Natural Gas Conversion to Value-Added Chemicals by Microwave Catalytic Processes

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Natural Gas Conversion to Value-Added Chemicals by Microwave Catalytic Processes

Brandon M. Robinson

Dissertation submitted
to the Benjamin M. Statler College of Engineering and Mineral Resources
at West Virginia University

in partial satisfaction of the requirements for the degree of

Doctor of Philosophy in
Chemical Engineering

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Morgantown, West Virginia
2021

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Abstract
Natural Gas Conversion to Value-Added Chemicals by Microwave Catalytic Processes
Brandon M. Robinson

Ethane is the second-largest component in natural gas and is typically separated out to minimize condensation in the pipelines. The technical difficulties and cost associated with the transportation and the storage of ethane have led companies to start burning natural gas to produce power or flaring which attributes to the global CO$_2$ emission problem. The conversion of ethane to higher-value liquid products is of increasing importance so that the natural gas can be safely utilized and cost-effectively transported. Existing commercial technologies used to convert ethane to liquid chemical products are typically based on the indirect syngas route, such as dry and steam reforming. Although, the direct conversion of ethane to aromatic products by non-oxidative dehydroaromatization has been studied for several decades, due to technical challenges no commercialization has occurred. The challenges include the design of highly selective catalysts and reactors systems to facilitate long-term catalyst stability. Conventional catalytic technologies have resulted in little or no progress towards commercialization. Thus, novel reaction engineering concepts are required, not only to develop a robust catalyst but also to revolutionize the entire process by applying non-conventional heating. The selective heating nature of microwave irradiation has demonstrated energy efficiency by lowering bulk catalyst temperatures and achieve higher selectivity due to suppressing further side reactions of undesired products.

This research aims to develop a method to increase catalyst stability, reactor efficiency, and product selectivity for the ethane dehydroaromatization reaction (EDHA). Molybdenum loaded zeolite supported H/ZSM-5 catalysts were studied for the EDHA reaction under thermally heated and/or microwave heated conditions. Promoters such as Fe and Zn were tested for the EDHA reaction over five reaction and regeneration cycles. The ability of the microwave to regenerate a deactivated catalyst in a microwave reactor was also tested under an O$_2$ and a CO$_2$ atmosphere. The reaction mechanism of EDHA was further investigated by using two different heating modes. A microwave fixed-bed reactor (MWFB) was used and its performance was compared to a conventional thermal fixed-bed reactor (CTFB). Catalyst bed preheating by thermally heated hot air and catalyst bed fluidization were investigated to enhance the utilization of the catalyst bed and the selectivity to aromatics for the microwave heated EDHA reaction.
This work is dedicated to my family, friends, loved one, and everyone who has supported me throughout my Ph.D. education.

This is for you!
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Table of Contents

Chapter 1: Introduction ........................................................................................................... 1
  1.1 Research Objective ........................................................................................................ 1
  1.2 Natural Gas Utilization and Demand for Ethylene and BTX ......................................... 2
  1.3 Direct Conversion of Light Hydrocarbons .................................................................... 4
    1.3.1 Zeolite Supports ...................................................................................................... 4
    1.3.2 Molybdenum Metal Catalyst ................................................................................... 5
    1.3.3 Metal Promotors ..................................................................................................... 6
  1.5 Microwave Technology ................................................................................................. 7

Chapter 2: Experimental ........................................................................................................ 9
  2.1 Reactor Configuration and Experimental Conditions .................................................. 9
    2.1.1 Non-Oxidative Ethane DHA Promoter Screening for Catalyst Stability .................. 9
    2.1.2 Catalytic Direct Conversion of Ethane to Value-Added Chemicals Under Microwave Irradiation .......................................................................................................................... 9
    2.1.3 CO₂ Regeneration of a Non-Oxidative Methane Dehydroaromatization Coked Catalyst ........................................................................................................................................... 11
    2.1.4 A Systems Approach to Increase Aromatic Selectivity for Non-Oxidative Ethane Conversion in a Microwave Reactor .................................................................................................................. 13
    2.1.5 Catalyst Performance Under Microwave Irradiation for the Methane DHA Reaction 14
    2.1.6 Microwave Induced Methane Plasma Process for the High Conversion of Methane .. 15
    2.1.7 Reactor Setup and Conditions for MW-Enhanced Catalytic Conversion of Ethane to Aromatics with CO₂ .................................................................................................................. 16
    2.1.8 Reactor Setup and Conditions for Microwave-Assisted Methanol Production......... 16
    2.1.9 Reactor Setup and Conditions for Microwave-Assisted Oxidative Ethane Dehydrogenation ................................................................................................................................. 17
  2.2 Catalyst Preparation ....................................................................................................... 18
2.3 Product Analysis ................................................................................................................... 19
  2.3.1 Agilent 3000A Micro-GC ......................................................................................... 19
  2.3.2 Inficon Fusion Micro-GC ...................................................................................... 19
  2.3.3 Prima BT Mass Spectrometer ................................................................................. 20
2.4. Product Analysis Calculations. ....................................................................................... 20
2.5 Catalyst Characterization ................................................................................................. 21
  2.5.1 Powder X-ray Diffraction (XRD) ........................................................................... 21
  2.5.2 Surface Area Measurement .................................................................................. 21
  2.5.3 Ammonia Temperature-Programmed-Desorption ................................................ 21
  2.5.4 Transmission Electron Microscope with Energy Dispersive X-ray Spectroscopy (TEM-EDS) ................................................................................................................. 22
  2.5.5 Temperature Programmed Oxidation (TPO) ........................................................ 22
  2.5.6 Temperature Programmed Reduction (TPR) ......................................................... 23
  2.5.7 Thermogravimetric Analysis (TGA) ...................................................................... 23
  2.5.8 Inductively Coupled Plasma Optical Spectroscopy (ICP-OES) ............................ 24
  2.5.9: XPS Spectroscopy ............................................................................................... 24

Chapter 3: Stability of Fe- and Zn-Promoted Mo/ZSM-5 Catalysts for Ethane
Dehydroaromatization in Cyclic Operation Mode ................................................................. 25
  3.1 Catalyst Characterization ............................................................................................... 26
  3.2 Catalyst Performance in Ethane Dehydroaromatization ........................................... 29
  3.3. Mechanistic Study of Catalyst Deactivation and Regeneration ............................... 34
  3.4: Conclusion on Stability of Fe- and Zn-Promoted Mo/ZSM-5 Catalysts for Ethane Dehydroaromatization in Cyclic Operation Mode ......................................................... 40
  3.5. Supplementary Materials......................................................................................... 41

Chapter 4: Catalytic Direct Conversion of Ethane to Value-Added Chemicals Under Microwave Irradiation ................................................................................................................. 49
Chapter 4: Catalyst Performance Under Microwave Irradiation vs Conventional Thermally Hearted Reactors

4.1 Catalyst Performance Under Microwave Irradiation vs Conventional Thermally Hearted Reactors

4.0. Catalyst Characterization

4.0.1 Surface Area and Acidity

4.0.2. X-Ray Diffraction

4.1 Catalyst Performance Under Microwave Irradiation vs Conventional Thermally Hearted Reactors

4.2. Investigation of Catalyst Deactivation

4.2.1. Transmission Electron Microscopy

4.2.2. Carbon Analysis by TPO and TGA

4.3: Conclusion

Chapter 5: Microwave Carbon Dioxide Regeneration on a DHA Catalyst

5.0 Experimental Justification for Methane DHA and Fluidized Microwave CO2 Regeneration

5.1 Methane Dehydroaromatization CO2 Regeneration in a Microwave Fluidized Reactor

5.2: Reactivity of the 2.5%Mo/ZSM-5 and the 10%Mo/ZSM-5 CO2-Regenerated Catalyst

5.3: Conclusion of CO2-Regeneration on a DHA Catalyst by Microwave Heating

Chapter 6: A Systems Approach to Increase Aromatic Selectivity for Non-Oxidative Ethane Conversion in a Microwave Reactor

6.1 Fixed-bed EDHA Testing in Microwave, Hybrid, or Thermally Heated Reactor

6.2 Fluidization of an Ethane DHA Catalyst Under Thermal and Microwave Heating

6.1.1 Results for Fixed-bed EDHA Testing in Microwave, Hybrid, or Thermally Heated Reactor

6.2.1 Thermal Fluidization

6.2.2 Microwave Fluidization

6.2.3 Microwave Fluidized Bed Temperature Distribution and Control

6.2.4 Characterization of Spent Fluidized Catalyst Under Thermal and Microwave Heating
6.3 Comparison and Conclusion on Thermal, Microwave, and Hybrid Heated Reactions .... 111
Chapter 7: Supporting Projects and Future Perspectives in Microwave Enhanced Activation of
Methane or Ethane C-H Bond.............................................................................................................. 113
7.1 Activation of C-H Bond by Microwave Catalysis for The Methane DHA Reaction ...... 113
7.1.2 Catalyst Performance Under Microwave Irradiation for the Methane DHA Reaction
.............................................................................................................................................................. 114
7.2 Microwave Induced Methane Plasma Process for High Conversion of Methane......... 115
7.2.1 Results for Microwave Induced Plasma Process for Catalytic Conversion of Methane
.............................................................................................................................................................. 116
7.3 MW-Enhanced Catalytic Conversion of Ethane to Aromatics with CO₂ ..................... 117
7.3.2 Results for Microwave Oxidative Ethane DHA Reaction with CO₂......................... 119
7.4 Microwave-Assisted Methanol Production........................................................................... 120
7.4.1 Simultaneously Production of Aromatics and Methanol from Ethane and CO₂ under
Low Pressure ...................................................................................................................................... 121
7.3 Microwave Ethane Dehydrogenation to Ethylene ......................................................... 123
7.3.1 Introduction ................................................................................................................................. 123
7.3.3 Proof-of-Concept ....................................................................................................................... 124
Chapter 8: Publication to Date........................................................................................................... 125
8.1 Journal Articles (Lead author)............................................................................................... 125
8.2 Journal Articles (Co-author)................................................................................................. 125
8.4 AIChE and ACS Presentations.................................................................................................. 126
Chapter 9: References......................................................................................................................... 127
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon Nanotubes</td>
</tr>
<tr>
<td>CTFB</td>
<td>Conventional Fixed Bed</td>
</tr>
<tr>
<td>DHA</td>
<td>Dehydroaromatization</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>HDPE</td>
<td>High Density Polyethylene</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively Coupled Plasma Optical Spectroscopy</td>
</tr>
<tr>
<td>LDPE</td>
<td>Low Density Polyethylene</td>
</tr>
<tr>
<td>MTA</td>
<td>Methane to Alcohols</td>
</tr>
<tr>
<td>MTO</td>
<td>Methane to Olefin</td>
</tr>
<tr>
<td>MW</td>
<td>Microwave</td>
</tr>
<tr>
<td>MWFB</td>
<td>Microwave Fixed Bed</td>
</tr>
<tr>
<td>MWFL</td>
<td>Microwave Fluidized</td>
</tr>
<tr>
<td>MWFR</td>
<td>Microwave Fluidized Regeneration</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards</td>
</tr>
<tr>
<td>ODE</td>
<td>Oxidative Dehydrogenation of Ethane</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinyl Chloride</td>
</tr>
<tr>
<td>SCD</td>
<td>Segmented Array Coupled Device</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TFB</td>
<td>Thermal Fixed Bed</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>TOS</td>
<td>Time on Stream</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature Programmed Desorption</td>
</tr>
<tr>
<td>TPO</td>
<td>Temperature Programmed Oxidation</td>
</tr>
<tr>
<td>TPR</td>
<td>Temperature Programmed Reduction</td>
</tr>
<tr>
<td>UHP</td>
<td>Ultra-High Purity</td>
</tr>
<tr>
<td>WHSV</td>
<td>Weight Hour Space Velocity</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
</tbody>
</table>
List of Figures

Figure 1.1: Summary of major research objectives for the natural gas conversion to value-added chemical by microwave processes................................................................. 1
Figure 1.2: Global key thermoplastic production [million tons] per year and forecasted future production of thermoplastics. (PET, HDPE, PVC, LDPE, PP, PS, and others) [6] ........... 3
Figure 1.3: Microwave irradiation in the conversion of natural gas over metal-promoted zeolite. 8
Figure 2.1: Cross-sectional cut-away of the 6.6550 GHz microwave cavity. ......................... 10
Figure 2.2: CAD render of (a) Mono-mode high temperature cavity (b) Cut away of the cavity. 12
Figure 2.3: Fluidization tube used in all fluidization experiments. ........................................ 12
Figure 2.4: Thermally pre-heated catalyst bed (a) schematic of concentric tubes and gas flows paths, and (b) image of the thermally heated setup........................................... 14
Figure 2.5: Reactor setup for the microwave induced methane plasma process. .................. 15
Figure 2.6: Reactor setup for microwave methanol production. (a) methanol production at 82-psi form CO₂ and hydrogen, (b) Co-processing of ethane and CO₂ to from methanol and aromatics............................................................. 17
Figure 3.1: The major research objective for chapter 1 for the conversion of natural gas to value-added chemical. .......................................................................................... 25
Figure 3.2: Graphical explanation of the methodology and summary of the results. .......... 26
Figure 3.3: XRD patterns of fresh and spent catalysts after five cycles. ............................ 27
Figure 3.4: Nitrogen absorption-desorption isotherms for the fresh catalyst. .................... 28
Figure 3.5: Ethane conversion and average aromatic selectivity for each reaction cycle. .... 32
Figure 3.6: Comparison of time-on-stream between benzene concentrations for five reaction ... 33
Figure 3.7: Comparison of the total aromatic yields per reaction cycle in mole percent of benzene and toluene..................................................................................... 34
Figure 3.8: TEM images of spent catalysts before regeneration: (a) Mo and (b) MoFe and EDS data. a: N/F stands for not found. ................................................................. 36
Figure 3.9: (a) and (b) are both TEM images of the spent MoZn catalyst and EDS analysis. a: N/F stands for not found................................................................. 36
Figure 3.10: (a) and (b) are both TEM images of the spent MoFeZn catalyst and EDS analysis. a: N/F stands for not found......................................................... 37
Figure 3.11: TPO (solid) and TGA (dotted) profiles of the spent catalyst after 5 reaction cycles.

Figure 3.12: TPR profiles of the fresh versus regenerated fifth cycle catalyst.

Figure S3.13: Ammonia temperature-programmed desorption of the fresh catalysts.

Figure S3.14: Comparison of time-on-stream toluene concentration changes for five reaction cycles.

Figure S3.15: Comparison of time-on-stream hydrogen concentration changes for five reaction cycles.

Figure S3.16: Comparison of time-on-stream methane concentration changes for five reaction cycles.

Figure 4.1: The major research objective for chapter 4 is to elucidate the effects that microwave heating has on the reaction productivity and product distribution for the conversion of ethane to value-added chemical.

Figure 4.2: Graphical illustration of the microwaves selective heating nature and energy saving potential.

Figure 4.3: XRD patterns of (a) Fresh MoFe/ZSM-5, (b) MWFB spent catalyst, and (c) CTFB spent catalyst.

Figure 4.4: Comparison of the conversion and formation rates for the MoFe/ZSM-5 catalyst in MWFB at 375°C and CTFB at 660°C. (a) percent ethane conversion, (b) hydrogen formation, (c) benzene formation, and (d) toluene formation.

Figure 4.5: Comparison of the formation rates for the MoFe/ZSM-5 catalyst in MWFB at 375°C and CTFB at 660°C. (a) methane formation and (b) ethylene formation.

Figure 4.6: Compares the hydrocarbon selectivity’s of the major carbon products for the MWFB at 375°C and CTFB at 660°C. (a) methane selectivity, (b) ethylene selectivity, (c) benzene selectivity, and (d) toluene selectivity.

Figure 4.7: TEM image of the spent MWFB MoFe/ZSM-5 catalyst after 36 min of reaction.

Figure 4.8: TEM images of the spent CTFB MoFe/ZSM-5 catalyst after 36 min of reaction.

Figure 4.9: TPO (black) and TGA (blue) for spent catalysts under MWFB (dotted) and CTFB (solid) reactors. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article).

Figure 5.1: The major research objective for chapter 5.
Figure 5.2: Results for three cycles of thermally heated dehydroaromatization reaction and microwave fixed-bed CO\(_2\) regeneration for the EDHA and MDHA. [30-minutes of EDHA at 600°C in 30% ethane/N\(_2\) and 0.5g catalyst, 30-minutes of MDHA at 700°C in 30% methane/N\(_2\) and 0.5g catalyst, and microwave CO\(_2\) fixed-bed regeneration at 550°C for 30 minutes in 30% CO\(_2\)/N\(_2\)].

Figure 5.3: Image of 4%Mo/ZSM-5 catalyst bed after three thermally heated reaction and microwave fixed-bed regeneration cycles. [30-minutes of EDHA at 600°C in 30% ethane/N\(_2\) and 0.5g catalyst, and microwave CO\(_2\) fixed-bed regeneration at 550°C for 30 minutes in 30% CO\(_2\)/N\(_2\)].

Figure 5.4: Microwave fluidized CO\(_2\)-Regeneration of two MDHA coked catalyst (left) 10%-Mo/ZSM-5 and (Right) 2.5%-Mo/ZSM-5 where the top of each shows the tracked ion intensities of CO\(_2\), CO, and O\(_2\). The bottom graph of each show the temperature profile and the forward and reverse power profile of the microwave reactor. [10°C ramp to 800°C in 10% CO\(_2\)/He, hold for 30-minutes, 0.75g catalyst at 100-mL/min].

Figure 5.5: Thermal images of the microwave heated fluidized bed after reaching 800°C for the CO\(_2\) regeneration of the coked 2.5%Mo-ZSM-5 MDHA catalyst. (a-d) shows the formation and the cycling of hot particles in the catalyst bed.

Figure 5.6: The thermally heated fixed-bed regeneration of the coked 2.5%Mo-ZSM-5 catalyst (left) in 10%-CO\(_2\) (TFB-CO\(_2\)) and (right) 10%-O\(_2\) (TFB-O\(_2\)).

Figure 5.7: TGA and DSC curves for the coked and the regenerated catalyst. [Dynamic-HiRes 20°C max ramp to 800°C in air at 150mL/min].

Figure 5.8: CO\(_2\)-temperature programed oxidation (CO\(_2\)-TPO) of the 10%Mo/ZSM-5 catalyst.

Figure 5.9: XPS spectra of the 2.5%Mo/ZSM-5 samples with deconvoluted peak curves.

Figure 5.10: XPS spectra of the 10%Mo/ZSM-5 samples with deconvoluted peak curves.

Figure 5.11: Temperature programed reduction of the fresh, TFB-CO\(_2\), MWFL-CO\(_2\), and TFB-O\(_2\).

Figure 5.12: TEM of the 10%Mo/ZSM-5 catalyst where (a) is the fresh catalyst, (b) is the carburized catalyst, (c) is the spent catalyst, and (d) is the MWFR-10 regenerated catalyst.

Figure 5.13: XRD of the 10%Mo/ZSM-5 catalyst samples.

Figure 5.14: XRD of the 2.5%Mo/ZSM-5 catalyst samples.
Figure 5.15: Thermal fixed bed MDHA reactivity testing of the 2.5%-Mo/ZSM-5. Where (a) is the methane conversion, (b) is the ethylene selectivity, (c) is the benzene selectivity, and (d) is the total aromatic production. [700°C, 0.3g of catalyst at 30mL/min of 30%CH₄ in N₂]

Figure 5.16: Thermal fixed bed MDHA reactivity testing of the 10%-Mo/ZSM-5. Where (a) is the methane conversion, (b) is the ethylene selectivity, (c) is the benzene selectivity, and (d) is the total aromatic production. [700°C, 0.3g of catalyst at 30mL/min of 30%CH₄ in N₂]

Figure 6.1: The major research objective for chapter 6.

Figure 6.2: Graphical illustration of the three microwave heating processes.

Figure 6.3: Microwave fixed-bed data for the MWFB350, where (a) is the temperature profile, (b) is the forward and reflected power profiles, and (c) is the collected reaction data. The vertical dashed line depicts the point in time the gas was switched from 1.5% ethane to 30% ethane which denotes time zero.

Figure 6.4: Microwave fixed-bed data for the MWFB375, where (a) is the temperature profile, (b) is the forward and reflected power profiles, and (c) is the collected reaction data. The vertical dashed line depicts the point in time the gas was switched from 1.5% ethane to 30% ethane which denotes time zero.

Figure 6.5: Microwave fixed-bed data for the MWFB425, where (a) is the temperature profile, (b) is the forward and reflected power profiles, and (c) is the collected reaction data. The vertical dashed line depicts the point in time the gas was switched from 1.5% ethane to 30% ethane which denotes time zero.

Figure 6.6: Thermal Images of the MWFB350 where (a) shows onset of hotspot formation, (b) is the pulsating of the hotspot by microwave power, and (c) is the ending temperature distribution after the thermal hotspot event. The time is in seconds where time zero is the 18-minute mark in microwave run time for the MWFB350, the images are recorded in IR radiation counts, and the arrows represent increases and decreases in counts due to the hotspot.

Figure 6.7: Thermal Images of the MWFB375 where (a) shows onset of hotspot formation, (b) is the rapid thermal runway and hotspot formation, (c) is the pulsating of the hotspot by microwave power, and (d) is the ending temperature distribution after the thermal hotspot event. The time is in seconds where time zero is the 21-minute mark in microwave run time.
for the MWFB375, the images are recorded in IR radiation counts, and the arrows represent increases and decreases in counts due to the hotspot. 

Figure 6.8: Image of the hotspot from within the center of the (a) MWFB350 and (b) MWFB425 reaction.

Figure 6.9: Image of the hotspot that was formed in the MWFB375 reaction. (a) The catalyst inside the tube, and (b) is an image of the agglomerated hotspot and the dispersed catalyst bed showing overall low catalyst bed utilization by low coke deposits.

Figure 6.10: Microwave fixed-bed data for the MWHybrid, where (a) is the temperature profile, (b) is the forward and reflected power profiles, and (c) is the collected reaction data. The vertical dashed line depicts the point in time the gas was switched from 1.5% ethane to 30% ethane which denotes time zero.

Figure 6.11: Comparison between microwave heating, thermal heating, and microwave hybrid heating.

Figure 6.12: XRD of the carburized, TFB615, MWFB350, MWFB375, MWFB425, MWHybrid, and the concentrated hotspot.

Figure 6.13: Oxidative thermogravimetric weight loss and Heat flow curves of the spent TFB615, MWFB350, MWFB375, MWFB425, MWHybrid, and the concentrated hotspot.

Figure 6.14: 6%Mo/ZSM-5 spent samples where (a) is the MWFB425 and (b) is the concentrated hotpot sample after TGA regeneration in air to 1100°C.

Figure 6.15: Comparison of ethane conversion and product selectivity’s for the (a) TFL650, (b) TFL615, (c) TFL575, and (d) TFB615. [0.75g cat—100mL/min of 30% ethane].

Figure 6.16: Microwave fluidized data for the MWFL500 reaction, where (a) is the temperature profile, (b) is the forward and reflected power profiles, and (c) is the collected reaction data. The vertical dashed line depicts the point in time the gas was switched from 1.5% ethane to 30% ethane which denotes time zero.

Figure 6.17: MWFL500 temperature distribution within the catalyst fluidized bed at 34:30 of microwave program time the beginning of the reaction (a), (b) 64:00, and (C) 93:04 minutes of microwave program run time.

Figure 6.18: Microwave fluidized data for the MWFL575 reaction, where (a) is the temperature profile, (b) is the forward and reflected power profiles, and (c) is the collected reaction data.
The vertical dashed line depicts the point in time the gas was switched from 1.5% ethane to 30% ethane which denotes time zero. ................................................................. 103

Figure 6.19: MWFL575 temperature distribution within the catalyst fluidized bed at (a) 29:00, (b) 60:00, and (c) 87:45 minutes of microwave program run time. ................................................. 104

Figure 6.20: Microwave fluidized data for the MWFL600 reaction, where (a) is the temperature profile, (b) is the forward and reflected power profiles, and (c) is the collected reaction data. The vertical dashed line depicts the point in time the gas was switched from 1.5% ethane to 30% ethane which denotes time zero. ................................................................. 105

Figure 6.21: MWFL600 temperature distribution within the catalyst fluidized bed at (a) 34.00, (b) 50.00, (C) 59.10, (d) 65.00, (e) 75.05, and (f) 86.00 minutes of microwave program run time................................................................. 106

Figure 6.22: Microwave fluidized data for the MWFL475 reaction, where (a) is the temperature profile, (b) is the forward and reflected power profiles, and (c) is the collected reaction data. The vertical dashed line depicts the point in time the gas was switched from 1.5% ethane to 30% ethane which denotes time zero. ................................................................. 107

Figure 6.23: XRD of the Carburized, fluidized thermal (TFL) spent catalyst and the microwave fluidized bed (MWFL) spent catalyst................................................................. 109

Figure 6.24: Oxidative thermogravimetric weight loss (solid lines) and Heat flow curves (dashed lines) of fluidized thermal (TFL) spent catalyst and the microwave fluidized bed (MWFL) spent catalyst................................................................. 110

Figure 6.25: Thermal, microwave, and hybrid fixed-bed mode compared to thermal and microwaves fluidized mode for the average production rate, ethane conversion, and product selectivity’s for the EDHA reaction. ................................................................. 112

Figure 7.1: Equilibrium conversion of methane dehydroaromatization in a thermally heated reactor................................................................. 114

Figure 7.2: Methane conversion for the dehydroaromatization reaction at 450°C and 600°C. ................................................................. 115

Figure 7.3: Microwave induced methane plasma process reactor system exit gas concentrations. ................................................................. 117

Figure 7.4: Efficient reactor concept to produce liquid products from ethane and CO₂. ................................................................. 118
Figure 7.5: Ethane DHA with CO\textsubscript{2} in thermal catalytic and MW catalytic fixed-bed reactors, (a) effect of temperature on conversion (b) effect of temperature on aromatics (BTX) formation rate. .................................................................................................................................................. 119

Figure 7.6: Methanol concentration for the direct microwave CO\textsubscript{2} hydrogenation and dual reactor co-processing of ethane and CO\textsubscript{2}........................................................................................................................................ 122

Figure 7.7: Product distribution at the exit of the reactor for the co-processing of ethane and CO\textsubscript{2}. .......................................................................................................................................................................................... 123

Figure 7.8: Proof of concept data for the microwave oxidative dehydrogenation of ethane to ethylene........................................................................................................................................................................... 124

Figure 7.9: Image of catalyst bed after 150 min of TOS, displaying low coke formation for the microwave oxidative dehydrogenation of ethane to ethylene. .................................................................................. 124

List of Tables:

Table 2.1: Catalyst compositions used for natural gas conversion to value-added chemicals. .... 18
Table 2.2: List of Agilent 3000A micro-GC column configuration .............................................. 19
Table 2.3: List of Inficon Fusion micro-GC column configuration ............................................. 19
Table 2.4: List of Inficon Fusion micro-GC column configuration use for methanol analysis... 20
Table 3.1: Surface area and micropore results of the fresh catalyst ........................................... 29
Table 3.2: Catalyst Composition Analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP–OES).......................................................................................................................... 30
Table 3.3: TGA results of the spent catalyst obtained at the end of the fifth reaction cycle. ...... 38
Table S3.4: The change of benzene concentration between cycles (ppm) ................................. 41
Table S3.5: The change of toluene concentration between Cycles (ppm)................................. 42
Table S3.6: The change of hydrogen concentration between cycles (%) ............................... 43
Table S3.7: The change of ethane concentration between cycles (%) ................................. 44
Table 4.1: The surface area and acidity of fresh catalyst before and after catalyst loading. ...... 51
Table 7.1: Microwave methanol synthesis temperature survey.................................................. 122
Chapter 1: Introduction

1.1 Research Objective

It was stated by the National Academies of Sciences Engineering Medicine that the way to commercialization of the direct conversion of natural gas to value-added chemicals, is by the identification of ways to manage carbon flow. Preferentially carbon needs to be place in the products rather than in coke. Increased understanding and new approaches for solving this issue would increase reaction productivity, reduce energy use, and extend catalyst lifetime [1]. The Primary objective of this research is to assess the approach of microwave selective heating for the reaction productivity, energy use, and its effects on catalyst lifetime for the conversion of ethane to value-added chemicals such as hydrogen, ethylene, benzene, and toluene. The objectives of the research are outlined in Figure 1.1.

\[\text{Non-oxidative Ethane Conversion Promoter Screening for Catalyst Stability} \]

“Fe and/or Zn metal promoted Mo/ZSM-5 was tested to determine the effects on reaction productivity and catalyst lifetime for the dehydroaromatization reaction over multiple reaction and regeneration cycles”

\[\downarrow\]

\[\text{Non-oxidative Ethane Conversion by Microwave Heating} \]

“Microwave heating was used to determine the effects on reaction productivity, energy input, carbon distribution in the product stream, and on coke formation”

\[\downarrow\]

\[\text{CO}_2 \text{ Regeneration of a Non-Oxidative Natural Gas Conversion Catalyst} \]

“The regeneration by CO\textsubscript{2} in a microwave reactor could increasing reaction productivity by lowering the induction period and produce valuable CO\textsubscript{2} form and not CO\textsubscript{2} that is associated with oxygen regeneration”

\[\downarrow\]

\[\text{Systems Approach to Increase Aromatic Selectivity for Non-Oxidative Ethane Conversion in a Microwave Reactor} \]

“The use of microwave fluidization and catalyst pre-heating could improve the total aromatic selectivity of the microwave by increasing catalyst bed utilization”

**Figure 1.1:** Summary of major research objectives for the natural gas conversion to value-added chemical by microwave processes.
1.2 Natural Gas Utilization and Demand for Ethylene and BTX

The production of natural gas in the United States has reached 33.6 million cubic feet in 2020 [2]. Natural gas consists primarily of methane, which is often further refined in industry to produce hydrogen (steam reforming) and fuels. Ethane is the second largest component in natural gas and is typically separated out to minimize condensation in the pipelines. The technical difficulties and cost associated with the transportation and the storage of ethane has led companies to start burning natural gas to produce power or flaring it. In 2012 approximately 3.5% of natural gas production went to flaring, which certainly would attribute to the global CO₂ emission problem [3]. Therefore, developing low-cost technologies would be needed to utilize these waste fuels.

The increase in the world's overall population and economic growth has directly affected the demand for chemicals that can be produced from ethane. The conversion of ethane to higher-value products such as, hydrogen, ethylene, and liquid products such as benzene, toluene, and xylene (BTX) is of increasing importance in the energy and petrochemical industry. Ethylene is typically manufactured into polyethylene, ethylene glycol, ethylene dichloride, and styrene. BTX chemicals are important in the production of fuels, plastics, resins, synthetic fibers, rubbers, detergents and even pharmaceuticals. Ethylene and benzene are major component of thermoplastics commonly used in food packaging and commercial products. The global demand for ethylene is forecasted to increase from 188.43 million tons per year in 2019 to 311.32 million tons per year by 2030, and BTX is forecasted to increase from 111.2 million tons per year in 2017 to 141.0 million tons per year tons in 2023 worldwide [4][5]. This demand is driven by markets such as that of thermoplastics as seen in Figure 1.3. A significant increase in the use of thermoplastics for which ethylene and benzene are major building block of has been occurring since 1980 and is forecasted to increase 21.26% from 2020 to 2030 [6].
The conventional process to produce ethylene is typically from the steam cracking of naphtha. The steam cracking of ethane (ethane cracker) to produce ethylene is a much more cost-effective approach due to the large price difference associated with feedstock cost, where ethane is $55.10 per ton and naphtha $173.79 per ton [7]. Steam cracking of naphtha to ethane is a non-catalytic energy intensive pyrolysis process that combines steam with the feed stock to suppress coke deposition in the reactor tubes. The addition of the steam produces large amounts of carbon dioxide emissions at a rate of 1.8-2 kg of CO$_2$ per kilogram of ethylene produced for naphtha cracking [8]. In the steam cracking of ethane, the aromatic products associated with the steam cracking of naphtha are not produced. The BTX industry is under strain, naphtha crackers are being retrofitted due to the current abundance of natural gas [9]. The production of liquid products such as BTX from ethane are typically based on the indirect syngas route, such as dry and steam reforming. This is where a complete oxidation of ethane is required to produce syngas followed by Fischer-Tropsch reaction to produce new hydrocarbons with higher molecular weight such as diesel [10][11]. In general, indirect conversion of light alkanes by the syngas route is capital-intensive accounting for up to 50% of the capital cost incurred and energy inefficient due to several intermediate production steps [12]. Thus, direct catalytic conversion of light alkanes to higher-value products could be a cost-effective solution in the future.
1.3 Direct Conversion of Light Hydrocarbons.

Non-oxidative ethane dehydroaromatization (EDHA) is the reaction of ethane over a metal supported acid catalyst that enables the direct conversion of ethane to ethylene and aromatics. The EDHA reaction is thermodynamically unfavored requiring temperatures of 600°C to facilitate the reaction to aromatics. However, EDHA can be facilitated at much lower temperatures than pyrolysis, thus has a large energy saving potential. The EDHA reaction is often described as a two-step process, where ethane is first dehydrogenated to ethylene and then oligomerization to longer olefins, which are then further aromatized by the support. Although, the direct conversion of ethane to aromatic products by non-oxidative dehydroaromatization has been studied for several decades, no commercialization has occurred for this technology due to technical challenges. The direct transformation of ethane into aromatic hydrocarbons requires high activation energies and typically yields low conversion to aromatics even with increasing reaction temperatures[13][14]. The high reaction temperatures (500–700°C) which are needed to facilitate the endothermic reaction, lead to low selectivity to aromatic products, coking, and catalyst deactivation [15]. Conventional catalytic technologies have resulted in little or no progress towards the commercialization of this technology. Thus, novel reaction engineering concepts are required, not only to develop a robust catalyst but also to revolutionize the entire process by applying nonconventional heating processes that reduce catalyst deactivation.

1.3.1 Zeolite Supports

Direct conversion of natural gas (methane or ethane) is typically carried out over oxide supports such as zeolites. Zeolites have a unique shape selectivity in heterogenous catalyst due to their, pore size, 3D-structure, solid acidity, ion exchangeability, and thermal stability [16]. Zeolites are crystalline oxides that are formed by tetrahedra SiO$_4$ and AlO$_4$ bonded at the corners to produce three-dimensional (3D) structures. The zeolite MFI-type (ZSM-5) structure is formed by 10 membered rings that form a micropore-channel system with pores that consist of straight and sinusoidal channels [17]. ZSM-5 has a pore size of 0.52-0.55nm in diameter and the 3D-structure allows for the formation and transportation of benzene and toluene aromatic hydrocarbons, while the size of the pores is small enough to exclude larger highly polyaromatics compounds [18]. ZSM-5 can be synthesized in various SiO$_2$/Al$_2$O$_3$ ratios (SAR) that effect its physical surface area.
and its chemical properties. Changes in the SAR does not result in a change in the zeolites physical structure but changes in the acidity of the zeolite occur [19]. The acidic properties of ZSM-5 can directly affect the catalytic activity, deactivation, and product distribution. The acidity of ZSM-5 is typically discussed in terms of Brønsted and Lewis acidity. Decreasing the SAR increases the acidity and decrease the B/L acidity ratio [20]. Low SAR ZSM-5 has been shown to produce more aromatic products due to the high acid strength sites facilitating the aromatization of reaction intermediates to aromatics. The concertation of the acid sites have also been determined to directly influence the anchoring and dispersion of metal loadings of molybdenum [21].

1.3.2 Molybdenum Metal Catalyst

Molybdenum supported on H/ZSM-5 is a well-studied catalyst and has shown good activity towards the aromatization of methane and ethane [22][23][24]. When the molybdenum is calcined on the H/ZSM-5 support, the MoO₃ started to migrate and form a chelate with the Brønsted acid sites on the surface and inside the pore structure of H/ZSM-5 zeolite support [25]. When the catalyst is reduced in the presence of ethane, it forms Mo-carbides, which is proposed to be the active phase of Mo that catalyzes the dehydrogenation step of ethane to ethylene [23][26][27][28][29]. Mo-oxy-carbide, the in-between phase of Mo-carbides, are thought to be a transient metastable phase and are shown to be active for C-H bond activation during the carburization of the MoO₃ species [29]. The effects of Mo-metal loading weight percentage have also been studied on H/ZSM-5. It was found that after 2%Mo loading the activity begins to level off, but instead increases with the amount of carbon present after the activation period. However, catalysts with low Mo loadings of less than 2-wt% were shown not to contain little to no Mo-carbide species, but mainly Mo-oxy-carbide species that do not completely reduce to Mo₂C [30]. This also suggest that full carburization is only achievable in larger Mo particles, and nearly impossible to fully carburize the mono- or dimeric species of Mo that is located on the Al framework of zeolite. Furthermore, it has been demonstrated that the catalytic activity does not linearly increase with Mo loading, and that it is believed a hydrocarbon pool mechanism occurs [12] [31]. Recent DFT analysis of Mo carbide nanoparticles suggest that the C/Mo ratio is important to the location of the Mo species [32]. Mo-carbide species with C/Mo ratios greater than 1.5 are more likely to migrate to the external surface of the zeolite, whereas C/Mo ratios less than 1.5 prefer to stay inside the pores. The reaction mechanism for ethane dehydroaromatization
is thought to be very similar to that of methane DHA. The initial conversion of ethane over Mo-oxo species result in the formation of ethylene and small amounts of benzene. As the Mo-oxo species are transformed to Mo-carbides the reaction shifts to a radical mechanism. Where ethane is likely reduced on the Mo-centers leading to radical hydrocarbon species. These species are then thought to add to the hydrocarbon pool mechanism, where polyaromatic products build up inside the zeolite pores that interact with the Mo$_2$C to produce benzene $^{[33]}[34]$. 

1.3.3 Metal Promoters

Different metal promoters are added and tested on Mo/ZSM-5 $^{[35]}[36][37]$. The addition of Fe to Mo/ZSM-5 was found to improve the activity and stability of Mo/ZSM-5 $^{[25]}[38][39][40][41]$. The addition of Fe suppressed the formation of low-temperature amorphous coke by the formation of carbon nanotubes (CNT) which acted as a competitor for the coke precursors. The selectivity to CNT formation was believed to increase gas diffusion into the pores due to the decreased formation of amorphous surface coke that can cause pore blockage and thus rapid deactivation. Our previous study on methane dehydroaromatization reaction suggested that the addition of Fe to Mo/ZSM-5 catalyst acted as a stabilizer where little to no decrease in both aromatic selectivity and yield were observed over five reaction and regeneration cycles $^{[38]}$. The possibility of the addition of a third promoter on the catalyst, such a Zn, could increase the aromatic yield, especially for the ethane compared to methane dehydroaromatization reaction, because it requires lower activation temperatures, which will increase the Zn stability, especially at lower loadings. It was found that Mo/ZSM-5 showed higher benzene selectivity and a lower total number of strong acid sites when Zn was added $^{[42]}[43]$. However, a recent study has determined that the most active Zn metals were located inside the micropore but suffered from evaporation, which led to very rapid deactivation during the dehydroaromatization reaction of methane $^{[44]}$. Furthermore, it was reported that there were two types of Zn species present during the dehydroaromatization of methane: one being a ZnO species that is loosely bound and easily reduced, and the second is the Zn species that is bound to the acid sites of ZSM-5 supports and is a more reactive and stable [Zn(OH)$_x$]. The amount of [Zn(OH)$_x$] present was dependent upon the Zn loading. At higher loading, most Zn was present in the ZnO form $^{[45]}$. 
1.5 Microwave Technology

Conventional catalytic technologies have resulted in little or no progress towards the commercialization of this technology. Thus, novel reaction engineering concepts are required, not only to develop a robust catalyst but also to revolutionize the entire process by applying nonconventional heating processes that reduce catalyst deactivation. Microwave heating is a rapidly emerging tool in chemical reactions due to microwave’s unique characteristics of selective material heating, rapid non-contact heating, and quick start-up and shut-down operation [46,47]. Microwave induced thermal effects within solids are generated due to the oscillating electric and magnetic fields of microwaves. The thermal effects of the electric field are typically generated under high frequencies when the dipoles are not able to align with the oscillating electric field sufficiently. This causes friction and collisions between the dipoles that results in the generation of heat [48,49]. Depending on the material, heating can be caused by electrical resistance due to the collisions of charges being transported by the oscillating electrical current. Thermal effects from the magnetic field contribute to microwave heating especially in metal oxides, such as ferrites and other magnetic materials, by including eddy currents, hysteresis losses, and magnetic resonance [50–52]. In heterogeneous catalysis, of gas-solid phases, microwave heating has demonstrated the ability to be energy efficient by lowering bulk catalyst temperatures and achieving higher selectivity due to suppressing further side reactions of undesired products [53–55]. The enhanced activity of heterogeneous reaction, observed under microwave irradiation, is attributed to microwave thermal and non-thermal effects as mentioned in literature [56–58]. Microwave thermal effects can be attributed to the localization of heat in a material when placed in the microwave field, also known as a hot spot [56,59,60]. Zhang et al. reported the formation of hot-spots as large as 90–1000 micrometers and temperatures of 100–200 °C higher than the bulk temperature of the catalyst bed [61]. The formation of a hotspot can explain most of the catalytic effects generated in a microwave-assisted reaction. However, microwave non-thermal effects have been reported by Stiegman et al. where the activation energy for the Boudouard reaction was lowered under microwave reaction for the reaction of carbon and CO₂ [62], NO decomposition [63], ammonia synthesis [64,65], and DHA [66] are also other reaction examples where non-thermal effects of microwave energy were observed. A microwave field acting on a metal particle can generate the transfer of free electrons from the conduction band within the metal particle to its surface. It is suggested that the sharing of these free electrons at the surface of the metal can
facilitate dipole-dipole like interactions between the catalyst metal sites and the gas phase molecules \([64–66]\). As illustrated in Figure 1.3 from our previous publication \([66]\), proposes that catalytic materials themselves have dielectric properties that allow them to absorb MW energy. Coupling of the MW field with certain features of the catalyst, like dipoles on the surface, can affect charge distributions at specific sites which enables the electromagnetic energy to impact electronic interactions, extend the dipole formation and/or charge transfers which can lead to increases in conversion and selectivity.

**Figure 1.3:** Microwave irradiation in the conversion of natural gas over metal-promoted zeolite.
Chapter 2: Experimental

2.1 Reactor Configuration and Experimental Conditions.

2.1.1 Non-Oxidative Ethane DHA Promoter Screening for Catalyst Stability.

The reactions were carried out in a Micromeritics Autochem 2950 analyzer connected with a micro gas chromatograph (micro-GC) for gas analysis. The micrometrics unit internal valves and line temperatures were maintained at 150 °C, and a 150–170 °C heated trace line attached to the inlet of the micro-GC was used to maintain the products in the gas phase. For each experiment, 200 mg of catalyst was loaded into a quartz tube reactor. The reaction was carried out under atmospheric pressure and continuous flow conditions. The catalyst was heated to 615 °C in argon at a flow rate of 50 mL/min with the heating rate of 10 °C/min. Pure ethane was mixed with argon to create a 36% ethane mixture, which then flowed over the catalyst at 50 mL/min. After 21 min of reaction, helium was introduced to purge ethane in the system. The catalyst remained at 615 °C, where it was regenerated for 95 min in a flow of 2% oxygen in helium. After catalyst regeneration, helium was introduced to purge remaining oxygen in the system and the catalyst was ready for the next 21 min reaction cycle. A total of five reaction cycles (1 fresh and 4 regenerated) were performed for each catalyst. All reactant gases were purchased from AirGas with ultrahigh-purity (UHP) grade. Catalyst powder were pressed and sieved between 70 and 100 mesh particle size. The products were analyzed be an Agilent 3000A 4-column micro-GC.

2.1.2 Catalytic Direct Conversion of Ethane to Value-Added Chemicals Under Microwave Irradiation

The catalytic reaction of ethane dehydroaromatization were evaluated under two different heating modes, using microwave irradiation (MWFB) and conventional thermal (CTFB) heating. The catalyst was evaluated at 375°C (bulk catalyst temperature) in a Lambada MC1330200 microwave reactor operated at a fixed frequency of 6.650GHz. The only heat supplied to the reaction was from the microwave heating of the catalyst. The bulk catalyst temperature and quartz tube reactor temperature were measured by two different IR pyrometers. A short-wave IR pyrometer was used to observe the temperature of the catalyst be through the glass. Figure 2.1 depicts a cross-sectional cut-away of the microwave cavity and the location of the pyrometers. The reaction temperature


was maintained by controlling the forward microwave power window (between 0–180W). The quartz tube with the catalyst penetrated through the H-plane axis of the waveguide in a horizontal fixed bed setup. The catalyst was also evaluated under the same ethane conversion using a conventional thermal horizontal furnace at 660°C. The reaction temperature was monitored using a K-type thermocouple in the catalyst bed. The reactor temperature remained constant during the reaction time in both heating methods. Catalyst evaluations were carried out in a fixed bed setup with continuous flow in quartz tubes (8 mm-ID, 12mm-OD, and 381 mm-L). 0.4800g of pelletized MoFe/ZSM-5 was loaded into the center of the quartz tube and held in place by quartz wool. Catalyst powder were pressed and sieved between 70 and 100 mesh particle size. The catalyst was pre-reduced at 550°C for one-hour in a 10% H₂ –90 %N₂ environment in a tubular furnace. The catalyst was then heated by the designated heating method at 5°C/min under an inert flow of N₂ to reaction temperature. The reaction was carried out in an atmosphere of 36 % ethane balance of N₂ at 50mL/min. After 36 minutes of reaction time, the catalyst cooled to room temperature in an inert flow of N₂. The products were analyzed be an Agilent 3000A 4-column micro-GC.

**Figure 2.1**: Cross-sectional cut-away of the 6.6550 GHz microwave cavity.
2.1.3 CO₂ Regeneration of a Non-Oxidative Methane Dehydroaromatization Coked Catalyst

The effects of microwave catalytic regeneration will be tested by fixed bed followed by microwave CO₂ regeneration. The catalyst was first carburized in a flow 100mL/min of 90% hydrogen and 10% methane at 700°C for 10mins. The reaction was carried out in a Micromeritics Autochem 2920 analyzer connected to an Agilent 3000A 4-column micro-GC for product analysis. The micromeritics unit internal valves and line temperatures were maintained at 150 °C, and a 150–170 °C heated trace line attached to the inlet of the micro-GC was used to maintain the products in the gas phase. For each experiment, 300 mg of catalyst was loaded into a U-shaped quartz tube. The catalyst was heated to 750 °C in nitrogen at a flow rate of 30 mL/min with the heating rate of 10 °C/min. UHP methane was mixed with UHP nitrogen to create a 30% methane mixture, which was then flowed over the catalyst at 30 mL/min. After 30 min of reaction, nitrogen was introduced to purge methane from the system. Catalyst regeneration was performed in a Sairem 3kW magnetron (GMP30KIP) and in a Sairem 900 W solid state (GMS1000MS) microwave mono-mode reactor system with automatic 4-stub tunning and PID control. The temperature of the catalyst was monitored by a pyrometer with an optical wavelength of 1.5 and a spot size of 3 mm when focused on the catalyst bed. A FLIR A6260 short wave IR camera with an InGaAs detector, 25mm lens and a ND1 filter was used as the primary determination of temperature for all reactions. The 3kW magnetron microwave was set a temperature of 700°C and the 900W solid state microwave was set to a temperature ramp of 10°C/min to 800°C and held for 90 mins. A mono-mode high temperature cavity was used with the fluidization tube penetrating perpendicular to the H-field of the cavity depicted in Figure 2.2. In both cases the catalyst was fluidized in a specially designed quartz fluidization tube as depicted in Figure 2.3. The catalyst regenerations were conducted in an atmosphere of 10% UHP CO₂ mixed with UHP Nitrogen at a flow rate of 150mL/min. The catalyst powder was pressed and sieved between 34 and 45 mesh particle size before the reactions.
Figure 2.2: CAD render of (a) Mono-mode high temperature cavity (b) Cut away of the cavity.

Figure 2.3: Fluidization tube used in all fluidization experiments.
2.1.4 A Systems Approach to Increase Aromatic Selectivity for Non-Oxidative Ethane Conversion in a Microwave Reactor.

The catalytic testing was performed using five different reactor configurations utilizing thermal, microwave, and thermal + microwave heating (hybrid). The microwave heated reactions were carried out in a Sairem 900 W solid state (GMS1000MS) microwave mono-mode reactor system with automatic 4-stub tuning and PID control. The temperature of the catalyst was monitored by a pyrometer with an optical wavelength of 1.8 and a spot size of 3mm when focused on the catalyst bed. A FLIR A6260 short wave IR camera with an InGaAs detector, 25mm lens and a ND1 filter was used as the primary determination of temperature for all reactions. A mono-mode high temperature cavity was used and is depicted in Figure 2.2. The thermally heated reactions were carried out in a conventional tubular furnace with a heated length of 6 inches and PID control. Thermal pre-heating was performed by passing hot air through concentric tubes, as seen in Figure 2.4, at a flow rate high enough to maintain the temperature of the catalyst bed at 410°C without microwave irradiation. In thermal pre-heating, the microwave was only used to raise and maintain the temperature to 475°C. For all the experiments a micromeritics PID engineers gas blending box was used to control the gas flow to the system. A UHP 30% ethane mix was used in the experiment and was flowed a rate of 100mL/min. 1.5% ethane was flowed during the heating phase of each reaction for all reactor setups to allow microwave hotspot formation before the start of the reaction. 0.75g of 6%Mo/ZSM-5 pressed and sieved to 35/45 mesh was loaded for each method of testing and the temperatures of the reaction were varied for each method. All reaction products were analyzed by an online Inficon Fusion 4-column micro-GC with the reactor exit gas lines heat traced to 150°C.
Figure 2.4: Thermally pre-heated catalyst bed (a) schematic of concentric tubes and gas flows paths, and (b) image of the thermally heated setup.

2.1.5 Catalyst Performance Under Microwave Irradiation for the Methane DHA Reaction

The catalytic reaction of methane dehydroaromatization was evaluated at 450°C and 600°C (bulk catalyst temperature) in Sairem 3kW 2.45GHz magnetron microwave reactor complete with a 4-stub automatic tuner and sliding short. The only heat supplied to the reaction was from the microwave heating of the catalyst. The bulk catalyst temperature was measured by short wave IR pyrometer. The reaction temperature was maintained by controlling the forward microwave power. The quartz tube with the catalyst, penetrated through the H-field plane of the waveguide in a vertical fixed bed setup. 0.4800g of pelletized 4%Mo/ZSM-5 was loaded into the center of the quartz tube and held in place by quartz wool. The catalyst was pre-reduced at 550°C for one-hour in a 10%H2–90%N2 environment in a tubular furnace. The reaction was carried out in an atmosphere of 36% CH4 balanced in N2 at 50mL/min. All reaction products were analyzed by an online Inficon Fusion 4-column micro-GC with the reactor exit gas lines heat traced to 150°C.
2.1.6 Microwave Induced Methane Plasma Process for the High Conversion of Methane

The process of methane conversion to C$_2$+ products was tested in a dual reactor zone setup as seen in Figure 2.5. A 3kW 2.45GHz magnetron microwave reactor complete with a 4-stub automatic tuner and sliding short by Sairem was used to initiate and maintain the methane plasma. A single quartz reactor tube with an internal diameter of 8mm was fed through the microwave zone and a tubular furnace. 0.50g of 4%Mo/ZSM-5 was placed inside the heated zone of the tubular furnace supported by quartz wool. The 4%Mo/ZSM-5 catalyst was then heated to 400$^\circ$C at a rate of 10$^\circ$C/min. A 2%CH$_4$ in argon mixture was fed to the reactor system at a rate of 75mL/min at atmospheric pressure. The gas mixture was flowed for 54 mins without the ignition of methane plasma. After 54 mins, the microwave was set to 1000-W and the plasma was ignited by a static discharge device. The power required to maintain the plasma was manually controlled. The gas products form the plasma zone was flowed across the catalyst in the tubular furnace where aromatization of ethylene and acetylene is thermodynamically possible. The temperature of 400$^\circ$C in the tubular furnace was chosen so that ethylene and acetylene could be aromatized efficiently with little coke formation. All reaction products were analyzed by an online Inficon Fusion 4-column micro-GC with the reactor exit gas lines heat traced to 150$^\circ$C.

![Figure 2.5: Reactor setup for the microwave induced methane plasma process.](image)
2.1.7 Reactor Setup and Conditions for MW-Enhanced Catalytic Conversion of Ethane to Aromatics with CO₂

Oxidative ethane dehydroaromatization with CO₂ as an oxidant was carried out over a 4%Mo/ZSM-5 catalyst. A Sairem 3kW 2.45GHz magnetron microwave reactor complete with a 4-stub automatic tuner and sliding short as well as a thermally heated fixed bed reactor was used to facilitate the reactions. The feedstock consisted of a constant C₂H₆:CO₂ ratio of 3:1 with a WHSV of 6000 and at atmospheric pressure. The reaction temperature was raised and then held at each temperature for 30mins for product analysis. All reaction products were analyzed by an online Inficon Fusion 4-column micro-GC.

2.1.8 Reactor Setup and Conditions for Microwave-Assisted Methanol Production.

Methanol production was performed in Sairem 3kW 2.45GHz magnetron microwave reactor complete with a 4-stub automatic tuner and sliding short. Figure 2.6a shows the reactor set up for the synthesis of methanol by the direct processing of CO₂ and hydrogen. 0.6g of the methanol synthesis catalyst (CuZnZr) was loaded into a high-pressure quartz reactor tube held in place by quartz wool. The reactor tube was then loaded into the microwave reactor where the temperature would be measured by a short-wave IR pyrometer. 22.5% CO₂, 67.5% hydrogen and 10% N₂ was fed to the reactor setup. The pressure in the reactor was maintained at 82psi. The temperature was first raised to 3 different temperatures of 160°C, 100°C, and 260°C. The concentrations of methanol were tracked by a 4-column micro-GC. Figure 2.6a shows the reactor setup for the synthesis of methanol from co-processing of ethane and CO₂. For the co-processing of ethane and CO₂, two reactors will be used as seen in Figure 2.6b. 0.5g of 4%Mo/ZSM-5 was loaded into the high-pressure quartz tube along with the methanol synthesis catalyst. The thermally heated DHA reactor was brought to a temperature of 600°C under a gas flow mixture of 22.5% CO₂, 67.5% ethane and 10% N₂. The pressure in the system was 82-psi and the and the methanol catalyst was maintained at 200°C by the microwave reactor. All reaction products were analyzed by an online Inficon Fusion 4-column micro-GC with the reactor exit gas lines heat traced to 150°C.
2.1.9 Reactor Setup and Conditions for Microwave-Assisted Oxidative Ethane Dehydrogenation

Oxidative-CO$_2$ dehydrogenation of ethane was carried out in a Sairem 3kW 2.45GHz magnetron microwave reactor complete with a 4-stub automatic tuner and sliding short. 1.5g of 4%Mo/Al catalyst was loaded into a high-pressure quartz reactor tube held in place by quartz wool. The catalyst was heated to low temperature of 275°C where the temperature of the catalyst was measured by a short-wave IR pyrometer. 10% ethane and 50% CO$_2$ in N$_2$ was then passed over the catalyst at a 6000 GHSV. All reaction products were analyzed by an online Inficon Fusion 4-column micro-GC with the reactor exit gas lines heat traced to 150°C.
2.2 Catalyst Preparation

The zeolite catalyst support ZSM-5 was purchased from Zeolyst, Inc with a silica/alumina ratio of 23 in the ammonium form (NH₄-ZSM-5). The zeolite was first calcined at 550°C for ten hours in air to convert the zeolite from the ammonium form to its protonated form (H/ZSM-5). Gamma-aluminum oxide support was purchased form Sigma-Aldrich, no pre-treatment was performed before metal impregnation. The metal precursors of Ammonium heptamolybdate tetrahydrate, zinc nitrate hexahydrate, iron (II) chloride, and gallium nitrate hydrate were purchased from Acrons Organics. All catalysts were prepared by conventional incipient wetness co-impregnation. The catalysts were then dried at 105°C for five hours, the dried powders were then calcined in air at 550°C for four hours. The chemical compositions of the synthesized catalyst are show in Table 2.1.

Table 2.1: Catalyst compositions used for natural gas conversion to value-added chemicals.

<table>
<thead>
<tr>
<th>Catalytic Investigations</th>
<th>Loading (weight %)</th>
<th>ICP (weight %)</th>
<th>Support</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mo</td>
<td>Fe</td>
<td>Zn</td>
</tr>
<tr>
<td>Promoter Stability [Ch.3]</td>
<td>4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>MW vs Thermal [Ch.4]</td>
<td>3.5</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>MW Regeneration [Ch.5]</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MW aromatic selectivity improvements [Ch.6]</td>
<td>6</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Supporting Projects Catalyst

<table>
<thead>
<tr>
<th>Supporting Projects Catalyst</th>
<th>Loading</th>
<th>ICP</th>
<th>Support</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW CH₄ DHA [Ch.7.1]</td>
<td>4%Mo</td>
<td></td>
<td>H/ZSM-5¹</td>
</tr>
<tr>
<td>MW + Plasma CH₄ DHA [Ch 7.2]</td>
<td>4%Mo</td>
<td>ICP</td>
<td>H/ZSM-5¹</td>
</tr>
<tr>
<td>MW Ethane + CO₂ to aromatics [Ch7.3]</td>
<td>4%Mo</td>
<td>Not</td>
<td>H/ZSM-5¹</td>
</tr>
<tr>
<td>MW Ethane + CO₂ to ethylene [Ch. 7.5]</td>
<td>4%Ga</td>
<td>Performed</td>
<td>Ga-AlOx</td>
</tr>
<tr>
<td>MW Ethane + CO₂ methanol [Ch.7.4]</td>
<td>4%Mo and (CuZnZr)</td>
<td></td>
<td>H/ZSM-5¹</td>
</tr>
</tbody>
</table>

¹-Zeolite H/ZSM-5 of Silica to alumina ratio (SAR) of 23
2.3 Product Analysis

2.3.1 Agilent 3000A Micro-GC

The Agilent 3000A four-channel micro-GC was configured according to Table 2.2. The GC was calibrated with external standard mixed component gas cylinders purchased from Airgas. The micro-GC allowed for the analysis of hydrogen, nitrogen, methane, ethane, ethylene, benzene, and toluene. Xylene was not traced, and naphthalene was separated out of the analysis stream.

Table 2.2: List of Agilent 3000A micro-GC column configuration

<table>
<thead>
<tr>
<th>Channel</th>
<th>Injector</th>
<th>Analytical Column</th>
<th>Pre-Column</th>
<th>Carrier Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Backflush</td>
<td>Molsieve-[10m]</td>
<td>Plot-U-[3m]</td>
<td>Argon</td>
</tr>
<tr>
<td>B</td>
<td>Backflush</td>
<td>PLOT-U-[8m]</td>
<td>PLOT-Q-[1m]</td>
<td>Helium</td>
</tr>
<tr>
<td>C</td>
<td>Backflush</td>
<td>Aluminum-[10m]</td>
<td>Aluminum-[1m]</td>
<td>Helium</td>
</tr>
<tr>
<td>D</td>
<td>Variable Volume</td>
<td>OV-1-[10m]</td>
<td></td>
<td>Helium</td>
</tr>
</tbody>
</table>

2.3.2 Inficon Fusion Micro-GC

The Inficon Fusion micro-GC four-channel micro-GC was configured according to Table 2.3. The GC was calibrated with external standard mixed component gas cylinders purchased from Airgas. The micro-GC allowed for the analysis of hydrogen, nitrogen, methane, ethane, ethylene, benzene, and toluene. Xylene was not traced, and naphthalene was separated out of the analysis stream. For methanol analysis the micro-GC configured column are listed in Table 2.4.

Table 2.3: List of Inficon Fusion micro-GC column configuration

<table>
<thead>
<tr>
<th>Channel</th>
<th>Injector</th>
<th>Analytical Column</th>
<th>Pre-Column</th>
<th>Carrier Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Backflush</td>
<td>Molsieve-[10m]</td>
<td>Plot-U-[3m]</td>
<td>Argon</td>
</tr>
<tr>
<td>B</td>
<td>Backflush</td>
<td>PLOT-U-[8m]</td>
<td>PLOT-Q-[1m]</td>
<td>Helium</td>
</tr>
<tr>
<td>C</td>
<td>Backflush</td>
<td>Aluminum-[10m]</td>
<td>Aluminum-[1m]</td>
<td>Helium</td>
</tr>
<tr>
<td>D</td>
<td>Variable Volume</td>
<td>Rxi-1ms-[20m]</td>
<td></td>
<td>Helium</td>
</tr>
</tbody>
</table>
Table 2.4: List of Inficon Fusion micro-GC column configuration use for methanol analysis.

<table>
<thead>
<tr>
<th>Channel</th>
<th>Injector</th>
<th>Analytical Column</th>
<th>Pre-Column</th>
<th>Carrier Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Backflush</td>
<td>Molsieve-[10m]</td>
<td>Plot-U-[3m]</td>
<td>Argon</td>
</tr>
<tr>
<td>B</td>
<td>Backflush</td>
<td>PLOT-U-[8m]</td>
<td>PLOT-Q-[1m]</td>
<td>Helium</td>
</tr>
<tr>
<td>C</td>
<td>Variable Volume</td>
<td>Stabilwax-[10m]</td>
<td></td>
<td>Helium</td>
</tr>
<tr>
<td>D</td>
<td>Variable Volume</td>
<td>Rxi-1ms-[20m]</td>
<td></td>
<td>Helium</td>
</tr>
</tbody>
</table>

2.3.3 Prima BT Mass Spectrometer.

Thermo Scientific Prima BT laboratory bench-top gas analysis mass spectrometer was used of the online gas analysis in the CO₂ temperature ramp regeneration experiment. The mass spectrometer was configured with a scanning laminated electromagnet with a mass range of 1-150 amu. The faraday detector was used with the mass spectrometer set to run in ion scanning mode. The ions that were tracked consisted of helium-4, carbon monoxide-28, oxygen-32, and carbon dioxide-44.

2.4. Product Analysis Calculations.

The ethane conversion, flow rate, product selectivity, and product production rate are defined in equations 1-4, respectively and used for all gas chromatograph product analysis.

\[
\text{conversion} \, (\%) = \frac{\text{ethane fed (sccm)} - \left[ \frac{\text{ethane (mol\%)}}{100} \times \frac{\text{Inert fed (sccm)}}{\text{Inert (mol\%)}} \times 100 \right]}{\text{ethane fed (SCCM)}} \times 100
\]

\[
\text{product flow rate (mol/min)} = \frac{\text{product (mol\%)} \times \frac{\text{Inert fed (sccm)}}{\text{Inert (mol\%)}} \times [1000 \times 0.08206(25 + 273)]}{100}
\]

\[
\text{product selectivity} \, (\%) = \frac{\text{product (mol\%)} \times \text{product carbon #}}{\left[ \text{component fed (mol \%)} - \text{component out (mol \%)} \right] \times \text{component carbon #}} \times 100
\]

\[
\text{production Rate} \left( \frac{\text{g Product}}{\text{g catalyst} \times \text{hour}} \right) = \frac{\text{product flow rate (mol/min)} \times \text{product molecular weight (g/mol)} \times 60 \text{ min/hour}}{\text{grams catalyst}}
\]
2.5 Catalyst Characterization
2.5.1 Powder X-ray Diffraction (XRD)

The XRD patterns of the powdered samples were captured using a PANalytical X’Pert Pro set to 45kV and 40mA. Samples were scanned from 5° up to 80° (2θ) using Cu Kα radiation.

**Applications:**

- XRD of the Mo, MoFe, MoZn, MoFeZn loaded on H/ZSM-5 before and after five reaction and regeneration cycles.
- XRD of the fresh and spent MoFe/ZSM-5 used the MWFB vs CTFB study.
- XRD of the 10%Mo/ZSM-5, fresh, thermal spent, MW CO₂ regenerated, and MW CO₂ regenerated spent catalyst.
- XRD of fresh and spent 6%Mo/ZSM-5 catalyst used in the systems approach to increase aromatic selectivity and catalyst bed utilization.

2.5.2 Surface Area Measurement

Surface area measurements were carried out using a Micromeritics ASAP 2020+. The samples were degassed for ten hours at 300°C under vacuum. Nitrogen was used as an absorption gas to calculate the Brunauer-Emmett-Teller (BET) model, and the t-plot method for micropore volumes, external surface area and micropore area.

**Applications:**

- BET of fresh Mo, MoFe, MoZn, MoFeZn loaded on H/ZSM-5.
- BET of fresh MoFe/ZSM-5 used in the MWFB vs CTFB study.

2.5.3 Ammonia Temperature-Programmed-Desorption

Ammonia temperature programmed desorption (NH₃-TPD) experiments were carried out using a Micromeritics Autochem 2950 equipped with a thermal conductivity detector. The samples were heated to 300 °C at 5 °C/min for 60min under an inert flow of He to remove moisture and then allowed to cool to 150 °C. The catalyst was then dosed with 15 % ammonia for 30 min at 30 mL/min. A baseline was determined by flowing helium over the sample for 30 min at 30 mL/min.
to remove weekly bounded ammonia from the catalyst surface. The samples were then heated to 700 °C at 5 °C/min in 30 mL/min He.

**Applications:**
- NH3-TPD of the fresh Mo, MoFe, MoZn, MoFeZn loaded on H/ZSM-5.
- NH3-TPD of the fresh MoFe/ZSM-5 used in the MWFB vs CTFB study.

### 2.5.4 Transmission Electron Microscope with Energy Dispersive X-ray Spectroscopy (TEM-EDS)

Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100. The energy-dispersive spectroscopy (EDS) was obtained with an Oxford EDS. The samples were taken from the center of the catalyst bed in both the microwave and the conventional fixed bed. The samples were prepared by sonication in acetone for 15min. The sample was then loaded via a glass dropper onto a formvar coated copper grid. The sample was dried suspended in air for one hour then placed in a grid storage container.

**Applications:**
- TEM of the Mo, MoFe, MoZn, MoFeZn loaded on H/ZSM-5 before and after five reaction and regeneration cycles.
- TEM of the fresh and spent MoFe/ZSM-5 used the MWFB vs CTFB study.
- TEM of the 10%Mo/ZSM-5, fresh, thermal spent, MW CO₂ regenerated, and MW CO₂ regenerated spent catalyst.
- TEM of fresh and spent 6%Mo/ZSM-5 catalyst used in the systems approach to increase aromatic selectivity and catalyst bed utilization.

### 2.5.5 Temperature Programmed Oxidation (TPO)

TPO was performed on a Micromeritics Autochem 2950 HP equipped with a thermal conductivity detector was used to determine the TPO profile. 0.2000g of coked catalyst was loaded into the tubular reactor supported by quartz wool. The coked catalyst was first heated to 300 °C with a ramp rate of 5 °C/ min in a flow of N₂ at 30 mL/min for two hours to remove moisture. The sample was cooled to ambient temperature where it was then heated in the presence of 10 % oxygen or 10%CO₂ at a ramp rate of 5 °C/min 700 °C.
Applications:

- TPO of the Mo, MoFe, MoZn, MoFeZn loaded on H/ZSM-5 after five reaction and regeneration cycles.
- TPO of the spent MoFe/ZSM-5 used the MWFB vs CTFB study.
- TPO-CO$_2$ of the 10%Mo/ZSM-5, fresh, carb, thermal spent, MW CO$_2$ regenerated catalyst

2.5.6 Temperature Programmed Reduction (TPR)

TPR was carried out in a Micromeritics AutoChem 2950 equipped with a thermal conductivity detector. The samples were heated to 300 °C at 10 °C/min for 60 min under an inert flow of He to remove moisture and then cooled to 100 °C. Premixed 10% hydrogen in argon was then flowed for 20 min over the catalyst for 25 mL/min to achieve a baseline. Once a baseline was achieved, the samples were heated to 900 °C at 5 °C/min.

Applications:

- TPR of the Mo, MoFe, MoZn, MoFeZn loaded on H/ZSM-5 before and after five reaction and regeneration cycles.
- TPR of the 10%Mo/ZSM-5, fresh, carb, thermal spent, MW CO$_2$ regenerated catalyst

2.5.7 Thermogravimetric Analysis (TGA)

TGA of the coked catalyst was carried out using a TA Instruments SDT 650. Two methods were used for coke determination. The first: The 90-μL sample cups were tared and then the sample was loaded into cups and placed into the balance and allowed to purge with N$_2$ for 1h. The sample was then heated to 300 °C at 5 °C/min and held for 120 min under inert flow of N$_2$ to dry the sample. The sample was cooled to 150 °C and allowed to equilibrate. The gas flow was switched to 10 % O$_2$ and after 60 min the temperature was ramped at 5 °C/min to 700 °C and held for 60 mins. The second method used HiRes-dynamic resolution technique. The 90-μL sample cups were tared and then the sample was loaded into cups and placed into the balance. The samples were ramped at a max of 20°C/min in air with a hi-res factor of 6 and a sensitivity of 1.

Applications:

- TGA of the Mo, MoFe, MoZn, MoFeZn loaded on H/ZSM-5 before and after five reaction and regeneration cycles.
• TGA of the fresh and spent MoFe/ZSM-5 used the MWFB vs CTFB study.
• TGA of the 10%Mo/ZSM-5, fresh, thermal spent, MW CO₂ regenerated, and MW CO₂ regenerated spent catalyst.
• TGA of fresh and spent 6%Mo/ZSM-5 catalyst used in the systems approach to increase aromatic selectivity and catalyst bed utilization.

2.5.8 Inductively Coupled Plasma Optical Spectroscopy (ICP-OES)

All trace metals were analyzed using ICP–OES on an Optima 7300 DV (PerkinElmer, Waltham, MA, U.S.A.), which is a dual-view spectrometer with solid-state segmented-array charge coupled device (SCD) detectors. Calibration standards were purchased from Inorganic Ventures (Christiansburg, VA, U.S.A.) and are traceable to National Institute of Standards and Technology (NIST) standard reference materials. Fe, Mo, and Zn were measured after digestion in aqua regia acid. A total of 12 mg of each sample was digested in 12 mL of aqua regia (9 mL of HCl and 3 mL of HNO₃) acid and then further diluted 100-fold using a mixture of high-purity 2% nitric acid prior to analysis.

Applications:
• ICP of the Mo, MoFe, MoZn, MoFeZn loaded on H/ZSM-5 before and after five reaction and regeneration cycles.
• ICP of the fresh MoFe/ZSM-5 used the MWFB vs CTFB study.
• ICP of the fresh 10%Mo/ZSM-5 used in the MW CO₂ regenerated study.
• ICP of fresh and spent 6%Mo/ZSM-5 catalyst used in the systems approach to increase aromatic selectivity and catalyst bed utilization.

2.5.9: XPS Spectroscopy

Physical electronic PHI 5000 VersaProbe XPS instrument was used for obtaining survey and detailed scans for the C-1s and the Mo-3d spectra. Peak analysis and fitting were performed using OriginLabs Gaussian peak fitting function.

Applications:
• XPS of the fresh, carb, spent, and regenerated 10%Mo/ZSM-5 and 2.5% Mo/ZSM-5 catalyst used in the MW CO₂ regenerated study.
Chapter 3: Stability of Fe- and Zn-Promoted Mo/ZSM-5 Catalysts for Ethane Dehydroaromatization in Cyclic Operation Mode

For the direct conversion of ethane to reach commercialization, improvements need to be made in terms of product selectivity and catalyst lifetime. As stated in chapter 1, the National Academies of Sciences Engineering Medicine stated that the way to commercialization for the direct conversion of natural gas to value-added chemicals, is by the identification of ways to manage carbon flow. Preferentially carbon needs to be placed in the products rather than in coke. Increased understanding and new approaches for solving this issue would increase reaction productivity, reduce energy use, and extend catalyst lifetime [1]. Therefore, the objective of this study is to elucidate the effects that metal promoters have on the catalysts deactivation mechanisms and explore the effects of short reaction and regeneration cycling to explore the effects of catalyst lifetime and productivity for practiced in petroleum refineries as stated in Figure 3.1.

Figure 3.1: The major research objective for chapter 1 for the conversion of natural gas to value-added chemical.

In this study Mo/ZSM-5 was used as the base catalyst and the effects of Fe and/or Zn metal loadings were tested to determine their effects on reaction mechanism and catalyst stability. The catalyst was thermally heated in a fixed bed reactor and 36% ethane was flowed for a short time of 21 minutes. After the reaction, the catalyst was then regenerated for 90 minutes in 2% oxygen. This process was cycled five times and the reaction products were monitored. Figure 3.2 summarizes graphically the results and depicts the method of cyclic regeneration. The reactor setup and reaction conditions are discussed in Chapter 2, section 2.1.1 and the catalyst metal loadings are shown in Table 2.1.
Figure 3.2: Graphical explanation of the methodology and summary of the results.

3.1 Catalyst Characterization

As illustrated in Figure 3.3, the XRD patterns of the freshly prepared catalysts are compared to the regenerated catalyst. Considering the diffraction angles of 22–25°, almost no changes were observed in the fresh catalyst diffraction pattern compared to the regenerated catalyst, indicating that the ZSM5 structure retained its crystallinity throughout the reaction and regeneration cycles. Furthermore, metal oxide peaks corresponding to Mo, Fe, or Zn could not be observed, indicating that the metal loadings were homogeneously dispersed, and their particle sizes were small below the XRD detection limits [67].
Figure 3.3: XRD patterns of fresh and spent catalysts after five cycles.

The nitrogen adsorption and desorption plot are shown in Figure 3.4 for the fresh catalysts. The plot of H/ZSM-5 and all four-metal loaded ZSM-5 catalysts represent a type II isotherm. The large hysteresis loop observed in the range of \( P/P_0 = 0.40 - 1.0 \) indicates that the catalyst has a mesoporous structure, where nitrogen condenses on the external surfaces of the crystallites and on the spaces in between.

A summary of the surface area and micropore analysis is shown in Table 3.1. The addition of Mo to the unprompted zeolite resulted in a decrease in the total surface area, including the micropore area and the external surface area of the catalyst. As the total weight percent of the loaded metals increased, the surface area of catalysts decreased. The addition of Fe to Mo/ZSM-5 resulted in a further decrease in the external surface area. However, their micropore area did not change compared to Mo/ZSM-5, suggesting that the Fe metal particles did not diffuse into the micropore structure of the zeolite. The addition of Zn to the Mo/ZSM-5 catalyst showed similar effects compared to Fe on the micropore area and external surface area. This suggests that Zn occupies the external acid sites on the ZSM-5 structure with little to no diffusion into the pores of the ZSM-
For the MoFeZn/ZSM-5 catalyst, there was a total decrease in both the micropore area and external surface area compared to pure H/ZSM-5.

Figure S3.13 of the Supporting Information represents NH$_3$- TPD profiles of H/ZSM-5 and all four fresh catalysts. Pure H/ZSM-5 exhibits two NH$_3$ desorption peaks at 223 and 427 °C, representing weak acid sites (mostly Lewis acid) and strong acid sites (mostly Brønsted acid), respectively. The presence of Mo particles anchored to the Brønsted acid sites on the external surface and inside the pores is evident from the decrease of the higher temperature peak shown in Figure S3.13 of the Supporting Information and confirmed by the BET analysis above [68,69]. The addition of Fe and Zn to Mo/ZSM-5 did not cause a further decrease in the Brønsted acid strength. Based on the temperature shift and changes in peak shape, Figure S1 the addition of Mo, Fe, and Zn has less impact on Lewis acid sites compared to Brønsted acid sites.

![Figure 3.4: Nitrogen absorption-desorption isotherms for the fresh catalyst.](image)
Table 3.1: Surface area and micropore results of the fresh catalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>total surface area (m²/g)</th>
<th>micropore area (m²/g)</th>
<th>external area (m²/g)</th>
<th>pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM-5</td>
<td>352</td>
<td>250</td>
<td>102</td>
<td>0.12</td>
</tr>
<tr>
<td>Mo</td>
<td>298</td>
<td>228</td>
<td>70</td>
<td>0.11</td>
</tr>
<tr>
<td>MoFe</td>
<td>294</td>
<td>228</td>
<td>66</td>
<td>0.11</td>
</tr>
<tr>
<td>MoZn</td>
<td>295</td>
<td>228</td>
<td>67</td>
<td>0.11</td>
</tr>
<tr>
<td>MoFeZn</td>
<td>292</td>
<td>227</td>
<td>66</td>
<td>0.11</td>
</tr>
</tbody>
</table>

*aCalculated using the BET method. bCalculated using the t-plot method.

3.2 Catalyst Performance in Ethane Dehydroaromatization.

Figure 3.5 depicts the conversion and selectivity of each catalyst toward ethane dehydroaromatization. The second cycle was chosen as a basis for comparison throughout this study as a result of the presence of the induction period in the fresh catalyst, making it very difficult to compare the activity in the first cycle. The promoting effect of metals on ZSM-5 was ranked on the basis of ethane conversion. The ethane conversion level for the second cycle (Figure 3.5a) was found in the order of MoFe > Mo > MoFeZn > MoZn, whereas for the fifth cycle (Figure 3.5b), the conversion level followed the order of Mo > MoZn ≈ MoFeZn > MoFe. The aromatic selectivity of these catalysts with respect to regeneration cycles is shown in Figure 3.5c. Although the selectivity of the MoFe catalyst to aromatics was relatively lower than others, it showed stable aromatic selectivity with little to no decrease in the average selectivity from the second to fourth reaction cycle and even a slight increase on the fifth cycle. The MoZn catalyst showed a slight increase in the overall average aromatic selectivity from the first to third reaction cycle. However, a decrease was observed from the third to fifth reaction cycle. The MoFeZn catalyst exhibited a trend similar to the MoZn catalyst; however, the slope of the deactivation of aromatic selectivity was less severe from the third to fifth cycle. This suggest that Fe had a stabilizing effect on the MoFeZn catalyst as it did in the MoFe catalyst. It was reported in the literature that the presence of Zn can promote selectivity to aromatics in ethane aromatization as a result of the type of Zn sites formed [43,45]. The increase in selectivity to aromatics on MoZn and MoFeZn catalysts over the first to third cycles could be due to the formation of zinc hydroxyl species. However, after the third reaction cycle, a decline in aromatic selectivity was observed possibly as a result of the loss of the Zn species [44]. Meanwhile, the presence of Zn causes the loss of Mo, which will be
discussed later in this paper. Table 3.2 showed the ICP analysis of spent catalysts after five reaction/regeneration cycles; the Zn content decreased by nearly 50%. This could be explained by the loss of the volatile unbound ZnO species, thus leaving the more stable and active \([\text{Zn(OH)}]^+\) species bound to the acid sites of the zeolite surface [45].

**Table 3.2:** Catalyst Composition Analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP–OES)

<table>
<thead>
<tr>
<th>catalyst</th>
<th>fresh</th>
<th>spent</th>
<th>change</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mo</td>
<td>Fe</td>
<td>Zn</td>
</tr>
<tr>
<td>Mo</td>
<td>3.26</td>
<td>0.43</td>
<td>0.46</td>
</tr>
<tr>
<td>MoFe</td>
<td>3.39</td>
<td>0.43</td>
<td>0.44</td>
</tr>
<tr>
<td>MoZn</td>
<td>3.44</td>
<td>0.43</td>
<td>0.44</td>
</tr>
<tr>
<td>MoFeZn</td>
<td>3.36</td>
<td>0.45</td>
<td>0.44</td>
</tr>
</tbody>
</table>

“Spent catalyst = regenerated fifth cycle catalyst.

Figure 3.6 shows the benzene concentration as a function of time-on-stream (TOS) for all the catalysts studied. Overall, the Mo/ZSM-5 catalyst showed the highest benzene concentration, followed by MoFe, MoFeZn, and MoZn catalysts. To study the commercial viability of cyclic regeneration, for each catalyst, the extent of deactivation between each regeneration cycle was analyzed. Ideally, a stable catalyst should exhibit the characteristics that the time-on-stream benzene concentration in all five cycles falls on the same line. This indicates that the catalyst is regenerable and can be used repeatedly. In contrast, if a divergence of the benzene concentration between cycles is observed, that is an indication of either irreversible deactivation or an inefficient regeneration process. Understanding the cause of the “divergence” between cycles is thus important in developing a commercially viable catalyst and regeneration process. The numerical data in Figure 3.6 are quantitatively broken down to give the percent change in the benzene concentration from cycle to cycle for each catalyst and then an overall change from the second to fifth reaction cycle. Results are summarized in Table S3.4 of the Supporting Information where it is shown that the MoFe catalyst exhibits little to no decrease in the benzene concentration from cycle to cycle. The other three catalysts suffer from the loss of activity and irreversibility between cycles, with the Mo catalyst being the most significant. Similarly, MoFe exhibits the same behavior toward the toluene formation during these 5 reaction cycles (Figure S3.14 of the Supporting Information). The variation in the toluene concentration was the minimum among other catalysts.
studied during these five reaction cycles, yet they still show some toluene loss from cycle to cycle. This could be attributed to the buildup of coke on the interior surface of the pores, resulting in a decrease in the diameter of the pore. Furthermore, the decrease in the pore diameter could lead to the toluene disproportionation reaction to form benzene and xylene \[70\]. This may be an explanation that, for the MoFe catalyst, little to no decrease in the benzene concentration was observed between cycles, whereas a slight decrease in the toluene concentration continued. Figure 3.7 depicts the distribution of total aromatic yields of all four catalysts. The total aromatic (benzene and toluene) yield follows the order of Mo > MoFeZn > MoFe > MoZn supported on ZSM-5. For each catalyst, starting from the second cycle, a trend of decrease in the total aromatic yield is observed on Mo, MoZn, and MoFeZn catalysts. However, the MoFe catalyst shows no decrease in the benzene yield but a slight decrease in the total aromatic yield as a result of the toluene disproportionation reaction. Illustrated in Figure S3.15 of the Supporting Information is the comparison of the hydrogen production rates between all catalysts studied. The initial activity of hydrogen production rates is in the following order: MoFeZn > Mo ≈ MoFe > MoZn, where Mo and MoFe catalysts exhibited comparable hydrogen production rates and the MoZn catalyst was the lowest. MoFeZn showed the highest initial production rate, probably attributed to the higher metal loading. The MoFe catalyst shows the least amount of reduction in the hydrogen concentration per cycle (Table S3.6 of the Supporting Information). The result is consistent with the time-on-stream changes of benzene and toluene concentrations, as illustrated in Figure 3.6 and Figure S3.14 of the Supporting Information. Figure S3.16 of the Supporting Information depicts the time-on-steam methane formation rate for all catalysts studied. The activity of methane formation is in the order of MoFeZn > Mo ≈ MoFe > MoZn supported on H/ZSM-5. The changes in the methane concentration between cycles are summarized in Table S3.7 of the Supporting Information. From the second to fifth cycle, Mo and MoFeZn exhibited comparable changes in the methane formation rate, whereas the MoFe catalyst resulted in little to no change in the methane concentration. The result is consistent with the findings from the concentration changes for benzene, toluene, and hydrogen shown in Figure 3.4 and Figures S3.14 and Figure S3.15 of the Supporting Information.
Figure 3.5: Ethane conversion and average aromatic selectivity for each reaction cycle.
Figure 3.6: Comparison of time-on-stream between benzene concentrations for five reaction cycles.
Figure 3.7: Comparison of the total aromatic yields per reaction cycle in mole percent of benzene and toluene.

3.3. Mechanistic Study of Catalyst Deactivation and Regeneration

To elucidate the catalyst deactivation mechanism and the effectiveness of regeneration, TEM/EDS analysis was carried out. The TEM images of all four catalysts are shown in Figures 3.8−3.10. Figure 3.8a shows TEM of the spent Mo catalyst after five reaction cycles. Agglomeration of Mo particles was observed, as confirmed using EDS analysis (spot 1). The spent MoFe catalyst is shown in Figure 3.8b along with the EDS analysis for spots 1 and 2. The formation of CNTs was observed. Spot 1 contains a high concentration of carbon along with agglomerated metal particles that have a Fe/Mo atomic ratio of 12.65. Spot 1 does not show any support structure (Si and Al), indicating that the metal agglomerates have leached out the surface of the catalyst during the reaction. Spot 2 also contains a large amount of carbon; however, the agglomerated particle shows a Fe/Mo ratio of 1.2 and is located on the surface of the zeolite. This would suggest that, at a larger Fe/Mo ratio, the agglomerated MoFe particles tend to leave the surface of the catalyst. In addition, both tip-growth and base-grown CNTs can be observed in TEM analysis. The TEM images of the spent MoZn catalyst are shown in panels a and b of Figure 3.9. Spot 1 contains a large atomic
percentage of Mo and Zn, with a Zn/Mo atomic ratio of 1.78, located on a support structure with some carbon deposited. On spot 2, the presence Mo and Zn are not observed, indicating that the metal particles are not located in this area or that the density of metal particles is too small as a result of the even dispersion. Spot 3 contains a high concentration of Mo and Zn, with a Zn/Mo atomic ratio of 0.97. On spot 4, Zn or Mo is not found, suggesting the uniform dispersion in that area or the migration of metals to the spot 3 area. The TEM image of the spent MoFeZn catalyst is shown in panels a and b of Figure 3.10. On spot 1, the TEM image shows agglomerated Mo and Fe particles that are not located on the zeolite support. On spot 1, the Fe/Mo atomic ratio is 1.63. This is representative of tip-growth CNT, where the Mo–Fe agglomerates pushed out to leave the surface of the zeolite support. Spot 2 contains agglomerated Fe and Mo, with a much lower Fe/Mo ratio of 0.47. Spot 3 is another spot where a lower Fe/Mo ratio of 0.40 is observed. The lower atomic ratios could be explained by Masiero et al. [71], where Fe interacted structurally with Mo to form a new binary phase of Fe$_2$(MoO$_4$)$_3$. In calculating the atomic ratio of Fe and Mo in Fe$_2$(MoO$_4$)$_3$, we find a Fe/Mo atomic ratio of about 0.41. Furthermore, the Fe/Mo ratio in Fe$_2$(MoO$_4$)$_3$ coincides with what was found in the EDS analysis on spots 2 and 3. It may be possible that Fe$_2$(MoO$_4$)$_3$ is formed on the MoFeZn catalyst. It appears that, at lower Fe/Mo ratios, the Fe and Mo agglomerates stay attached to the zeolite support structure, whereas at higher Fe/Mo ratios, the excess amounts of Fe allow for agglomerated particles to detach from the surface. ICP results shown in Table 3.1 indicate a small loss in Fe particles in the spent catalysts containing Fe, which suggest that most Fe particles are deposited back onto the surface of the catalyst during regeneration. However, some Fe particles are speculated to be deposited onto the reactor walls. ICP analysis also suggests that the MoFeZn catalyst lost less Mo than the MoZn catalyst, indicating that Fe is a more stable promoter for Mo than Zn. The loss of Zn and Fe particles from the catalyst surface follow different mechanisms. To elaborate, the loss of Zn is due to the presence of the volatile state of zinc oxide [45]. In contrast, the loss of Fe occurs in a more random way, which is mainly due to the formation of tip-growth CNTs extending randomly away from the catalyst surface.
**Figure 3.8:** TEM images of spent catalysts before regeneration: (a) Mo and (b) MoFe and EDS data. a: N/F stands for not found.

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<td>Mo</td>
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**Figure 3.9:** (a) and (b) are both TEM images of the spent MoZn catalyst and EDS analysis. a: N/F stands for not found.

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<th>Spot (2)</th>
<th>Spot (3)</th>
<th>Spot (4)</th>
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<td>N/F⁰</td>
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</table>
Figure 3.10: (a) and (b) are both TEM images of the spent MoFeZn catalyst and EDS analysis. a: N/F stands for not found.

The TPO profiles were only used qualitatively to characterize types of coke formed on the catalyst surfaces during reaction based on the peak shape and burn-off temperatures. Figure 3.11 shows the TPO and TGA profiles of the spent catalysts obtained after the fifth reaction cycle. The peak shape of Mo and MoZn catalysts would suggest the presence of a single temperature burning carbonaceous species with resulting peak temperatures of 445 °C. The twin peak TPO spectra was observed on MoFe and MoFeZn catalysts. The second peak is associated with the presence of higher burning temperature carbon species (516 °C). The TPO analysis suggests that the addition of Fe results in the formation of a higher ordered coke species, e.g., CNTs, as observed from TEM analysis. The TGA profile of the spent Mo and MoZn catalysts results in one continuous negative curvature, whereas for MoFe and MoFeZn catalysts, the TGA curvature has a positive rise in slope at the temperature of the lowest point between the two peaks in the TPO profiles. The TGA results for all four catalysts are summarized in Table 3.3. As shown in Table 3.3, MoFe and MoFeZn catalysts are more selective toward coke formation, which is consistent with literature reports [71–73]. The Mo catalyst showed the highest conversion but still had about 25% less coke than the MoFe catalyst.
Figure 3.11: TPO (solid) and TGA (dotted) profiles of the spent catalyst after 5 reaction cycles.

Table 3.3: TGA results of the spent catalyst obtained at the end of the fifth reaction cycle.

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<th>carbon formation (g g⁻¹ of catalyst min⁻¹)</th>
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Figure 3.12 shows the TPR profiles for the fresh and regenerated catalysts (fifth cycle). For both Mo and MoZn catalysts, a temperature shift of 51 °C (first peak from 473 to 422 °C) is observed between fresh and spent catalysts. However, for the catalysts containing Fe, only a 27 °C shift in the temperature of the first peak is observed, which is evident of the presence of a more stable metal state. For the spent catalyst obtained after five cycles, the peak shape of MoFe is identical to
MoFeZn, whereas the peak shape of Mo is almost identical to MoZn. This is mainly attributed to the loss of Zn over the course of the five cycles, as shown in the ICP analysis; therefore, the impact of Zn on stabilizing Mo gradually diminished as the reaction cycles proceed.

Figure 3.12: TPR profiles of the fresh versus regenerated fifth cycle catalyst.
3.4: Conclusion on Stability of Fe- and Zn-Promoted Mo/ZSM-5 Catalysts for Ethane Dehydroaromatization in Cyclic Operation Mode

The stability of Fe and Zn promoted Mo/ZSM-5 in ethane dehydroaromatization was evaluated over five cycles of reaction and regeneration. All catalysts were found to maintain their zeolite crystalline structure. Mo was determined to be in the pores and on the exterior surface with strong interactions with Brönsted acid sites. On Fe and Zn promoted Mo/ZSM-5 catalysts, Fe and Zn were located mainly on the exterior surface. The Mo containing ZSM-5 catalyst exhibited the highest conversion and aromatic yield, however, the Mo containing catalyst suffered a loss in activity between reaction cycles. The addition of Zn resulted in an increase in aromatic selectivity during early reaction cycles but suffered a decrease in selectivity in the consecutive reaction cycles. The promoting effect of Zn was short lived in the cyclic operation due to the loss of almost 50% of the Zn over the course of the five reaction cycles. The initial increase in selectivity was attributed to the formation of zinc hydroxide species [Zn(OH)]+.

The addition of Fe resulted in great stability in aromatic selectivity, total aromatic yield, and hydrogen formation rate over the course of five reaction cycles. The improved stability was attributed to the formation of CNTs that allowed for improved gas diffusion into the pores. At lower Fe/Mo atomic ratios, the agglomerated particles were found on the surface of the catalyst resulting in the favored base growth CNTs. At higher Fe/Mo ratios, tip-growth CNTs were observed, which was believed to be the cause of the loss of Fe and Mo. MoZn lost more Mo then MoFeZn suggesting that Mo was more stable in the presence of Fe than it was with Zn. Metal particles of lower Fe/Mo atomic ratio would result in even greater stability.

This research provides fundamental insights into that effects that metal promoters have on the catalysts deactivation mechanisms and explore the effects of short reaction and regeneration cycling. The innovation of finding a stable aromatic production catalyst for the cyclic regeneration will lead to the prolonged life span of the catalyst thus preventing the need for costly catalyst bed replenishment.
### 3.5. Supplementary Materials.

**Table S3.4:** The change of benzene concentration between cycles (ppm)

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Table S3.6: The change of hydrogen concentration between cycles (%)

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Table S3.7: The change of ethane concentration between cycles (%)

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<td>-0.05</td>
<td>0.00</td>
<td>0.04</td>
<td>0.03</td>
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</table>
Figure S3.13: Ammonia temperature-programed desorption of the fresh catalysts.
Figure S3.14: Comparison of time-on-stream toluene concentration changes for five reaction cycles
Figure S3.15: Comparison of time-on-stream hydrogen concentration changes for five reaction cycles
Figure S3.16: Comparison of time-on-stream methane concentration changes for five reaction cycles
Chapter 4: Catalytic Direct Conversion of Ethane to Value-Added Chemicals Under Microwave Irradiation

For the direct conversion of ethane to reach commercialization, it is apparent that new technological approaches are needed to facilitate the conversion of ethane to value-added liquid products. The use of microwave irradiation has a promising selective heating nature that could change the classical product distribution of the ethane dehydroaromatization reaction, while cutting energy cost, increasing the reaction productivity, and changing the distribution of coke formation. As stated in chapter 1, the National Academies of Sciences Engineering Medicine stated that the way to commercialization for the direct conversion of natural gas to value-added chemicals is by the approach of adopting new technologies, increasing reaction productivity and by the identification of ways to manage carbon flow [1]. The objective of Chapter 4.1 is to elucidate the thermal effects (selective heating) of microwave irradiation that could result in mechanistic differences in product formation, reaction productivity, and factors causing catalyst deactivation for the conversion of ethane to value-added chemical.

**Non-oxidative Ethane Conversion by Microwave Heating**

“Microwave heating was used to determine the effects on reaction productivity, energy input, carbon distribution in the product stream, and on coke formation”

**Figure 4.1:** The major research objective for chapter 4 is to elucidate the effects that microwave heating has on the reaction productivity and product distribution for the conversion of ethane to value-added chemical.

As discussed in Figure 1.3 catalytic materials themselves have dielectric properties that allow them to absorb MW energy. Different materials can absorb microwaves and produce heat at different rates, based on the dielectric properties of that material. Figure 4.2 depicts the theoretical mechanism for the selective heating nature of MW’s for a supported metal catalyst. The thermally heated catalyst bed has a uniform temperature throughout for all active metal sites and catalyst support. Whereas the microwaves selective heating nature heats the catalyst support (a poor microwave absorber) to a temperature of 375 °C, while the dielectric favorable active metal sites are heated to a temperature of 660 °C. The microwaves relatively cooler surrounding temperature significantly inhibits coke formation that would occur from unwanted side reactions as well as the
thermal cracking of natural gas compounds on reactor walls and other reactor components that would be at elevated temperatures when heated traditionally. The microwaves ability to heat a catalyst to a 285 °C lower temperature demonstration a potential for greater energy efficiency for heterogenous catalytic reactions. The reactor setup and reaction condition are discussed in chapter 2, section 2.1.2 and the catalyst support and metal loadings are shown in Table 2.1.

Figure 4.2: Graphical illustration of the microwaves selective heating nature and energy saving potential.

4.0. Catalyst Characterization
4.0.1 Surface Area and Acidity
Table 4.1 shows a summary of the surface area and NH3-TPD results of H/ZSM-5 support and the freshly prepared MoFe/ZSM-5 catalyst. The addition of Mo and Fe to the unpromoted zeolite resulted in a decrease of total surface area, including the micropore and the external surface area of the catalyst. It has been shown previously that Mo is located mainly on the external surface but also can diffuses into the pores [74]. Iron particles are expected to be located external of the pores structure of the zeolite with this impregnation method [38]. The acidity of the H/ZSM-5 as seen in Table 4.1 has two desorption peaks at temperatures of 229°C and 408°C. The higher desorption temperature peaks correspond to the strong acid sites (mostly Brönsted acid sites) and the lower desorption temperature corresponds to the weak acid sites (mostly Lewis acid sites) [37,75]. The
addition of Mo and Fe to the H/ZSM-5 support resulted in a reduction in the temperature and the amount of ammonia desorbed. This suggests that the metal promotors are anchored to the Brönsted acid sites located on the zeolite support.

Table 4.1: The surface area and acidity of fresh catalyst before and after catalyst loading.

<table>
<thead>
<tr>
<th></th>
<th>Surface Area</th>
<th>total surface area (m²/g)</th>
<th>micropore area (m²/g)</th>
<th>external area (m³/g)</th>
<th>pore volume (cm³/g)</th>
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</thead>
<tbody>
<tr>
<td>HZSM-5</td>
<td>333.3</td>
<td>242.8</td>
<td>90.4</td>
<td>0.122</td>
<td></td>
</tr>
<tr>
<td>MoFe/ZSM-5</td>
<td>286.6</td>
<td>214.1</td>
<td>72.5</td>
<td>0.107</td>
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<table>
<thead>
<tr>
<th>Acidity</th>
<th>weak acidity</th>
<th>strong acidity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp [°C]</td>
<td>Area [a.u./g]</td>
</tr>
<tr>
<td>HZSM-5</td>
<td>229.8</td>
<td>38.62</td>
</tr>
<tr>
<td>MoFe/ZSM-5</td>
<td>224.6</td>
<td>38.98</td>
</tr>
</tbody>
</table>

4.0.2. X-Ray Diffraction

Figure 4.3 illustrates the x-ray diffraction patterns for the fresh catalyst and compares the spectra to the spent MWFB and spent CTFB catalysts. By comparing the diffraction patterns of the fresh and spent catalysts at diffraction angles between 22° and 25°, almost no changes were observed. No crystalline carbon peaks were observed which suggests the formation of mostly amorphous carbon or that the amount of carbon was too little to detect. The carbon build-up also contributed to the decrease in peak intensity after reaction which could be due to the formation of coke on the surface of the zeolite. This indicates that the ZSM-5 maintained its crystallinity in both the conventional thermal and microwave reactors. Metal oxide peaks were not observed in the fresh and spent catalysts, this could suggest that the metal loadings were evenly distributed, and the metal particles were of small particle size that could not be detectable under the XRD instrument.
Figure 4.3: XRD patterns of (a) Fresh MoFe/ZSM-5, (b) MWFB spent catalyst, and (c) CTFB spent catalyst.

4.1 Catalyst Performance Under Microwave Irradiation vs Conventional Thermally Hearted Reactors.

The catalyst performance in MWFB and CTFB is compared in Figure 4.4–4.6. In Figure 4.4(a) the ethane conversion is plotted as a function of time on stream during the reaction. The catalyst was tested over different reaction temperature thermally (CTFB) and the conversion at which the two methods coincide was determined. The CTFB required a bulk temperature of 660 °C to obtain the same conversion of ethane as in the MWFB at 375 °C. This temperature difference is attributed to the mechanism of selective microwave heating. The zeolite support is an inefficient absorber of microwaves due to high SiO₂ content, therefore most of the heat generated comes from the selective heated metal sites of Mo and Fe species on the zeolite surface. For direct ethane conversion on ZSM-5 zeolite, ethane is firstly converted to ethylene on metal sites (Mo₂C), and the aromatics are produced from the oligomerization of ethylene intermediate [39]. In other words,
due to the selective heating feature of microwave irradiation, the microscopic “hotspot” temperature on metal sites can reach around 660°C while the bulk catalyst temperature is at 375 °C in the MWFB reactor. The deactivation trend of the MWFB and the CTFB was very similar over the course of the 36 min of the reaction. The initial absorbed power required by the microwave system was 38 W to maintain the bulk catalyst temperature at 375°C under inert flow. After the start of the reaction, only 11 W were needed to maintain the bulk catalyst temperature at 375 °C. This can be attributed to the formation of coke, given that carbon is a good absorber of microwaves. As seen in Figure 4.4–4.6, the formation rate and selectivity of methane, benzene, and toluene were higher in the CTFB than in the MWFB reactor throughout the reaction. However, the formation rate and selectivity of ethylene was much higher in the MWFB than in the CTFB reactor. Ethylene acts as the major intermediate to aromatic formation [12]. It is suggested that the microwaves induce dipoles on the metal sites located on the surface of the catalyst [12,63–65]. These dipoles could facilitate electron transfer between ethane and the metal site to accelerate the formation of ethylene via the dehydrogenation process. At 10-min time on stream, Figure 4.6(b) shows that the CTFB had an 11.5 % carbon selectivity to ethylene, whereas the MWFB had a higher (38 %) carbon selectivity to ethylene. Although the ethane deactivation curve for MWFB and CTFB appeared to be similar, the coke formation mechanism and type of coke are different between the two method, coke formation is further discussed below. Different coke would affect active sites (dehydrogenation sites and aromatization sites) differently, which could affect temperature distribution on the catalyst surface differently for the MWFB, therefore we observed different product selectivity. The low aromatic selectivity could be due to the inefficient dehydroaromatization of ethylene. Y. kuo et al. [76] reported different surface temperature affect selectivity differently for ethylene dehydroaromatization. It was reported that the benzene selectivity for ethylene dehydroaromatization over a Ga/ZSM-5 catalyst sharply decreased from 20 % to 0 %, between 400–300 °C, while maintaining a high ethylene conversion. The low bulk temperature of 375°C along with possible uneven heat distribution throughout the catalyst bed could allow only parts of the catalyst bed to be fully utilized throughout the reaction.
Figure 4.4: Comparison of the conversion and formation rates for the MoFe/ZSM-5 catalyst in MWFB at 375°C and CTFB at 660°C. (a) percent ethane conversion, (b) hydrogen formation, (c) benzene formation, and (d) toluene formation.

Figure 4.5: Comparison of the formation rates for the MoFe/ZSM-5 catalyst in MWFB at 375°C and CTFB at 660°C. (a) methane formation and (b) ethylene formation.
Figure 4.6: Compares the hydrocarbon selectivity’s of the major carbon products for the MWFB at 375 °C and CTFB at 660 °C. (a) methane selectivity, (b) ethylene selectivity, (c) benzene selectivity, and (d) toluene selectivity.

4.2. Investigation of Catalyst Deactivation
4.2.1. Transmission Electron Microscopy

TEM images of the MWFB spent catalyst are shown in Figure 4.7, where the sample was taken from the center of the catalytic bed. The EDS of the 4 spots shown in Figure 4.7 confirms that the dark spots are made up of Mo and Fe agglomerated metal particles on the catalyst surfaces. Several agglomerations of metal particles up to 60 nm in diameter can be distinguished. The TEM images of CTFB spent catalyst and EDS spots can be seen in Figure 4.8. The EDS confirms the dark spots are agglomerated metal Mo and Fe particles of much smaller diameter. The largest metal agglomerations on the CTFB spent sample are of only between 10 and 20 nm. The MWFB spent sample’s larger particle agglomerations are attributed to the selective heating nature of the
microwave. The results imply that anchoring Mo and Fe in the structure of ZSM-5 is necessary to prevent metal agglomeration on the surface due to the mobility of Mo and Fe on the zeolite surface. The fresh catalyst TEM images are not given since the fresh catalyst had little to no metal agglomerations visible. Furthermore, the formation of carbon structures was observed in both the MWFB and CTFB spent samples, agreeing with literature on Fe promoted catalysts under thermal conventional reaction conditions [25,38,41,66]. The formation of CNTs with distinct tubular walls and diameters up to 20-nm can be seen in CTFB samples in Figure 4.6. In comparison, the MWFB spent sample resulted in the formation of unordered CNT-like structures with diameters as large as 60-nm. The CNTs formed have little to no open voids with several encapsulations within the tube structure. CNTs are very good microwave absorbers as well as electric conductors [77,78]. The results suggest that the coke formations themselves can be altered by electron restructuring due to the induced electron transfer by the MWFB fields at the agglomerated metal sites or by rapid thermal gradients at the metal particle site.

![Figure 4.7: TEM image of the spent MWFB MoFe/ZSM-5 catalyst after 36 min of reaction.](image-url)
4.2.2. Carbon Analysis by TPO and TGA

The TPO and TGA profiles of the spent catalyst obtained are shown in Figure 4.9. TPO profiles are used for qualitative purpose to determine how structurally ordered coke is based on peak shape and oxidation burn-off temperature. The TPO and TGA profiles of spent CTFB sample suggest that at least three types of coke, were formed due to the appearance of three temperature peaks at 459°C, 542°C, and 601°C. The MWFB spent sample temperature profile only had one distinct peak at 562°C. This temperature is between the middle and the higher temperature peak of the CTFB and is believed to contain two of the three CTFB peaks. The microwave was more selective to forming the higher burn-off temperature coke species and less selective towards the formation of the lower temperature burning amorphous carbon. Amorphous carbon has been shown to lead to faster deactivation due to pore and acid site blockage [25,37,38]. The decreased selectivity to
amorphous carbon suggests that the catalyst could remain active for longer periods if the MW power reaching the metal active sites remain constant. The total weight loss in the spent MWFB was only 4.04 % compared to a total weight loss of 9.839 % for the spent CTFB. Furthermore, the total weight loss suggests that the fixed bed was more selective to overall coke formation throughout the 36 min of reaction time.

Figure 4.9: TPO (black) and TGA (blue) for spent catalysts under MWFB (dotted) and CTFB (solid) reactors. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article).
4.3: Conclusion

In this study, it was experimentally determined that the microscopic “hotspot” temperature of metal particles on the zeolite could reach about 660 °C while the bulk catalyst temperature was only 375 °C due to the selective heating feature of microwave. The CTFB had higher formation rates and selectivity’s to hydrogen, methane, benzene, and toluene than the MWFB. However, the MWFB had higher formation rates and selectivity’s to ethylene. The low selectivity to aromatics was not due to the lack of ethylene in the stream but, was attributed to low bulk temperature and uneven heat distribution resulting in the inability of ethylene to diffuse into the catalyst pore structure efficiently. Metal particle agglomeration is a key factor of catalyst deactivation, and more severe agglomeration was observed in MWFB. TEM analysis also revealed that the MWFB induced the formation of nonuniform CNT with little to no tubular structure up to 60 nm in diameter, while the CTFB had very uniform CNT formation with distinct wall structures up to 20 nm in diameter. The presence of multiple types of coke in the CTFB was observed, whereas the MWFB only contained one type of higher burn-off temperature coke. TGA confirmed that the CTFB resulted in more carbon formation than the MWFB sample which suggests that the lower bulk temperature prevented the formation of amorphous carbon which is one of the leading causes of zeolite deactivation.
Chapter 5: Microwave Carbon Dioxide Regeneration on a DHA Catalyst

Oxidative regeneration using air was discussed in chapter 3. Oxidative regeneration using CO\(_2\) to remove coke by the Boudouard reaction: CO\(_2\) + C= 2CO will be explored. The advantage of CO\(_2\) regeneration is the mitigation of carbon dioxide and the production of a carbon monoxide, a valuable product. The Boudouard reaction is endothermic in nature, which can avoid metal sintering by negating hotspot formations and over oxidation of promoters that normally takes place in oxidative regeneration. Under microwave irradiation the thermodynamics of the Boudouard reaction have been shown to dramatically differ from the conventional fixed bed. It was found that there is a dramatic shift in equilibrium so that the temperature at which carbon monoxide becomes the major product drops from 643°C in the conventional thermal reaction to 213°C in the microwave \[79–84\]. Therefore, it becomes apparent that there is a need to test carbon dioxide regeneration of a catalyst under microwave irradiation. The objective of chapter 5, as seen in Figure 5.1, is to determine the ability of the microwave to regenerate a DHA catalyst in an atmosphere of CO\(_2\) and evaluate its effects on energy efficiency and catalyst reaction productivity.

**CO\(_2\) Regeneration of a Non-Oxidative Natural Gas Conversion Catalyst**

“The regeneration by CO\(_2\) in a microwave reactor could increasing reaction productivity by lowering the induction period and produce valuable CO form and not CO\(_2\) that is associated with oxygen regeneration”

**Figure 5.1:** The major research objective for chapter 5.

**5.0 Experimental Justification for Methane DHA and Fluidized Microwave CO\(_2\) Regeneration**

Microwave regeneration of an ethane or methane dehydroaromatization coked catalyst was tested on the ability of the microwave to active the reverse Boudouard reaction. The CO\(_2\) regeneration was tested in an ex-situ reactor configuration, where the EDHA reaction was carried out in a thermally heated fixed-bed tubular reactor and then moved to the microwave 2.45 GHz reactor for the regeneration step without catalyst bed disturbance. Figure 5.2 shows the catalytic performance
for the three cycles of reaction and regeneration for ethane (a-b) or methane (c-d) dehydroaromatization reaction. With each subsequent cycle of reaction and regeneration the catalyst conversion is decreasing for ethane dehydroaromatization (EDHA) reaction. Figure 5.3 is an image of the ethane coked catalyst after the second regeneration cycle. Non-uniform coke removal is occurring in the radial direction, which suggest that the center of the catalyst bed is the hottest region. Figure 5.2 also shows a similar trend for the methane dehydroaromatization (MDHA) reaction, with each recurrent cycle, the catalyst activity was decreasing. A similar coke removal distribution for the methane regenerated catalyst was observed that resembled Figure 5.3. It is apparent that the methane dehydroaromatization reaction exhibited a benefit from the CO\(_2\) microwave regeneration. For the first cycle, MDHA reaction showed the presence of an induction period in methane and benzene selectivity. However, the subsequent reaction cycles do not show this large induction period. It is thought that this is due to the formation of a molybdenum-oxy-carbide type species that is more stable under the CO\(_2\) regeneration and did not completely re-oxidize to MoO\(_3\) [85]. The EDHA reaction shows almost no promotional effect from the CO\(_2\) regeneration and only shows a slight induction period for benzene selectivity in the fresh catalyst thought to be due to the formation of CO and CO\(_2\) in the initial reduction of the molybdenum oxide species to the molybdenum carbide species. Due to the higher operating conditions of MDHA, it is thought that the higher temperatures required to facilitate the reverse Boudouard reaction would be more suitable for MDHA and could possibly have higher adverse effects from temperatures that the EDHA catalyzed reaction is normally not subjected to. The promotional effect achieved on the induction period for the methane DHA reaction from the CO\(_2\) regeneration, as seen in Figure 5.2, would allow the catalyst to be initially more selective to the desired aromatic products while producing a higher conversion rate. Combining short reaction and regeneration times, as discussed in chapter 4, with CO\(_2\) regeneration could allow for the increased productivity for the MDHA reaction. Therefore, in chapter 5, the reaction of interest for CO\(_2\) regeneration by microwaves is the is the MDHA reaction.
Figure 5.2: Results for three cycles of thermally heated dehydroaromatization reaction and microwave fixed-bed CO$_2$ regeneration for the EDHA and MDHA. [30-minutes of EDHA at 600$^\circ$C in 30% ethane/N$_2$ and 0.5g catalyst, 30-minutes of MDHA at 700$^\circ$C in 30% methane/N$_2$ and 0.5g catalyst, and microwave CO$_2$ fixed-bed regeneration at 550$^\circ$C for 30 minutes in 30% CO$_2$/N$_2$]
Figure 5.3: Image of 4%Mo/ZSM-5 catalyst bed after three thermally heated reaction and microwave fixed-bed regeneration cycles. [30-minutes of EDHA at 600°C in 30% ethane/N₂ and 0.5g catalyst, and microwave CO₂ fixed-bed regeneration at 550°C for 30 minutes in 30% CO₂/N₂]

5.1 Methane Dehydroaromatization CO₂ Regeneration in a Microwave Fluidized Reactor

A 2.5%-Mo/ZSM-5 and a 10%-Mo/ZSM-5 methane dehydroaromatization deactivated catalyst was tested for catalytic activity before and after catalyst regeneration by CO₂ in a microwave fluidization configuration. The catalyst was first carburized by raising the temperature of the catalyst in a thermally heated reactor at 10°C/min in a flow of 10%CH₄ in H₂ and held at 700°C for 10 minutes. The gas flow was then switched to 30% methane at a flow of 50 mL/min, where catalyst coking/deactivation occur for 120 minutes for the 2.5%Mo/ZMS-5 and 30 minutes for the 10%Mo/ZSM-5. The microwave fluidized reactor will be used for CO₂ regeneration to facilitate the activation of the entire catalyst bed and prevent partial regeneration as seen previously in Figure 5.3. To test the temperature required to activate CO₂ in a microwave fluidized bed a 0.75g of coked 40/60 mesh 2.5%-Mo/ZMS-5 or 10%-Mo/ZSM-5 catalyst was loaded into a fluidized reactor tube as seen in Figure 2.3. The catalyst was regenerated in a stream of 10%-CO₂ at a rate of 100 mL/min. The temperature was increased in the microwave fluidized bed at a rate of 10°C/min to 800°C. The regenerations were held for 90-minutes where the regeneration process was monitored by a mass spectrometer. Figure 5.4 shows the microwave temperature and power profile (bottom) and the ion intensities of CO₂, CO, and O₂ (top). The microwave forward and the reverse power profiles are shown for the heating and holding phase. The difference in the forward
and reverse power is the amount of power required to heat the catalyst to the desired temperature, the absorbed power. A thermal imager set to 189-fps with a calibrated temperature range of 575-900°C was used to image the temperature profile of the 2.5%Mo-/ZSM-5 fluidized microwave heated catalyst after reaching the 800°C setpoint is shown in Figure 5.5. The thermal profile in the figure depicts the fluidization in 4 frame skip intervals of the catalyst in the tube. Where, (a) is the formation of a hot pocket near the bottom of the tube, (b) is the rising of that hot pocket to the center of the tube, (c) is the dispersion and continued rising of the hot pocket, and (d) is the dispersion of the hotspot and the beginning of the formation of another hot pocket at the bottom of the tube. The temperature in the fluidized bed had an observed average temperature of 780.6°C, maximum temperature of 898.2°C, average maximum of 861.6°C, a minimum temperature of 651.7°C, and an average minimum temperature of 722.4°C over the 15 second thermal video recording. This shows that a temperature distribution of 246.5°C is occurring as the fluidization is taking place when considering the average max and minimum values. The large temperature distribution can be attributed to the selective heating nature of microwave and to thermofluidic effect of the fluidization [86]. It was previously demonstrated that the microwave heating of fluidized highly absorbing SiC pearls produce a non-uniform overheated reaction zones in the center of a fluidized bed, depending on the fluidization length. Therefore, with non-optimized fluidization tested here the, mixing of the hot center with the cooler outer walls of the reaction tube is probably the largest contribution to the large temperature distribution.
Figure 5.4: Microwave fluidized CO$_2$-Regeneration of two MDHA coked catalyst (left) 10\%-Mo/ZSM-5 and (Right) 2.5\%-Mo/ZSM-5 where the top of each shows the tracked ion intensities of CO$_2$, CO, and O$_2$. The bottom graph of each show the temperature profile and the forward and reverse power profile of the microwave reactor. [10$^\circ$C ramp to 800$^\circ$C in 10\% CO$_2$/He, hold for 30-minutes, 0.75g catalyst at 100-mL/min]
Figure 5.5: Thermal images of the microwave heated fluidized bed after reaching 800°C for the CO₂ regeneration of the coked 2.5%Mo-ZSM-5 MDHA catalyst. (a-d) shows the formation and the cycling of hot particles in the catalyst bed.

The MWFR-2.5 and MWFR-10 regeneration is in close agreement with that of the thermal TFB-CO₂ reaction as seen in Figure 5.6. Figure 5.6 shows the thermally heated fixed-bed 10%-CO₂ (TFB-CO₂) and 10%-O₂ (TFB-O₂) regeneration reactions for the 2.5%Mo-ZSM-5 coked catalyst. An online mass spectrometer and a thermal conductivity detector was used to track the changes in gas concentration as the temperature of the coked catalyst was raised at a ramp of 10°C/min and then held at regeneration temperature until the regeneration was near complete. The formation of CO from CO₂ starts to form at 475-500°C bulk temperatures for the MWFR-2.5, MWFR-10, and TFB-CO₂ regenerations. Similar trends in catalyst CO₂ regeneration has been reported previously for a Co-Mo containing catalyst [87]. The CO formation continues to increase in reaction rate until the maximum set point temperature is reached for the MWFR-2.5, MWFR-10, and TFB-CO₂ regenerations. This is in good agreement with the Boudouard reaction thermodynamics, which requires temperature typically greater than 643°C to make CO the more favored product and this increases with increasing temperatures [62]. In current reported literature the microwave has
demonstrated the ability to lower the enthalpy of reaction nearly 5.5x that of the thermal reactions from 183 KJ/mol at 825°C to 33.4 KJ/mol by measure of equilibrium constants as a function of temperature [62]. A 3.2x lowering of the enthalpies from 148.9 KJ/mol to 47.1 KJ/mol were also reported by comparing conventional heating to microwave heating for the bordered reaction [88]. The thermodynamic values listed above are in the absence of a metal catalyst.

![Figure 5.6](image.png)

**Figure 5.6:** The thermally heated fixed-bed regeneration of the coked 2.5%Mo-ZSM-5 catalyst (left) in 10%-CO₂ (TFB-CO₂) and (right) 10%-O₂ (TFB-O₂).

The temperature ramp for the MWFR-2.5 and MWFR-10 catalyst regenerations showed an increase in the rate of forward power and a divergence of the forward and reverse power indicating a loss in the total amount of microwave absorption. Throughout the reaction a steady increase occurred in the amount of forward and absorbed power needed to maintain the reaction temperature. The increase in microwave forward power and absorbed power is indicative of the loss of well microwave absorbing coke. TGA analysis, as seen in Figure 5.7, shows that the MWFR-10 coked catalyst had 1.693% weight loss and one order of coke whereas the 2.5%Mo/ZSM-5 catalyst lost 4.409% weight and had only one order of coke formations. The 2.5%Mo/ZSM-5 coked catalyst only displayed a sharp exothermic re-oxidation in the DSC curve.
at 483°C and the 10%Mo-ZSM-5 coked catalyst at 460°C. The MWFR-2.5 appeared to experience only one order of coke loss in the TGA at 562°C. Whereas the MWFR-10 exhibited a weight increase at 450°C from reoxidation determined by DSC signal, followed by a small order of coke loss at 485°C. It has been demonstrated that the oxidation of the Mo-carbide spices to Mo-oxides and oxycarbide can facilitate rapid combustion of soft proximity coke spices [89]. This observation is in close agreement with in the CO₂-TPO, as seen in Figure 5.8, of the 10%Mo/ZSM-5 catalyst, it can be seen that the formation of CO at the low temperatures observed in the TFB-CO₂ and the MWFR suggest that the formation of CO must be coming from the oxidation of Mo₂C. Which is indicative of the soft coke peak seen in the CO₂-TPO peak at 750°C for CO₂, followed by the hard coke formation at 850°C for the 10%Mo/ZSM-5 coked catalyst. Mo₂C on H/ZSM-5 has been previously reported to start oxidizing as low as 300°C in the presence of pure CO₂ and increasing in rate with increasing temperature [90]. However, it has been shown that the temperature at which Mo₂C oxidizes in CO₂ is increased with increasing CO concentration in the system [91]. In the CO₂-TPO of the 10%Mo-ZSM-5 catalyst, the reoxidation by CO₂ continues out to 850°C before reaching a maximum peak. The CO₂-TPO also shows that the MWFR-10 resulted in the almost complete removal of coke with only a small peak appearing at 850°C. With the wide temperature distribution of up to 900°C observed temperature, the MWFR was efficient at the removed the coke from the catalyst surface. TFB-CO₂ 2.5%Mo/ZSM-5 regenerated catalyst with a percent weight loss of 1.841% after being exposed to CO₂ for 180mins at 800°C, which was more than the MWFR-2.5 regenerated catalyst at 1.01% after being exposed for 90 minutes at 800°C. This indicates that the microwave is at least twice faster at removing coke via the Boudouard reaction than a thermally headed fixed bed operated at the same conditions. The effect of microwave selective heating with the possible electronic interactions on the metal catalyst could increase the rate of the soft coke combustion. The overall rate of the Boudouard reaction increase can also be attributed to the uneven temperature distribution in the fluidized bed. The TFB-O₂ regeneration, shows the conversion of O₂ and carbon into CO and CO₂ starting at temperatures of about 450°C and steadily increasing till the setpoint temperature. The ion intensity of O₂ and the TCD signal indicate that there is an uptake in O₂. TGA-DTG curve indicates that there is an exothermic uptake in weight occurring at 450°C from the reoxidation of the molybdenum spices [92]. The O₂ regenerated catalyst exhibited a small amount of weight loss due to incomplete regeneration of coke at 0.292 %.
Figure 5.7: TGA and DSC curves for the coked and the regenerated catalyst. [Dynamic-HiRes 20°C max ramp to 800°C in air at 150mL/min]
XPS was performed on the fresh, carburized, spent TFB-O₂ regenerated, TFB-CO₂ regenerated, and the MWFR regenerated catalyst. Figure 5.9 and Figure 5.10, show the XPS spectra for the 2.5%Mo/ZSM-5 and the 10%Mo/ZSM-5 coked catalyst display the typical Mo(3d⁵/₂) peaks at 233.3-233.6eV which are attributed to the Mo⁶⁺ state catalyst samples [93]. Upon carburization both the catalyst displayed the conversion of the Mo⁶⁺ to a mixture of Mo⁶⁺ and Mo⁴⁺ species. After reacting the catalyst in methane DHA (coking), the 10%Mo/ZSM-5 catalyst showed a Mo₂C peak at 228.9 eV. However, the 2.5%Mo/ZSM-5 catalyst only displayed a small shift in the Mo⁶⁺ and Mo⁴⁺ species this was attributed to the low metal loading of 2.5%Mo. It has been previously discussed that at low metal loading the MoOₓ are atomically dispersed into the pores of the zeolite, therefore XPS and XRD are insensitive to the detection of low amount of Mo₂C. The formation of
the Mo$_2$C species is also inhibited until further reaction, detachment, and migration occurs [94]. When the 2.5%Mo/ZSM-5 coked catalyst is regenerated by oxygen, it reverts fully back to its Mo$^{6+}$ state. But when the 10%Mo or the 2.5%Mo catalyst are treated under CO$_2$ by thermal or microwave conditions, the result is that a percentage of the Mo$^{4+}$ states are maintained.

![Figure 5.9: XPS spectra of the 2.5%Mo/ZSM-5 samples with deconvoluted peak curves.](image)
Temperature programed reduction in H$_2$, as seen in Figure 5.11, show the disappearance of the strong uptake of hydrogen at 485°C which is attributed to the MoO$_3$(Mo$^{6+}$) to MoO$_2$(Mo$^{4+}$) and 550°C MoO$_2$(Mo$^{4+}$) to MoO(Mo$^{2+}$) indicating that the catalyst was not fully re-oxidized. The 675°C reduction temperature is generally attributed to the well dispersed MoO$_2$ further reduction to Mo [95] [96]. This is contradictory to the oxidative state changes observed in the XPS spectra for the 2.5%Mo/ZSM-5 catalyst. In comparing the XPS with the TPR the low Mo$^{6+}$ compared to the high Mo$^{2+}$ in the TPR suggest that the Mo6+ is located on the surface of the zeolite, whereas the Mo$^{2+}$ could exist in higher concentration in the pores and less susceptible to reoxidation due to binding with Al framework [97]. The TFB-CO$_2$ and the MWFR both display reduced oxidation states. The MWFR regeneration was noticed to have a slightly higher oxidation temperature then that of the TFB-CO$_2$. It is thought that this shift in temperature could be due to the increases in
metal particle diameters. TEM images of the 10%Mo/ZSM-5 catalyst samples are seen in Figure 5.12. The fresh catalyst (a) shows no agglomerations on the catalyst suggesting that the metal loading is well dispersed. Image (b-d) show the increase size of agglomerated Mo metal particle for the carburized, spent, and MWFR-10. XRD did not find any losses in zeolite crystallinity as seen in Figure 5.13 and Figure 5.14. No crystalline peaks of the metal loading could be observed by XRD, for the 2.5%Mo/ZSM-5 loading which confirms that the 2.5%Mo loading is well dispersed on the zeolite surface. The 10%Mo/ZSM-5 higher metal loading showed distinct MoO₂ and Mo₂C carbide peaks in the carburized and MWFR-10 sample, which confirms the XPS results of the catalyst maintaining some form of molybdenum carbide to oxycarbide structure.

![Temperature programmed reduction of the fresh, TFB-CO₂, MWFL-CO₂, and TFB-O₂.](image)

**Figure 5.11:** Temperature programmed reduction of the fresh, TFB-CO₂, MWFL-CO₂, and TFB-O₂.
Figure 5.12: TEM of the 10%Mo/ZSM-5 catalyst where (a) is the fresh catalyst, (b) is the carburized catalyst, (c) is the spent catalyst, and (d) is the MWFR-10 regenerated catalyst.

Figure 5.13: XRD of the 10%Mo/ZSM-5 catalyst samples.
Figure 5.14: XRD of the 2.5%Mo/ZSM-5 catalyst samples.

5.2: Reactivity of the 2.5%Mo/ZSM-5 and the 10%Mo/ZSM-5 CO2-Regenerated Catalyst

The catalytic testing of the 2.5%Mo/ZSM-5 catalyst, as seen in Figure 5.15, indicate the CO2 could regenerate the catalyst by removing the carbon deposits. MWFR-2.5 resulted in the overall loss of methane conversion compared to the fresh catalyst and the carburized catalyst. The carburized catalyst loss in conversion can be attributed to the overall lower metal loading of 2.5-wt%. Due to the low metal loading the Mo2C species is believed to not of been completely formed during the initial carburization and coking of the catalyst and would of potently not of stayed as a Mo-oxycarbide [30]. The MWFR-2.5 loss in conversion from the carburized starting point is believed to be due to metal agglomeration as indicated by the 10%Mo/ZSM-5 catalyst TEM showing significantly more metal agglomerations than when compared to the spent. Also, the incomplete regeneration of the MWFR-2.5 could of lead to further activity decreases due to the entrapment of
the low metal loaded species within the pores that were diffusion limited to the larger CO\textsubscript{2} molecule from the build-up of carbon. The MWFR-2.5 compared to the carburized resulted in the increases in ethylene selectively which suggest the formation of a more oxygenated states of Mo\textsubscript{2}C that inhibits the C-C bond dissociation and promotes the formation of ethylene [98] [99]. The reduction in benzene production is also believed to be due to the incomplete regeneration and due to the reoxidation of the Mo\textsubscript{2}C. Mo\textsubscript{2}C is considered the most active in the formation of aromatic compound for Mo/ZSM-5 [89]. The H\textsubscript{2}-TPR showed very little reoxidation of the lower oxidative states of the MWFR-2.5 after regeneration, but the shift to a higher oxidative state was observed. The increase in a different oxidative state or form of molybdenum could attributed to the loss of the more active Mo\textsubscript{2}C phase in the CO\textsubscript{2} rich atmosphere [32].

The 10\%Mo/ZSM-5 catalyst reactivity, as seen in Figure 5.16, shows that the 10\%Mo/ZSM-5 MWFR-10 regenerated catalyst had overall comparable conversion and selectivity’s to the fresh and carburized catalyst. The carburized catalyst exhibited no methane conversion induction period, and the MWFR-10 catalyst induction period was reduced in magnitude from that of the fresh catalyst. This is attributed to the MWFR-10 catalyst not being completely re-oxidized by the CO\textsubscript{2}, as shown in the XPS and TGA. The retention of the oxide spices of the mixture of Mo\textsuperscript{6+} and Mo\textsuperscript{4+} resulted in a faster catalyst reactivation due to a faster reduction period which would result in less CO\textsubscript{2} and CO production at the initial start of the reaction. This is indicated by the higher selectivity to ethylene and benzene then the fresh catalyst at the start of the reaction. Therefore, if the catalyst were to be utilized in a short reaction and regeneration approach, more of the Mo\textsubscript{2}C could be maintained while facilitating a higher initial selectivity to desired products.
Figure 5.15: Thermal fixed bed MDHA reactivity testing of the 2.5%-Mo/ZSM-5. Where (a) is the methane conversion, (b) is the ethylene selectivity, (c) is the benzene selectivity, and (d) is the total aromatic production. [700°C, 0.3g of catalyst at 30mL/min of 30%CH₄ in N₂]
Figure 5.16: Thermal fixed bed MDHA reactivity testing of the 10%-Mo/ZSM-5. Where (a) is the methane conversion, (b) is the ethylene selectivity, (c) is the benzene selectivity, and (d) is the total aromatic production. [700°C, 0.3g of catalyst at 30mL/min of 30%CH₄ in N₂]

5.3: Conclusion of CO₂-Regeneration on a DHA Catalyst by Microwave Heating.

In this study, the regeneration of a 2.5%Mo/ZSM-5 and 10%Mo/ZSM-5 catalyst under microwave fluidized heating conditions with CO₂ as the oxidant. The Boudouard reaction is a very endothermic reaction that requires high temperatures to make the production of CO form CO₂ and carbon favorable. The microwave fluidized CO₂ regeneration was tested alongside a thermally heated fixed-bed CO₂ regeneration for the 2.5%Mo/ZSM-5 methane coked catalyst. It was determined that the microwave in the fluidized state resulted into very similar CO₂ consumption and CO production curves. The temperature in both heating methods resulted in the formation of CO and CO₂ at temperatures starting at near 450-500°C. This goes against currently reported literature for the reverse Boudouard reaction ability of the microwave to lower the enthalpy of reaction by nearly 5.5x that of the thermal reactions, from 183. KJ/mol at 825°C to 33.4 KJ/mol by measure of equilibrium constants as a function of temperature [62]. The activation of the
Boudouard reaction was not seen at low temperatures, but the time needed for the fluidized microwave CO\(_2\) regeneration was cut in half when compared to the thermally heated CO\(_2\) regeneration. The MWFR-2.5 regeneration removed more coke in 90 mins than the TFB-CO\(_2\) at the same temperature and ramp rate was able to do in 180 mins. However, the MWFR-2.5 regenerated catalyst was not able to regain the initial activity of the carburized or fresh state. This is believed to be due to its low 2.5\% metal loading which allows the Mo to be well dispersed in the pores and the possible diffusion limitation of CO\(_2\) caused by pores size restricting coke formation. The 10\%Mo/ZSM-5 catalyst was coked in methane for 30 mins and regenerated for a shorter period of 30 mins in the microwave CO\(_2\) fluidized bed. The 10\%ZSM-5 catalyst reactivity after catalyst regeneration showed improved reduction in the induction period as to when it was compared to the fresh catalyst for conversion, benzene, ethylene, and aromatic production rate. XPS, XRD, and TGA all confirmed the presence of molybdenum that is not fully re-oxidized back to its initial MoO\(_6\) state. Therefore if the reaction was operated in pulsed or short cycles of reaction and regeneration, the microwave operated in a fluidized bed could effectively remove the coke from the catalyst and facilitate a higher productivity by preventing the over oxidation of the molybdenum active species. Moreover, pulsing of CO\(_2\) or a constant feed of a low loading of CO\(_2\) would be more beneficial to the reaction [32] [31]. The combination of microwaves carbon activating selectivity with the benefits of Co-feeding or pulsing CO\(_2\) could have large benefits in the rates of activation of coke or Mo-oxycarbide and Mo\(_2\)C cycling that is highly sought after for ethane dehydrogenation reaction to ethylene.
Chapter 6: A Systems Approach to Increase Aromatic Selectivity for Non-Oxidative Ethane Conversion in a Microwave Reactor

In Chapter 4, the microwave selective heating nature was discussed and its effect on ethane conversion and selectivity as well as coke distribution for the non-oxidative dehydroaromatization reaction of ethane to aromatics (EDHA). It was demonstrated that microwave heating is efficient at the dehydrogenation of ethane to ethylene but lacked the capability to efficiently aromatize the abundant amount of ethylene into the target products benzene and toluene. The low aromatic selectivity was attributed to the underutilization of the catalyst bed due to hotspot formation that drives the high conversion at low temperatures. The objective of chapter 6, as seen in Figure 6.1, is to take a systems approach by changing the microwave reactor configurations so that catalyst bed utilization can be increased. The reactor configurations were also tested in a thermally heated reactor to compare how the different configuration would change known thermal reaction mechanism. Chapter 6 will test the conclusions draw in chapter 4 and elute the effects of temperature distributions on microwave ethane dehydroaromatization. A 6%Mo/ZSM-5 catalyst was tested in thermal, microwave, and hybrid setups for fixed bed and/or fluidized bed configurations for the EDHA reaction. The goal was to determine how to increase aromatic productivity in the microwave reactor. Typically, the microwave reactor has been tested for fixed bed dehydroaromatization [66,100–102]. This is the first known reporting of the utilization of microwave fluidization and/or hybrid heating for the ethane dehydroaromatization reaction.

Figure 6.1: The major research objective for chapter 6.

In this chapter the effects of different reactor configurations have been explored to provide insight into more effective ways to conduct ethane dehydroaromatization experiments by microwave processes. Three different configurations of microwave heating have been tested as seen in Figure 6.2. Conventional thermally heated fixed bed and fluidized bed configurations were also tested at
the same conditions. 0.75g of the 6%Mo/ZSM-5 catalyst, shown in Table 2.1, was used with a gas flow rate of 100mL/min all experiments. To allow for easier microwave heating and more uniform temperature distribution, the catalyst was pre-carburized in a feed of 10%CH₄/90%H₂ followed by 10 minutes of reaction in 90% methane at 700°C to coke the catalyst. 1.5% ethane was flowed during the heating phase, this was to facilitate more optimum temperature control and allow hotspot formation before the flow of 30% ethane. In previous experiments from chapter 4.0, it was discovered that the sudden onset of a high endothermic reaction can cause major instability in temperature control due to the onset of hotspot formation shortly after the reaction gas has started. The reactor setups and experimental conditions are discussed further in chapter 2.1.4.

**Figure 6.2:** Graphical illustration of the three microwave heating processes
6.1 Fixed-bed EDHA Testing in Microwave, Hybrid, or Thermally Heated Reactor

In chapter 4.0, ethane dehydroaromatization was discussed to compare differences in catalyst deactivation and catalyst product distribution at a thermal temperature of equivalent ethane conversion for a 375°C microwave heated catalyst bed. In section 6.1, a 2.45Ghz microwave reactor system was used to test the catalyst activity in a microwave heated, hybrid heated, or thermally heated fixed-bed reactor. The 2.45 GHz microwave system has a waveguide the size of 3.4-inch x 1.7-inch, whereas the reactor used in chapter 4.0, had a much smaller waveguide of 1.59 inches x 0.795 inches. This allows for the loading of more catalyst; different reactor configurations, and the lower microwave frequency will result in a larger microwave penetration depth into the catalyst bed [103]. In chapter 4, It was thought that the underutilization of the catalyst bed led to high ethylene yield and low aromatic production. The formation of hotspots within the catalyst bed were apparent in chapter 4, but at the time no definite method to determine temperature distribution was available. Therefore, to determine the effects of catalyst bed utilization in a fixed-bed reactor setup the utilization of a larger waveguide, a lower microwave frequency, a thermal imager, and additionally testing of a hybrid heated reactor.

6.1.1 Results for Fixed-bed EDHA Testing in Microwave, Hybrid, or Thermally Heated Reactor

The EDHA reaction was studied in a microwave heated fixed-bed (MWFB) over three temperature consisting of 350°C, 375°C, and 425°C. The catalyst beds were thermal imaged at different times through the reactions and the product distributions were discussed in respect to conversion and temperature distribution. Figures 6.3-6.5 shows the temperature profile (a), microwave power profile (b), and on the EDHA reaction conversion and product distribution (c) for the MWFB350, MWFB375, and MWFB425 respectively. The MWFB reactions all initially facilitated high conversions of ethane over the first 6 minutes of reaction. The high initial conversion can be attributed to temperature spikes within the catalyst bed associated with hotspot formation. The formation of the hotspot was detected by the sharp reduction and convergence of forward and reverse power starting between 325°C-350°C for all MWFB reactions. This indicates that a high microwave absorbing hotspot was forming in the 1.5% ethane feed at these temperatures. The hotspot also resulted in initial unstable microwave temperature control of the catalyst bed. This is due to the sudden change in the dielectric properties of the catalyst and from coke formation which
will influence the amount of power needed to heat the catalyst [78]. In all three MWFB reactions the power required rapidly drops before the start of the 30% ethane feed. The microwave controller was setup with adaptive PID tuning, thus it required 10-15 minutes to regain control and hold the bulk temperature of the catalyst to +/- 5°C.

The catalyst temperature distribution and formation of the hotspots was recorded on a FLIR A26260 short wave-IR thermal imager and is shown in Figure 6.6 for the MWFB350 and Figure 6.7 for the MWFB375 reactions. Figure 6.6a and Figure 6.7a, shows the induction periods leading to hotspot formation in both the MWFB350 and the MWFB375 reactions. In the range of 18-23.13 minutes and for 21-25.5 minutes of microwave program time for the MWFB350 and MWFB375 respectively, the catalyst bed temperature distribution shrinks to a more localized area, which is in alignment with the start of the convergence and reduction of the forward and reflected power. Figures 6.6b and Figure 6.7b-c show the sudden onset of a rapid temperature increase, followed by pulsating/flashing hotspots detected by the thermal imager in the MWFB350 and MWFB375 reactions. The temperature pulses are due to the inefficiency of the microwaves ability to control the temperature of a catalyst with rapidly changing dielectric properties. Figure 6.6c and Figure 6.7d show the catalyst bed temperature distribution of the MWFB350 and MWFB375 respectively, after the temperature pulsing has subsided. The 900-Watt solid-state microwave used in this experiment can step the power 1-watt at a time, thus the pulsing of the catalyst bed does subside after the PID adaptive tuning has regained control of the temperature. Figure 6.8a shows the hotspot agglomerated particle for the MWFB350 and Figure 6.8b shows the agglomerated particle for MWFB425 catalyst. Figure 6.9a is an image of the catalyst bed still inside the tube. If image (a) is compared to (b) the brown deposits on the quartz tube are also present on the catalyst surface. The brown deposits are well microwave absorbing regions, if the sample is compared to Figure 6.7, the hot region expels directly from the area of the deposit seen in Figure 6.9a. Taking a closer look at Figure 6.8b and 6.9b, it can be seen that a large amount of the catalyst bed is not active in the reaction due the low amount of coked catalyst particles.

The 1.5% ethane feed during the heating phase of the MWFB reactions is likely the cause of the formation of graphitized coke species. Microwaves ability to delocalize the pi-electrons within coke formations make graphitized coke not only a good microwave absorber but also a good heat
producer [46]. It is thought the combination of coke deposition of graphitized species due to the internal high temperatures and the formation of the Mo2C species. of the catalyst fixed-bed would facilitate the microwave to preferentially absorbed in this area with respect to the rest of the catalyst bed [101]. If the localized heat generation is not able to displace the heat fast enough to colder nearby catalyst particles, then a hotspot will form from the newly formed hotspot [104]. Each of the MWFB reactions displayed the hotspot formation within 30°C bulk temperature of each other during the temperature ramp. This is indicative of the sharp decrease in the amount of power required followed by the sudden onset of very rapid heating of 2 sec, as seen in Figure 6.6b.

The microwave fixed-bed reaction product distribution and ethane conversion were tracked and are shown in Figures 6.3c-6.5c. The average ethane conversion increase with increasing temperature setpoint in the order of MWFB425>MWFB375>MWFB350. The changes in ethane conversion that occur throughout the run can be directly correlated back to the forward and reverse power for that MWFB reactions. In Figure 6.4, at 55 minutes of microwave program time a 2-watt increase in the amount of absorbed power occurs. The absorption of the 2-watts facilitates a higher conversion for the following point. In figure 6.5, an increase in power absorption occurs at 42 mins and again at 77 mins of microwave program time. This shows that microwave power is directly affecting the rate of the reaction with no temperature increase detected on the pyrometer. The selectivity for ethylene also increased as the temperature of the reactions were increased. As determined in Chapter 4.0, the microwave fixed-bed reaction is very good at facilitating the production of ethylene over other products. Also, as discussed in chapter 4.0, the microwave fixed-bed has a low selectivity to the hydrogenolysis reaction of ethane to methane and a low selectivity for aromatic products. Molybdenum loaded H/ZSM-5 operated at 500°C, in thermally heated systems, have been shown to have a relatively high ethylene selectivity and a low selectivity to benzene and toluene [31]. The aromatization of ethylene over Mo/ZSM-5 has also shown low selectivity’s at thermal temperatures below 500°C. The thermal images also confirm that the catalyst bed is un-uniformly heated and underutilized. Therefore, the large amount of ethylene produced by the microwave reactor was not able to be efficiently converted to aromatics.
Figure 6.3: Microwave fixed-bed data for the MWFB350, where (a) is the temperature profile, (b) is the forward and reflected power profiles, and (c) is the collected reaction data. The vertical dashed line depicts the point in time the gas was switched from 1.5% ethane to 30% ethane which denotes time zero.
Figure 6.4: Microwave fixed-bed data for the MWFB375, where (a) is the temperature profile, (b) is the forward and reflected power profiles, and (c) is the collected reaction data. The vertical dashed line depicts the point in time the gas was switched from 1.5% ethane to 30% ethane which denotes time zero.
Figure 6.5: Microwave fixed-bed data for the MWFB425, where (a) is the temperature profile, (b) is the forward and reflected power profiles, and (c) is the collected reaction data. The vertical dashed line depicts the point in time the gas was switched from 1.5% ethane to 30% ethane which denotes time zero.
Figure 6.6: Thermal Images of the MWFB350 where (a) shows onset of hotspot formation, (b) is the pulsating of the hotspot by microwave power, and (c) is the ending temperature distribution after the thermal hotspot event. The time is in seconds where time zero is the 18-minute mark in microwave run time for the MWFB350, the images are recorded in IR radiation counts, and the arrows represent increases and decreases in counts due to the hotspot.
Figure 6.7: Thermal Images of the MWFB375 where (a) shows onset of hotspot formation, (b) is the rapid thermal runway and hotspot formation, (c) is the pulsating of the hotspot by microwave power, and (d) is the ending temperature distribution after the thermal hotspot event. The time is in seconds where time zero is the 21-minute mark in microwave run time for the MWFB375, the images are recorded in IR radiation counts, and the arrows represent increases and decreases in counts due to the hotspot.
**Figure 6.8:** Image of the hotspot from within the center of the (a) MWFB350 and (b) MWFB425 reaction.

**Figure 6.9:** Image of the hotspot that was formed in the MWFB375 reaction. (a) The catalyst inside the tube, and (b) is an image of the agglomerated hotspot and the dispersed catalyst bed showing overall low catalyst bed utilization by low coke deposits.
To test the theory of catalyst bed underutilization further, a hybrid reactor configuration was employed to heat the catalyst bed to 410°C by thermally heating hot air and passing it through concentric tubes as discussed in section 2.1.4 and Figures 2.4 and 6.2. The microwave was then used to raise the catalyst temperature to 475°C to facilitate the EDHA reaction. Figure 6.10 shows the microwave temperature, power, and reaction profiles for the MWhybrid reaction. The 410°C catalyst pre-heating was verified at the start of the microwave and at the end of the microwave program. Once again in the microwave fixed-bed a hotspot formation can be seen occurring at a temperature of 475°C. The formation of the hotspot at the higher temperature as compared to the MWFB would be due to the temperature difference within the catalyst bed. In the MWFB, the only heat source was the microwaves alone, however, now in the MWhybrid fixed-bed the catalyst is already at 410°C before the microwaves are turned on. In hotspot formation a temperature gradient is needed to facilitate the formation of coke or the dielectric properties changes to the catalyst.

The reaction products of the MWFB350, the MWhybrid reactor, and the thermally heated fixed-bed (TFB615) are compared in Figure 6.11. The MWhybrid reactor unconventional conversion trend is due to hotspot formation and the manual power changes during the reaction to induce a more controlled temperature profile, such as the one achieved in the last 15-mins of the reaction. The MWFB350 and the TFB615 had close to the same conversion after the first 6 mins of the reaction. The product selectivity to ethylene are in the order of MWFB350>MWHybrid>TFB615. The MWHybrid reactor show a decrease in overall ethylene selectivity when compared to just microwave heating. However, the MWHybrid exhibited a larger selectivity to aromatic than just MWFB350 alone. This supports the theory of catalyst bed underutilization put forth in chapter 4 and once again in this section 6.1. It is now confirmed that the addition of heat to the catalyst bed would increase catalyst bed utilization and provide enough energy to facilitate the aromatization of ethylene to benzene by the catalyst support. However, the thermally heated fixed-bed reactor still had the highest selectivity to aromatics for the EDHA reaction.

Although a path forward to increase aromatic selectivity has been identified with the MWHybrid heating, the formation of hotspots is still present. XRD characterization, as seen in Figure 6.12, the hotspots are detrimental to the zeolite structure. For the MWFB and the MWHybrid show little to no loss of H/ZSM-5 crystallinity. However, a large change in H/ZSM-5 crystallinity is observed.
when an XRD of a crushed hotspot that was concentrated on top of a carburized sample is analyzed. Significant reduction of the major zeolite peaks at 7.9, 8.8, 23.0, 23.9, and 24.3 [2θ] along with boarding of the angles between 20-30 degrees [105]. The formation of three new peaks are present at 41.9, 42.9, 43.5 degrees. These peaks suggest the formation of crystalline phases that are normally not present in Mo/ZSM-5 samples. The peaks were not identifiable in the other microwave heated samples due to the dilution of the hotspot with the rest of the crystalline catalyst bed.

TGA analysis of the spent samples are shown in Figure 6.13. The spent samples weight loss percent can be correlated to the conversion of the MWFB samples in the order of MWFB350 < MWFB375 < MWFB475. The MWFB samples each contain two orders of coke, where the corresponding temperature provided by the DSC signal are 446°C, 505°C, 564°C. The MWHybrid sample lost the higher amount of weight percentage. The type of coke formed on the MWHybrid sample consisted mostly of the two lower orders of coke at 446°C, and 505°C. The hotspot sample extracted from the center of a different microwave fixed-bed sample that was run under the same conditions 350°C, only 3.33% of weight loss occurred in the sample. The hotspot sample also only had one single order of carbon. In comparing the other samples to the hotspot sample, a small shoulder in the DSC signal for the MWFB and the MWHybrid spent samples can be seen that correspond to the hotspots higher order carbon burn off temperature at 625°C. The MWFB samples are all expected to have this higher order of coke that is displayed in the hotspot sample. However, the MWFB and MWHybrid samples were prepared by mortar and pestle to try to disperse the agglomerated hotspot as well as possible among the rest of the catalyst bed before further characterization. With only a 3.33% of weight loss in the hotspot sample and XRD confirming that the zeolite structure was degraded in the hotspot sample, it is most likely that the hotspot is a degradation and the formation of a well microwave absorbing material that is not carbon dense. Figure 6.14 is an image of a regenerated (a) MWFB425 sample and (b) Hotspot sample after TGA analysis to 1100°C in air. This shows that the structure that is left over from the hotspot sample is of no longer a well-structured H/ZSM-5. The sample is dark in color and there should be no carbon left on the sample after 1100°C treatment in air. Small dark piece of sample can also be seen in the MWFB425 regenerated sample, indicating that the same substance could be present in smaller quantity due to dispersion.
Figure 6.10: Microwave fixed-bed data for the MWHybrid, where (a) is the temperature profile, (b) is the forward and reflected power profiles, and (c) is the collected reaction data. The vertical dashed line depicts the point in time the gas was switched from 1.5% ethane to 30% ethane which denotes time zero.
**Figure 6.11:** Comparison between microwave heating, thermal heating, and microwave hybrid heating.
Figure 6.12: XRD of the carburized, TFB615, MWFB350, MWFB375, MWFB425, MWHybrid, and the concentrated hotspot.
Figure 6.13: Oxidative thermogravimetric weight loss and Heat flow curves of the spent TFB615, MWFB350, MWFB375, MWFB425, MWHybrid, and the concentrated hotspot.

Figure 6.14: 6%Mo/ZSM-5 spent samples where (a) is the MWFB425 and (b) is the concentrated hotspot sample after TGA regeneration in air to 1100°C.
6.2 Fluidization of an Ethane DHA Catalyst Under Thermal and Microwave Heating

The results of chapter 4 and in section 6.1 has provided insights on the interaction of the microwave EDHA reaction when operated in fixed-bed mode. The formation of the hotspot does allow for high ethane conversion to ethylene. But the overall low bulk temperature of the catalyst bed results in the inability of the catalyst to produce aromatics. The MWHybrid reaction demonstrated that the 410°C pre-heated catalyst was able to become more selective to aromatics. Temperatures above 410°C could facilitate higher benzene selectivity, but in the current setup, as shown in Figure 2.4, 410°C was the highest temperature able to be maintained by the system without the use of microwaves. Therefore, to further test the effects of catalyst bed utilization and to reduce hotspot formation, the use of a fluidized bed was employed. The goal of this section is not the optimization of fluidization, but the comparison of MW heating and temperature distribution in the same in a fluidized bed setup.

6.2.1 Thermal Fluidization

The effects of fluidization were first tested in a thermal fluidized bed rector (TFL) setup, as described in section 2.4 and illustrated in Figure 6.2. The EDHA thermally heated fluidized reaction were conducted at 650°C (TFL650), 615°C (TFL615), and 575°C (TFL575). The TFL samples were compared to the thermally heated TFB615 reaction form section 6.1 so that influence of fluidization could be compared before testing of the microwave heated catalyst. Figure 6.15 shows the reaction conversion and product selectivity’s for the TFB and TFL reactions. The TFL setup resulted in the loss of ethane conversion when compared to the thermally heated reaction. This suggest that the bubble size of the fluidized bed was not optimal and allowed for the bypass of ethane without complete reactions. The TFL650 and TFL615 reactions resulted in a higher ethylene selectivity but were not able to achieve the same aromatic selectivity as the TFB615.
Figure 6.15: Comparison of ethane conversion and product selectivity’s for the (a) TFL650, (b) TFL615, TFL575, and TFB615. [0.75g cat—100mL/min of 30% ethane]
6.2.2 Microwave Fluidization

6.2.3 Microwave Fluidized Bed Temperature Distribution and Control.

The effects of fluidization on the EDHA microwave heated reaction were tested in the reactor setup described in section 2.4 and illustrated in Figure 6.2. The EDHA microwave heated fluidized reaction was conducted at 600°C (MWFL600), 575°C (MWFL575), and 500°C (MWFL500) according to the thermal imager averaged bed temperature. The ethane conversion increased with increasing average catalyst bed temperature in the order of MWFL425 < MWFL500 < MWFL575 < MWFL600. The ethylene selectivity decreased, and the benzene selectivity increased with increasing temperatures. Figures 6.16, 6.18, and 6.20 shows that the catalyst bed is reaching temperatures throughout the catalyst bed hot enough to activate ethylene [106–108]. By use of the thermal imager at 144fps, the temperature distribution of the catalyst bed was recorded and averaged over the viewable area of the catalyst bed. The viewable area was 2/3 of the size of the catalyst bed viewed form one side of the catalyst bed, which is much larger than the 2.5mm spot size of the pyrometer. The thermal imager allows for a more accurate temperature description of what is taking place within the catalyst bed during the fluidization and was used as a validation of the real temperature of the catalyst bed. Also, throughout the MWFL reactions, the thermal imager was used periodically to take 30 second videos at 144fps. The recordings were reprocessed and the maximum temperature, average maximum temperature, minimum temperature, and the average minimum temperature was calculated over the video recordings length for the viewable catalyst bed.

The MWFL500 temperature profile, as seen in Figure 6.17a, shows that the pyrometer is in a disagreement with the thermal imager on absolute temperature of the catalyst bed. The temperature discrepancy can be explained by comparing the maximum and minimum temperature values in Figure 6.17a with the MWFL500 thermal images captured at 34:30 minutes of microwave program time before the start of the reaction, as seen in Figure 6.18. The progression of the fluidized bubbling bed can also be seen in Figure 6.19, where (b) is a hot gas bubble forming near the bottom of the tube, (c) rising to the top, and (d) merging with the hotter upper region. There is not one absolute temperature occurring, by examining the maximum and minimum values in the recording further shows that a 300°C temperature gradient within the catalyst bed is occurring over the 30 second recording. The pyrometer and the thermal imager are seeing hot regions bubbling within.
the tube reaching temperature of 700°C. The thermal imager is averaging a larger area and therefore a larger temperature distribution across the catalyst bed, therefore if the catalyst bed has areas of much lower temperature, the thermal imager will take that into account. The fluidized bubbling of hot and cold regions also creates a noisy temperature signal that could trigger a sensor break in the Eurotherm microwave controller. A sensor break will cause the microwave to reduce power to a safe level, this effect can be seen in Figure 6.18 on the MWFL575 at 35 minutes and in Figure 6.20 at 54 minutes. To mitigate a sensor break, the pyrometer was set to average the temperature for four seconds. The four seconds of averaging causes a lag within the microwave control system. The results are an unstable temperature control due the averaging time to detect a deviation in temperature. A careful balance must be made between the possibility of a temperature break and the response time of the microwave to temperature fluctuations. The catalyst can experience rapid temperature swings determined by the power given by the microwave (forward power) and absorbed by the catalyst (forward power – reflected power). Preventing temperature overshoot is necessary to prevent thermal dielectric property runaways, like the example shown in Figure 6.7.

In Figure 6.18, the average temperature profile of the thermal imager increased while the pyrometer remained constant with time on steam. This can be explained by the temperature distribution in the catalyst bed decreases with time as show in Figure 6.19 by the thermal imager and in Figure 17a max and min temperature values for the MWFL575. In Figure 6.20, the average temperature profile of the thermal imager for the MWFL600 reaction was in close agreement with the pyrometer, however this effect is due to the upper temperature limit of 748.9°C of the calibrated range used in the recording of the temperature distribution. For this reason, the thermal imager should have had a higher average catalyst bed temperature than what is shown in Figure 6.20a and in Figure 6.21. For the MWFL425, as seen in Figure 6.22, the overall catalyst bed temperature was too low to accurately measure an average temperature due to the thermal imagers calibrated range of 383.7-743.9°C. Figure 6.16c, 6.18c, and 6.20c shows the catalytic activity of the MWFL500, MWFL575, and MWFL600 reactions respectively.
Figure 6.16: Microwave fluidized data for the MWFL500 reaction, where (a) is the temperature profile, (b) is the forward and reflected power profiles, and (c) is the collected reaction data. The vertical dashed line depicts the point in time the gas was switched from 1.5% ethane to 30% ethane which denotes time zero.
Figure 6.17: MWFL500 temperature distribution within the catalyst fluidized bed at 34:30 of microwave program time the beginning of the reaction (a), (b) 64:00, and (C) 93:04 minutes of microwave program run time.
Figure 6.18: Microwave fluidized data for the MWFL575 reaction, where (a) is the temperature profile, (b) is the forward and reflected power profiles, and (c) is the collected reaction data. The vertical dashed line depicts the point in time the gas was switched from 1.5% ethane to 30% ethane which denotes time zero.
Figure 6.19: MWFL575 temperature distribution within the catalyst fluidized bed at (a) 29:00, (b) 60:00, and (c) 87:45 minutes of microwave program run time.
Figure 6.20: Microwave fluidized data for the MWFL600 reaction, where (a) is the temperature profile, (b) is the forward and reflected power profiles, and (c) is the collected reaction data. The vertical dashed line depicts the point in time the gas was switched form 1.5% ethane to 30% ethane which denotes time zero.
**Figure 6.21:** MWFL600 temperature distribution within the catalyst fluidized bed at (a) 34.00, (b) 50.00, (C) 59.10, (d) 65.00, (e) 75.05, and (f) 86.00 minutes of microwave program run time.
Figure 6.22: Microwave fluidized data for the MWFL475 reaction, where (a) is the temperature profile, (b) is the forward and reflected power profiles, and (c) is the collected reaction data. The vertical dashed line depicts the point in time the gas was switched form 1.5% ethane to 30% ethane which denotes time zero.
6.2.4 Characterization of Spent Fluidized Catalyst Under Thermal and Microwave Heating

XRD analysis of the spent fluidized samples shown in Figure 6.23, determines that the zeolites-maintained crystallinity after the reactions. MWFL600 and TFL650 show decreases in intensity in 7.5- and 8-degree spectral peaks. This is attributed to the higher level of coke formation as seen in Figure 6.24, where TFL650 lost 5.533% weight and MWFL600 lost 8.817%. All the samples exhibited reoxidation from 350-441°C indicated by the weight increase and DSC signal, except for MWFL600. At 441°C and then again at 520°C, the samples experience the same coke burn off temperatures except for the MWFL600. This shift to higher order coke can be attributed to the higher temperatures observed by the thermal imager that were occurring within the MWFL600 fluidized bed.
Figure 6.23: XRD of the Carburized, fluidized thermal (TFL) spent catalyst and the microwave fluidized bed (MWFL) spent catalyst.
**Figure 6.24:** Oxidative thermogravimetric weight loss (solid lines) and Heat flow curves (dashed lines) of fluidized thermal (TFL) spent catalyst and the microwave fluidized bed (MWFL) spent catalyst.
6.3 Comparison and Conclusion on Thermal, Microwave, and Hybrid Heated Reactions

A 6%Mo/ZSM-5 catalyst was tested in thermal, microwave, and hybrid setups for fixed-bed and fluidized bed configurations for the EDHA reaction. The catalyst was first tested in a TFB615 and then compared the microwave fixed-bed reactions of MWFB350, MWFB375, MWFB425, and MWHybrid. The TFB615 was the most selective to benzene formation and average benzene yield. The MWFB reactions facilitated a higher conversion of ethane due to hotspot formation. However, as previously reported in chapter 4.0, the MWFB reactions were not able to convert the large amount of ethylene produced into aromatic products. By use of the thermal imager, it was confirmed that the catalyst bed was being underutilized due to the low temperature distribution after hotspot formation, as seen in Figures 6.6 and 6.7. The use of a MWHybrid heated reactor, heated to 410°C by thermally hot air followed by microwave heating to 475°C resulted in a higher benzene selectivity and aromatic yield then the MWFB reactions at 350°C, 375°C, and 425°C. This further supports the claim of catalyst bed underutilization by hotspot formation. However, XRD confirmed that the hotspots generated are detrimental to the zeolite structure along with TGA confirming the formation of a high temperature burring order of coke. It was also noticed that the zeolite structure had degraded and changed color in the hotspot sample after reoxidation in air at 1100°C. To avoid such issues of hotspot degrading the catalyst structure and to facilitate the use of more of the catalyst bed, fluidization in a microwave reactor was tested.

To understand the effects of the non-optimized fluidization setup used, a comparison between thermal fluidization and fixed-bed fluidization at the same temperature was made. The TFB615 resulted in more conversion and selectivity to aromatics then the TFL615. This indicates that the fluidization had large bubbles that resulted in the bypass of unreacted gas. As the temperatures increased in the thermal fluidized bed the benzene selectivity, ethane conversion, and aromatic production rate increased. However, in the thermal fluidized bed at 650°C (TFL650) was still not able to facilitate a higher selectivity to aromatics then the fixed-bed at 615°C (TFL615).

The microwave fluidized bed reactor was compared over four temperatures so that the effects of increasing temperatures could be correlated in both thermal and microwave heating processes, Figure 6.25, illustrates the results summary of the microwave modes tested. The microwave fluidized bed at 425°C (MWFL425) was found not active for EDHA, the 6%Mo/ZSM-5 catalyst
at 425°C was only able to convert an average of 4% of the incoming ethane. This is contradiictive to the microwave fixed-bed where MWFB425 had the highest average conversion at 37%, due to hotspot formation. In the fixed-bed mode, the internal temperature of the catalyst cannot be monitored by pyrometers or thermal imagers, therefore the real temperature within the catalyst bed is unknown. Whereas within a fluidized bed the hot particles are bubbling and cycling in and out of the center of the fluidized tube. The effects of the fluidization prevent the sudden onset of rapid hotspot formations leading to catalyst degradation. However, the average amount of absorbed microwave power was about 3x that of the microwave fixed-bed for all microwave temperatures as seen in Figure 6.25. The microwave fluidized bed at 575°C (MWFL575) and MWFL600 was able to surpass the TFB615 conversion and benzene production rate. But the TFB615 reactor remained the most selective approach to aromatic within the study. It has been demonstrated we were able to increase the catalyst selectivity to aromatics and facilitate a higher aromatic production rates than previously possible within a microwave fixed-bed reactor by using unconventional methods, such as fluidized beds and hybrid heating systems, for the microwave heated ethane dehydroaromatization reaction.

**Figure 6.25:** Thermal, microwave, and hybrid fixed-bed mode compared to thermal and microwaves fluidized mode for the average production rate, ethane conversion, and product selectivity’s for the EDHA reaction.
Further process development for the use of microwaves to induce C-H bond activation in gas phase heterogenous catalytic reactions was explored. Supporting projects were conducted with methane and ethane to elucidate reaction mechanisms and the feasibility of the C-H bond activation. Methane DHA by microwave induced catalyst heating and microwave induced plasma catalysis was explored to lower the required energy input and increase methane conversion. Continued process development for ethane was carried out in oxidative atmospheres consisting of CO\textsubscript{2} to determine the mechanistic differences that the microwave facilitated for the oxidative conversion of ethane to aromatics and/or methanol.

7.1 Activation of C-H Bond by Microwave Catalysis for The Methane DHA Reaction

Methane dehydroaromatization is a thermodynamically limited process, as seen in Figure 7.1, that suffers from coke deposition and relatively fast deactivation. Molybdenum loadings on H/ZSM-5 are typically used in the range 3–6 weight percent [109–111]. The conversion of methane at low temperatures are reported to be in the range of 10–15\% at 700\^°C. The reported selectivity to aromatics for the thermally heated reactor is in the range 60–90\% at 700\^°C. In Section 3.0, the catalytic activation of ethane for the dehydroaromatization reaction was discussed. The results of section 3.0 showed that microwave required a 285\^°C lower catalyst temperature, to activate ethane, than what the thermally heated fixed-bed required. The energy saving concept for microwave conversion of ethane to aromatics was tested to determine the activation temperatures required to maintain the conversion for methane dehydroaromatization.
7.1.2 Catalyst Performance Under Microwave Irradiation for the Methane DHA Reaction

Figure 7.2 shows the methane conversion in the microwave at a bulk temperature of 450°C and 600°C. Under microwave conditions, initial methane conversion of 50% can be achieved at temperature of 450-600°C. The microwave heated catalyst exhibited a rapid deactivation trend in methane conversion. This can be attributed to the under-utilization of the catalyst bed, combined with rapid coke formations within the hotspot region. Figure 7.1. shows the equilibrium conversion of methane dehydroaromatization in a thermally heated reactor. The microwave reactors methane conversion is higher than the equilibrium methane conversion at 700°C (12%) in a thermal reactor. The hypothesis is that there may be the presence of localized non-equilibrium regime that facilitates the reaction to produce compositions above thermodynamic equilibrium. The results for methane DHA further confirm the results in section 3, that the microwave reactor can activate the C-H bond at lower bulk temperatures then thermally heated reactors. Microwave facilitated methane DHA research was not continued for this thesis dissertation for reasons of repeatability caused by rapid deactivation due to coke formations, and catalyst bed underutilization.
Figure 7.2: Methane conversion for the dehydroaromatization reaction at 450°C and 600°C.

The preliminary results offer insights on traditional fixed-bed deactivation and regeneration along with the innovative use of microwaves to heat the solid electromagnetic sensitive catalyst. Given the preliminary results it becomes more apparent that more research is needed to find ways to efficiently utilize the whole catalyst bed, drive energy efficiency, and reduce catalyst coking. Coke formation is a very good microwave absorber, and the build-up of coke can lead to hotspot formations, microwave leakage, and catalyst deactivation. The use of oxidants such as CO₂ should be explored as a regeneration gas and as a reactive gas for various reactions with natural gas in a microwave. In addition, understanding the activation of CO₂ and ethane under microwave catalytic conditions become critical. Different from oxidation dehydrogenation of ethane using oxygen where poor selectivity is obtained due to highly exothermic nature, dehydrogenation of ethane in the presence of CO₂ is endothermic reaction, and the reaction can be better controlled under microwave irradiation. The Future research are summarized in the following section projects are listed below.

7.2 Microwave Induced Methane Plasma Process for High Conversion of Methane

The direct conversion of methane into C₂+ chemicals is a significant challenge due to the high activation energy of methane and the low conversions achieved even at reaction temperatures above 700°C [13,14,112,113]. In microwave discharges, methane can be converted to ethylene and acetylene without high temperatures or a catalyst present by dimerization of methyl radicals.
to form ethane, followed by subsequent dehydrogenation reactions [114,115]. In microwave discharges, the product distribution is shifted with increasing input power from ethane to ethylene and finally to acetylene [115,116]. M. Heintze at el. showed that over 90% methane conversion could be achieved with a selectivity of up to 80% acetylene [57,117]. Generally, this process is conducted under vacuum, however, at atmospheric pressures the initial capital and running cost of the reactor system can be greatly reduced. The combination of microwave discharge of methane with a bi-functional catalyst such as Mo/ZSM-5, could prove to be a low temperature, low coking solution to the direct conversion of methane to liquid products.

7.2.1 Results for Microwave Induced Plasma Process for Catalytic Conversion of Methane

The process of methane conversion to C$_2$+ products was tested in a dual reactor zone setup as seen in Figure 2.5. 0.50g of 4%Mo/ZSM-5 was placed inside the heated zone of the tubular furnace at 400°C and a methane plasma was initiated upstream and fed down to the catalyst. The reaction conditions and reactor configuration are discussed further in section 2.1.6. Figure 7.3 shows the exit gas concentrations from the reactor system. Under non-plasma conditions no conversion of methane was observed for the first 54 mins of the reaction. Once the plasma was ignited, the single pass conversion of methane was over 97%. With this high methane conversion, capital intensive recycle of unconverted methane would not be necessary to drive a profit. The outlet gas contained primary hydrogen with ethane, ethylene, benzene, and toluene. At 70 min of TOS the aromatic selectivity was 8.87%, the ethylene selectivity was 20%, and the selectivity of ethane was 5.56%. The ethane concentration in the stream would not be thermodynamically capable of reacting at the 400°C temperature to produce aromatics. Microwave induced methane plasma process research was not continued for this thesis dissertation for the following reasons. Under atmospheric conditions plasma temperature control was unstable due to the buildup of coke deposits on the quartz walls within the waveguide. As the quartz tube becomes coated in a layer of carbon, the microwave would require increased power to maintain the plasma. This suggest that the carbon is shielding the plasma zone from the microwave irradiation.
7.3 MW-Enhanced Catalytic Conversion of Ethane to Aromatics with CO₂

In 2018, Yao et. al. reported oxidative dehydrogenation of ethane with CO₂ using Mo₂C as a catalyst [98]. They have discovered that CO₂ was able to transform into CO via two pathways:

1. \[ \text{CO}_2 + * = \text{CO} + \text{O}^\circ \], where the surface O\(^\circ\) is responsible for ethane dehydrogenation
2. Reverse Boudouard reaction with carbon formed on catalyst: \[ \text{CO}_2 + \text{C} = 2\text{CO} \]

The aforementioned pathways can be potentially exploited to improve DHA conversion and yields as the presence of CO₂ can offer a mild source of oxygen that can improve the activation of the C₂⁺ compounds as well as limit the deleterious effects of carbon formation that normally plagues the DHA reaction. However, introducing CO₂ leads to the potential of over oxidizing the hydrocarbons into syngas, which requires developing a catalyst that selectively activates the C-H
bond but minimizes C-C cleavage [118]. This can be controlled by the addition of promoters (Fe) and the reactivity of the surface oxygen. Figure 7.4 illustrates an efficient reactor concept that utilizes ethane and CO$_2$ at the well head to produce liquid products. The microwave reactor coupled with secondary heat source (burner) could dramatically decrease the amount of energy required by the microwave to produce liquid products. The burner is fueled by the non-condensable products CO and H$_2$ to generate heat form the combustion of CO and H$_2$, the CO$_2$ produced from combustion could be recycled.

**Figure 7.4:** Efficient reactor concept to produce liquid products from ethane and CO$_2$. 
7.3.2 Results for Microwave Oxidative Ethane DHA Reaction with CO₂

As shown in Figure 7.5, initial conversion of ethane and CO₂ in a MW fixed-bed reactor is observed at 325°C bulk catalyst temperature, and continues to increase, reaching ~60%. In contrast, in a thermally heated fixed-bed reactor, ethane conversion starts from 500°C, and remains relatively insensitive to the temperature increase. The effect of temperature on aromatics formation rate is shown in Figure 7.5b. The MW reactor is operated in the temperature range of 325-475°C, whereas the thermally heated reactor is operated in the temperature range of 500-600°C. The catalyst under MW exposure shows an aromatics formation rate that continues to increase with temperature. At 475°C in MW reactor, the BTX formation rate is nearly double that which corresponds to the thermal fixed-bed reactor at 550°C. This illustrates the promising activity that can be achieved for a catalyst that would be properly designed to take advantage of the selective heating of active sites while the catalyst is exposed to MW irradiation. Although not shown, the spent MW catalyst was lighter in appearance compared to the traditionally heated catalyst, qualitatively indicating carbon formation was less pronounced over the duration of the experiment.

![Figure 7.5: Ethane DHA with CO₂ in thermal catalytic and MW catalytic fixed-bed reactors, (a) effect of temperature on conversion (b) effect of temperature on aromatics (BTX) formation rate.](image)
7.4 Microwave-Assisted Methanol Production.

The results illustrated in the above sections are relevant to aromatics formation from the ethane DHA with CO₂ as an oxidant reaction:

\[ \text{CO}_2 + 3\text{C}_2\text{H}_6 \rightleftharpoons \text{C}_6\text{H}_6 + \text{CO} + \text{H}_2\text{O} + 5\text{H}_2 \]

We have explored alternative use for CO and H₂ produced from the reaction. Although CO₂ is an oxidant in the reaction, turning into CO after DHA. It will be beneficial if we can convert CO and H₂ into liquid chemicals, such as methanol, in the same DHA reactor:

\[ \text{CO}_2 + 3\text{C}_2\text{H}_6 = \text{C}_6\text{H}_6 + \text{CH}_3\text{OH} + \text{H}_2\text{O} + 3\text{H}_2 \]

Methanol is a key chemical intermediated which can be converted to olefins and aromatics via commercial process (MTO and MTA).

The challenge is: DHA is operated under relatively high temperature and ambient pressure whereas methanol synthesis is operated under lower temperature and high pressure (220°C, 70 bar). The use of microwave technology, like the reactor setup as seen in Figure 2.6a, could improve the aromatic synthesis and allow for lower pressure methanol synthesis. The microwave fields provide energy to the reaction through relaxation processes. These relaxations include dipolar or Debye processes, which involve the coupling of the radiation with dipoles in the solid catalyst. These dipoles can be defect sites (i.e. atomic vacancies) in the catalysts or dangling bonds on the surface of the catalyst. The dipoles would allow the catalyst surface to facilitate selective bond activation effects enabling electron sharing between reaction intermediates and catalyst surface, thus lowering activation energy which in turn can affect reaction rates.

Section 7.3 discusses the microwave catalytic conversion of ethane to aromatics with CO₂. This process produces excess hydrogen along with unreacted CO₂, which could be further utilized to produce methanol in the catalyst bed. This transformative approach relies on the use of microwaves to enable the conversion of ethane into hydrogen and aromatics, and simultaneously hydrogenate CO₂ into methanol, the reaction pathways are:
Dehydroaromatization: \[3C_2H_6 = C_6H_6 + 6H_2\]  
Methanol Synthesis: \[3H_2 + CO_2 = CH_3OH + H_2O\]

Overall Reaction: \[CO_2 + 3C_2H_6 = C_6H_6 + CH_3OH + H_2O + 3H_2\]

However, the high reaction temperatures required to activate ethane under microwave irradiation was found to dissociate methanol. Therefore, the approach of using a thermal-microwave hybrid heating system, as seen in Figure 2.6b, consisting of one thermally heated reactor (oxidative DHA) and one microwave reactor (methanol synthesis) was considered for the simultaneously conversion of ethane and CO\(_2\) into aromatics, CO and H\(_2\), followed by the simultaneous production of methanol. The production of aromatics and methanol without the need of high pressures or separation processes would result in significant energy savings.

**7.4.1 Simultaneously Production of Aromatics and Methanol from Ethane and CO\(_2\) under Low Pressure**

The temperature survey results are illustrated in Table 7.1, which lists the amount of methanol produced at each temperature. 200°C achieved the highest amount of methanol production. 160°C was too low to facilitate the reaction, whereas 240°C caused methanol decomposition. Methanol synthesis from CO\(_2\) and hydrogen typically requires high pressures. However, here it has been shown that it is possible to produce methanol in a microwave at lower pressures than possible in a thermally heated reactor. Figure 4.8 displays the methanol concentration over time for the 200°C microwave reaction temperature. The methanol concentration for the co-processing of ethane and CO\(_2\) can also be seen in Figure 4.8. The concentration of methanol in the co-processing method is significant less than the direct processing method. Figure 4.9 gives the conversion of ethane and concentrations of the gas at the exit of the reactor. The CO\(_2\) and hydrogen atmosphere will undergo the water gas shift reaction to produce CO. If H\(_2\) and CO\(_2\) concentrations are compared to the methanol concentration produced in the co-processing reaction, it is apparent that with increasing CO\(_2\) and decreasing H\(_2\) concentration, the amount of methanol produced was decreased with TOS. The ratio of CO\(_2)/(H_2)\) in the direct processing experiment was 0.33 whereas in the outlet gas of the co-processing experiment it was closer to 0.45. This suggest that the optimum feed concentrations of ethane and CO\(_2\) need to be optimized to achieve the desired ratio of hydrogen.
and CO₂ needed to facilitate CO₂ hydrogenation to methanol. Higher pressures could force more methanol formation for the co-processing technique. Microwave enhanced co-processing of methanol from ethane and CO₂ was not continued for this thesis dissertation for the reasons of pressure limitations to current reactor design.

Table 7.1: Microwave methanol synthesis temperature survey.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Methanol (avg conc %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>160°C</td>
<td>0.013</td>
</tr>
<tr>
<td>200°C</td>
<td>0.041</td>
</tr>
<tr>
<td>240°C</td>
<td>0.010</td>
</tr>
</tbody>
</table>

Figure 7.6: Methanol concentration for the direct microwave CO₂ hydrogenation and dual reactor co-processing of ethane and CO₂.
7.3 Microwave Ethane Dehydrogenation to Ethylene
7.3.1 Introduction

Ethylene is a valuable chemical intermediate that is used in industrially important products such as HDPE, LDPE, PVC, ethylene glycol, and styrene. Typically, ethylene is produced by the energy intensive process with temperature above 800°C and the use of large amounts of steam. Compared to steam cracking ethylene production by direct catalytic oxidative dehydration of ethane (ODE) is thermodynamically favored, therefore the coke formation is significantly less due to the lower reaction temperatures [84,119,120]. Transition metal oxides such as Mo, Cr, Ga, and V are typically used as catalyst and have been shown to activate ethane at temperatures between 400-550°C [84,119,120]. Support materials such as alumina oxide, titanium oxide, and silicon oxide are common supports for ODE catalyst [84,119,120]. Ethylene production by the ethane oxidative dehydrogenation process combined with microwave technology could drive the efficiency of the ethylene production process, due to the rapid and selective heating along with the high energy efficiency of the microwave.
7.3.3 Proof-of-Concept

The proof-of-concept results showed that ethylene can be produced from the dehydrogenation of ethane by use of carbon dioxide as a oxidant in a microwave reactor system. Figure 5.6 is an image of the spent catalyst inside the tube after 150 min of TOS. From the image it can be seen that there is little coke formation on the catalyst surface and that only a small portion of the catalyst bed was used during the 150 min reaction.

![Conversion and Selectivity at 275°C](image)

**Figure 7.8:** Proof of concept data for the microwave oxidative dehydrogenation of ethane to ethylene.

![Image of catalyst bed after 150 min of TOS](image)

**Figure 7.9:** Image of catalyst bed after 150 min of TOS, displaying low coke formation for the microwave oxidative dehydrogenation of ethane to ethylene.
Chapter 8: Publication to Date

8.1 Journal Articles (Lead author)


8.2 Journal Articles (Co-author)


• Jianli Hu, Changle Jiang, I-Wen Wang, Brandon Robinson, Xinwei Bai, Microwave Catalysis for Modular Production of Carbon Nanomaterials from Natural Gas, U.S. Provisional patent filed Application No.: 63/020,933, May 6, 2020

8.4 AIChE and ACS Presentations

• Thermal-Microwave Hybrid Reactor Configuration for Energy Efficient Production of Aromatics from Natural Gas, AIChE National Meeting, San Francisco, 2020
• Microwave Assisted Catalytic Conversion of Ethane to Aromatics for a more Efficient approach over A Conventional Fixed-Bed Reactor, AIChE National Meeting, Orlando, 2019
• Stability of Fe- and Zn-Promoted Mo/ZSM-5 Catalysts for Ethane Dehydroaromatization, ACS National Meeting, Boston, 2018
• Stability of Fe- and Zn-Promoted Mo/ZSM-5 Catalysts for Ethane Dehydroaromatization, AIChE National Meeting, Pittsburgh, 2018
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