ABSTRACT

Title of Dissertation: **NANO STRUCTURED MATERIALS FOR ENERGY APPLICATIONS**

Lu Liu, Doctor of Philosophy, 2017

Dissertation directed by: Michael R. Zachariah, Professor
Department of Chemical and Biomolecular Engineering and Department of Chemistry and Biochemistry

This dissertation addressed the applications of nanostructured materials as oxygen carriers (OCs) and catalysts in poly lactic acid (PLA) thermal decomposition. In chapter 1-4, the stability and cyclibility of metal oxides and supported metal oxides as OCs were evaluated in an isothermal fixed bed reactor at different temperatures for 50 cycles with methane as fuel, up to 15h while their structural, physical and chemical properties were identified using XRD, SEM, TEM, BET, XPS and Ar/H2-TPR. In chapter 5, aerosol synthesized Bi2O3 was found to be a useful catalyst in thermal PLA decomposition, which could lower the on-set decomposition temperature by ~75 T. The developed study protocol could be applied to various metal oxides and polymers to study their catalytic thermal decompositions as well.
NANO STRUCTURED MATERIAL FOR ENERGY APPLICATIONS

by

Lu Liu

Dissertation submitted to the Faculty of the Graduate School of the University of Maryland, College Park, in partial fulfillment of the requirements for the degree of Doctor of Philosophy 2017

Advisory Committee:
Professor Michael R. Zachariah, Chair
Professor Sheryl Ehrman, Dean’s representative
Professor Bryan Eichhorn
Professor Zhihong Nie
Professor Efrain Rodriguez
Dedication

To

My parents

Junhui Liu (刘俊辉) and Ping Li (李平),

And my husband

Peng Zhao (赵鹏).

Thank you for your unconditional love and support. Thank you for your unwavering faith and absolute belief in my abilities. You have sacrificed so much and waited so long for this moment to come true and I dedicate this dissertation to you.
Acknowledgements

I owe my gratitude to all those who have guided and helped me along this journey.

First and foremost, I would like to express my sincere thanks and respect to my advisor, Professor Michael Zachariah, for guiding me throughout the years of my graduate study, who is the most brilliant person I have met. It is my honor for me to work with him, with his invaluable ideas, experience, eternal passion and rigorous attitude for research and life.

I thank my advisory committees, Professor Efrain Rodriguez, Professor Zhihong Nie, Professor Bryan Eichhorn and Professor Sheryl Ehrman for their time, input and help in reading my dissertation and providing valuable comments. Moreover, I would like to thank Dr. Rodriguez for insightful discussions on my perovskite OC work. I would like to thank Dr. Dongxia Liu for advice and suggestions on the zeolite work. I would like to thank Dr. Stanislav Stoliarov for reading and editing my catalytic Poly Lactic-acid (PLA) thermal decomposition work.

I would like to thank Dr. Xiaofei Ma, who mentored me in my first two years of PhD study. I learned much from his knowledge and experience in combustion and aerosol synthesis & measurement techniques. I would like to thank Yiqing Wu and Dr. Jing Li, with whom I collaborated with zeolite and PLA work respectively. Yiqing did the material synthesis, elemental analysis and BET in zeolite work and Jing finished the kinetic analysis in the PLA work. I learned a lot from them.
Also, I would like to thank all Zachariah group members (Dr. Guoqiang Jian, Dr. Xiaofei Ma, Xizheng Wang, Tao Wu, Dr. Mingdong Li, Dr. Lei Zhou, Dr. Wenbo Zhou, Yong Yang, Rian You, Jiaojie Tan, Philip Guerieri, Jeffery DeLisio, Scott Holdren Garth Egan, Nichloas Piekiel and Rohit Jacob) for their help for make my Ph.D. journey real and enjoyable.

Last but definitely not least, I owe my thanks to my family for all their love and support. I am indebted to my parents for raising me and supporting me in all my pursuits. Most importantly, I am very grateful to my husband, Peng Zhao, for his love and support on my way to finish my Ph.D.

Lu Liu
刘璐
Table of Contents

Dedication .................................................................................................................. ii
Table of Contents ......................................................................................................... v
List of Tables ................................................................................................................ vii
List of Figures ............................................................................................................... viii

Chapter 1: Introduction ............................................................................................. 1
  1.1 Energy utilization and nanostructures ................................................................. 1
     1.1.1 Energy utilization and climate change ......................................................... 1
     1.1.2 Nanostructures ......................................................................................... 13
     1.1.3 Synthetic methods of nanostructures ......................................................... 13
  1.2 Applications ......................................................................................................... 18
     1.2.1 Oxygen Carriers in Chemical Looping Combustion ................................... 18
     1.2.2 Catalysts in Thermal Poly Lactic Acid Decomposition .............................. 23
  1.3 Scope of the Thesis ............................................................................................. 26
  1.4 List of Publications .............................................................................................. 29

Chapter 2: Alkali Metal doped Fe₂O₃ and Fe₂O₃-Al₂O₃ Composites as Oxygen Carrier .................................................................................................................. 30
  2.1 Introduction ......................................................................................................... 30
  2.2 Experimental Approach ....................................................................................... 31
     2.2.1 Oxygen Carrier Synthesis ........................................................................ 31
     2.2.2 Fixed bed reactivity test for CLC OCs ...................................................... 32
  2.3 Results and Discussion ........................................................................................ 35
  2.4 Conclusion and Outlook ....................................................................................... 61

Chapter 3: Novel Support: Silicalite-1 zeolite for Fe-based Oxygen Carriers .......... 62
  3.1 Introduction ......................................................................................................... 62
  3.2 Experimental Section ........................................................................................ 64
     3.2.1 Material synthesis ...................................................................................... 64
     3.2.2 Characterizations ...................................................................................... 68
  3.3 Results and discussion ......................................................................................... 70
     3.3.1 Structural properties of OCs .................................................................... 70
     3.3.2 Composition and porosity of OCs ............................................................ 74
     3.3.3 OC performance tests in CLC ................................................................. 78
  3.4 Conclusion ........................................................................................................... 92

Chapter 4: Perovskite Oxides as Oxygen Carriers .................................................... 93
  4.1 Introduction ......................................................................................................... 93
  4.2 Experimental Approach ...................................................................................... 94
     4.2.1 Perovskite OC synthesis .......................................................................... 94
     4.2.2 Material Characterizations ...................................................................... 95
     4.2.3 Fixed bed reactor reactivity test .............................................................. 96
  4.3 Results and Discussion ....................................................................................... 97
     4.3.1 Textual properties of OCs ...................................................................... 97
Chapter 5: Thermal Decomposition and Kinetics of Poly (Lactic Acid)
Sacrificial Polymer Catalyzed by Metal Oxide Nanoparticles

5.1 Introduction
5.2 Experimental Approach
5.2.1 Catalyst synthesis
5.2.2 Incorporation of nano-catalysts into PLA
5.2.3 Material characterizations
5.3 Results and Discussion
5.3.1 Material textural properties
5.3.2 Thermal tests and kinetic analysis
5.4 Conclusions and Outlook

Chapter 6: Conclusions and Future Work

6.1 Conclusions
6.2 Future Work
6.2.1 Develop kinetic models for alkaline additives added OCs and zeolite supported OCs
6.2.2 Study the effectiveness of alkaline or alkaline earth ions’ addition to Cu-, Mn-, Ni-based OCs
6.2.3 Study the effectiveness of zeolite support to Cu-, Mn-, Ni-based OCs
6.2.4 Extend the 3d electronegativity rule of transition metal to other energy related applications
6.2.5 Study the catalytic effects of other aerosol synthesized metal oxides to bio-degradable polymers

Chapter 7: References
List of Tables

Table 2.1. XRD identifications of different OCs’ sample before and after 50-cycle CLC tests.

Table 3.1. Textual properties and elemental composition of the OCs.

Table 3.2. Reaction equations in different reduction stages of CLC and corresponding CO₂ yields.

Table 4.1. Le Bail refinement results for as synthesized samples.

Table 4.2. Le Bail refinement results for samples post fixed bed reactor studies.

Table 5.1. Kinetic parameters for PLA, PLA/Fe₃O₃, PLA/Bi₂O₃ and PLA/CuO.
List of Figures

Figure 1.1. History of total and per capita human energy use and world population.

Figure 1.2. Energy flow charts of the relative size of primary energy resources and end uses in the United States in 2015, with fuels compared on a common energy unit basis. The chart is produced by Lawrence Livermore National Lab (https://flowcharts.llnl.gov/).

Figure 1.3. Global surface temperature changes from 1880 to 2015, with the year 2015 ranking as the warmest on record (data from NASA/GISS http://climate.nasa.gov/vital-signs/global-temperature/).

Figure 1.4. Keeling curve of atmospheric carbon dioxide concentration, measured at Mauna Loa Observatory (from Wikipedia, http://en.wikipedia.org/wiki/Keeling_Curve).

Figure 1.5. All CO₂ emissions in US, by source (from Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-1023).

Figure 1.6. Schematic overview of pre-combustion technology.

Figure 1.7. Schematic overview of oxyfuel combustion technology.

Figure 1.8. General schemes of chemical looping combustion.

Figure 1.9. Configuration of a pressure typed nebulizer.

Figure 1.10. Configuration of spray pyrolysis set up.
Figure 1.11. Schematic overview of oxygen transport in CLC. (http://theconversation.com/chemical-looping-a-carbon-capture-technology-for-the-future-12435).

Figure 1.12. Perovskite crystal structure.

Figure 1.13. Chemistry of the decomposition from PLA to lactide.

Figure 2.1. Schematic diagram of CLC system.

Figure 2.2. SEM images and Particle-size distributions of as-synthesized Fe$_2$O$_3$ a), b) 4.8mol% K 95.2mol% Fe$_2$O$_3$, c) produced by spray pyrolysis measured using a differential mobility analyzer (DMA) coupled with a condensation particle counter (CPC).

Figure 2.3. a) Effect of temperature on temporal CO$_2$ conversion for the 1$^{st}$ cycles of Fe$_2$O$_3$ in the CH$_4$ step, b) Comparison of potassium added vs. neat iron oxide CO$_2$ temporal conversion for the 1$^{st}$ cycle CH$_4$ step at 1023 K.

Figure 2.4. CO$_2$ yield per gram Fe$_2$O$_3$ for a) Fe$_2$O$_3$, b) Fe$_2$O$_3$·K (95.2mol% Fe$_2$O$_3$ with 4.8mol% K), c) 1Fe1Al(50 mol% Fe$_2$O$_3$/ 50 mol% Al$_2$O$_3$), d) 1Fe1Al·K (2.6 mol% K 48.7 mol% Fe$_2$O$_3$/ 48.7 mol% Al$_2$O$_3$) at 750 °C, 850 °C, 950 °C.

Figure 2.5. TEM images of alkaline doped OCs after 50 cycles CLC test at 1023 K of a) 4.8mol% Na / 95.2mol% Fe$_2$O$_3$ (b) 4.8mol% K / 95.2mol% Fe$_2$O$_3$ (c) 2.6 mol% Cs 48.7 mol% Fe$_2$O$_3$/48.7 mol% Al$_2$O$_3$ (d) 2.6 mol% K 48.7 mol% Fe$_2$O$_3$/48.7 mol% Al$_2$O$_3$. 
Figure 2.6. HRTEM images of alkaline doped OCs after 50 cycles CLC test at 1023 K of (a) 95.2 mol% Fe$_2$O$_3$/4.8 mol% Na (b) 95.2 mol% Fe$_2$O$_3$/4.8mol% K (c) 48.7 mol% Fe$_2$O$_3$/48.7 mol% Al$_2$O$_3$ with 2.6 mol% Cs.

Figure 2.7. CO$_2$ yield per gram of Fe$_2$O$_3$ for different OCs at 1023 K as a function of cycle number.

Figure 2.8. CO$_2$ selectivity- $\gamma_{CO_2}$ of different OCs at 1023 K.

Figure 2.9. XPS and deconvolution results for Fe 2p core-level of a) Fe$_2$O$_3$ b) 4.8 mol% K 95.2 mol% Fe$_2$O$_3$ after 50 CLC cycles at 1023 K.

Figure 2.10. SEM images of OCs after direct synthesis, 1 h thermal annealing at 1023 K, and 50 cycles CLC test at 1023 K.

Figure 2.11. TEM and elemental mapping results for 50 mol% Fe$_2$O$_3$/50 mol% Al$_2$O$_3$: (a, c) as synthesized; (b, d) after 50 CLC cycles at 1023 K.

Figure 2.12. TEM and elemental mapping: 48.7 mol% Fe$_2$O$_3$/48.7 mol% Al$_2$O$_3$ with 2.6 mol% K after 50 CLC cycles at 1023 K.

Figure 2.13. TEM Elementary Mapping result 2.6 % Na 48.7mol% Fe$_2$O$_3$/ 48.7mol% Al$_2$O$_3$ after 50 CLC cycles at 1023 K.

Scheme 3.1. Synthesis procedure to prepare Fe$_2$O$_3$@silicalite-1 OC.

Figure 3.1. Morphology of OC samples viewed by SEM images of a) Fe$_2$O$_3$@Si, c) Fe$_2$O$_3$e/Si-12, and e) Fe$_2$O$_3$/Si-24, and TEM images of b) Fe$_2$O$_3$@Si, d) Fe$_2$O$_3$/Si-12, and f) Fe$_2$O$_3$/Si-24, respectively.
Figure 3.2. XRD patterns of silicalite-1, Fe$_2$O$_3$ and silicalite-1 supported OCs.

Figure 3.3. a) Ar ad-/desorption isotherms of OCs and b) NLDFT pore size distributions of OCs derived from the adsorption branch of their Ar ad-/desorption isotherms.

Figure 3.4. CO$_2$ yield in CH$_4$ step at a) 1023K and b) 1223K of Fe$_2$O$_3$, Fe$_2$O$_3$@Si, Fe$_2$O$_3$/Si-12, Fe$_2$O$_3$/Si-24 during 50 cycle CLC reaction.

Figure 3.5. XRD patterns of Fe$_2$O$_3$ and silicalite-1 supported Fe$_2$O$_3$ OCs after 50 cycle CLC reaction tests.

Figure 3.6. CH$_4$ to CO$_2$ selectivity, $\gamma_{CO_2}$, at a) 1023K and b) 1223K, respectively, over Fe$_2$O$_3$, Fe$_2$O$_3$@Si, Fe$_2$O$_3$/Si-12 and Fe$_2$O$_3$/Si-24 samples during 50 cycle CLC reaction.

Figure 3.7. The evolution profile of CO$_2$ a) and H$_2$ b) in the reduction step during the 30$^{th}$ CLC cycle at 1023 K (open symbol) and 1223 K (filled symbol) for all OCs.

Figure 3.8. SEM images of the OCs (a) and (b): Fe$_2$O$_3$, (c) and (d): Fe$_2$O$_3$@Si, (e) and (f): Fe$_2$O$_3$/Si-12 and (g) and (h): Fe$_2$O$_3$/Si-24 after 50 cycle CLC reaction at 1023 and 1223 K, respectively.

Figure 4.1. SEM of LaCrO$_3$ 1a) and 1b) shows the spherical morphology.

Figure 4.2. Powder XRD patterns for each of the tested samples.

Figure 4.3. a) TEM, b) SEM and c) HRTEM and d) SAED shows the perovskite crystal structure of the post-reaction La$_{0.5}$Ca$_{0.5}$CoO$_3$.

Figure 4.4. Powder XRD of post fixed bed reactor study samples.
Figure 4.5. Le Bail fitting of La$_{0.5}$Ca$_{0.5}$CoO$_3$ in the orthorhombic *Pnma* space group. Shown are the observed (black circles), refined (red line), difference (blue line) and locations of allowed reflections (blue tick marks).

Figure 4.6. Le Bail fitting of LaCu$_{0.5}$Mn$_{0.5}$O$_3$ in the orthorhombic *Pbnm* space group. Shown are the observed (black circles), refined (red line), difference (blue line) and locations of allowed reflections (blue tick marks).

Figure 4.7. Le Bail fitting of LaNiO$_3$ in the orthorhombic *Pbnm* space group. Shown are the observed (black circles), refined (red line), difference (blue line) and locations of allowed reflections (blue tick marks).

Figure 4.8. TGA-MS of as-synthesized perovskites with m/z=32 ion current displayed (All mass loss curves superimposed on top of one another).

Figure 4.9. (a) OSC (δ) and (b) CH$_4$ selectivity to CO$_2$ of tested perovskites in 50 cycles with methane at 750 °C in a fixed-bed reactor.

Figure 4.10. The relation of OSC (δ) and (a) the $\lambda_B$ (B site electronegativity) in methane total oxidation and (b) the e$_g$ electron occupancy.

Figure 5.1. SEM of nanoparticles a) Bi$_2$O$_3$, b) CuO, c) Fe$_2$O$_3$, prepared from spray pyrolysis.

Figure 5.2. Particle-size distributions of Fe$_2$O$_3$, CuO, Bi$_2$O$_3$ as-synthesized by spray pyrolysis measured using a differential mobility analyzer (DMA) coupled with a condensation particle counter (CPC).

Figure 5.3. N$_2$ adsorption/desorption isotherms of Fe$_2$O$_3$, CuO, Bi$_2$O$_3$. 
Figure 5.4. XRD of nanoparticles-Bi$_2$O$_3$, Fe$_2$O$_3$, CuO from spray pyrolysis.

Figure 5.5. SEM of cross-sectioned a) and b) PLA, c) PLA/Fe$_2$O$_3$, d) PLA/CuO films.

Figure 5.6. SEM of cross-sectioned PLA/Bi$_2$O$_3$ film.

Figure 5.7. TGA of PLA and PLA/MOs.

Figure 5.8. DTG plots of PLA and PLA/MOs.

Figure 5.9. DSC test of PLA and PLA/MOs.

Figure 5.10. Experimental and simulated DTG of PLA & PLA/MO composites at 10 K min$^{-1}$.

Figure 5.11. HRR of PLA, PLA/Fe$_2$O$_3$, PLA/Bi$_2$O$_3$ and PLA/CuO.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CLC</td>
<td>Chemical Looping Combustion</td>
</tr>
<tr>
<td>OC</td>
<td>Oxygen Carrier</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-Ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Coupled Plasma-Optical Emission Spectroscopy</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmett and Teller Theory</td>
</tr>
<tr>
<td>TG</td>
<td>Thermogravimetry</td>
</tr>
<tr>
<td>TPR</td>
<td>Temperature Programed Reduction</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential Thermal Analysis</td>
</tr>
<tr>
<td>DSC</td>
<td>Digital Scanning Calorimetry</td>
</tr>
<tr>
<td>DMA</td>
<td>Differential Mobility Analyzer</td>
</tr>
<tr>
<td>CPC</td>
<td>Condensation Particle Counter</td>
</tr>
<tr>
<td>PLA</td>
<td>Poly Lactic Acid</td>
</tr>
</tbody>
</table>
Chapter 1: Introduction

1.1 Energy utilization and nanostructures

1.1.1 Energy utilization and climate change

Since the industrial revolution two or three hundred years ago, daily life style of human society has been changed in all aspects, including increased amount of food and consumer goods produced, significantly elongated distances travelled, as well as drastically increased human population. All of these aspects are based on the growing energy consumption to maintain the enhanced quality of human life. As shown in Figure 1.1, the energy consumption has grown by more than 20 times in the 20th century, which was caused by both the population explosion and the energy consumed per pita.

As indicated by Figure 1.2, which is the energy flow chart in the U. S in 2015, the major energy resources are fossil fuels, including coal, natural gas, petroleum, which cover more than 80% of the total energy resource. Also, combustion is still the major approach for energy conversion, including more than 85% (fossil fuel & biomass) of the total world energy, which is the sum of the 95% in transportation, 67% in electricity generation and approximately 50% in all other sectors.
Figure 1.1. History of total and per capita human energy use and world population.
Figure 1.2. Energy flow charts of the relative size of primary energy resources and end uses in the United States in 2015, with fuels compared on a common energy unit basis. The chart is produced by Lawrence Livermore National Lab.

Estimated U.S. Energy Consumption in 2015: 97.5 Quads
Increased energy consumption has been widely acknowledged as the reason for global climate change. The global temperature has increased ~1 °C in the past one hundred years, which has exceeded the temperature increase in the previous thousands of years, while nationwide temperature is 0.6 °C higher than the 1981-2010 average, as shown in Figure 1.3. It has been widely acknowledged that CO₂ is the major greenhouse gas, shown in Figure 1.4, accounting for half the greenhouse gas effect, causing global warming.² It mainly comes from fossil fuel and biomass combustion, which is the major energy source for modern industries, offering more than 80% of the global energy consumption.³ Although CO₂ emission also comes from lots of natural sources such as decomposition, ocean release and respiration, a lot of evidence has shown that human related CO₂ emission is the major source of CO₂ increase since industrial revolution, indicated by Figure 1.5.⁴
Figure 1.3. Global surface temperature changes from 1880 to 2015, with the year 2015 ranking as the warmest on record (data from NASA/GISS http://climate.nasa.gov/vital-signs/global-temperature/).
Figure 1.4. Keeling curve of atmospheric carbon dioxide concentration, measured at Mauna Loa Observatory (http://en.wikipedia.org/wiki/Keeling_Curve).
Figure 1.5. All CO₂ emissions in US, by source (from Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2023).
Traditional combustion involves the high temperature redox reaction between hydrocarbon and oxidizer; usually air (80% N₂). Novel combustion techniques for power plant with carbon dioxide capture have been proposed to efficiently reduce major greenhouse gas-\(\text{CO}_2\) emission, including pre-combustion\(^5\), post combustion\(^6\), oxy-fuel combustion\(^7\) and chemical looping combustion\(^8\).

Pre-combustion refers to removing of carbon species in the fuel before combustion, shown in Figure 1.6, by gasification process of hydrocarbon at high temperature and pressure to form syngas, and then syngas undergoes water-gas shift reaction to convert CO to \(\text{CO}_2\), producing a mixture with \(\text{H}_2\) and high concentration \(\text{CO}_2\) (more than 50%). The \(\text{CO}_2\) could be easily separated and leaves carbon-free fuel content to combust.

In oxyfuel combustion, shown in Figure 1.7, pure oxygen instead of air (80% \(\text{N}_2\)) is used as oxidizer, and the product from hydrocarbon with pure oxygen will only be steam and \(\text{CO}_2\), thus pure \(\text{CO}_2\) stream could be obtained by water condensation.
Figure 1.6. Schematic overview of pre-combustion technology.\textsuperscript{9}
Figure 1.7. Schematic overview of oxyfuel combustion technology.⁹
Chemical looping combustion is a two-step combustion technique, shown in Figure 1.8, and it utilizes metal oxides instead of air (80% N₂) as the oxidizer to burn hydrocarbon fuels such that the separation of CO₂ from N₂ is avoided, and hydrocarbons are converted to carbon dioxide and water while reduced metal oxides are transferred into an air reactor, and further oxidized back to the original form. With both reactions occurring below 1100 °C, chemical looping combustion could avoid NOₓ formation as well.

The exploration of novel combustion technologies requires the study of novel materials, which make the applications of those technologies possible. One of these approaches involves the use of nanostructured materials.
Figure 1.8. General schemes of chemical looping combustion.
1.1.2 Nanostructures

The nanoscale covers from 0.1 nm to 100 nm dimension, and nanomaterials are materials composed of units within this scale range. Single atom and molecule’s diameter are several Angstroms (Å), while 1 Å = 0.1 nm. Nanomaterials offer large surface to volume ratio, which are highly related to their synthesis, processing and applications. The smaller the particle size, the higher surface to volume ratio. The existence of high percentage surface to volume ratio helps promote the surface energy, thus the atomic diffusion, leading to many size dependent phenomena. Thus, nanomaterials have attracted a lot of interests for more than decades in various applications, because of their superior mechanical, electrical and catalytic performances.

1.1.3 Synthetic methods of nanostructures

Here we utilize the aerosol synthetic method to obtain nano-structured metal oxides. Aerosol includes a suspension of fine liquid droplets or particles, up to 100 µm, in a gas phase, which could be natural, such as fog and cloud, or artificial, such as dust, haze, mist, fume and smoke. A common method for large scale industrial production of nanomaterials is the aerosol based processes because it is simple, highly scalable and continuous, compared to wet chemical synthesis. The usage and applications of aerosol has started decades before the basic aerosol science and engineering are well understood. For instance, generation of pigments, including carbon black and titania, is from aerosol method while fumed silica and titania are generated from their chloride precursors by flame pyrolysis. The aerosol synthetic method involves thermal decomposition of aerosols precursors generated by a
nebulizer and carried by a gas flow through a hot zone. When precursors are sprayed onto a hot surface or into hot atmosphere beyond their decomposition temperature, the target particles will be formed in the hot zone. This synthetic method includes flame synthesis, where particles are sprayed into high temperature flame\textsuperscript{19}, or spray pyrolysis\textsuperscript{20} where precursor droplets are sprayed into a flameless high temperature reactor. It follows the droplet-to-droplet mechanism, where each droplet is a microreactor as they are carried by the carrier gas into the hot zone where reaction occurs. The first step in the aerosol-assisted synthesis is breakage of precursor solutions into fine droplets through a nebulizer. A nebulizer utilizes either shear force, ultrasonic energy or electrical force to break precursor solution into fine droplets. A widely used atomizer is the ultrasonic nebulizer type because of energy efficiency, affordability and inherent low velocity of the initial precursors, which breaks up the precursors into droplets through vibrations from the ultrasonic energy. Another pressure typed nebulizer is widely used in industries due to its stability and economy. It is the one we used in our lab, with its configurations shown in Figure 1.9. According to Bernoulli’s Principle and Venturi Effect, $P_1 < P_2 = P_0 = 1$ atm, therefore liquid flow will be sucked up from the atomizer and then broke into droplets by shear force from the compressed air flow.

The spray pyrolysis utilized in our lab is described in Figure 1.10, it is a process for preparing particles or films by first generating droplets form a precursor solution, then solvent evaporating and decomposing precursors in a reactor. Briefly, particles are formed through an aerosol “droplet-to-particle” process, and unlike liquid synthetic methods, it could produce particles continuously. This process has
been widely used in the preparation of particles in various applications, including solid oxide fuel cell, lithium ion batteries and catalysts. Various nanomaterials could be prepared through spray pyrolysis, including solid/porous/hollow metal, metal oxides\textsuperscript{20} and sulfides\textsuperscript{21}, nanocomposites\textsuperscript{22}, highly porous carbons\textsuperscript{23} etc.
Figure 1.9. Configuration of a pressure typed nebulizer.
Figure 1.10. Configuration of spray pyrolysis set up.
1.2 Applications

1.2.1 Oxygen Carriers in Chemical Looping Combustion

Chemical looping combustion is a novel combustion technique that offers little carbon footprint with little energy penalties.\textsuperscript{24} The wide applications of chemical looping combustion depend on the explorations of proper oxygen carriers, which should 1) be stable under repeated oxidation/reduction cycles; 2) show fast kinetics both at oxidation and reduction steps; 3) little coking formation from hydrocarbon decomposition at reduction step; 4) economically feasible and 5) environmentally benign. Therefore, single or mixed (Cu-, Mn-, Co-, Fe-, Ni-) transition metal based oxides and Ca-based alkaline earth sulfates have been tested as oxygen carriers.\textsuperscript{24}
Figure 1.11. Schematic overview of oxygen transport in CLC. (http://theconversation.com/chemical-looping-a-carbon-capture-technology-for-the-future-12435).
Copper oxide has a relatively low melting and decomposition temperature, below 800 °C, and will go through chemical looping oxygen uncoupling (CLOU) process during the reaction with hydrocarbon, which releases oxygen to react with fuels. Its low melting point leads to a tendency for sintering and defluidization in reactors, therefore, a supporting material is usually utilized to overcome those issues. Manganese oxide and cobalt oxide will follow the CLOU reaction path in the fuel reactor with oxygen releasing occurring before reaction with hydrocarbon.

Nickel and iron oxides are non-CLOU metal oxides, and oxygen will stay in the solids to react with hydrocarbon. Iron oxides are widely studied OC material, since it is inexpensive, environmental benign and earth abundant, with high melting point and mechanical strength. However, it is easy to sinter and shows slow reduction kinetics. After applying proper support materials, improved reactivity and recyclability will make it a good performing OC.

Mixed metal oxides, including Mn-Fe, Mn-Ni, Mn-Mg, and Mn-Cu are explored as OCs, showing synergistic effects. Naturally occurring minerals, such as ilmenite, are also potential candidates as OC, which is reduced to Fe₂TiO₅ and oxidized to FeTiO₃ in multiple cycles. It exhibits high oxygen storage capability compared to Fe₂O₃ to Fe₃O₄ redox cycle. Perovskites, shown in Figure 1.12, usually with chemical formulated as ABO₃, are known for high oxygen conductivity, thermal stability and fast oxygen-diffusion. The ideal perovskite structure is cubic symmetry, with B cation in 6-fold coordination and A cation in a 12-fold coordination, shown in Figure 1.12. Perovskite has been proved to be qualified oxygen carriers with long time stability offering fast oxygen transportation.
Figure 1.12. Perovskite crystal structure.
1.2.1.3 Supporting Materials

Supporting materials are added to provide enhanced chemical and mechanical stability, recyclability as well as oxygen transport ability to OCs. Inert supports, such as MgAl$_2$O$_4$\textsuperscript{35}, Al$_2$O$_3$\textsuperscript{36}, TiO$_2$\textsuperscript{37}, SiO$_2$\textsuperscript{38}, ZrO$_2$\textsuperscript{24}, are used as support materials to offer extra stability and prolong recyclability of mixed and single metal oxide OCs.

For example, Cu-based OCs show high reaction rates and high oxygen transfer capacity with almost complete fuel conversion, however, its proneness to decompose at low temperatures (~950 K) and tendency to sinter makes it impractical to use pure CuO in CLC applications. Therefore, to improve Cu-based OCs, various supports have been utilized, including Al$_2$O$_3$, MgAl$_2$O$_4$, SiO$_2$, TiO$_2$, Yttria stabilized zirconia (YSZ) etc.\textsuperscript{39,40,41,42,43,44,45}

Fe-based OCs attract continuous research interests because of their low cost, environmental benign, and abundance in nature. However, they suffer from weak redox characteristics and sintering; thus various supports are used in Fe-based OCs to improve performance.\textsuperscript{38,37,36}

Reducible oxides (CeO$_2$, La$_2$O$_3$) are studied as supports for NiO to ensure complete conversion of fuel to CO$_2$ compared to inert supports (Al$_2$O$_3$, SiO$_2$).\textsuperscript{46a} Veser \textit{et al.} has added lanthanum doped ceria as low as 2% to iron based oxygen carriers to double the effective oxygen carrying capacity.\textsuperscript{46b}

1.2.1.4 Promoter additives to Oxygen Carriers

Phase separation is another reason for oxygen carrier materials degradation with OCs’ phase segregating and sintering. Additives, such as alkali or alkali earth ions\textsuperscript{47,48} are added to prevent phase separation between OC and support and improve oxygen
utilization, with only less than 5% addition. Those ions could assist in binding OC and supports, thus reducing the potential of phase separation. The promoter additives do not work as support to the OCs since they are usually less than 5% and if too much additives are added, there would be negative effects to OCs’ reactivity.

Besides the exploration of MOs as OCs, we also studied the MOs as catalytic thermal decomposition catalysts of bio-friendly polymer, Poly Lactic Acid (PLA). PLA has been used as sacrificial polymer in the fabrication of battery separators and can be employed in 0D-3D Vaporization of a Sacrificial Component (VaSC) fabrication.

1.2.2 Catalysts in Thermal Poly Lactic Acid Decomposition

1.2.2.1 Poly Lactic Acid thermal decomposition

Bio-based polymers have attracted much attention due to their economic and ecological benefits. Lactic acid is mainly produced from plants (mainly from starch and sugar) including corn, potatoes and beets, and bacteria could generate its monomers also. The chemistry of the interconversion between lactide and poly lactic acid is shown in Figure 1.13.
Figure 1.13. Chemistry of the decomposition from PLA to lactide.
PLA is known as the most promising candidate of substituting the petroleum-based polymers in packaging\textsuperscript{51} and fiber technology.\textsuperscript{52} PLA has been explored as one of the two major 3-D printing inks (the other one being ABS (Acrylonitrile butadiene styrene)) due to its good thermoplasticity.\textsuperscript{53} Compared to ABS, PLA offers biodegradability and biocompatibility. Because of its relative low thermal decomposition temperature (more than 200 °C lower than thermal stable polymers, such as polyimide (PI), epoxies, Poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP), etc., PLA has also been explored as a sacrificial component from 0D to 3D to create complex-shaped molds after thermal removal with thermal stable polymer copolymers.\textsuperscript{53,54,55,56} Porous materials could not only regulate fluids transport in filtration,\textsuperscript{57} but also facilitate ion exchange in battery electrodes\textsuperscript{58} and separator films\textsuperscript{59}.

1.2.2.2 Catalysts for PLA thermal decomposition

To further enlarge the thermal decomposition temperature difference between PLA and stable polymer mold copolymer, catalysts, such as alkali earth metal oxides\textsuperscript{60}, rare metal (scandium (III) triflates (CF\textsubscript{3}SO\textsubscript{3}-))\textsuperscript{61}, and tin containing compounds\textsuperscript{62}, have been added into PLA to further lower its thermal decomposition temperature. The addition of catalysts into PLA could be achieved through surface treatment\textsuperscript{54}, solvent evaporation casting\textsuperscript{55}, or vane extruding\textsuperscript{62}.

By adding these catalysts, the decomposition of PLA could be further lowered, which could greatly shorten the heat treatment of PLA removal time, thus keeping the thermal stable polymers' integrity and stability.\textsuperscript{60,53}
1.3 Scope of the Thesis

In chapter 2, alkaline (K-, Na-, and Cs-) doped iron oxide and alumina supported iron oxides were synthesized from one step aerosol spray pyrolysis and tested as OCs in fixed bed reactor with methane as fuel. In this study alkali metal doped Fe$_2$O$_3$ and Fe$_2$O$_3$/Al$_2$O$_3$ composite oxygen carriers were synthesized from spray pyrolysis, and the reactivity and stability as oxygen carrier materials were evaluated in a fixed bed reactor for 50 isothermal redox cycles using CH$_4$ as the fuel. We find that both Fe$_2$O$_3$ and Fe$_2$O$_3$/Al$_2$O$_3$ composite showed reactivity degradation over multiple cycles, with clear phase separation between Fe and Al, in the composites. In contrast, alkali metal doping (~ 5 mol%) with Na, K, Cs was found to stabilize the reactivity of the Fe$_2$O$_3$ over the 50 redox cycles and prevent phase Fe-Al separation in the composite. Methane to CO$_2$ selectivity was found to be relevant to dopant type, which decreased in the order of dopant type K, Cs, Na. The best performing alkali metal, K, enhanced long term stability significantly, with no observed degradation in kinetics and total conversion performance in the methane step, as well as reduced coke formation. Adding an alumina matrix to K doped Fe$_2$O$_3$ helped promote CO$_2$ generation as well as minimize coking, and was found to be the best performing material.

In chapter 3, silicalite-1 has been explored as the supporting material for iron oxide as OCs for the first time. We employed a silicalite-1 zeolite support to achieve OCs with high resistance against sintering and coking in CLC. Iron oxides (Fe$_2$O$_3$) with methane fuel were employed to demonstrate the approach and to quantify the influence of silicalite-1 support on conversion efficiency, durability, and selectivity of these OCs in CLC cycles. Two iron oxide-zeolite geometrical structures, a core-shell
Fe$_2$O$_3$@silicalite-1 and an Fe$_2$O$_3$-impregnated silicalite-1 (Fe$_2$O$_3$/silicalite-1), were created to improve Fe$_2$O$_3$ stability. The CLC tests showed that both structures led to less aggregation of Fe$_2$O$_3$ OCs at 1223 K. A comparison between Fe$_2$O$_3$/silicalite-1 and Fe$_2$O$_3$@silicalite-1 in CLC tests illustrates that Fe$_2$O$_3$ impregnated in zeolite had higher durability than in the core-shell structure. The selectivity of CH$_4$ to CO$_2$ followed the order of Fe$_2$O$_3$/silicalite-1 > Fe$_2$O$_3$@silicalite-1 >> bare Fe$_2$O$_3$. The high selectivity of Fe$_2$O$_3$/silicalite-1 to CO$_2$ in CLC tests can be attributed to the encapsulation of Fe$_2$O$_3$ inside channels of silicalite-1 that provides physical barriers for aggregation of OCs in CLC cycles as well as coke deposition on OCs. In conclusion, our study of the structure-function relation for silicalite-1 supported Fe$_2$O$_3$ OCs can form the basis for the development of silicalite-1 as efficient support in chemical looping applications.

Perovskite oxides, chemical formulated as ABO$_3$, has been studied as novel OCs in CLC due to its thermal stability and faster reaction kinetics. In chapter 4, ten perovskite type OCs, La$_x$Ca$_{1-x}$B(Cr-, Mn-, Fe-, Co-, Ni-)O$_3$ were synthesized from spray pyrolysis and tested with methane as fuel in the fixed bed reactor at 1023 K. It has been found that the oxygen storage capacity (OSC) has negligible change with changing A site from Ca to La while there exists an inverted volcano shaped relationship between OSC and B site electronegativity. Thus 3$d$ transition metal B site electronegativity could be used as a powerful descriptor in the OSC of perovskites with CH$_4$ total combustion thus could provide useful design rule in choosing perovskite type OCs in CLC and might also provide some design insight for other energy related applications of perovskites.
Also we explored Bi$_2$O$_3$, CuO and Fe$_2$O$_3$ nanoparticles synthesized from spray pyrolysis, as catalysts for PLA thermal decomposition in chapter 5. Poly Lactic Acid (PLA) has been used as sacrificial polymer in the fabrication of battery separators and can be employed in 0D-3D Vaporization of a Sacrificial Component (VaSC) fabrication. In this study, 1wt% PLA/Fe$_2$O$_3$, PLA/CuO, PLA/Bi$_2$O$_3$ composites are prepared by solvent evaporation casting. Scanning Electron Microscopy (SEM) images indicate that the embedded nanoparticles are well dispersed in the polymer matrix and X-Ray Diffraction (XRD) verifies the crystallinity of these Metal Oxides (MOs). Thermal stability analysis of PLA and PLA/MO composites is performed using a Thermogravimetric Analyzer (TGA) and Differential Scanning Calorimeter (DSC). The overall heat of combustion is measured by Microscale Combustion Calorimetry (MCC) and is found to be insensitive to the presence of nanoparticles. The overall catalytic effects of the three metal oxides trends as: Bi$_2$O$_3$>Fe$_2$O$_3$>CuO ≈ inert material. PLA/Bi$_2$O$_3$ decomposition onset temperature (T$_{5\%}$) and maximum mass loss decomposition temperature (T$_{\text{max}}$) are lowered by approximately 75 K and 100 K respectively compared to the neat PLA. The as-synthesized Bi$_2$O$_3$ is identified as the most effective additive among those proposed in the literature to catalyze the PLA thermal decomposition process. A numerical pyrolysis modeling tool, ThermaKin, is utilized to analyze thermogravimetric data of all the PLA/MOs and to produce a description of the decomposition kinetics, which can be utilized for modeling of thermal vaporization of these sacrificial materials.
1.4 List of Publications


Chapter 2: Alkali Metal doped Fe\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} Composites as Oxygen Carrier

2.1 Introduction

Chemical Looping Combustion (CLC) involves a two-step process in which metal oxides as the oxygen carrier (OC) replacing air in order to avoid direct contact between fuel and air.\textsuperscript{5} Current primary interests in CLC lie in the potential advantages of burning hydrocarbons or coal in a nitrogen-free environment so as to enable more efficient/economical CO\textsubscript{2} sequestering as well as avoid NO\textsubscript{x} formation.\textsuperscript{63,64} However, finding good oxygen carriers is one of the major challenges in any widespread implementation of CLC.\textsuperscript{8} The important properties of oxygen carriers are high reactivity to both reduction and oxidation, as well as high mechanical stability and recyclability over multiple cycles, low cost and environmental benign.\textsuperscript{39,65} Metal oxides including copper-, iron- nickel-, and mixed-oxide have been studied, however, Fe-based oxygen carriers while economical, have shown relatively slow reduction rate and a propensity for physical and chemical degradation over time.\textsuperscript{66,67,68} Fe\textsubscript{2}O\textsubscript{3} can be sequentially reduced to Fe\textsubscript{3}O\textsubscript{4}, FeO, and finally Fe, with different CO\textsubscript{2} conversions.\textsuperscript{69} The economic advantages of an iron-based material coupled with its high melting point and environmental benign have continued to maintain interest as these materials. In an effort to enhance active surface area, pore volume, sintering resistance, long term stability and recyclability, support materials including Al\textsubscript{2}O\textsubscript{3},...
SiO₂, MgO, TiO₂, ZrO₂, CeO₂ have been employed. The performance improvement with supported OCs was often attributed to enhanced intra-particle gaseous diffusivity, as well as electronic or O²⁻ mobility considering the reactions between OC and fuel are gas-solid or solid-solid reactions.

In order to enhance the reactivity of Fe₂O₃, we have referred to the fact that alkali metal doping of catalysts has been known to improve selectivity, activity or prolong lifetime of metal/metal oxide catalysts. Specifically, activity decreases in the order of Cs, K, Na, Li, attributed to the decreasing size, polarization and electronegativity. While strictly speaking the oxygen carrier is considered a reactant and not a catalyst one might expect that some of the same principles that improve catalyst may also improve oxidation performance. With that logic, in this study we demonstrate that K doped Fe₂O₃ offers significant improvement in performance, both cycling and a lower coke formation potential in the reduction step with methane, while other alkali metals are not as effective. Further enhancement is seen when alumina is included to make composite alkali doped particles. In both cases no long-term degradation in performance is observed.

2.2 Experimental Approach

2.2.1 Oxygen Carrier Synthesis

All oxygen carriers studied were in-house synthesized by aerosol spray pyrolysis. Briefly speaking, the system consists of an atomizer (to produce aerosol droplets), silica-gel diffusion drier (to remove solvent), a high temperature furnace, and a sample collector (to collect nanoparticles). The aerosol of precursor solution is
generated using a collision-type nebulizer with an initial droplet diameter is about 1 µm, which is dried by passing through diffusion dryer. The aerosol is then passed through a tube furnace operated at 873 K to create the solid particle with a residence time of ~1 s. Particles exiting the aerosol reactor are then collected on a 0.4 µm DTTP Millipore filter. To thermally decompose all nitrates completely, all particles were annealed at 1023 K for 1 h before the CLC test.

The precursors for the Fe$_2$O$_3$, Al$_2$O$_3$ and alkali metal components were Fe(NO$_3$)$_3$·9H$_2$O, Al(NO$_3$)$_3$·9H$_2$O and MNO$_3$ (M= Na, K, Cs) respectively at a total concentration of 0.2 M. For the samples tested in this work, a 5 mole% of alkali metal relative to Fe was added, in each case, such as 4.8mol% K/95.2mol% Fe$_2$O$_3$ (Fe$_2$O$_3$·K), 4.8mol% Cs/95.2mol% Fe$_2$O$_3$ (Fe$_2$O$_3$·Cs), 50mol% Fe$_2$O$_3$/ 50mol% Al$_2$O$_3$ (1Fe1Al), 2.6mol% K 48.7mol% Fe$_2$O$_3$/ 48.7mol% Al$_2$O$_3$ (1Fe1Al·K), 2.6mol% Na 48.7mol% Fe$_2$O$_3$/ 48.7mol% Al$_2$O$_3$ (1Fe1Al·Na), 1.3mol% Na 1.3mol% Na 48.7mol% Fe$_2$O$_3$/ 48.7mol% Al$_2$O$_3$ (1Fe1Al·1K1Na).

### 2.2.2 Fixed bed reactivity test for CLC OCs

The reactivity of oxygen carriers was tested in a vertically oriented fixed bed reactor placed in an electrically heated isothermal furnace. While industrial practice probably favors the use of fluidized-beds, there are examples of designs for full scale fixed bed reactors for CLC$^{77,78}$. From a laboratory standpoint fixed bed studies are widely used due to the simplicity of operation and the small samples that can be utilized$^{79, 46a, 80, 81}$. This latter point was of particular interest to us since our focus is on materials synthesis and rapid screening. Readers will also note that our materials are nanoscale. Obviously this length scale is not practical in fluidized beds, however particles of the
type described here are easily generated by spray pyrolysis methods at various sizes\textsuperscript{17}. Finally it is possible to construct micro-size particles comprised of nanoparticles by spray induced aggregation that offers accessible surface areas that greatly exceed the corresponding external surface area\textsuperscript{82}.

About 200 mg sample materials were used for each test. The quartz flow reactor has a length of 61 cm, with a 1 cm I.D, as shown in Figure 2.1. The particles were first annealed at 1023 K for 1 hour, and then exposed alternatively to 11% methane for 2 min and 20% oxygen for 5 min simulating the CLC system. Argon is introduced for 300 s after each period, to avoid oxygen and methane mixing during the switch between oxidation and reduction. 50 cycles were achieved in this test.
Figure 2.1. Schematic diagram of CLC system.
MKS Mass Flow Controllers (MFCs) for the three gases were regulated by a Labview VI program. The reactor effluent was characterized by a mass spectrometer (Stanford Research UGA 300) operating with a mass resolution <0.5 atomic mass unit (amu) at 10% of peak height and a detection limit <1 ppm. Argon was used as an inert internal standard to determine the volume change of gaseous reactants and products during the reaction so as to assign concentrations. By varying flow rates of CH$_4$, O$_2$ with fixed Ar flow rate, calibrations of mass spectrometer for different gases with different concentrations were accomplished. Crystal structures of OCs were characterized by X-Ray Diffraction (XRD) with a Bruker Smart1000 using Cu Kα radiation. Transmission electron microscopy (TEM) and elemental mapping were performed using a field-emission transmission electron microscope (JEOL JEM 2100F). Scanning electron microscopy (SEM) and Energy-Dispersive X-ray (SEM-EDX) results were obtained by Hitachi SU-70 SEM.

2.3 Results and Discussion

A differential mobility analyzer (DMA) coupled with a condensation particle counter (CPC) described in our previous work, was utilized to obtain the size distribution of the as-synthesized particles.$^{80}$ As shown in Figure 2.2c, the Fe$_2$O$_3$ particle diameter peaks at 84 nm without K and 87 nm with 5mol% K, implying that particle size effects can be ignored in any comparison. Similar results were obtained with other dopants (Na, Cs).
Figure 2.2. SEM images and Particle-size distributions of as-synthesized Fe$_2$O$_3$ a), b) 4.8mol% K 95.2mol% Fe$_2$O$_3$, c) produced by spray pyrolysis measured using a differential mobility analyzer (DMA) coupled with a condensation particle counter (CPC).
The multiple-cycle test in the fixed bed reactor examines the reactivity and stability of the selected oxygen carriers. Figure 2.3a illustrates the temporal dependence of oxygen carrier reduction with CH$_4$ reaction to CO$_2$ of neat Fe$_2$O$_3$ sample at the 1$^{st}$ cycles. Normalized time is the real time normalized by the pulse length. The conversion-time plot shows a sigmoidal shape, indicating that the gas-solid reaction may proceed following the JMA model.$^{83, 84}$ Since this study primary focuses on total yield, selectivity and cycling stability, the data presented subsequently are under conditions of steady conditions ($i.e.$ long times) so that temperature dependence of kinetics cannot be evaluated. Figure 2.3b shows that adding potassium results in a slight improvement in the kinetics without changing final yield. This is important since any long-term stability improvements though the addition of potassium should not ultimately degrade kinetic performance. Assuming that both cases share the same reaction order, the temporal conversion plots yield a reaction rate for the potassium added case roughly twice that for the neat iron oxide.
Figure 2.3. a) Effect of temperature on temporal CO$_2$ conversion for the 1$^{st}$ cycles of Fe$_2$O$_3$ in the CH$_4$ step, b) Comparison of potassium added vs. neat iron oxide CO$_2$ temporal conversion for the 1$^{st}$ cycle CH$_4$ step at 1023 K.
Figure 2.4. shows the performance behavior at different temperatures for unmixed (Figure 2.4a, 2.4c), and K added OCs’ multicycle performance (Figure 2.4b, 2.4d). Theoretically, the conversion from Fe₂O₃ to Fe₃O₄ should give a CO₂ yield of 0.52 mmol/g from Fe₂O₃ to FeO, 1.56 mmol/g and from Fe₂O₃ to Fe, 4.69 mmol/g. Equilibrium calculation shows that Fe₂O₃ to Fe₃O₄ under methane leads to 100% CO₂, but that subsequent partial reduction to FeO gives a mixture of CO and CO₂. Our experimental results could not reliably quantify this point due to relative high mass 28 (N₂) background in our mass spectrometer. It is clear that for the 1st cycle of the neat Fe₂O₃ (Figure 2.4a) and 50mol% Fe₂O₃/50mol% Al₂O₃ (Figure 2.4c) samples, the Fe₂O₃ got converted to Fe₃O₄ after CH₄ step.

Also, it demonstrates that from Figure 2.4a that for pure Fe₂O₃ performance degrades steadily after each cycle, which has also been reported by others and is one of the problems plaguing many OCs. Addition of aluminum nitrate to create an alumina stabilizing matrix (Figure 2.4c) for the Fe₂O₃ exhibited essentially identical behavior to the neat Fe₂O₃ oxide case, implying that at least under the synthetic strategy pursued here, the alumina offered no advantages. For both cases before K⁺ addition (Figure 2.4a and 2.4c), CO₂ generation degraded to almost one third its first cycle at the 50th cycle. The addition of K however, shown in Figure 2.4b and Figure 2.4d stabilized the performance even up to 1223 K, with no temperature dependence to the conversion or stability over the 50 cycles studied. At various loadings, 80mol% Fe₂O₃, 20mol% Al₂O₃, 67mol% Fe₂O₃ 33mol% Al₂O₃ OCs were also tested, with no difference in performance detected. The degradation may be attributed to the decreasing oxygen-ion transport within the lattice or a reduction in the oxygen
Meanwhile, adding K+ to the Fe₂O₃/Al₂O₃ composite also helped modify the degradation problem (Figure 2.4d). To be more specific, 2.6mol% K 48.7 mol%Fe₂O₃ 48.7mol% Al₂O₃ OC also gave a steady CO₂ yield of Fe₂O₃ to Fe₃O₄ as the Fe₂O₃ case during those 50 cycles. What is responsible for this effect will be specified later in this work.
Figure 2.4. CO$_2$ yield per gram Fe$_2$O$_3$ for a) Fe$_2$O$_3$, b) Fe$_2$O$_3$·K (95.2mol% Fe$_2$O$_3$ with 4.8mol% K), c) 1Fe1Al(50 mol% Fe$_2$O$_3$/ 50 mol% Al$_2$O$_3$), d) 1Fe1Al·K (2.6 mol% K 48.7 mol% Fe$_2$O$_3$/ 48.7 mol% Al$_2$O$_3$) at 750 °C, 850 °C, 950 °C.
Next we turn to the effects of alkali metals as dopants. To compare the effects of different alkali doping, we chose to use Na, K and Cs to vary the size, polarization and electronegativity of the dopant. Plots of the CO\textsubscript{2} yields per gram Fe\textsubscript{2}O\textsubscript{3} for different oxygen carriers (OCs) for 50 redox cycles is presented in Figure 2.5. The first thing to note is that addition of the alkali metal dopant clearly stabilizes the long term stability of the CO\textsubscript{2} conversion with no apparent decreases in performance over time, but only K offers high oxygen transport capacity for iron oxide. Usually, alkaline ions are considered as catalysts; however, they only prevent performance degradation instead of improving performance compared to the neat Fe\textsubscript{2}O\textsubscript{3} initially in our case. Alkaline metals are thought to act as an electron donor for the iron based materials, and that the synergistic effects are ascribed to the weakening of the Fe-O bond.\textsuperscript{88, 87} The Na added OC sample showed the worst performance which can be attributed to its smaller radius, lower electronegativity, consistent with previous work on the role of alkaline metals on catalytic activity.\textsuperscript{75}

On that basis, however, Cs should perform better than K, but clearly did not. TEM images of reacted OCs (Figure 2.5 and Figure 2.6) show that Cs was not retained after thermal processing (at least at significant levels within the iron oxide lattice) but phase-separated into small primary particles decorating the surface (TEM-EDX identified that metal elements of the small grains on the bulk Fe\textsubscript{2}O\textsubscript{3} surface are mainly Cs), possibly because of the increased atom size. Alkali metals have also been shown to improve selectivity, reduce coking or prolong lifetime of metal/metal oxide catalysts for various reactions.\textsuperscript{88, 73, 87, 88} At least for the conversion addition of
aluminum oxide stabilizer there appears to be no advantage, but it is included here because of a subsequent discussion on selectivity.
Figure 2.5. TEM images of alkaline doped OCs after 50 cycles CLC test at 1023 K of (a) 4.8mol% Na / 95.2mol% Fe₂O₃ (b) 4.8mol% K / 95.2mol% Fe₂O₃ (c) 2.6 mol% Cs 48.7 mol% Fe₂O₃/48.7 mol% Al₂O₃ (d) 2.6 mol% K 48.7 mol% Fe₂O₃/48.7 mol% Al₂O₃.
Figure 2.6. HRTEM images of alkaline doped OCs after 50 cycles CLC test at 1023 K of (a) 95.2 mol% Fe$_2$O$_3$/4.8 mol% Na (b) 95.2 mol% Fe$_2$O$_3$/4.8mol% K (c) 48.7 mol% Fe$_2$O$_3$/48.7 mol% Al$_2$O$_3$ with 2.6 mol% Cs.
Figure 2.7. CO$_2$ yield per gram of Fe$_2$O$_3$ for different OCs at 1023 K as a function of cycle number.
Because one of the primary motivations of CLC today is CO$_2$ sequestering, selectivity is extremely important, specifically with respect to coking, which may occur from a number of side reactions including the Boudouard reaction (1) and methane pyrolysis (2).\textsuperscript{85,81,89}

\[2\text{CO} \rightarrow \text{C} + \text{CO}_2\] (1)

\[\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \text{ (pyrolysis)}\] (2)

The second reaction is endothermic while the first reaction is exothermic. Furthermore, methane decomposition is thermodynamically preferred at high temperatures while the Boudouard reaction is favored at low temperatures. Carbon formation comes from the two reactions mentioned above, and then burned away in the oxidation step.\textsuperscript{81,42} Therefore the amount of CO$_2$ observed in the oxidation step can be directly used to determine the extent of coke formation in the methane step. The two different side reactions can be differentiated by the amount of hydrogen generated during the methane step, as it results only from methane decompostion (reaction (2)). As the amount of hydrogen generated during the methane step was double the amount of CO$_2$ generated during the oxidation step, we can conclude that methane decompostion is the primary side reaction. We define CO$_2$ selectivity (based on the amount of CO$_2$ measured during the fuel step) as:

\[\gamma_{CO_2} = \frac{n_{CO_2}}{n_C + n_{CO_2}}\]

where $n_{CO_2}$ is determined directly during the fuel step, and $n_C$ is measured indirectly by the amount of CO$_2$ measured during the oxidation step.
Thus the selectivity represents the amount of methane that is reacting with the OCs rather than decomposing. $\gamma_{CO_2}$ of different OCs at 1023 K for 50 cycles is shown in Figure 2.6. It is evident that addition of alkaline metals improves CO$_2$ selectivity against coking and that potassium works best in the context of selectivity. The addition of the alumina support provides further improvement. This 48.7 mol% Fe$_2$O$_3$/48.7 mol% Al$_2$O$_3$/2.6 mol% K material clearly offers superior performance in both reactivity stability and CO$_2$ selectivity. This result implies that alkali metals promote oxidation over pyrolysis although the mechanism is not well understood.
Figure 2.8. CO₂ selectivity – $\gamma_{\text{CO}_2}$ of different OCs at 1023 K.
Phase identification of oxygen carriers was determined using XRD (Table 2.1), indicating that all iron oxides were $\gamma$-Fe$_2$O$_3$ or Fe$_3$O$_4$. Even though the samples were obtained after CH$_4$ step cooled down to room temperature in Ar, the high temperature reduced phase gets easily oxidized and thus all XRD patterns gave peaks assigned to Fe$_2$O$_3$ and four reduced samples (OC samples after CH$_4$ step) gave peaks of Fe$_3$O$_4$. No signals for K-Fe-O may come from two reasons: 1) K-Fe forms very fine particles beyond limit of XRD detection 2) K-Fe forms solid solutions. From HR-TEM results (Figure 2.7 and 2.8), the second one is more reasonable since K-Fe stayed homogeneously distributed in the particle. Also, The XPS and deconvolution results for Fe 2p core-level (Figure 2.9) of 4.8mol% K 95.2mol% Fe$_2$O$_3$ sample showed very similar patterns and main peaks of Fe 2p3/2 around 710.8 eV, which demonstrates no chemical bonding between K and Fe, which means that K$^+$ may move around in Fe$_2$O$_3$ crystal as ion interstitials. XRD analysis on the Al$_2$O$_3$ supported sample has two major phases: Fe$_2$O$_3$ and Al$_2$O$_3$, with no mixed Fe-Al-O phase formation and no mixed Fe-K-Al-O phase formation is detected (e.g. KFeO$_2$). Moreover, XPS also gave the same information.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$ (Maghemite-Q)</td>
<td>Fe$_2$O$_3$(Maghemite-Q)</td>
</tr>
<tr>
<td>50mol% Fe$_2$O$_3$ / 50mol% Al$_2$O$_3$</td>
<td>Fe$_2$O$_3$ (Maghemite-Q), Al$_2$O$_3$</td>
</tr>
<tr>
<td>4.8mol% Na 95.2mol% Fe$_2$O$_3$</td>
<td>NaNO$_3$, Fe$_2$O$_3$ (Maghemite-Q)</td>
</tr>
<tr>
<td>4.8mol% K 95.2mol% Fe$_2$O$_3$</td>
<td>KNO$_3$, Fe$_2$O$_3$ (Maghemite-Q)</td>
</tr>
<tr>
<td>2.4mol% Na 2.4mol% K 95.2mol% Fe$_2$O$_3$</td>
<td>NaNO$_3$, KNO$_3$, Fe$_2$O$_3$ (Maghemite-Q)</td>
</tr>
<tr>
<td>4.8mol% Cs 95.2mol% Fe$_2$O$_3$</td>
<td>Amorphous</td>
</tr>
<tr>
<td>Fe$_2$O$_3$ after 1 h sinter at 1023 K</td>
<td>Fe$_2$O$_3$ (Maghemite-Q)</td>
</tr>
<tr>
<td>4.8mol% K 95.2mol% Fe$_2$O$_3$ after 1 h</td>
<td>Fe$_2$O$_3$ (Maghemite-Q)</td>
</tr>
<tr>
<td>sinter at 1023 K</td>
<td></td>
</tr>
<tr>
<td>50mol% Fe$_2$O$_3$ / 50mol% Al$_2$O$_3$ after 1 h</td>
<td>Fe$_2$O$_3$ (Maghemite-Q), Al$_2$O$_3$</td>
</tr>
<tr>
<td>sinter at 1023 K</td>
<td></td>
</tr>
<tr>
<td>4.8mol% Na 95.2mol% Fe$_2$O$_3$ after 1 h</td>
<td>Fe$_2$O$_3$ (Maghemite-Q)</td>
</tr>
<tr>
<td>sinter at 1023 K</td>
<td></td>
</tr>
<tr>
<td>2.4mol% Na 2.4mol% K 95.2mol% Fe$_2$O$_3$ after 1 h</td>
<td>Fe$_2$O$_3$ (Maghemite-Q)</td>
</tr>
<tr>
<td>sinter at 1023 K</td>
<td></td>
</tr>
<tr>
<td>4.8mol% Cs 95.2mol% Fe$_2$O$_3$ after 1 h</td>
<td>Fe$_2$O$_3$ (Maghemite-Q)</td>
</tr>
<tr>
<td>sinter at 1023 K</td>
<td></td>
</tr>
<tr>
<td>Fe$_2$O$_3$ after 50 cycles at 1023 K</td>
<td>Fe$_3$O$_4$, Fe$_2$O$_3$ (Maghemite-Q)</td>
</tr>
<tr>
<td>Fe$_2$O$_3$ after 50 cycles at 1123 K</td>
<td>Fe$_3$O$_4$, Fe$_2$O$_3$ (Maghemite-Q)</td>
</tr>
<tr>
<td>Fe$_2$O$_3$ after 50 cycles at 1223 K</td>
<td>Fe$_3$O$_4$, Fe$_2$O$_3$ (Maghemite-Q)</td>
</tr>
<tr>
<td>4.8mol% K 95.2mol% Fe$_2$O$_3$ after 50</td>
<td>Fe$_3$O$_4$, Fe$_2$O$_3$ (Maghemite-Q)</td>
</tr>
<tr>
<td>Temperature</td>
<td>Composition</td>
</tr>
<tr>
<td>-------------</td>
<td>-------------</td>
</tr>
<tr>
<td>1023 K</td>
<td>4.8mol% K 95.2mol% Fe₂O₃</td>
</tr>
<tr>
<td>1123 K</td>
<td>4.8mol% K 95.2mol% Fe₂O₃</td>
</tr>
<tr>
<td>50 cycles at 1223 K</td>
<td>2.6mol% K 48.7mol% Fe₂O₃/48.7mol% Al₂O₃</td>
</tr>
<tr>
<td>50 cycles at 1123 K</td>
<td>2.6mol% K 48.7mol% Fe₂O₃/48.7mol% Al₂O₃</td>
</tr>
<tr>
<td>50 cycles at 1223 K</td>
<td>2.4mol% Na 2.4mol% K 95.2mol% Fe₂O₃</td>
</tr>
<tr>
<td>50 cycles at 1023 K</td>
<td>4.8mol% Cs 95.2mol% Fe₂O₃</td>
</tr>
</tbody>
</table>

Table 2.1. XRD identifications of different OCs’ sample before and after 50-cycle CLC tests.
Figure 2.9. XPS and deconvolution results for Fe 2p core-level of a) Fe$_2$O$_3$ b) 4.8 mol% K 95.2 mol% Fe$_2$O$_3$ after 50 CLC cycles at 1023 K.
The SEM micrographs, of the OCs are shown in Figure 2.10. Consistent with the size distribution measurements in Figure 2.2 the as produced particles from spray pyrolysis were spherical ~0.1-1 μm. After ~ 1 h thermal annealing at 1023 K, particles maintained their spherical shapes. After 50 cycles (15 hours), particles clearly showed evidence of some sintering, although for all but the smallest particles the characteristic length scales are still nominally the same. The Na doped sample (not shown), was essentially indistinguishable from the K counterparts despite the fact that the reactivity was much lower. It is worth noticing that all particles displayed similar amounts of sintering, regardless of alkali metal doping. It can be implied that sintering does not account for the reactivity differences.
**Figure 2.10.** SEM images of OCs after direct synthesis, 1 h thermal annealing at 1023 K, and 50 cycles CLC test at 1023 K.
TEM elemental mapping is shown in Figure 2.11 and Figure 2.12, for the as prepared 50 mol% Fe₂O₃/50 mol% Al₂O₃ (Figure 2.11a, 2.11c), after multi-cycles at 1023 K (Figure 2.11b, 2.11d) and 2.6 mol% K 48.7 mol% Fe₂O₃/48.7 mol% Al₂O₃ after multi-cycle CLC at 1023 K. Figure 2.11a, 2.11c show that the as-produced material the iron is homogeneously dispersed within the alumina matrix, but that after CLC (Figure 2.11b, 2.11d), considerable morphological changes have occurred accompanied with a significant phase separation between Fe and Al. This is also consistent with the fact as shown in Figure 2.4 that the Al additions to iron oxide have minimal performance effects and shows the same general trend of decreasing activity with time. However, 2.6 mol% K 48.7 mol% Fe₂O₃/48.7 mol% Al₂O₃ composite, as shown in Figure 2.12 clearly stabilizes the structure from both morphological sintering effects but also phase separation between Al and Fe.

Similar results (Figure 2.13) were achieved with the Na sample after 50 cycles, but recall that the Na containing sample did not perform well. The mapping results indicate that the alkaline metal helps to retard phase separation within the alumina support, which may account for the long-term stability of 2.6 mol% K 48.7 mol% Fe₂O₃/48.7 mol% Al₂O₃ OC relative to the nascent iron oxide, and little alkaline metal loss. Potassium ions movement may exist as a binder for Fe-Al, thus preventing phase separation between the two. This result indicates that alkaline effect here is more than catalytic surface effect; it is a whole particle effect. Additional TEM images in the supporting information (Figure 2.7, 2.8), indicates that Cs however, did not stay in iron oxide, and was found to phase separate to the surface of the OC surface. This separation may be attributed to the larger size of the Cs⁺ (~181 pm) ion.
compared to $\text{K}^+$ (~152 pm) and $\text{Na}^+$ (~116 pm), as well its higher ion polarization.\textsuperscript{75-86,91} Previous catalysis studies have seen similar trends in the tendency for Cs phase separation.\textsuperscript{72,73-74}
Figure 2.11. TEM and elemental mapping results for 50 mol% Fe$_2$O$_3$/50 mol% Al$_2$O$_3$: (a, c) As synthesized; (b, d) after 50 CLC cycles at 1023 K.
Figure 2.12. TEM and elemental mapping: 48.7 mol% Fe$_2$O$_3$/48.7 mol% Al$_2$O$_3$ with 2.6 mol% K after 50 CLC cycles at 1023 K.
Figure 2.13. TEM Elementary Mapping result 2.6 % Na 48.7mol% Fe$_2$O$_3$/ 48.7mol% Al$_2$O$_3$ after 50 CLC cycles at 1023 K.
Our experimental approach is not amenable to identify the root cause of the potassium effect, however unlike a catalysis which is a pure surface effect, we are driving the OC within the whole particle, and thus we expect whatever the alkali metal effect it must involve more than surface effects. This may involve changing oxygen-ion transport within the lattice or a reduction in the oxygen binding energy. The fact that Na with its lower electronegativity performs worse is consistent with this, with the Cs, because of its instability within the lattice not providing any useful insights on this point. The stability of iron within the alumina implies that the alkali metal (both K and Na) stiffens the alumina matrix from moving around and offers a stable path for oxygen transport to the surface, which may help to explain the improved selectivity (i.e. reduction in coking).

2.4 Conclusion and Outlook

We demonstrate that addition of potassium to iron oxide nanoparticles during synthesis can significantly enhance its performance in long-term CLC tests of methane oxidation. This was however not true for Na or Cs addition. In the latter Cs addition was not incorporated within the lattice but was found to phase separate into small Cs particles at the surface of the iron oxide. Synthesis of particles with an alumina matrix was found to have minimal effect for nascent iron oxide performance, but when added in combination with potassium yielded the best performance in terms of long-term stability as well as CO$_2$ selectivity with respect to coking.
Chapter 3: Novel Support: Silicalite-1 zeolite for Fe-based Oxygen Carriers

3.1 Introduction

The capture of CO$_2$ released from fuel combustion is being actively studied to mitigate the effects of climate change.$^4$ A number of processes such as pre-combustion$^6$, oxy-fuel combustion and post-combustion$^9$ have been explored for CO$_2$ capture from fossil fuel combustion processes. However, all these techniques are energy intensive, resulting in a decrease of the overall combustion efficiency.

Chemical looping combustion (CLC) is being explored as a next generation combustion technology, since it operates with the same thermodynamic efficiency as air based combustion, but with a potential of near-zero CO$_2$ emission.$^2$,$^{92}$ CLC involves a two-step process, in which metal oxides serve as the oxygen source rather than air so that the direct contact between fuel and air is avoided. Hydrocarbon fuels are oxidized by metal oxides to water steam and CO$_2$ in the first step, from which a pure CO$_2$ stream, could be realized by single steam condensation.$^{63,64}$ The reduced metal oxide is then regenerated by combustion in air in the second step to complete the combustion cycle. The isolation of hydrocarbon fuels from air in CLC processes achieves a pure CO$_2$ stream for direct sequestration in an ideal situation, and avoids NO$_x$ formation by recovery of metal oxides at moderate temperature in air. Because of the multi-cycling nature of the process, the choice of metal oxides as oxygen carriers (OCs), with excellent activity, and long-term stability is critical to enabling
implementation of CLC into industrial scale. Metal oxides based on copper-, iron-, nickel-, manganese- et al., as well as their mixtures are the most promising OC’s candidates for CLC cycles because of their earth abundance, low cost, mechanical stability and recyclability. Among them, Fe-based OCs have received intensive research efforts because of its low cost, high melting point and excellent mechanical strength at high temperature. The practical application of iron oxide OCs in CLC, however, has been impeded by serious sintering and low reduction rate by fuels. Eventually, the iron oxide OCs encounter agglomeration and deactivation and thus durability loss in multiple CLC cycles. The introduction of support materials for iron oxide OCs is being studied to conquer the durability and deactivation issues in CLC cycles. Currently, inert supports including Al₂O₃, SiO₂, MgAl₂O₄, TiO₂ and ZrO₂, CeO₂ and active supports such as perovskites have been considered for Fe₂O₃ OCs. The support materials help to promote dispersion of OC particles and provide physical/chemical barriers against OC migration into aggregates. The interaction between support and OC can also facilitate the reduction rate of OCs for fuel combustion. It should be noted that all these support materials are oxides and their mixtures.

In the present work, we report a new type of support, a silicalite-1 zeolite, for Fe₂O₃ OCs in CLC. Silicalite-1 is the aluminum-free form of zeolite, with a mordenite framework inverted (MFI) structure consisting of two intersected 10 member ring (MR) microporous channels, one straight and one sinusoidal, with diameter of ~0.55 nm. Silicalite-1 is thermally stable (up to ~1550 K) and mechanically stable, making it a potential desired inert support for Fe₂O₃ to form
durable OCs in CLC, which, to our knowledge, has not yet been explored. In this study, two silicalite-1 supported Fe₂O₃ structures; a) core-shell Fe₂O₃@silicalite-1 and b) Fe₂O₃-impregnated silicalite-1 (Fe₂O₃/silicalite-1) were created for CLC and tested with methane fuel in a fixed bed reactor. The encapsulation of Fe₂O₃ inside silicalite-1 shell or within its channels provides physical barriers for avoiding aggregations of OCs during CLC cycling, while the unique microporous structure of zeolite allows transport of methane in and CO₂ out of Fe₂O₃ OC. An added benefit is we find that these structures reduce coke deposition on Fe₂O₃.

3.2 Experimental Section

3.2.1 Material synthesis

3.2.1.1 Preparation of core-shell Fe₂O₃@silicalite-1 OCs

Fe₂O₃ particles were prepared by dissolving 20.2 g of Fe(NO₃)₃·9H₂O (99.99% trace metals basis, Sigma-Aldrich) in 50 mL deionized (DI) water under rigorous stirring, followed by addition of 30 mL KOH (≥85%, Sigma-Aldrich) solution (5 mol·L⁻¹) to form a Fe(OH)₃ suspension. After adjusting pH of the suspension to ~10 by drop wise addition of NH₄OH solution (28.0-30.0%, Sigma-Aldrich), the mixture was stirred for 0.5 h and then transferred to a Teflon-lined stainless steel autoclave and held at 453 K for 5 h. Finally, the sample was then filtrated, washed with DI water and ethanol alternatively four times, and dried at 343 K for 12 h to form Fe₂O₃ particles.
Scheme 3.1. Synthesis procedure to prepare Fe$_2$O$_3$@silicalite-1 OC.
Scheme 3.1 shows the procedure to prepare the Fe$_2$O$_3$@silicalite-1 core-shell structure with Fe$_2$O$_3$ as the core and silicalite-1 as the shell. First, a SiO$_2$ shell was created on Fe$_2$O$_3$ particles to form core-shell Fe$_2$O$_3$@SiO$_2$ structure. In this synthesis, 0.1 g as-synthesized Fe$_2$O$_3$ particles were firstly dispersed in a solution of 40 mL 2-propanol (99.5%, Sigma-Aldrich), 1.42 g DI water and 1.1 g NH$_4$OH solution (28.0-30.0%) by ultra-sonication for 1 h. Secondly, a SiO$_2$ precursor solution was prepared by mixing 1 g tetraethyl orthosilicate (TEOS) (98%, Sigma-Aldrich) with 2 mL 2-propanol and the resultant mixture was added into Fe$_2$O$_3$ suspension at a rate of 0.4 mL h$^{-1}$ via a syringe pump (NE-1000, New Era Pump System). After stirring the mixture for 12 h, the resultant Fe$_2$O$_3$@SiO$_2$ particles were collected by centrifugation, washed with DI water four times, and then dried at 343 K overnight. Thirdly, a vapor phase transformation process was carried out to convert SiO$_2$ into silicalite-1 under assistance of silicalite-1 seeds to form the core-shell Fe$_2$O$_3$@silicalite-1 structure according to a previously reported method.$^{101,102}$ In this synthesis step, the as-prepared Fe$_2$O$_3$@SiO$_2$ particles were firstly dispersed in 4 mL DI water by ultrasonication. 2 g poly-(diallyldimethylammonium chloride) (PDDA, 20 wt% in H$_2$O, Sigma-Aldrich) was mixed with 1 mL DI water and the resultant mixture was added into the Fe$_2$O$_3$@SiO$_2$ suspension. After the mixture was stirred for 0.5 h, the particles were centrifuged and washed with diluted NH$_4$OH (2 wt %) solution four times. The as-obtained wet paste was then dispersed in 10 mL 1 wt% zeolite seed suspension for 0.67 h. The mixture was finally collected by centrifugation, washed with DI water four times and then dried at 343 K overnight. The as-prepared Fe$_2$O$_3$@SiO$_2$ particles coated with PDDA and silicalite-1 seeds were transferred into
a glass vial, which was placed in a Teflon-lined stainless steel autoclave containing 2.0 g trimethylamine (99%, Sigma-Aldrich), 0.2 g ethylene diamine (99.5%, Sigma-Aldrich), and 0.4 mL DI water. The autoclave was heated at 413 K for three days to transform amorphous SiO$_2$ shell into silicalite-1 shell. Finally, the sample was calcined at 823 K for 4 hours at a ramp rate 1 K min$^{-1}$ under flowing air (100 mL min$^{-1}$, Airgas). The Fe$_2$O$_3$@silicalite-1 sample was designated as Fe$_2$O$_3$@Si.

For the synthesis of silicalite-1 seeds, typically, 0.43 g NaOH (99%, Sigma-Aldrich) was dissolved in 15 mL DI water, followed by addition of 15 g tetrapropylammonium hydroxide aqueous solution (TPAOH, 40 wt%, Alfa-Aesar) and 9.5 g of fumed silica (Sigma-Aldrich). The mixture was stirred at room temperature for 0.25 h and then heated at 353 K under stirring until a clear mixture was obtained. The resultant clear mixture was placed in a Teflon-lined stainless steel autoclave, which was rotated at a speed of 30 rpm and under temperature of 403 K for 8h in a convection oven. Finally, the silicalite-1 nanoparticles were centrifuged and washed with DI water for 4 times and then dispersed in DI water to form 1 wt% silicalite-1 seed solution.

3.2.1.2 Preparation of Fe$_2$O$_3$/silicalite-1 composite
Silicalite-1 zeolite was synthesized by a hydrothermal method using a recipe of 1TPAOH: 8.5TEOS: 0.17NaOH: 34CH$_3$CH$_2$OH: 484H$_2$O. In a typical synthesis, 0.032 g NaOH was firstly dissolved in 20.2 g DI water, followed by addition of 1.22 g TPAOH (40wt%) aqueous solution. 4.25 g TEOS was added and then the resultant mixture was held under rigorous stirring at room temperature for 24 h. Finally,
crystallization of silicalite-1 zeolite was conducted for 2 days in the autoclaves tumbling vertically in an oven at 423 K. After crystallization, the zeolite product was centrifuged, washed with DI water till pH ~ 9, and dried at 343 K overnight. Afterwards, the zeolite sample was calcined at 823 K for 6 h with a ramp rate at 1 K min\(^{-1}\) under flowing air (100 mL min\(^{-1}\)).

The synthesis of Fe\(_2\)O\(_3\)/silicalite-1 composite was done by an impregnation method. Typically, 0.35 g of Fe(NO\(_3\))\(_3\) was dissolved in 0.2 g DI water and the resultant aqueous solution was added to 1 g silicalite-1 dropwise under rigorous stirring to form the 12 wt\% Fe\(_2\)O\(_3\)/silicalite-1 sample. The process was repeated to make the 24 wt\% Fe\(_2\)O\(_3\)/silicalite-1, in which 0.70 g of Fe(NO\(_3\))\(_3\) was used. The as-prepared 12 wt\% Fe\(_2\)O\(_3\)/silicalite-1 and 24 wt\% Fe\(_2\)O\(_3\)/silicalite-1 were dried at 393 K overnight, followed by calcination at 823 K for 4 h with a ramp rate of 1.67 K min\(^{-1}\) under air flow (100 mL min\(^{-1}\)). We designate the 12 wt\% Fe\(_2\)O\(_3\)/silicalite-1 and 24 wt\% Fe\(_2\)O\(_3\)/silicalite-1 as Fe\(_2\)O\(_3\)/Si-12 and Fe\(_2\)O\(_3\)/Si-24, respectively.

3.2.2 Characterizations

The morphologies of the zeolite supported Fe\(_2\)O\(_3\) OC samples were characterized by scanning electron microscopy (SEM, Hitachi SU-70) and transmission electron microscopy (TEM, JEOL JEM 2100 FEG). The porosity, pore size, and surface area of these samples were obtained by argon (Ar) adsorption-desorption isotherms measured at 87 K with an Autosorb-iQ analyzer (Quantachrome Instruments). Crystal structures of OCs were characterized by X-Ray diffraction (XRD) with a Bruker Smart1000 under Cu K\(\alpha\) beam. Fe and Si contents of the samples were determined by
inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 4300 DV instrument, Perkin-Elmer).

The cyclability and reactivity of OCs with CH$_4$ as fuel was carried out in a vertically oriented fixed bed reactor in an electrically heated isothermal furnace, as reported in a previous publication.$^{94}$ Mass flow controllers (MFC, MKS) regulated by a Labview VI program were utilized for gas reactant flow rate control. The reactor effluent was characterized by an online mass spectrometer (Stanford Research UGA 300) operating with a mass resolution < 0.5, atomic mass unit (a.m.u.), at 10 % of peak height and a detection limit < 1 ppm. Ar was used as an inert internal standard to determine the volume change of gaseous reactants and products during the reaction so as to assign concentrations. By varying the flow rates of CH$_4$ and O$_2$ with a fixed Ar flow rate at 200 mL min$^{-1}$, calibrations for the mass spectrometer were obtained for CO$_2$, CO, CH$_4$ and H$_2$. About 200 mg of OC was used for each test, and for the supported OCs, samples containing this amount of Fe$_2$O$_3$ were used. The powders were packed within a quartz reactor tube of 610 mm length, with outer diameter (O.D.) 12.5 mm and inner diameter (I.D.) 10 mm, as described in our previous work.$^{94}$ The particles were first annealed at 1023 K for 1 hour, and then exposed alternatively to 11% methane for 2 min, and 20% oxygen for 5 min simulating the CLC reaction cycles with argon as the inert balance gas. Argon was introduced for 5 min during the shift from methane to oxygen to avoid direct contact between oxygen and methane. The CLC tests were run continuously for 50 cycles, up to 15 h.
3.3 Results and discussion

3.3.1 Structural properties of OCs

SEM and TEM images in Figure 3.1 show the morphologies of synthesized core-shell Fe$_2$O$_3$@Si and Fe$_2$O$_3$/Si composite OCs. Fe$_2$O$_3$@Si consists of uniform spherical particles of diameter at ~ 1 µm (Figure 3.1a). The thickness of the silicalite-1 shell is ~ 100 nm and the Fe$_2$O$_3$ core has a diameter of ~ 900 nm (Figure 3.1b). Figure 3.1c) and 3.1e) are SEM images of Fe$_2$O$_3$/Si-12 and Fe$_2$O$_3$/Si-24, respectively, and both samples show a typical coffin-like morphology of silicalite-1, indicating that the loading of Fe$_2$O$_3$ and subsequent calcination did not change the morphology of the silicalite-1 support. Moreover, a comparison between the Fe$_2$O$_3$/Si-12 and Fe$_2$O$_3$/Si-24 samples (as evidenced by TEM images in Figure 3.1d) and 3.1f) indicates that there are more debris-like particle aggregates on the silicalite-1 in Fe$_2$O$_3$/Si-24 than Fe$_2$O$_3$/Si-12, which can be attributed to the high loading of Fe$_2$O$_3$ in Fe$_2$O$_3$/Si-24.
Figure 3.1. Morphology of OC samples viewed by SEM images of a) Fe$_2$O$_3$@Si, c) Fe$_2$O$_3$/Si-12, and e) Fe$_2$O$_3$/Si-24, and TEM images of b) Fe$_2$O$_3$@Si, d) Fe$_2$O$_3$/Si-12, and f) Fe$_2$O$_3$/Si-24, respectively.
The XRD patterns in Figure 3.2 identify the existence of both Fe$_2$O$_3$ and silicalite-1 crystalline phases in these three OC samples. For comparison purpose, the XRD patterns of silicalite-1 and Fe$_2$O$_3$, respectively, are included in Figure 3.2. Apparently, Fe$_2$O$_3$@Si contains the characteristic peaks of both hematite Fe$_2$O$_3$ ($2\theta = 33^\circ$, $35^\circ$ and $54^\circ$) and silicalite-1 ($2\theta = 23^\circ$ and $24^\circ$), confirming the existence of silicalite-1 and Fe$_2$O$_3$ in this sample, consistent with morphology observation in Figure 3.1. XRD patterns of Fe$_2$O$_3$/Si-12 and Fe$_2$O$_3$/Si-24 in Figure 3.2 show the characteristic peaks of silicalite-1, consistent with the silicalite-1 crystal viewed in Figure 3.1. The intensity of diffraction peaks corresponding to Fe$_2$O$_3$ in Fe$_2$O$_3$/Si-12 is much smaller than that in Fe$_2$O$_3$/Si-24, which can be ascribed to the lower loading of Fe$_2$O$_3$ OCs in the former sample.
Figure 3.2. XRD patterns of silicalite-1, Fe$_2$O$_3$ and silicalite-1 supported OCs.
3.3.2 Composition and porosity of OCs

The concentrations of Fe$_2$O$_3$ in the OC samples were measured by ICP-OES, as summarized in Table 3.1. The weight percentage of Fe$_2$O$_3$ in Fe$_2$O$_3$/Si-12 and Fe$_2$O$_3$/Si-24 were 11 wt% and 24 wt%, respectively, same as the Fe$_2$O$_3$ concentrations used in the sample preparation recipe. The concentration of Fe$_2$O$_3$ in the Fe$_2$O$_3$@Si core-shell sample is 22 wt%, comparable to that in Fe$_2$O$_3$/Si-24.
Table 3.1. Textual properties and elemental compositions of the OCs.

<table>
<thead>
<tr>
<th>OC</th>
<th>( f_{\text{Fe}_2\text{O}_3}^a )</th>
<th>( S_{\text{total}}^b )</th>
<th>( V_{\text{total}}^c )</th>
<th>( V_{\text{micro}}^d )</th>
<th>( V_{\text{meso}}^e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Fe}_2\text{O}_3@\text{Si} )</td>
<td>21</td>
<td>178</td>
<td>0.107</td>
<td>0.044</td>
<td>0.063</td>
</tr>
<tr>
<td>Silicalite-1</td>
<td>NA</td>
<td>396</td>
<td>0.208</td>
<td>0.113</td>
<td>0.093</td>
</tr>
<tr>
<td>( \text{Fe}_2\text{O}_3/\text{Si-12} )</td>
<td>11</td>
<td>360</td>
<td>0.196</td>
<td>0.110</td>
<td>0.086</td>
</tr>
<tr>
<td>( \text{Fe}_2\text{O}_3/\text{Si-24} )</td>
<td>24</td>
<td>309</td>
<td>0.161</td>
<td>0.100</td>
<td>0.061</td>
</tr>
</tbody>
</table>

\( a \) Determined by ICP-OES; \( b \) Calculated from multi-point BET method; \( c \) Calculated from the adsorption branch at \( P/P_0=0.95 \); \( d \) Calculated from \( t \)-plot method; \( e \) \( V_{\text{meso}}=V_{\text{total}}-V_{\text{micro}} \).
Ar adsorption-desorption isotherms in Figure 3.3 are used to characterize the porosity of silicalite-1, Fe$_2$O$_3$/Si-12, Fe$_2$O$_3$/Si-24 and Fe$_2$O$_3$@Si samples. At the low relative pressure ($p/p_0 < 0.05$), the Ar uptake follows the order of Fe$_2$O$_3$/Si-24 < Fe$_2$O$_3$/Si-12 < silicalite-1, implying that the microporosity of silicalite-1 decreases with the increase of Fe$_2$O$_3$ loading. Fe$_2$O$_3$@Si (22 wt%) and Fe$_2$O$_3$/Si-24 (24 wt%) have similar Fe$_2$O$_3$ loadings, but the former sample has much lower Ar uptake and thus microporosity. The low Ar uptake in Fe$_2$O$_3$@Si sample might result from the existence of a portion of amorphous SiO$_2$ or not-well-crystallized zeolite in the silicalite-1 shell.

The pore size distributions of the OC samples are shown in Figure 3.3b, which are derived from the adsorption branch of the Ar ad-/desorption isotherms using non-local density functional theory (NLDFT) method. The intensity of the micropore peaks, centered at ~5 Å, shows the trend of silicalite-1 > Fe$_2$O$_3$/Si-12 > Fe$_2$O$_3$/Si-24, consistent with the Ar isotherm data in Figure 3.3a), indicating that high Fe$_2$O$_3$ loading leads to more Fe$_2$O$_3$ loading in the microporous channels of silicalite-1. The Fe$_2$O$_3$@Si sample has the lowest micropore peak intensity, which might be due to the amorphous SiO$_2$, or not-well-crystallized silicalite-1, as discussed above. The second peak located at 8 Å might be due to the reminiscence of a phase transition in Ar adsorbate according to previous reports. The intensity of the mesopore peak in all OCs is very low, which suggests the absence of mesoporosity in these zeolite-supported OC samples.
Figure 3.3. a) Ar ad-/desorption isotherms of OCs and b) NLDFT pore size distributions of OCs derived from the adsorption branch of their Ar ad-/desorption isotherms.
3.3.3 OC performance tests in CLC

Table 3.2 lists the possible reactions occurring in different reduction stages of the CLC tests with Fe$_2$O$_3$ OCs and methane fuel. The CO$_2$ yield in each reaction is computed according to the equation stoichiometry.
Table 3.2. Reaction equations in different reduction stages of CLC and corresponding \( \text{CO}_2 \) yields.

<table>
<thead>
<tr>
<th></th>
<th>Reaction Equation</th>
<th>( \text{CO}<em>2 ) yield (mmol/g(</em>{\text{Fe}_2\text{O}_3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>( \frac{1}{4} \text{CH}_4 + 3\text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe}_3\text{O}_4 + \frac{1}{4} \text{CO}_2 + \frac{1}{2} \text{H}_2\text{O} )</td>
<td>0.52</td>
</tr>
<tr>
<td>(2)</td>
<td>( \frac{1}{4} \text{CH}_4 + \text{Fe}_2\text{O}_3 \rightarrow 2\text{FeO} + \frac{1}{4} \text{CO}_2 + \frac{1}{2} \text{H}_2\text{O} )</td>
<td>1.56</td>
</tr>
<tr>
<td>(3)</td>
<td>( \frac{3}{4} \text{CH}_4 + \text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe} + \frac{3}{4} \text{CO}_2 + \frac{3}{2} \text{H}_2\text{O} )</td>
<td>4.69</td>
</tr>
</tbody>
</table>
Our measured CO$_2$ yield stabilized at 0.52 mmol/g-Fe$_2$O$_3$ for all OC samples at both 1023 K and 1223 K for a 50 cycle CLC test, as shown in Figure 3.4. The CO$_2$ yield suggests that all OC samples did methane conversion preferentially following the first reaction equation in Table 3.2, which means Fe$_2$O$_3$ is reduced into Fe$_3$O$_4$ phase. The XRD patterns in Figure 3.5 show the existence of Fe$_3$O$_4$ in the OC samples after the CLC test, which is consistent with the conclusion that Fe$_2$O$_3$ reduced to Fe$_3$O$_4$ in the CH$_4$ reduction step drawn from CO$_2$ yield data in Figure 3.4. The silicalite-1 support did not influence the reaction nature of Fe$_2$O$_3$ OCs in the CLC tests, which is consistent with the chemical and thermal inertness of silicalite-1 zeolite in the CLC conditions. The consistence in CO$_2$ yield across all these CLC 50 cycles, up to 15 hours, indicates that all OCs were stable and did not experience obvious activity degradation. Additionally, Figure 3.4 shows the reaction temperature does not influence the reaction nature of the Fe$_2$O$_3$ OCs in the tested CLC conditions.
Figure 3.4. CO₂ yield in CH₄ step at a) 1023K and b) 1223K of Fe₂O₃, Fe₂O₃@Si, Fe₂O₃/Si-12, Fe₂O₃/Si-24 during 50 cycle CLC reaction.
Figure 3.5. XRD patterns of Fe$_2$O$_3$ and silicalite-1 supported Fe$_2$O$_3$ OCs after 50 cycle CLC reaction tests.
Since the primary motivation of developing CLC process is for CO$_2$ sequestration, the exclusive formation of CO$_2$ versus other by-products such as coke (C) from methane fuel over OCs in the reaction is desired. In the present study, we did not observe any other gaseous carbon-based product except CO$_2$ in the reduction stage of OCs. In the regeneration (or oxidation) stage of OCs, CO$_2$ product was also observed, which results from the combustion of coke species deposited on OCs during the reduction stage in the CLC tests. Additionally, H$_2$ product was detected in the reduction stage of OCs.

It is noted that two nominal side reactions, Boudouard reaction (3.1) and methane decomposition (3.2), could occur in CLC of methane fuel.$^{85}$

$$2\text{CO} \rightarrow \text{C} + \text{CO}_2 \quad (3.1)$$

$$\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \quad (3.2)$$

The thermodynamic analysis shows that the methane decomposition reaction is endothermic while the Boudouard reaction is exothermic. Therefore, the methane decomposition reaction is thermodynamically preferred at high temperature reaction conditions while the Boudouard reaction is favored at low temperatures.$^{39}$ The absence of CO product and presence of H$_2$ in the reduction stage of the CLC test indicate that methane decomposition is the side reaction in our study. Thus, the selectivity of CO$_2$ ($\gamma_{\text{CO}_2}$) is analyzed based on the ratio of CO$_2$ amount ($n_{\text{CO}_2}$) to total carbon-based species (i.e., the summation of $n_{\text{CO}_2}$ and the amount of C ($n_C$)) in the reduction stage, as shown in equation (3.3). It should be noted that coke generated from the methane decomposition during the reduction step will subsequently be
oxidized to CO\textsubscript{2} during the OC regeneration step (the O\textsubscript{2} oxidation step). The amount of coke was quantitied based on the CO\textsubscript{2} emission from the oxidation step.

\[
\gamma_{\text{CO}_2} = \frac{n_{\text{CO}_2}}{n_C + n_{\text{CO}_2}} \quad (3.3)
\]

Figure 3.6 reveals CO\textsubscript{2} selectivity in CLC tests over Fe\textsubscript{2}O\textsubscript{3} and silicalite-1 supported Fe\textsubscript{2}O\textsubscript{3} OCs at two different tempreatures. At 1023 K (Figure 3.6a), all the supported OCs (Fe\textsubscript{2}O\textsubscript{3}@Si, Fe\textsubscript{2}O\textsubscript{3}/Si-12 and Fe\textsubscript{2}O\textsubscript{3}/Si-24) showed similar CO\textsubscript{2} selectivity, ~97% and was slightly higher than bare Fe\textsubscript{2}O\textsubscript{3} OCs that had a CO\textsubscript{2} selectivity of ~95%. When the temperature was raised to 1223 K (Figure 3.6b), significant differences in CO\textsubscript{2} selectivity across these four OC samples were observed. The bare Fe\textsubscript{2}O\textsubscript{3} OC only had a selectivity of ~65%. The Fe\textsubscript{2}O\textsubscript{3}@Si had a better performance than bare Fe\textsubscript{2}O\textsubscript{3}, showing a selectivity of ~87%, but much less than Fe\textsubscript{2}O\textsubscript{3}/Si-12 and Fe\textsubscript{2}O\textsubscript{3}/Si-24 OCs. As shown in Figure 3.6b, both Fe\textsubscript{2}O\textsubscript{3}/Si-12 and Fe\textsubscript{2}O\textsubscript{3}/Si-24 had minimal performance degradation in the reduction stage, with a selectivity ~95%. The slight differences in CO\textsubscript{2} selectivity at relatively lower temperature (1023 K) and significant differences at higher temperature (1223 K) across these four OC samples suggest higher reaction temperature may change the structures of the OC samples, and thus alters their selectivity in the CLC reaction. Apparently, the Fe\textsubscript{2}O\textsubscript{3}-impregnated silicalite-1 samples have the best stability than others in the CLC tests.
To further understand the CO$_2$ selectivity at different temperatures over these OC samples discussed above, we monitored the temporal evolution of CO$_2$ and H$_2$ in
the reduction step of CLC process (shown in Figure 3.7). In the CO₂ evolution profile at 1023 K shown in Figure 3.7a, the CO₂ yield initially increased with the reduction time, reached a maximum, and then decreased. The peaking of CO₂ signal for reaction over the silicalite-1 supported Fe₂O₃ OCs emerged earlier than the bare Fe₂O₃ OC sample. This is due to the large particle size of bare Fe₂O₃ without any zeolite support, which causes sluggish reaction kinetics compared to the reaction over smaller Fe₂O₃ particle sizes in the silicalite-1 supported Fe₂O₃ OCs.²⁹,⁴⁵,⁶⁶ At higher reaction temperature (1223 K), the emergence of the maxima in CO₂ evolution profile over every sample is earlier than that at 1023 K, suggesting the reaction rate is facilitated due to the increase in reaction temperature. But again, the peaking of the CO₂ signal for reaction over the bare Fe₂O₃ lagged behind all other silicalite-1 supported Fe₂O₃ OCs. It should be noted that the CO₂ peak area resulted from reaction over every OC sample or every tested temperature is the same. This is consistent with the total yield of CO₂ was independent of the temperature or OC sample, as evidenced in Figure 3.5 above.

For the evolution profiles of H₂ in the CLC tests (shown in Figure 3.7b), all OCs showed nearly zero H₂ production at 1023 K, indicating the insignificant methane decomposition to form coke during CLC reaction, consistent with the selectivity data presented in Figure 3.6a. At reaction temperature of 1223 K, the H₂ evolution profile of bare Fe₂O₃ exhibited a pronounced H₂ peak, followed by the medium sized peak from Fe₂O₃@Si sample and invisible peak from Fe₂O₃/Si-24 and Fe₂O₃/Si-12. The emergence of H₂ signal in the CLC tests indicates coke was being formed from methane decomposition reaction. Quite clearly, the resistance to coking in the CLC
tests at 1223 K follows the sequence of Fe$_2$O$_3$/Si-24 $\sim$ Fe$_2$O$_3$/Si-12 $>$ Fe$_2$O$_3$@Si $>>$ Fe$_2$O$_3$. This analysis fits well with the conclusion drawn from CO$_2$ selectivity data illustrated in Figure 3.6b. It is worth noting that H$_2$ production does not occur concurrently with CO$_2$ evolution, and instead, behind the CO$_2$ formation. This scenario indicates that the side reaction, methane decomposition, is strongly promoted when the labile framework oxygen in OCs is mostly consumed by the reduction of CH$_4$ to CO$_2$ at high temperatures. The zeolite support apparently helps the Fe$_2$O$_3$ OCs limit this side reaction, and thus promote the CO$_2$ selectivity in the CLC process.
Figure 3.7. The evolution profile of CO$_2$ a) and H$_2$ b) in the reduction step during the 30$^{th}$ CLC cycle at 1023 K (open symbol) and 1223 K (filled symbol) for all OCs.
To examine the morphological structure of OCs after high temperature CLC reaction, SEM observation and XRD measurements were conducted on the used OC samples. Figure 3.8a, c, e and g) show SEM images of the four OC samples after 50 cycle CLC at 1023 K. In comparison with the morphology of silicalite-1 supported Fe$_2$O$_3$ samples before CLC tests (Figure 3.1), the Fe$_2$O$_3$@Si particles lost their smooth surface feature in the core-shell structure, but still kept the spherical morphology. The Fe$_2$O$_3$/Si-12 and Fe$_2$O$_3$/Si-24 samples, however, have quite similar morphologies to those before CLC tests. The XRD patterns in Figure 3.5 confirmed the crystalline phase integrity of four OCs after reaction at 1023 K, since all of them do not have new peaks in the diffraction patterns. These data confirms that all the OCs can reserve their structural and chemical reactivity features at 1023 K in the CLC reactions.

Figure 3.8b, d, f and h show the morphologies of all investigated OCs after 50 cycle CLC at 1223 K. Both unsupported Fe$_2$O$_3$ and Fe$_2$O$_3$@Si seem to be sintered together to form large aggregates (Figure 3.8b and d, respectively). Particularly, the XRD patterns in Figure 3.5 indicate the transformation of silicalite-1 into amorphous SiO$_2$, consistent with the SEM observation on these two OC samples. The sintering of silicalite-1 shell of the Fe$_2$O$_3$@Si particles might be due to the low structural crystallinity of the silicalite-1 shell (∼100 nm thick), which is vulnerable to and prone to collapse at high temperature. Figure 8f and h illustrate that Fe$_2$O$_3$/Si-12 and Fe$_2$O$_3$/Si-24 have little morphological change after 50 cycles of CLC reaction at 1223 K. The XRD results in Figure 3.5 further confirm the presence of silicalite-1 zeolite phase in the samples after CLC tests. Compared to the thin silicalite-1 shell in
the Fe$_2$O$_3$@Si, the excellent structural stability of Fe$_2$O$_3$/silicalite-1 OCs should be ascribed to the large (~1 μm) and well-crystallized silicalite-1 crystals. Overall, the stable silicalite-1 zeolite provided physical barriers to avoid aggregation of active Fe$_2$O$_3$ OCs in CLC cycles, limited the coke deposition from side methane decomposition reaction, and thus led to high CO$_2$ selectivity in CLC of methane fuel.
Figure 3.8. SEM images of the OCs (a) and (b): Fe$_2$O$_3$, (c) and (d): Fe$_2$O$_3$@Si, (e) and (f): Fe$_2$O$_3$/Si-12 and (g) and (h): Fe$_2$O$_3$/Si-24 after 50 cycle CLC reaction at 1023 and 1223 K, respectively.
3.4 Conclusion

Silicalite-1 is explored as a novel support material for Fe$_2$O$_3$ to form supported OCs for CLC reaction with methane as the fuel. Two silicalite-1 supported Fe$_2$O$_3$ structures, core-shell Fe$_2$O$_3$@silicalite-1 and Fe$_2$O$_3$-impregnated silicalite-1 (Fe$_2$O$_3$/silicalite-1), were created to study their influences on CLC reaction at 1023 and 1223 K, respectively. After 50 cycles of CLC tests at 1023 K, both Fe$_2$O$_3$@silicalite-1 and Fe$_2$O$_3$/silicalite-1 OCs showed similar CO$_2$ yield and slightly higher CO$_2$ selectivity than bare Fe$_2$O$_3$ OCs. All the OC samples were able to preserve their structural integrity at 1023 K. An increase of reaction temperature to 1223 K resulted in significant sintering of bare Fe$_2$O$_3$ and Fe$_2$O$_3$@silicalite-1 OCs, and thus they showed inferior CO$_2$ selectivity than that of Fe$_2$O$_3$/silicalite-1 OCs. The larger silicalite-1 crystal in Fe$_2$O$_3$/silicalite-1 OCs keeps its structural integrity and provides physical barriers for Fe$_2$O$_3$ OCs against aggregation and coke deposition in CLC cycles. In conclusion, our study of the structure-function relation for silicalite-1 supported Fe$_2$O$_3$ OCs can form the basis for the development of silicalite-1 as an efficient support in chemical looping applications.
Chapter 4: Perovskite Oxides as Oxygen Carriers

4.1 Introduction

Chemical looping combustion (CLC) is a novel approach towards the combustion of fuels that utilizes a two-step redox process to achieve carbonaceous combustion, offering a smaller carbon footprint with no thermodynamic energy penalty. Instead of directly burning hydrocarbon in air, metal oxides are used as oxygen carriers (OC’s) in the fuel reactor where they are reduced while carbonaceous fuel is converted to carbon dioxide and water. The reduced OC's are regenerated in an air reactor, and through cycling these oxides, a flameless combustion is achieved with the temperature in air reactors often lower than 1300 K, thus avoiding NOx formation that is generated from traditional combustion with air (~80% N2). The resultant process under ideal conditions generates a pure CO2 stream, after steam condensation in the fuel reactor.

One of the significant roadblocks in implementation of CLC is finding the right OC, and the multiple considerations include high phase stability, redox activity, low cost, and being environmentally benign. Potential candidates studied as OC’s include binary oxides of first row transition metals, such as iron, copper, nickel, manganese, cobalt, and their mixed metal oxides. Perovskites have also been explored as novel OC’s considering their high redox
cyclic stabilities and superior oxygen transport capacities.\textsuperscript{32b} Perovskites are generally formulized as $ABO_3$, with $A$ and $B$ cations and the $O^{2-}$ anion and are natural candidates for OC's due to their high oxygen conductivity, thermal stability, ease of synthesis, and relatively low cost. In the perovskite structure, the $A$ cation is typically an alkali, alkaline earth, or lanthanide metal, and the $B$ cation a transition metal. Nevertheless, given the myriad of potential combinations of the $A$ and $B$ cations, choosing the optimal perovskite for CLC applications is daunting.\textsuperscript{33}

The role of the transition metal $B$ is more important than that of $A$ considering that it is the redox active metal that participates in the CLC reactions. Therefore, we have conducted a systematic study of 9 different La$_{1-x}$Ca$_x$BO$_3$ compositions where the $B$ site was varied between Cr to Cu. Furthermore, we included Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_3$ (BSCF) since it is a commonly used material in oxygen evolution catalysis. In this communication, we report trends of particular materials descriptors such as electronegativity versus our independent variable oxygen storage capacity (OSC) with CH$_4$ as the fuel. Our goal is to find various descriptors that could be utilized by future studies to select the optimal oxides for various CLC applications.

\textit{4.2 Experimental Approach}

\textbf{4.2.1 Perovskite OC synthesis}

All perovskites were synthesized in our laboratory using aerosol-assisted spray pyrolysis with metal nitrate aqueous solutions as precursors. All chemicals were
purchased from Sigma-Aldrich, including La(NO$_3$)$_3$·6H$_2$O (≥99.0% pure), Ca(NO$_3$)$_3$·4H$_2$O (≥99.0% pure), Mn(NO$_3$)$_2$·4H$_2$O (≥97.0% pure), Fe(NO$_3$)$_3$·9H$_2$O (≥98% pure), Ni(NO$_3$)$_2$·6H$_2$O (≥97.0% pure), Co(NO$_3$)$_2$·6H$_2$O (≥98% pure), Cu(NO$_3$)$_2$·3H$_2$O (≥98% pure), Cr(NO$_3$)$_3$·9H$_2$O (≥98% pure), Ba(NO$_3$)$_2$·9H$_2$O (≥98% pure) and Sr(NO$_3$)$_2$·9H$_2$O (≥99% pure).

The spray pyrolysis system consists of a stainless steel atomizer, silica-gel diffusion dryer, an isothermal tube furnace, and a stainless steel sample collector, as described in details in previous publications.\(^8\) The synthetic process can be described as a droplet-to-particle method, where the precursor droplets are decomposed into perovskite mixed metal oxides in the isothermal furnace during the thermal treatment. For the precursor solution, 0.20 M metal nitrates, 0.10 M citrate acid are dissolved in DI water. The atomizer is a collision-type nebulizer, which generates droplets with diameters approximately 1 μm in size. The precursor droplets were carried by compressed air gas with a flow rate of ~3 L/min into the diffusion dryer, then into the isothermal tube furnace at 1273 K to decompose the precursors into oxide particles with a ~1s residence time. Finally, particles exiting the aerosol reactor are collected on a 0.4 μm DTTP Millipore filter with 10%-20% porosity (purchased from EMD Millipore).

**4.2.2 Material Characterizations**

Crystal structures of OCs are characterized by X-Ray Diffraction (XRD) with a Bruker Smart1000 detector using Cu Kα radiation. Transmission Electron Microscopy (TEM) and High Resolution Transmission Electron Microscopy (HRTEM) are performed using a Field Emission Transmission Electron Microscope
(JEOL 2100 FE-TEM). Scanning Electron Microscopy (SEM) results are obtained by Hitachi SU-70 SEM. TGA (Thermal Gravimetric Analyzer) coupled MS (Mass spectroscopy) tests were conducted simultaneously in a SDT Q600 coupled with Discovery TM quadruple mass spectrometer from TA instruments, with an alumina sample crucible loaded with ~10 mg samples. Samples were first heated to 150 K to and held for 30 min then ramped at 10 K min$^{-1}$ to 1023 K and held for 30 min.

4.2.3 Fixed bed reactor reactivity test

Total methane oxidation and stability tests of the perovskites were performed in a vertically oriented fixed bed reactor placed in an electrically heated isothermal furnace at 1023 K. The effluent was sampled with a mass spectrometer (Stanford Research UGA 300) with a mass resolution of <0.5 atomic mass units (amu) at 10% of peak height and a detection limit <1 ppm. Argon was also used as an internal mass spectrometer standard for quantitative analysis of the effluent gases, and Ar flow rate were kept at a fixed value. By varying the flow rates of CH$_4$ and O$_2$ with a fixed Ar flow rate, calibrations of the mass spectrometer for different gases with different concentrations, including CO$_2$, CO, CH$_4$, H$_2$.

Nominally, a ~200 mg oxygen carrier sample is used for each test. The quartz flow reactor has a length of 61 cm, with a 1 cm inner diameter. The particles are first annealed at the reaction temperature for 1 hour, and then exposed alternatively to 11% methane for 2 min and 20% oxygen for 5 min simulating the CLC reactor. Argon is introduced for 300 s after each period, to purge the reactor and avoid oxygen and
methane mixing between the oxidation and reduction cycles. We achieved 50 cycles in this test as our previous study.

4.3 Results and Discussion

4.3.1 Textual properties of OCs

The Scanning Electron Microscopy (SEM) images of Figure 4.1 a) and 4.1 b) shows the spherical morphology of our spray pyrolysis synthesized LaCrO₃, while X-Ray diffraction (XRD) in Figure 4.2 confirms perovskite crystal structure. All samples were pseudocubic perovskites with Le Bail refinement performed in either the cubic (Pm-3m), orthorhombic (Pbnm), or rhombohedral (R-3c) space groups.

Powder X-ray Diffraction (XRD) experiments, performed on a Bruker D8 diffractometer with Cu Kα radiation, were used to characterize the as-synthesized materials, as shown in Figure 4.2. Table 4.1 presents the refined space group, crystallite size, and lattice parameters resulting from Le Bail fitting for each pattern. All refinements were performed with the TOPAS 4.2 software. While most samples could be adequately fit in the cubic space group and therefore should be considered pseudocubic, final refinements were performed in either cubic (Pm-3m), orthorhombic (Pbnm), or rhombohedral (R-3c) space groups depending on the presence of peak splitting and satellite peaks. Each sample had a crystallite size smaller than 35 nm, determined by the Scherrer equation, as expected with this synthesis technique. The exceptions were LaMn₀.₅Ni₀.₅O₃ and Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃ which had crystallite sizes of 77.8(5) and 66.3(4) nm, respectively. Each sample was phase pure except for LaMn₀.₅Cu₀.₅O₃, LaCoO₃, and La₀.₅Ca₀.₅CoO₃. LaCoO₃ and La₀.₅Ca₀.₅CoO₃ both had a weak and broad peak at approximately 28.5°.
(approximately 3.0 Å). This peak could be attributed to La$_2$O$_3$, however, it is not possible to definitively identify this phase as there are no other impurity peaks present at higher angles in the XRD patterns. For LaMn$_{0.5}$Cu$_{0.5}$O$_3$ there are impurity peaks present at approximately 29.5° and 35.5° 2θ (approximately 3.0 and 2.5 Å, respectively). The peak at 29.5° 2θ can possibly be attributed to La$_2$O$_3$ or Cu$_2$O and the peak at 35.5° 2θ to CuO. As with the previous samples, the lack of additional impurity peaks makes the definitive identification of these phases impossible. Other phases considered but ruled out include calcium oxide and carbonate, binary metal oxides, the metallic elements, and all oxygen deficient perovskite based phases present in the ICDD PDF-2 database. More crystallite info could be found in table 4.1.
Figure 4.1. SEM of LaCrO₃ a) and b) shows the spherical morphology.
Figure 4.2. Powder XRD patterns for each of the tested samples.
Table 4.1. Le Bail refinement results for as synthesized samples.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Symmetry</th>
<th>Crystallite size (nm)*</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Volume (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNiO₃</td>
<td>rhombohedral (R-3c)</td>
<td>25.4(2)</td>
<td>5.5058(4)</td>
<td>13.372(1)</td>
<td>351.13(6)</td>
<td></td>
</tr>
<tr>
<td>LaMnO₃</td>
<td>rhombohedral (R-3c)</td>
<td>20.1(1)</td>
<td>5.5190(4)</td>
<td>13.396(1)</td>
<td>353.37(7)</td>
<td></td>
</tr>
<tr>
<td>LaMn₀.₅Ni₀.₅O₃</td>
<td>rhombohedral (R-3c)</td>
<td>77.8(5)</td>
<td>5.6407(2)</td>
<td>13.8478(5)</td>
<td>381.80(3)</td>
<td></td>
</tr>
<tr>
<td>LaMn₀.₅Cu₀.₅O₃</td>
<td>cubic (Pm-3m)</td>
<td>13.1(1)</td>
<td>3.8888(7)</td>
<td></td>
<td>58.81(3)</td>
<td></td>
</tr>
<tr>
<td>LaCrO₃</td>
<td>orthorhombic (Pbnm)</td>
<td>34.3(2)</td>
<td>5.4695(3)</td>
<td>5.5177(3)</td>
<td>7.7598(5)</td>
<td>234.13(2)</td>
</tr>
<tr>
<td>LaCoO₃</td>
<td>rhombohedral (R-3c)</td>
<td>20.4(1)</td>
<td>5.4365(5)</td>
<td>13.130(2)</td>
<td>336.08(8)</td>
<td></td>
</tr>
<tr>
<td>La₀.₅Ca₀.₅MnO₃</td>
<td>cubic (Pm-3m)</td>
<td>12.7(1)</td>
<td>3.8376(4)</td>
<td></td>
<td>56.52(2)</td>
<td></td>
</tr>
<tr>
<td>La₀.₅Ca₀.₅FeO₃</td>
<td>orthorhombic (Pbnm)</td>
<td>25.6(2)</td>
<td>5.537(1)</td>
<td>5.571(1)</td>
<td>7.8556(5)</td>
<td>242.30(7)</td>
</tr>
<tr>
<td>La₀.₅Ca₀.₅CoO₃</td>
<td>rhombohedral (R-3c)</td>
<td>21.5(1)</td>
<td>5.4816(4)</td>
<td>13.535(1)</td>
<td>352.21(6)</td>
<td></td>
</tr>
<tr>
<td>Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃</td>
<td>cubic (Pm-3m)</td>
<td>66.3(4)</td>
<td>3.9927(1)</td>
<td></td>
<td>63.652(5)</td>
<td></td>
</tr>
</tbody>
</table>

* determined from the Scherrer equation
The post reaction La$_{0.5}$Ca$_{0.5}$CoO$_3$ TEM image is shown in Figure 4.3a) and HRTEM in Figure 4.3c). From Figure 4.3c), with a lattice spacing of 0.98 nm, while the selected area electron diffraction (SAED) in Figure 4.3d) verifies the (101) orientation in the cubic perovskite. SEM images in figure 4.3b) of post-reaction material indicates that sintering has taken place, although as will be discussed later this does not seem to impede performance over multiple cycles, consistent also with observation by others. HRTEM lattice image in Figure 4.3c) indicates that due to the 15 hours of high temperature operation, significant crystal growth is occurring as seen by the narrowing of the XRD spectral peaks of post-reaction samples in Figure 4.4.

Each of these XRD patterns is provided in Figure 4.3 of the Le Bailing fitting of each pattern showed that each sample was phase pure with all peaks being indexed in either the cubic ($Pm-3m$), orthorhombic ($Pbnm$), or rhombohedral ($R-3c$) space groups. Representative Le Bail refinements for La$_{0.5}$Ca$_{0.5}$CoO$_3$, LaCu$_{0.5}$Mn$_{0.5}$O$_3$, and LaNiO$_3$ are provided in Figures 4.5-4.7. Table 4.2 presents the refined space group, crystallite size, and lattice parameters resulting from the Le Bail fitting of each pattern. Considering impurity phases are no longer present in the post fixed bed experiment samples and that the OSC of these samples is steady over the 50 cycles tested, these impurity phases appear to have a minimal effect on the performance of these samples as oxygen carriers. All peaks were indexed in either the cubic ($Pm-3m$), orthorhombic ($Pbnm$), or rhombohedral ($R-3c$) space groups. TGA-MS data in Figure 4.8 implies that our perovskites did not release $O_2$ up to 1023 K, thus the OCs’ reaction with CH$_4$ follows the gas-solid reaction mechanism.
Figure 4.3. a) TEM, b) SEM and c) HRTEM and d) SAED shows the perovskite crystal structure of the post-reaction La$_{0.5}$Ca$_{0.5}$CoO$_3$. 
Figure 4.4. Powder XRD of post fixed bed reactor study samples.
Figure 4.5. Le Bail fitting of La$_{0.5}$Ca$_{0.5}$CoO$_3$ in the orthorhombic $Pnma$ space group. Shown are the observed (black circles), refined (red line), difference (blue line) and locations of allowed reflections (blue tick marks).
Figure 4.6. Le Bail fitting of $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$ in the orthorhombic $Pbnm$ space group. Shown are the observed (black circles), refined (red line), difference (blue line) and locations of allowed reflections (blue tick marks).
Figure 4.7. Le Bail fitting of LaNiO$_3$ in the orthorhombic $Pbnm$ space group. Shown are the observed (black circles), refined (red line), difference (blue line) and locations of allowed reflections (blue tick marks).
Table 4.2. Le Bail refinement results for samples post fixed bed reactor studies.

<table>
<thead>
<tr>
<th></th>
<th>Phase Symmetry</th>
<th>Crystallite size (nm)*</th>
<th>(a) (Å)</th>
<th>(b) (Å)</th>
<th>(c) (Å)</th>
<th>Volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{LaNiO}_3)</td>
<td>orthorhombic ((Pbnm))</td>
<td>57.8(5)</td>
<td>5.5394(4)</td>
<td>5.6513(3)</td>
<td>7.7449(4)</td>
<td>242.45(3)</td>
</tr>
<tr>
<td>(\text{LaMnO}_3)</td>
<td>rhombohedral ((R-3c))</td>
<td>38.8(4)</td>
<td>5.5193(3)</td>
<td>13.402(1)</td>
<td>353.56(5)</td>
<td></td>
</tr>
<tr>
<td>(\text{LaMn}<em>{0.5}\text{Ni}</em>{0.5}\text{O}_3)</td>
<td>rhombohedral ((R-3c))</td>
<td>48.1(5)</td>
<td>5.7053(5)</td>
<td>-</td>
<td>13.870(1)</td>
<td>390.96(7)</td>
</tr>
<tr>
<td>(\text{LaMn}<em>{0.5}\text{Cu}</em>{0.5}\text{O}_3)</td>
<td>orthorhombic ((Pbnm))</td>
<td>38.1(3)</td>
<td>5.5260(4)</td>
<td>5.6385(5)</td>
<td>7.7792(6)</td>
<td>242.39(3)</td>
</tr>
<tr>
<td>(\text{LaCrO}_3)</td>
<td>orthorhombic ((Pbnm))</td>
<td>67.3(5)</td>
<td>5.5149(2)</td>
<td>5.4776(2)</td>
<td>7.7610(4)</td>
<td>234.45(2)</td>
</tr>
<tr>
<td>(\text{LaCoO}_3)</td>
<td>orthorhombic ((Pbnm))</td>
<td>63.6(5)</td>
<td>5.5072(3)</td>
<td>5.5361(2)</td>
<td>7.7941(4)</td>
<td>237.62(2)</td>
</tr>
<tr>
<td>(\text{La}<em>{0.5}\text{Ca}</em>{0.5}\text{MnO}_3)</td>
<td>orthorhombic ((Pbnm))</td>
<td>70.6(8)</td>
<td>5.6727(3)</td>
<td>5.6513(4)</td>
<td>7.9691(5)</td>
<td>255.47(3)</td>
</tr>
<tr>
<td>(\text{La}<em>{0.5}\text{Ca}</em>{0.5}\text{FeO}_3)</td>
<td>orthorhombic ((Pbnm))</td>
<td>136(1)</td>
<td>5.5646(2)</td>
<td>5.5539(2)</td>
<td>7.8519(2)</td>
<td>242.67(1)</td>
</tr>
<tr>
<td>(\text{La}<em>{0.5}\text{Ca}</em>{0.5}\text{CoO}_3)</td>
<td>orthorhombic ((Pnma))</td>
<td>58(1)</td>
<td>5.5384(7)</td>
<td>5.5467(5)</td>
<td>7.7779(5)</td>
<td>238.94(4)</td>
</tr>
<tr>
<td>(\text{Ba}<em>{0.5}\text{Sr}</em>{0.5}\text{Co}<em>{0.8}\text{Fe}</em>{0.2}\text{O}_3)</td>
<td>cubic ((Pm-3m))</td>
<td>53.7(8)</td>
<td>3.9763(3)</td>
<td>-</td>
<td>-</td>
<td>62.87(2)</td>
</tr>
</tbody>
</table>

* determined from the Scherrer equation
Figure 4.8. TGA-MS of as-synthesized perovskites with m/z=32 ion current displayed (All mass loss curves superimposed on top of one another).
4.3.2 OC performance tests

In this study, we found that $A$ cation substitution has a negligible effect on OSC, but there exists an inverted volcano dependence for transferable oxygen during total methane oxidation with the $B$ cation's electronegativity (Pauling scale). The global reaction between perovskite and methane can be represented as,

$$4 ABO_3 + \delta \text{CH}_4 \rightarrow 4 ABO_{3-\delta} + \delta \text{CO}_2 + 2\delta \text{H}_2\text{O}$$

Thus we can define oxygen storage capacity (OSC) in CLC as $\delta$, which was measured by quantitative analysis of CO$_2$ in the fuel step. Figure 4.9a) shows the OSC ($\delta$) over 50 CLC cycles in the fixed bed reactor and clearly indicates that all perovskites are stable OCs. The amount of CO$_2$ produced was quantified from the effluent in the fuel step, and carbon coking generated from methane thermal decomposition, the major side reaction, is measured by the CO$_2$ species in the air step. Shown in Figure 4.9b), we define CO$_2$ selectivity as:

$$\gamma_{CO_2} = \frac{n_{CO_2}}{n_C + n_{CO_2}}$$

where $n_{CO_2}$ are the number of moles detected in the fuel step and $n_C$ the number of moles detected in the air step. All the perovskites expressed $\gamma_{CO_2}$ values higher than 95%, indicating their low coking ratio.$^{111}$
Figure 4.9. (a) OSC (δ) and (b) CH₄ selectivity to CO₂ of tested perovskites in 50 cycles with methane at 1023 K in a fixed-bed reactor.
In an attempt to provide some microscopic structural context to these results we show in Figure 4.10(a) the relationship between OSC and $\lambda_B$ ($B$ site electronegativity) on the Pauling Scale.$^{112}$ For the mixed $B$ site samples, a simple molar average was used for $\lambda_B$. The resulting plot shows an inverted volcano behavior. Since the OSC’s of the samples with mixed La and Ca occupancy on the $A$ site showed negligible difference, we concluded that substituting Ca for La on the $A$ site has a negligible effect of the OSC, which agrees with previous publications.$^{113,114,115,46a}$ This also makes sense considering that the $B$ metal is the redox active center of the perovskite. For comparison, we also plotted the average occupancy of the so-called $e_g$ orbital for the transition metal, as determined by Suntivich et al.$^{113b}$ versus OSC in Figure 4.10b). Although true $O_h$ symmetry is not present in all of these materials, the structural distortions are too minor to invert the basic crystal field splitting energies (i.e. make $t_{2g}$-derived states higher in energy than the $e_g$-derived ones). Therefore, we use $e_g$ only as a convenient label across various perovskites in searching for broad trends in properties such as catalytic activity or oxygen storage capacity. In cases where two transition metals are present, only the more catalytically active element was considered. Here, the trend appears less obvious than for $\lambda_B$, although a volcano-type relationship does seem plausible. Overall, $e_g$ occupancy does not appear to be as useful a descriptor as $B$-site electronegativity.

Utilizing a materials descriptor such as electronegativity provides a general understanding of OC design with $ABO_3$ perovskites given that the
underlying mechanisms are still unknown. Past studies have found that oxygen transport and mobility in perovskite structures are highly relevant to their other applications, thus considerable attention has been focused on partial substitutions for the A and B sites to find optimal combinations.\textsuperscript{116,32a} Recently, Imanieh \textit{et al.} explored the effect of substituted atom size on the reactivity of hydrocarbons with $ABO_3$ ($CaMnO_3$) perovskites in order to identify the optimal OC for CLC applications.\textsuperscript{117} At high reaction temperature (>1123 K) favoring $O_2$ release, CaMnO$_3$ perovskite with ~10\% Sr and Fe doped in the A and B sites, respectively, helps improve their oxygen storage capacity (OSC) due to higher crystalline distortion. X. Dai \textit{et al.} found that compared to Nd, Eu substitution for La on the A site maintains a relatively high catalytic activity and structural stability during redox reactions.\textsuperscript{118}

Since Bockris and Otagawa’s work in 1980s, descriptors correlating 5-coordinate surface ions’ electronic properties of perovskite oxides and their activities towards oxygen electrocatalysis have attracted a lot of interest.\textsuperscript{113a} It has been reported that the filling of $e_g$ manifold of the octahedral crystal field of the $B$ cations, mainly related to the oxygen binding to the perovskite surface\textsuperscript{13}, can be used as an efficient descriptor for reactivity in oxygen evolution reaction (OER) in fuel cell applications employing perovskites\textsuperscript{113b} and water-splitting reactions.\textsuperscript{114} Thus $e_g$ in perovskite, contributed to occupied valence band states, are responsible for the reactive states near Fermi level, could be used as an effective descriptor, consistent with Norskov’s d-band theory. From our own
results, however, it appears that $e_g$ occupancy is not as relevant for temperature-driven redox reactions.

The role of B-site electronegativity could be related to that of the B-O bond strength. Electronegativity, as defined by Mulliken, is the average of the ionization potential and the electron affinity. Therefore, the degree of hybridization between the $B d$-states and the O $2p$-states would be dependent on electronegativity.
Figure 4.10. The relation of OSC (δ) and (a) the $\lambda_B$ (B site electronegativity) in methane total oxidation and (b) the $e_g$ electron occupancy.
While we have not found a direct correlation between electronegativity and oxide conductivity yet, other workers have found oxygen vacancy formation as a useful descriptor for electrochemical applications of perovskite oxides. Kitchin et al. used density function theory (DFT) calculations to correlate the decrease in the oxygen vacancy formation energy to increasing atomic numbers from Cr to Cu in LaBO$_3$ and SrBO$_3$, which were explored as anode materials in SOFC’s.$^{119}$ Through DFT calculations, Carter et al. demonstrated that ion diffusion in the La$_{1-x}$Sr$_x$BO$_3$ family (B = Cr, Mn, Fe, Co) and Sr$_2$Fe$_{2-x}$Mo$_x$O$_6$ depends on two processes: oxygen vacancy formation and vacancy mediated oxygen migration, and found that oxygen vacancy formation energy could be used as a descriptor for oxide ion transport properties’ evaluation.$^{116}$

Yang et al. utilized X-ray Absorption Near Edge Structure (XANES) and fluorescence O K-edge to study the effects of the B and A site, respectively, on the electronic structure and found that changes in A site substitution have less of an effect relative to the B-site, and increasing the B site electron count can increase hybridization between the transition metal 3$d$ and oxygen 2$p$ states and therefore covalency.$^{115}$ Hong et al. reported that partial substitution of the B site could result in improved catalytic effects owing to lattice defects.$^{120}$ As to the reaction of perovskites with hydrocarbons, the activation of the C-H bond has been proposed to be important.$^{32a}$ For example, the reaction of oxides with methane can follow two pathways, the 4-centered (CH$_3$-B—H-O) transition state (σ-bond metathesis) and 3-centered (CH$_3$-B-H) transition state (dehydrogenation).$^{111,121}$ However, our studies are
not mechanistic in nature and we cannot propose any of these transition states in our oxides during CLC.

On the left side of the inverted plot (Figure 2a), the downward trend in the oxygen storage capacity includes $B$ cations with relative low electronegativity. As the $B$ site’s electronegativity increases, transition metal-oxygen bond covalency increases due to the decreased difference in electronegativity between the $B$ cation and oxygen anion. Previous computational studies on similar perovskites concluded that oxide vacancy formation is enhanced by weaker $B$—O bonds in La$B$O$_3$ perovskites. Therefore, the less electronegative metals would enhance oxygen vacancy formation under CLC conditions.

Interestingly, as electronegativity increases, the OSC starts to rise again after iron. The previous argument that the $B$—O bond strength diminishes oxide vacancy formation seems to be less important for this part of the trend. It has been widely accepted that the catalytic performance of metals follows the Sabatier’s principle (interactions between the catalyst and interface needs to be “just right”) and the $d$-band model (the existence of correlation between interaction energy and $d$-band center in transition metal catalysts). Nwosu et al. claims that mixed metal ions from 3$d$ transition metal whose average electronegativities are equivalent to those of noble metals should show similar catalytic performance. The study of catalysts for hydrocarbon cracking shows that metals with similar electronegativities would therefore lead to similar catalytic effects. Therefore, it could be that the $d$-band center is influenced by the deeper ionization potentials of the $B$ metals (which factors into $\lambda_B$) takes over as a more important parameter than $B$—O bond strength.
Considering the superior catalytic performance of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3 in OER\textsuperscript{113b}, we also prepared this perovskite to validate the inverted volcano plot with no lanthanum/calcium in \textit{A} site. As indicated in Figure 2a, the OSC of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3 fits reasonably well in the inverted volcano plot, indicating that this behavior is more universal and applies to other \textit{A} site OC perovskites with 3\textit{d} transition metals on the \textit{B} site.

\textit{4.4 Conclusions and Outlook}

Our study concludes that 3\textit{d} transition metal \textit{B} site electronegativity could be used as a powerful descriptor in the OSC of perovskites with CH\textsubscript{4} total combustion. We found an inverted volcano plot relationship for the lanthanum/calcium perovskite, and while the choice for the \textit{A} site (either La or Ca) has a negligible effect on the OSC, the choice of the \textit{B} site is more relevant towards the design of optimal OC’s. We propose that the limiting impactor of OSC in the total combustion of CH\textsubscript{4} by perovskite oxides is C-H bond activation. We propose that the inverted volcano plot is attributed to two different reaction mechanisms between the activation of C-H bond in methane in the series. This approach may offer a heuristic approach towards choosing and evaluating perovskite OC’s and possibly other energy related applications.
Chapter 5: Thermal Decomposition and Kinetics of Poly (Lactic Acid) Sacrificial Polymer Catalyzed by Metal Oxide Nanoparticles

5.1 Introduction

Poly Lactic Acid (PLA) is an environmentally friendly polymer produced from plants (mainly from starch and sugar) including corn, potatoes and sugar-beets, and has attracted attention for its biocompatibility, biodegradability, and thermoplastic processability.\(^{50}\) It has been reported that the greenhouse gas emission rate of PLA is approximately 1600 kg CO\(_2\)/metric ton, while that of polypropylene (PE), polystyrene (PS), polyethylene terephthalate (PET), and nylon are 1850, 2740, 4140, and 7150 kg CO\(_2\)/metric ton, respectively.\(^{126}\) Further, PLA’s low temperature of thermal degradation with minimal solid residue (gasified lactide) has made it an attractive candidate as a sacrificial component in polymer fabrication.\(^{56, 126-127}\)

PLA is also one of the two major plastics explored as 3D printing inks (the other being Acrylonitrile Butadiene Styrene (ABS)) because of its thermoplastic properties.\(^{52}\) Although ABS is currently the dominant 3D printing polymer, PLA offers the advantage of bio-compatibility. As a sacrificial component, PLA can be 3D printed to create complex-shaped molds\(^{54, 128}\). For example, White \textit{et al.}\(^{54}\) have
fabricated PLA as spheres (0D), fibers (1D), sheets (2D), and 3D printed sacrificial materials, leaving behind the reverse replica. Pitet et al.\textsuperscript{129} have explored PLA as a sacrificial component in copolymers to create porous membranes for battery separators utilizing the fact that its decomposition temperature is about 200 K lower than thermally stable polymers such as polyimide (PI), epoxies, Poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP), etc. The decomposition of neat PLA occurs above ~550K, which can lead to the thermal instability of other polymer blends in practical applications during prolonged heat treatment\textsuperscript{54}. Therefore, alkali earth metal oxides\textsuperscript{56}, rare metal (scandium (III) triflates (CF\textsubscript{3}SO\textsubscript{3}-))\textsuperscript{60}, and tin-containing compounds\textsuperscript{54, 61, 128b} were studied as catalysts for PLA thermal decomposition. Moore et al.\textsuperscript{54, 128a} added Sn-based reactants to lower the decomposition temperature by 90 K to effectively remove sacrificial PLA at a lower temperature while avoiding thermal damage to the epoxy mold. It was found that the same amount of SnO\textsubscript{x} additive works even better than tin (II) octoate to further reduce the total decomposition time at the same temperature.\textsuperscript{54} Mori et al. reported similar results using Sn-based compounds and recognized that these catalysts could enhance the breakage of ester bonds in the polymer backbone, thus promoting the fragmented polymer ends to experience chain backbiting and transesterification reactions before further depolymerization.\textsuperscript{61} Almost all of the previous studies used a high loading of more than 5 wt% catalyst.\textsuperscript{54, 56, 60-61, 128-129}

Addition of catalysts into PLA is usually achieved by surface treatment (including impregnation or solvent swelling)\textsuperscript{128a}, solvent evaporation casting\textsuperscript{54}, or vane extruding.\textsuperscript{130} Dong et al.\textsuperscript{128a} utilized solvent swelling to immobilize metal ions
(tin (II) octoate solution) into PLA fibers. Later, Moore et al. used solvent evaporation to imbed SnO$_x$ into PLA, further decreasing the decomposition temperature.$^{54}$ Solvent evaporation casting of PLA with specific viscosity was utilized by Guo et al. in a proposed 3D printing ink drying technique.$^{131}$ Zhang et al. utilized melt blending with a vane extruder with heating to get mono-dispersed PLA/TiO$_2$ nanocomposites.$^{130}$

It is widely known that controlling the removal process of the sacrificial materials is extremely difficult, requiring carefully designed thermal conditions and perfect timing to fully eliminate the sacrificial material at minimal cost, while also keeping the host material undamaged.$^{132}$ Therefore, catalysts are added to increase the decomposition temperature difference between the sacrificial materials and host materials to maintain the integrity of the host polymer.$^{54, 56, 60-61, 128-129}$ Usually the removal time for even nano-scale channels are hours to days and are highly non-linear relative to different heating conditions, which makes the control process hard to predict.$^{54, 128a, 132a}$ The severity of this problem increases as larger and more complex geometries are required with the rapid development of 3D printing using such sacrificial materials.$^{131}$ MOs have not been studied extensively as catalysts for PLA, especially at small loadings ($< 5\%$).

In this work, we employed 1 wt% MOs loading to study the catalytic effects of MOs. Bi$_2$O$_3$, CuO and Fe$_2$O$_3$ are synthesized by spray pyrolysis$^{76, 80, 133}$ and then uniformly embedded into PLA matrix using solvent evaporation casting. XRD and SEM are performed to verify the additives’ crystallinity and homogenous dispersion in the PLA matrix. The thermal properties of PLA/MOs composites relative to neat
PLA are measured by TGA (Thermogravimetric Analyzer), DSC (Differential Scanning Calorimeter), and MCC (Microscale Combustion Calorimeter) to examine the MOs catalytic effect on the PLA’s thermal degradation process and overall combustion heat. Thermal degradation simulations are performed to fit the experimental TGA curve with a number of first order chemical pyrolysis reaction models using a one dimensional pyrolysis model (TheraKin\textsuperscript{134} running under thermally thin mode). This kinetic fitting work is performed to reproduce the TGA data, which provides kinetic fundamentals to potentially further predict and control the removing process time and temperatures of PLA/MOs for different geometries or length scales in various heating environments in the future.

5.2 Experimental Approach

5.2.1 Catalyst synthesis

All metal oxide additives are in-house synthesized by aerosol spray pyrolysis.\textsuperscript{76, 80, 133} The spray pyrolysis system consists of an atomizer (to produce aerosol droplets), a silica-gel diffusion drier (to remove solvent), an isothermal furnace (to decompose precursor droplets), and a stainless steel sample collector with 0.4 µm DTTP Millipore filter (to collect nanoparticles). The aerosol droplets of precursor solution are generated using a collision-type nebulizer with an initial droplet diameter of approximately 1µm, which is then desiccated by passing through the silica-gel diffusion dryer. The dehydrated aerosol precursors then decompose into the solid metal oxide particles in the tube furnace set at 873 K for Fe\textsubscript{2}O\textsubscript{3} and CuO, or 1050°C for Bi\textsubscript{2}O\textsubscript{3}, with a residence time of about 1 s. Particles exiting the aerosol reactor are then collected on a 0.4 µm pore size DTTP Millipore filter with 10%-20% porosity.
The precursors used for the Bi₂O₃, Fe₂O₃, and CuO are Bi(NO₃)₃·5H₂O, Fe(NO₃)₃·9H₂O and Cu(NO₃)₂·3H₂O respectively, all from Sigma-Aldrich. A total precursor concentration of 0.200 M aqueous solution is used for MOs, and to dissolve Bi(NO₃)₃·5H₂O, 1:5 concentrated nitric acid and water mixture is used as the solvent. The aerosol spray pyrolysis is a droplet to droplet method. Lognormal poly-dispersed spherical solid particles are generated e.g. the Fe₂O₃ particles are spherical particles with a lognormal distribution peak at 84nm.133

5.2.2 Incorporation of nano-catalysts into PLA

PLA (Rejuven8 Plus Spartech) is obtained from Nature Works and used as received. The PLA sheets are 0.7 mm thick and cut into small pieces for solvent evaporation casting. 1.000 g PLA is first dissolved in 100.0 mL CH₂Cl₂ with magnetic stirring for 30 mins. Then 10.0 mg (1 wt%) MO is added to the solution and ultra-sonicated for 1 h. The solutions are then poured onto a watch glass and dried in a 323 K convection oven to for 12 h. Thin films of neat PLA (baseline reference) and PLA/MO composites are obtained after solvent evaporation. Small pieces of the as prepared thin films were then used for the thermal tests.

5.2.3 Material characterizations

Crystal structures of metal oxides are characterized by XRD with a Bruker Smart1000 using Cu Ka radiation. SEM results were obtained by Hitachi SU-70 SEM. For cross-sectional SEM images, samples are first fractured in liquid nitrogen and then sputter-coated with carbon. Nitrogen (N₂) adsorption-desorption isotherms and Brunauer–Emmett–Teller (BET) surface were measured at 77 K with a Micromeritics ASAP.
A Netzsch F3 Jupiter Simultaneous Thermal Analyzer (STA), employed in the thermal stability study, combines a TGA equipped with a 1 µg-resolution microbalance and DSC heat flow measurement with a steel furnace. Thus the STA can measure the TGA and DSC signals simultaneously during a single experiment. The PLA/MOs films were stored in a desiccator for 48 hours prior to testing, and then cut and pressed into Platinum-Rhodium crucibles with ventilation lids with a sample mass of 6-7 mg. The thermal decomposition experiments were performed at a heating rate of 10 K min\(^{-1}\) from 313 K to 873 K under 99.999% (UHP) N\(_2\) at a flow rate of 50 cm\(^3\)·min\(^{-1}\). A microscale combustion calorimeter (MCC) with 3 mg samples was used to measure the heat release rate and total heat of combustion. The MCC combines a condensed phase pyrolyzer and gas phase combustor. The samples are first decomposed in 80 cm\(^3\) min\(^{-1}\) UHP N\(_2\) flow, 60 K min\(^{-1}\) heating rate from 348 to 873 K inside the pyrolyzer, which is similar to the STA furnace, and then transferred to the combustor where the gaseous fuel (decomposition products) was burned at 1223 K to ensure complete combustion mixing with additional 20 cm\(^3\)·min\(^{-1}\) O\(_2\). The entire experimental measurement of HRR (Heat Release Rate) followed ASTM standard ASTM D 7309-07.\(^{135}\) The heat release rate is measured based on Thornton’s rule by measuring the O\(_2\) consumption rate of combustion.\(^{136}\)
5.3 Results and Discussion

5.3.1 Material textural properties

Figure 5.1 shows the SEM micrographs of spray pyrolysis synthesized Bi$_2$O$_3$, Fe$_2$O$_3$ and CuO nanoparticles, which are solid spherical particles with diameters from 50 nm to 1 µm following a log normal distribution with a peak (Fe$_2$O$_3$ at 84 nm$^{133}$, CuO at 86 nm and Bi$_2$O$_3$ at 87 nm, shown in Figure 5.2. Figure 5.3 shows BET surface area results: Fe$_2$O$_3$-13 m$^2$/g, CuO-23 m$^2$/g, Bi$_2$O$_3$-4 m$^2$/g), with Bi$_2$O$_3$ surface area being the lowest, indicating that surface area does not explain the superior catalytic activity of Bi$_2$O$_3$. The crystal structures of oxides are investigated from XRD shown in Figure 5.4. All peaks in Fe$_2$O$_3$ can be indexed to $\gamma$-Fe$_2$O$_3$ phase (JCPDS card No.: 39-1346); Bi$_2$O$_3$ with JCPDS card No.: 27-0050, while CuO peaks corresponds to tenorite with JCPDS card No.: 48-1548.
Figure 5.1. SEM of nanoparticles a) Bi$_2$O$_3$, b) CuO, c) Fe$_2$O$_3$, prepared from spray pyrolysis.
Figure 5.2. Particle-size distributions of Fe$_2$O$_3$, CuO, Bi$_2$O$_3$ as-synthesized by spray pyrolysis measured using a differential mobility analyzer (DMA) coupled with a condensation particle counter (CPC).
Figure 5.3. $N_2$ adsorption/desorption isotherms of $\text{Fe}_2\text{O}_3$, CuO, $\text{Bi}_2\text{O}_3$. 
Figure 5.4. XRD of nanoparticles-Bi$_2$O$_3$, Fe$_2$O$_3$, CuO from spray pyrolysis.
It is widely known that the dispersion of nanoparticles in polymer will greatly influence the both chemical and physical properties of the PLA/MO composites. Homogeneous dispersion of MO nanoparticles will affect the thermal and mechanical behaviors of PLA, such as wettability, UV transmittance, strength and ductility, elasticity, viscosity, antibacterial property. \(^{130}\)

Cross-sectional SEM images are taken to check the dispersion of MOs in the composites. PLA/MOs are first fractured in liquid nitrogen and then broken off for cross-sectional images. Figure 5.5a) and 5.5b) show neat PLA cross-sectional image without particles, while Figure 5.5c) and 5.5d) are PLA/Fe\(_2\)O\(_3\), PLA/CuO films images. It is clear from these images that all nanoparticles are well dispersed in the PLA films. Figure 5.4 shows the cross-sectional PLA/Bi\(_2\)O\(_3\) structure, and it is clear that spherical Bi\(_2\)O\(_3\) are uniformly dispersed in PLA and un-aggregated. The film is about 50 \(\mu\)m thick, indicated by low magnification image of Figure 5.6a) and Figure 5.6b). Moreover, Figure 5.6c) and 5.6d) give a closer view of the cross-sections, all showing that particles are coated and/or connected by PLA while separated from other nanoparticles.
Figure 5.5. SEM of cross-sectioned a) and b) PLA, c) PLA/Fe$_2$O$_3$, d) PLA/CuO films.
Figure 5.6. SEM of cross-sectioned PLA/Bi$_2$O$_3$ film.
5.3.2 Thermal tests and kinetic analysis

Figure 5.7 shows the TGA data of thermal decomposition mass loss under N₂ inert atmosphere. It is clear that the various types of MO additives affect the thermal stabilities of PLA/MOs differently, which can also be clearly seen in Figure 5.8 from Derivative Thermogravimetry (DTG) experimental curves (dotted lines). Specifically, the onset thermal degradation temperature for neat PLA as a reference is approximately $T_{5\%} \approx 580$ K. For PLA/Bi$_2$O$_3$, this temperature is 75 K lower ($T_{5\%} \approx 505$ K), while the effect of Fe$_2$O$_3$ is about 30 K decrease ($T_{5\%} \approx 550$ K) compared to neat PLA; CuO shows no noticeable effect. The thermal degradation temperatures at maximum weight loss ($T_{\text{max}}$), are 536 K (614 K for the second peak), 573 K, 634 K and 635 K for PLA/Bi$_2$O$_3$, PLA/Fe$_2$O$_3$, PLA/CuO and neat PLA respectively. These results show that the catalytic properties trend as: Bi$_2$O$_3$ > Fe$_2$O$_3$ > CuO. While the DSC signals reveal notable differences at the stage of decomposition, the addition of MOs does not significantly affect the melting point ~ 425 K or the heat of melting (as seen in DSC Figure 5.9). The heats of melting (the first peak integrals) are within 4% difference of their mean.
Figure 5.7. TGA of PLA and PLA/MOs.
Figure 5.8. DTG plots of PLA and PLA/MOs.
To better evaluate the decomposition kinetics at various heating conditions and scales, which are necessary as fundamentals to predict the catalytic effects of the MOs on the PLA decomposition, we have extracted phenomenological rate parameters using a numerical pyrolysis software - ThermaKin.\textsuperscript{134} ThermaKin solves the mass and energy conservation equations numerically for one or two-dimensional objects exposed to external (convective and/or radiative) heat. In this study, we use the thermally thin mode to simulate the thermal degradation processes inside the STA furnace. The material of the object (sample) is described by multiple components, which may interact chemically and physically. The neat PLA and PLA/MOs kinetics were characterized using the methodology reported in our recent publications.\textsuperscript{137} This methodology has been successfully applied to reproduce TGA and DSC signals of 15 non-charring and charring polymers.\textsuperscript{23,24} The resulting kinetic parameters were also shown to predict gasification or burning rates of these polymers at a wide range of thermal conditions.\textsuperscript{137-138} The results of this characterization is shown in Figure 5.10.

In the previous study, neat PLA was tested using STA and the kinetics of its decomposition was modeled using two consecutive first order reactions.\textsuperscript{137} One more reaction was employed to describe melting ($T_{\text{melt}} = 425$ K). This was done to use a minimum number of parameters to describe the entire time-resolved TGA and DSC curves. The kinetics of those reactions are parameterized with Arrhenius parameters ($A_x$, $E_x$ represent decomposition reaction $x$; while $A_m$, $E_m$ represent the melting) listed in Table 5.1. The value of the $\theta_x$ is calculated by the instantaneous mass (at the end stage of the reaction $x$) over its initial mass. Note that the $\theta_x$, obtained directly from the TGA experiments, corresponds to the remaining condensed phase residue yielded
in the reaction x. Those parameters are initially estimated using simple analytical expressions\textsuperscript{139} and then changed in small increments following the rules summarized in the previous studies until agreements with the experiment is reached (based on preset coefficient of determination and visual comparison). Each model reaction corresponds to tens or, perhaps, hundreds of elementary chemical processes operating within the same range of temperatures.

The MOs do not affect the phase transition as evident from DSC curves in Figure 5.9 (enlarged temperature range in the left corner). The kinetic parameters describing the melting were reported previously\textsuperscript{137}. For all the PLA composites, MOs are found to affect the thermal degradation process significantly, which is apparent in both the TGA and DSC measurements. The impact of MOs on the kinetics of decomposition is quantified through changes in the parameters of the first (major) reaction. The kinetic parameters are summarized in Table 5.1. With the exception of PLA/Bi\textsubscript{2}O\textsubscript{3}, the decomposition of all composites can be described by two consecutive reactions. The kinetics of the second reaction remain unaffected by the addition of MOs. In the case of PLA/Bi\textsubscript{2}O\textsubscript{3}, the thermal decomposition process consists of three consecutive reactions reflecting a more complex DTG signal. It has been widely concluded that the thermal decomposition of pure PLA is a one-stage reaction that involves the loss of ester groups in pure nitrogen and air,\textsuperscript{7,11} consistent with our observations for neat PLA and PLA/CuO in this study. Other researchers have also observed multiple reaction steps with the addition of other catalysts\textsuperscript{6}, although little information on mechanism is available. Our speculation for the existing second peak is that part of the PLA remains unaffected by the catalytic Bi\textsubscript{2}O\textsubscript{3} during the first
decomposition step, and it decomposes as neat PLA at a higher temperature to form the second peak. Further investigation is required to validate this hypothesis.

For all the materials, the solid lines in Figure 5.9 represent the numerical simulation results from the ThermaKin. All the simulation results fit the experimental data well and the calculated coefficients of determination of the experimental data and the fitted curves are all above 0.9.
Figure 5.9. DSC test of PLA and PLA/MOs.
Figure 5.10. Experimental and simulated DTG of PLA & PLA/MO composites at 10 K min⁻¹.
Table 5.2 Kinetic parameters for PLA, PLA/Fe$_2$O$_3$, PLA/Bi$_2$O$_3$ and PLA/CuO.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$A_1$</th>
<th>$E_1$</th>
<th>$\theta_1$</th>
<th>$A_2$</th>
<th>$E_2$</th>
<th>$\theta_2$</th>
<th>$A_3$</th>
<th>$E_3$</th>
<th>$\theta_3$</th>
<th>$A_m$</th>
<th>$E_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(s$^{-1}$)</td>
<td>(kJ mol$^{-1}$)</td>
<td></td>
<td>(s$^{-1}$)</td>
<td>(kJ mol$^{-1}$)</td>
<td></td>
<td>(s$^{-1}$)</td>
<td>(kJ mol$^{-1}$)</td>
<td></td>
<td>(s$^{-1}$)</td>
<td>(kJ mol$^{-1}$)</td>
</tr>
<tr>
<td>PLA</td>
<td>1.68E18</td>
<td>245</td>
<td>0.1</td>
<td>4.58E6</td>
<td>126</td>
<td>0.4</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>6.0E40</td>
<td>355</td>
</tr>
<tr>
<td>PLA+ Fe$_2$O$_3$</td>
<td>1.80E38</td>
<td>436</td>
<td>0.1</td>
<td>4.58E6</td>
<td>126</td>
<td>0.5</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>6.0E40</td>
<td>355</td>
</tr>
<tr>
<td>PLA+ Bi$_2$O$_3$</td>
<td>1.34E18</td>
<td>207</td>
<td>0.3</td>
<td>2.85E15</td>
<td>205.5</td>
<td>0.37</td>
<td>4.58E6</td>
<td>126</td>
<td>0.72</td>
<td>6.0E40</td>
<td>355</td>
</tr>
<tr>
<td>PLA+ CuO</td>
<td>1.68E18</td>
<td>245</td>
<td>0.1</td>
<td>4.58E6</td>
<td>126</td>
<td>0.4</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>6.0E40</td>
<td>355</td>
</tr>
</tbody>
</table>
The Heat Release Rate (HRR) is measured by MCC, as shown in the Figure 5.11. The heat release rate curves for all the PLA/MOs composites match the reaction peaks of TGA and DSC qualitatively but not quantitatively with respect to their peak temperatures. The corresponding heat release rate peaks in Figure 5.11 for all the samples shift to a higher temperature by approximately 27 ~ 28 K compared to the TGA and DSC results in Figures 5.7 & 5.9.
Figure 5.11. HRR of PLA, PLA/Fe$_2$O$_3$, PLA/Bi$_2$O$_3$ and PLA/CuO.
This temperature difference is caused by the relatively higher heating rate (60 K min\(^{-1}\)) utilized in the MCC compared to the heating rate (10 K min\(^{-1}\)) in the STA test. The integral of the heat release rate, which accounts for the heat of combustion of the gaseous decomposition products, is approximately equal for all tested samples yielding 19.5±0.8 kJ/g. Therefore, all of the these three types of 1wt% PLA/MOs affect the thermal degradation processes only in the condensed phase but have no effect on the heat of combustion.

5.4 Conclusions and Outlook

In this work, we offer a facile method to incorporate metal oxide additives and evaluate their catalytic effects on PLA thermal decomposition. More specifically, we have explored Bi\(_2\)O\(_3\), CuO and Fe\(_2\)O\(_3\) nanoparticles as catalysts for PLA thermal decomposition. Bi\(_2\)O\(_3\) is shown to be a highly effective catalyst for PLA thermal decomposition. With only 1wt% loading, it lowered the onset decomposition temperature (T\(_{5\%}\)) by 75 K and the decomposition temperature at the maximum weight loss (T\(_{\text{max}}\)) by approximate 100 K, comparable to the most effective catalysts studied so far. The same amount of Fe\(_2\)O\(_3\) and CuO nanoparticles have moderate and negligible effects on PLA thermal decomposition processes respectively. The overall catalytic effects of the three metal oxides trend as: Bi\(_2\)O\(_3\) > Fe\(_2\)O\(_3\) > CuO ≈ inert material.

The complete heats of combustion for the PLA/MOs composites have been measured by MCC, in which 1wt% MO additive catalyzes the thermal degradation processes differently in the condensed phase, and moreover, have negligible effect on the complete combustion heat in the gas phase as expected. PLA/MOs decomposition
was then quantitatively analysed to extract Arrhenious parameters for the decomposition kinetics, which offers possible explanations and predictions to evaluate thermal decomposition kinetics at other heating rate conditions.
Chapter 6: Conclusions and Future Work

6.1 Conclusions

This dissertation addressed the applications of nanostructured materials as oxygen carriers (OCs) and catalysts in poly lactic acid (PLA) thermal decomposition. The stability and cyclability of metal oxides and supported metal oxides as OCs were evaluated in an isothermal fixed bed reactor at different temperatures for 50 cycles with methane as fuel, up to 15h while their structural, physical and chemical properties were identified using XRD, SEM, TEM, BET, XPS and Ar/H\textsubscript{2}-TPR.

In chapter 2, alkaline (K-, Na-, and Cs-) doped iron oxide and alumina supported iron oxides were synthesized from on step aerosol spray pyrolysis and tested as OCs in fixed bed reactor with methane as fuel. We found that alkaline (K-, Na-) doped iron oxide and alumina supported iron oxides offers better stability and faster reduction kinetics as OCs in CLC reaction. The potassium doping promotes its reactivity most efficiently by binding the alumina support and iron oxide in the high temperature reactor and also offers less coking formation during reduction.

In chapter 3, silicalite-1 has been explored as the supporting material for iron oxide as OCs for the first time. Two kinds of structures, including Fe\textsubscript{2}O\textsubscript{3}@Si core-shell and Fe\textsubscript{2}O\textsubscript{3}@Si composite, are evaluated in the fixed bed reactor at both 1023 K and 1223 K. Both structures showed stable cyclic reactivity with no degradation in transferrable oxygen amount at both testing temperatures. At 1023 K, both OCs exhibited little morphological change after 15 h tests while at 1223 K, the core shell structure collapsed, with zeolite decomposed into SiO\textsubscript{2} and showed severe sintering;
the composite structure stayed both chemically and physically stable. Therefore, the composite structure worked as a better supporting material, offering both less coking and no sintering.

Perovskite oxides, chemical formulated as ABO$_3$, has been studied as novel OCs in CLC due to its thermal stability and faster reaction kinetics. In chapter 4, ten perovskite type OCs, La$_x$Ca$_{1-x}$BO$_3$ (Cr-, Mn-, Fe-, Co-, Ni-)O$_3$ were synthesized from spray pyrolysis and tested with methane as fuel in the fixed bed reactor at 1023 K. It has been found that the oxygen storage capacity (OSC) has negligible change with changing A site from Ca to La while there exists an inverted volcano shaped relationship between OSC and B site electronegativity. Thus 3$d$ transition metal $B$ site electronegativity could be used as a powerful descriptor in the OSC of perovskites with CH$_4$ total combustion thus could provide useful design rule in choosing perovskite type OCs in CLC and might also provide some design insight for other energy related applications of perovskites.

Also we explored Bi$_2$O$_3$, CuO and Fe$_2$O$_3$ nanoparticles synthesized from spray pyrolysis, as catalysts for PLA thermal decomposition in chapter 5. The overall catalytic effects of the three metal oxides trend as: Bi$_2$O$_3$ > Fe$_2$O$_3$ > CuO ≈ inert material. Bi$_2$O$_3$ is shown to be a highly effective catalyst for PLA thermal decomposition. With only 1wt% loading, it lowered the onset decomposition temperature ($T_{5\%}$) by 75 K and the decomposition temperature at the maximum weight loss ($T_{\text{max}}$) by approximate 100 K, comparable to the most effective catalysts studied so far. The same amount of Fe$_2$O$_3$ and CuO nanoparticles have moderate and negligible effects on PLA thermal decomposition processes respectively.
6.2 Future Work

6.2.1 Develop kinetic models for alkaline additives added OCs and zeolite supported OCs

Kinetic reaction models and mechanisms between metal oxides and fuel in CLC is an indispensable stage in order to design a CLC reactor. The main goal of kinetic study is to obtain the concentration change of a reactant or product as a function of time. TGA could be used as a useful tool for the kinetic study, providing the exact mass and heat change vs time. By changing the reaction temperature systematically, detailed reaction kinetics data (Ea & A) between metal oxides and fuel could be achieved.

6.2.2 Study the effectiveness of alkaline or alkaline earth ions’ addition to Cu-, Mn-, Ni- based OCs.

In chapter 2, it has been validated that the addition of alkaline ions to Fe-based OCs could effectively improve its reaction rate and support stability, as well as reducing coking formation. Those benefits may be applicable to other type OCs, such as Cu-, Mn- and Ni- based ones.

6.2.3 Study the effectiveness of zeolite support to Cu-, Mn-, Ni- based OCs.

In chapter 3, zeolite was explored as an effective novel support for Fe₂O₃ OC. It is worth studying its working conditions to other type OCs, such as Cu-, Mn- and Ni-based
6.2.4 Extend the 3d electronegativity rule of transition metal to other energy related applications

In chapter 4, it has been shown that there exists an inverted volcano plot between 3d transition metal B site electronegativity and OSC of perovskite type OCs, which could provide useful insights in perovskite type OC selection. This rule may be applicable to other energy related applications of perovskites, such as chemical looping methane reforming/water splitting or energetic materials.

6.2.5 Study the catalytic effects of other aerosol synthesized metal oxides to bio-degradable polymers

In chapter 5, aerosol synthesized Bi$_2$O$_3$ was found to be a useful catalyst in thermal PLA decomposition, which could lower the on-set decomposition temperature by ~75 T. The developed study protocol could be applied to various metal oxides and polymers to study their catalytic thermal decompositions as well.
Chapter 7: References


32. (a) Zhu, H.; Zhang, P.; Dai, S., Recent Advances of Lanthanum-Based Perovskite Oxides for Catalysis. *ACS Catalysis* **2015**, *5* (11), 6370-6385; (b) Sarshar, Z.; Kleitz, F.; Kaliaguine, S., Novel oxygen carriers for chemical looping...
combustion: La1−xCexBO3 (B = Co, Mn) perovskites synthesized by reactive grinding and nanocasting. *Energy & Environmental Science* **2011**, *4* (10), 4258.

33. Abad, A.; García-Labiano, F.; Gayán, P.; de Diego, L. F.; Adánez, J., Redox kinetics of CaMg0.1Ti0.125Mn0.775O2.9−δ for Chemical Looping Combustion (CLC) and Chemical Looping with Oxygen Uncoupling (CLOU). *Chemical Engineering Journal* **2015**, *269*, 67-81.


Ca/Cu Chemical Loops. Industrial & Engineering Chemistry Research 2013, 52 (4), 1481-1490.


