May 2020

Engineering Dopant Position in Structure-Controlled CeO2-ZrO2 Catalysts

Behnam Safavinia

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_theses

Part of the Catalysis and Reaction Engineering Commons

Recommended Citation
https://digitalcommons.lsu.edu/gradschool_theses/5147

This Thesis is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Master's Theses by an authorized graduate school editor of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.
ENGINEERING DOPANT POSITION IN STRUCTURE-CONTROLLED CEO2-ZRO2 NANOPARTICLES FOR REDOX CATALYTIC APPLICATIONS

A Thesis
Submitted to the Graduate Faculty of the
Louisiana State University and
Agriculture and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science
in
The Cain Department of Chemical Engineering

by
Behnam Safavinia
B.S., University of Arizona, 2017
August 2020
# TABLE OF CONTENTS

List of Tables .................................................................................................................................................. iv

List of Figures .................................................................................................................................................. v

Abstract .......................................................................................................................................................... vii

Chapter 1. Introduction .................................................................................................................................... 1
  1.1. Motivation .................................................................................................................................................. 3
  1.2. Function of Catalysts in DRM .................................................................................................................. 6
  1.3. Redox Catalysts (CeO$_2$) ....................................................................................................................... 9
  1.4. Synthesis and Structure .......................................................................................................................... 16
  1.5. Scope and Proposed Work ....................................................................................................................... 19

Chapter 2. Experimental Section .................................................................................................................... 21
  2.1. Materials .................................................................................................................................................. 21
  2.2. Co-precipitation/Molten Salt Synthesis ..................................................................................................... 21
  2.3. Adsorptive deposition ............................................................................................................................ 22
  2.4. X-ray Diffraction (XRD) ....................................................................................................................... 23
  2.5. Brunauer-Emmet-Teller (BET) Surface Analysis ....................................................................................... 23
  2.6. Transmission Electron Microscopy and Energy Dispersive X-ray Spectroscopy ................................. 24
  2.7. Raman Spectroscopy ............................................................................................................................. 24
  2.8. X-ray Spectroscopy .................................................................................................................................. 25
  2.9. Catalytic Characterizations .................................................................................................................... 25
  2.10. CO Chemisorption ................................................................................................................................... 26

Chapter 3. Ni:CZO Core Structure and Catalytic Performance ....................................................................... 27

Chapter 4. Ni:CZO Shell Deposition and Characterization ........................................................................... 43

Chapter 5. Conclusions and Future work ....................................................................................................... 49

Appendix A. Oxygen Vacancy Concentration Calculation ........................................................................... 51
Appendix B. Molten Salt Synthesis Procedure ................................................................. 52

Appendix C. Different Annealing Methods ................................................................. 53

Appendix D. Characterization Procedures (XRD, Raman, DSC/TGA, XPS, XAS) .......... 54

Chapter 6. Bibliography ............................................................................................ 65

Vita ............................................................................................................................. 78
List of Tables

Table 1.1. Enthalpy effect of removal of lattice oxygen in DRM reaction with change in the Zr content (Zhou, Shah et al. 2007) .......................................................... 10

Table 3.1. ICP-OES measurements for 5-20% Ni:CZO ICP-OES that is confirming the stoichiometry of CZO that is extracted from XRD. The stoichiometry reported for Ni is verifying that there is 9.3 mol% content in 20% Ni:CZO .................................................. 30

Table 3.2. Effect of increased Ni doping (mol%) on particle size, estimated oxygen vacancy concentrations (N) and catalytic activity. The activities are normalized to the surface area. .................................................................................. 31

Table 3.3. Fixed-bed reactor data for the 9.3 mol% Ni:CZO .......................................................... 33

Table 4.1. CO chemisorption was performed on the 4.6% Ni:CZO, 6.6% Ni:CZO, and 9.3% Ni:CZO catalysts to measure the dispersion of Ni on the surface as well as the moles of CO adsorbed on the surface of the catalysts. .............................. 45

Table 4.2. Effect of modifying the core Ni concentration on catalytic properties as well as active site dispersion of core-shell catalysts. .................................................. 47
List of Figures

Figure 1.1. CO₂ Emission by different sectors in the US (EPA 2015)..................................................2

Figure 1.2. Projection of world’s natural gas consumption and supply in 2050 (Usman, Daud et al. 2015)..................................................................................................................3

Figure 1.3. Energy-related U.S. greenhouse emissions by gas in 2005 (Department of Energy 2006).................................................................................................................................4

Figure 1.4. Schematic of carbon oxidation mechanism during C₂H₆ decomposition. (a) C₂H₆ is preferentially decomposed at the Ni/CeO₂ interface, and atomic C and H are generated. (b) Oxygen from the CeO₂ lattice oxidizes C and H. (c) H₂O, CO₂, and CO desorb from the CeO₂ surface and leave behind oxygen vacancies (Lawrence and Crozier 2018)..................................................8

Figure 1.5. Oxidation and reduction of Ceria along with formation of oxygen vacancies (Bulfin, Call et al. 2016)...........................................................................................................9

Figure 1.6. Crystal structure of disordered fluorite (Pokhrel, Wahid et al. 2016).....................................11

Figure 1.7. Correlation of the Ni content as a measure of Ni surface area (a) and Ni dispersion (b) Optimum Ni dispersion is achieved at 6.6 mol% Ni (Mette, Kühl et al. 2016)..........................................................13

Figure 1.8. Atomic structure of Ni adsorbed on a) CeO₂ and b) Ce₂O₃. Oₛ = surface oxygen atoms, Oₜₛ = subsurface oxygen atoms, Obulk = bulk oxygen atoms (Liu, Grinter et al. 2016).................................................................14

Figure 1.9. Different morphologies and structures of nanoparticles (He, Ichinose et al. 2003)..................17

Figure 1.10. High-resolution electron microscopy images of precipitated Ce₀.₅Zr₀.₅O₂ after sintering (900 °C, 2 h in air) (Stark, Maciejewski et al. 2003).........................................................18

Figure 3.1. a) XRD of CZO and 6.6 mol% Ni:CZO indicating no phase separation for these NPs. b) EDX confirming the presence of Ni in 6.6 mol% Ni:CZO. c) BF-STEM image of Ni:CZO (6.6 mol%) with observed d-spacing of 3.01 Å (d₂₂₂= 3.05 Å) and HRTEM image in the inset .........................................................29

Figure 3.2. XRD measurement of 4.6, 6.6, and 9.3% Ni:CZO. The stars represent cubic phase of CZO.........................................................................................................................30
Figure 3.3. (a) XRD of 9.3 mol% Ni:CZO and the reference catalyst showing greater phase separation for Ni and ZrO$_2$ in the reference catalyst. (b) Raman spectra showing an increase in the area of the LO band for the 9.3 mol% Ni:CZO compared to the reference catalyst.

Figure 3.4. Raman spectra for the CP/MSS particles with increasing Ni contents. The spectra show an increase in the ratio of peak intensities $I_{LO}/I_{F2g}$.

Figure 3.5. (a) XPS of the O 1s region showing an increase in the area of oxide ions with an increase in Ni doping. (b) Ce 3d XPS spectra of CZO with 4.6, 6.6, and 9.3 mol% Ni, displaying an increase in the peak areas $U_o$, $U'$, $V_o$, and $V'$, all of which correspond to Ce$^{3+}$, with respect to Ni content.

Figure 3.6. (a) XPS spectra of 9.3% Ni:CZO annealed in different environments to prove the capability to remove adsorbed OH on the surface. (b) XPS spectra of 9.3% Ni:CZO after gentle sputtering was performed and it is evident that the adsorbed species on the surface is removed.

Figure 3.7. Raman spectra showing a red shift in the $F_{2g}$ peak (boxed area) of the 9.3 mol% Ni:CZO as the synthesis reaction time is reduced.

Figure 3.8. XRD measurements of 20% Ni:CZO after 1, 3, and 6 h synthesis reaction times show only the cubic CZO structure.

Figure 4.1. (a) XRD plot of reference and core-shell catalysts. Less phase separation of Ni and ZrO$_2$ from cubic CZO is observed for the core-shell catalyst. (b) Raman spectra of the core-shell catalyst shows a higher area under the LO band.

Figure 4.2. XAS of the Ni L edge of core-shell NPs showing the transformation of surface Ni as the Ni concentration of the core is increased.
Abstract

CeO$_2$–ZrO$_2$ (CZO) nanoparticles (NPs) have application in many catalytic reactions, such as methane reforming, due to their oxygen cycling ability. Ni doping has been shown to improve the catalytic activity and acts as an active site for the decomposition of methane. In this work, Ni:CZO NPs were synthesized via a two-step co-precipitation/molten salt synthesis to compare Ni distribution, oxygen vacancy concentration, and catalytic activity relative to a reference state-of-the-art catalyst. To better understand the effects of Ni position and dispersion, and oxygen vacancy formation in these materials, the Ni concentration, reaction time, and deposition methods were varied. X-ray diffraction (XRD) measurements show a cubic phase with little to no segregation of Ni/NiO. Catalytic activity measurements displayed similar activity per surface area with an order of magnitude decrease in the coking rate for the particles synthesized by the molten salt method compared to a traditional insipient wetness impregnation synthesis. Additionally, this new approach resulted in an order of magnitude increase in oxygen vacancies which is attributed to the high dispersion of Ni$^{2+}$ ions in the NP core.

Tailoring active sites position and concentration on the catalyst surface has been shown to effect activity and stability of a catalyst. After an active Ni:CZO core has been finalized, a shell layer was subsequently deposited to active site concentration and dispersion. The robust structure of the core of the catalyst that is synthesized helps achieve better dispersion of active sites on the surface. Better dispersion of active sites along with availability of oxygen vacancies from the core resulted in a five-fold increase in catalytic activity per surface area and an order of magnitude decrease in coking. In this work, the role of Ni position on catalytic activity is probed to develop a two-step synthesis process which allows for spatially controlled dopant distribution for improved catalytic activity.
Chapter 1. Introduction

Fossil fuels are the world’s most important source of energy as population growth and new technologies demand increase consumption (Boden, Marland et al. 2009). Cracking, natural gas conversion, and petroleum production are used to convert the fossil fuel to more useable products (Archer, Eby et al. 2009). Additionally, these mid-range fossil fuels (C4-C12) are then converted into gasoline as a major product (Meisel 1976). Unfortunately, fuel utilization for transportation (Figure 1.1.) is one of the major sources of air pollution and the production of CO₂, a known greenhouse gas (EPA 2015). One approach to reduce the concentration of CO₂ in the atmosphere is CO₂ capturing and recycling (Yu, Huang et al. 2012). Reuse of CO₂ is very temperature sensitive and presence of a catalyst that can stabilize this chemical reaction is essential. The redox property of a catalyst in endothermic reactions such as dry reforming of methane (DRM, Equation 1.1) is crucial because of the need to transport oxygen to/from the reaction site (Jang, Shim et al. 2019).

\[ \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \]  

CeO₂ catalysts have typically been used for endothermic reactions due to their excellent redox property, phase stability and capability to incorporate metals (Lawrence, Brewer et al. 2011). In order to prepare thermodynamically stable catalysts for DRM reaction, it is necessary to understand the effects of synthetic approaches has on the formation of various and resistance to coking. In this chapter, a background and literature review of synthesis and utilization of CeO₂ catalysts is presented to motivate the need for a different synthesis of Ni doped CeO₂-ZrO₂ catalysts for application in the dry reforming of methane reaction. Specifically, the control of the positioning of the active site (Ni) is discussed to engineer the catalytic activity and coking rate of the catalyst under reaction conditions.
Figure 1.1. CO$_2$ Emission by different sectors in the US (EPA 2015).
1.1. Motivation

Sustainable production of energy is developing due to rapid increase in population and commercial/industrial demand (Chu and Majumdar 2012). The US is projected to consume over 20 trillion cubic feet of natural gas in 2050, as seen in Figure 1.2. (Usman, Daud et al. 2015). As leaders of innovation and technology, the US has taken the initiative to reduce air pollution and reduce emission of Hazardous Air Pollutants (HAPs) and Toxic Air Pollutants (TAPs) by setting in place laws and regulations that puts a cap on refineries emissions (Refinery Sector Rule, US EPA, 40 CFR 63 Subpart CC, Dec 2015). Air pollution not only effects the environment via the formation of acid rain and toxic algae, but can severely impact human health by promoting heart attacks, asthma, and birth defects (Brunekreef and Holgate 2002). Consumption of natural gas at the industrial level increases production of hydrocarbons, CO$_2$, and NO$_x$ (Oliveira and De França 2005). The presence of these compounds in the atmosphere is believed to cause the degradation of environment and increase ozone depletion. Thus, it is important to utilize and capture these environmental unfriendly gases and convert them into usable products to further prevent their growth.

![Figure 1.2. Projection of world’s natural gas consumption and supply in 2050 (Usman, Daud et al. 2015).](image-url)
As new approaches are being discovered for finding natural resource reserves, more processes and methods are being exploited for upscaling natural resources (Sachs and Warner 2001). The US is now the 4th leading country in number of shale gas reserves which means that the use of natural gas will only continue to increase (Hughes 2013). As the supply of natural gas increases, the industrial demand rises and conversion of natural gas to different compounds such as synthesis gas (syngas) becomes more crucial (Wilhelm, Simbeck et al. 2001). Without proper precautions, the production of different chemical compounds from natural gas causes an increase in emission of HAPs/TAPs. Flaring technology, which is combustion of unwanted or excess gases, has helped with lowering the emission of HAP/TAP pollutants to the atmosphere since it is more efficient than traditional venting (Kimura, Aoki et al. 2001). In addition to HAPs and TAPs, greenhouse gases are also produced during syngas production with 81.5% of the gas being CO₂ (Figure 1.3.) (Department of Energy 2006). CO₂ capture from the atmosphere has to be rapidly followed by storage or reuse, otherwise CO₂ will be emitted back to the atmosphere (Steeneveldt, Berger et al. 2006). Finally, employing CO₂ in catalytic activities reduces fossil fuel and natural gas carbon footprint on the environment.

Figure 1.3. Energy-related U.S. greenhouse emissions by gas in 2005 (Department of Energy 2006).
Natural gas conversion has tremendous environmental impacts and scientists have been exploring different catalysts, techniques, and processes to reduce its footprint through an energy efficient conversion process. One possible pathway is syngas (H₂ + CO) production, and is one of the major feed sources for production of fuel, diesel, fertilizers, and etc. (Rostrup-Nielsen 2000). Syngas is produced using different catalytic process such as, dry reforming of methane (DRM), steam reforming of methane (SRM), and partial oxidation of methane (POM), among others (Zou, Chen et al. 2017). In DRM, CO₂ is used as an oxygen source for breaking C-H bonds in methane. While the overall DRM temperature can be reduced with the help of a redox catalyst, the deactivation of the catalyst is significant (Guo, Lou et al. 2004). The three deactivation mechanisms are coking (carbon deposition), poisoning (surface deactivation), and sintering (particle agglomeration) (Yao, Jiang et al. 2016).
1.2. Function of Catalysts in DRM

Catalysts are backbone of many chemical reactions – lowering the activation energy and improving product selectivity and yield. The importance of catalysts is observed in syngas production, Equations 1.2 and 1.3, which shows that a redox catalyst stores oxygen from the first reaction and releases it in the second reaction in order to produce CO₂ (Sugiura 2003). As such, it is important not to use a catalyst with low selectivity for DRM as the CO:H₂ ratio can be lowered due to the reverse water-gas shift reaction (Equation 1.4) (Barroso-Quiroga and Castro-Luna 2010).

\[
CH_4 + O_2 \rightarrow CO + 2H_2 + O^* \quad (1.2)
\]

\[
CO + O^* \rightarrow CO_2 \quad (1.3)
\]

\[
CO_2 + H_2 \rightarrow CO + H_2O \quad (1.4)
\]

Breaking the C-H bond of methane is an essential step in DRM which can lead to coke formation, redox catalysts provide high oxygen concentration which can help avoid formation of coke (Kambolis, Matralis et al. 2010, Du, Zhang et al. 2012). Consequently, it is important for the catalyst used to have a high oxygen storage capacity (OSC), to shuttle excess oxygen during the C-O bond breaking (Skorodumova, Simak et al. 2002, Di Monte and Kašpar 2004). The presence of active metal sites on the surface is an important parameter in DRM catalysts because active sites are responsible for adsorbing and activating the CO₂ as one of the primary steps (Zhang, Wang et al. 2008). In addition to activating the CO₂, active sites such as, Mn, Fe, Co, Ni, and etc., promote the OSC of the catalyst by forming bonds with the support which can result in oxygen release (Kacimi, Barbier et al. 1993). Due to high catalytic activity plus abundance and lower market price
compared to the noble metals, Ni it has attracted a lot of attention for DRM reactions, among other catalytic process. As an example, Ni activated CeO$_2$ is used for the decomposition of C$_2$H$_6$, shown in Figure 1.4 (Lawrence and Crozier 2018). During the C$_2$H$_6$ decomposition, carbon (black spheres) adsorbs to the surface of Ni, followed by interaction with lattice oxygen (red spheres) to form CO/CO$_2$. Rare earth supports are one of the most used in catalysis due to their redox property and oxygen storage capability due to presence of different oxidation states. Of particular interest are CeO$_2$ based catalysts as they have applications in a wide range of catalytic reactions, such as three-way catalysis (Kim 1982), dry reforming of methane (Laosiripojana and Assabumrungrat 2005), water-gas shift reactions (Li, Fu et al. 2000), etc. (Montini, Melchionna et al. 2016), due to the ability of Ce to shuttle between the 3+/4+ oxidation states, facilitating oxygen storage/release without causing a phase change (Fornasiero, Balducci et al. 1996, Kašpar, Fornasiero et al. 1999, Zinkevich, Djurovic et al. 2006, Bulfin, Lowe et al. 2013, Montini, Melchionna et al. 2016). The redox ability of CeO$_2$ has further been improved by incorporating different dopants such as, La, Zr, Mg, and etc. which enhances the OSC by weakening the Ce-O bond (Jiang, Akkullu et al. 2019).
Figure 1.4. Schematic of carbon oxidation mechanism during C$_2$H$_6$ decomposition. (a) C$_2$H$_6$ is preferentially decomposed at the Ni/CeO$_2$ interface, and atomic C and H are generated. (b) Oxygen from the CeO$_2$ lattice oxidizes C and H. (c) H$_2$O, CO$_2$, and CO desorb from the CeO$_2$ surface and leave behind oxygen vacancies (Lawrence and Crozier 2018).
1.3. Redox Catalysts (CeO₂)

The wide use of ceria and ceria-based mixed oxides as active catalysts is associated with its unique ability to transition between Ce$^{3+}$ and Ce$^{4+}$ as shown in Figure 1.5 (Bunluesin, Gorte et al. 1998, Duprez, Descorme et al. 2001). This capability is taken advantage of in endothermic catalytic reaction such as, dry reforming of methane (Kašpar, Fornasiero et al. 1999). Studies have shown that OSC of CeO₂ is improved by incorporating Zr, weakening the Ce-O bond due to the smaller Zr$^{4+}$ ionic radius (Longo and Roitti 1971, Tsukuma and Shimada 1985, Fornasiero, Balducci et al. 1996, Montini, Melchionna et al. 2016). Incorporation of Zr$^{4+}$ between a 2:1 or 3:1 Ce:Zr ratio has been shown to maximize the OSC and catalytic activity (Trovarelli, Zamar et al. 1997, Madier, Descorme et al. 1999). This weakened Ce-O bond facilitates the formation of oxygen vacancies and enhances oxygen mobility within the bulk (Trovarelli, Zamar et al. 1997, Bedrane, Descorme et al. 2002). At high concentrations of Zr, the catalyst adapts a tetragonal phase which reduces the OSC of the catalyst. To achieve the highest oxygen mobility and OSC in CZO, a fluorite crystal structure is required due its high oxygen-ion diffusion property (Kim 1989).

![Figure 1.5. Oxidation and reduction of Ceria along with formation of oxygen vacancies (Bulfin, Call et al. 2016).](image)

Lattice oxygen helps prevent carbon deposition on the surface because availability of oxygen in the lattice of a catalyst helps the carbon to react with the lattice oxygen (Ramirez-Cabrera, Atkinson et al. 2004). The availability of oxygen from the bulk of the catalyst has a direct effect (entropic and enthalpic) on DRM reaction conditions, high concentration of lattice oxygen can reduce the activation barrier in removal of lattice oxygen in DRM (Zhou, Shah et al. 2007). The reduction thermodynamics (Table 1.2) show a clear dependence on Zr\(^{4+}\) content necessitating the optimum Ce:Zr ratio (Call, Roeb et al. 2015). As lattice oxygen increases, the availability of transport of lattice oxygen increases because of redox property of CZO and as mentioned above fluorite structure (Ce:Zr \(\sim 2:1\)) will provide the lattice oxygen/oxygen vacancy in CZO (Fornasiero, Balducci et al. 1996, Kamiya, Shimada et al. 2000, Skoro dumova, Simak et al. 2002, Zinkevich, Djurovic et al. 2006, Bulfin, Lowe et al. 2013). As seen in Figure 1.6, oxygen vacancies are randomly distributed in the disordered fluorite structure which helps oxygen mobility in a structure. This proves the claim that fluorite structure has high oxygen vacancy potential compared to other phases (Pokhrel, Wahid et al. 2016). Furthermore, fluorite structure of Ce\(_{0.8}\)Zr\(_{0.2}\)O\(_2\) helps disperse active sites easier due to high concentration of oxygen vacancies in the lattice of CZO which improves the coke resistivity of the catalyst (Roh, Potdar et al. 2004, Liu, Lau et al. 2009).

Table 1.1. Enthalpy effect of removal of lattice oxygen in DRM reaction with change in the Zr content (Zhou, Shah et al. 2007).

<table>
<thead>
<tr>
<th>Sample</th>
<th>-(\Delta H) (kJ/mol O(_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO(_2)</td>
<td>797</td>
</tr>
<tr>
<td>Ce(<em>{0.81})Zr(</em>{0.19})O(_2)</td>
<td>519</td>
</tr>
<tr>
<td>Ce(<em>{0.5})Zr(</em>{0.5})O(_2)</td>
<td>476</td>
</tr>
<tr>
<td>Ce(<em>{0.25})Zr(</em>{0.75})O(_2)</td>
<td>577</td>
</tr>
<tr>
<td>Ce(<em>{0.14})Zr(</em>{0.86})O(_2)</td>
<td>497</td>
</tr>
</tbody>
</table>
One of the challenges that is faced in having transition metals on the catalyst surface is the subsequent deactivation via sintering and coking (Rostrup-Nielsen and Trimm 1977, Trimm 1983, Wang, Lu et al. 1996, Descorme, Taha et al. 2002, Hu and Ruckenstein 2004, Roh, Potdar et al. 2004, Nandini, Pant et al. 2006, Theofanidis, Galvita et al. 2015, Mette, Kühl et al. 2016, Rogers, Mangarella et al. 2016). One method that has been explored to help reduce the coking rate is dispersing the active sites on the surface of the catalyst (Roh, Potdar et al. 2004, Laosiripojana and Assabumrungrat 2005, Xu and Wang 2005, Zhang, Liu et al. 2009, Koubaissy, Pietraszek et al. 2010, Xu, Liu et al. 2013, Carrasco, López-Durán et al. 2015). DRM is a highly endothermic reaction, with an enthalpy of reaction of +205 kJ/mol, and under high temperatures the catalysts experience rapid deactivation due to coke deposition and aggregation (Rostrup-Nielsen and Hansen 1993). Formation of coke occurs while CH$_4$ decomposes into carbon over large Ni facets (Hegarty, O’Connor et al. 1998, Koubaissy, Pietraszek et al. 2010). A challenge that many have faced is formation of Ni clusters on the surface due to poor dispersion of active sites, which results in high coking rates (Ginsburg, Piña et al. 2005, Djinović, Črnivec et al. 2012). Ni clusters on the surface

Figure 1.6. Crystal structure of disordered fluorite (Pokhrel, Wahid et al. 2016).
translates into poor interaction with the support due to smaller interaction between the active site and the support (Rostrup-Nielsen and Trimm 1977, Yao and Yao 1984, Su, Montreuil et al. 1985, Taha, Duprez et al. 1998, Zhou, Shah et al. 2007, Horváth, Stefler et al. 2011, Liu, Ye et al. 2011). As mentioned previously, the Ce:Zr ratio plays an important role in the availability of oxygen which helps prevent carbon from being fixed to the Ni surface (Bulfin, Lowe et al. 2013).

Demand of Ni-based catalysts has been growing and expanding over the past few decades owing to their availability and economic standpoint compared to other transition metals (Theofanidis, Galvita et al. 2015, Rogers, Mangarella et al. 2016). Ni has been used as an active mechanism in catalytic reactions because of its promising catalytic performance, conversion, and selectivity (Rostrup-Nielsen and Trimm 1977, Wang, Lu et al. 1996, Roh, Potdar et al. 2004). Ni content in catalysts directly effects the Ni surface area and dispersion (Figure 1.7), and an optimum Ni content has to be chosen in order to maximize the activity (Mette, Kühl et al. 2016). Homogeneously dispersing Ni over the surface of the catalyst has been shown to prevent coking because of the absence of Ni clusters on the surface (Liu, Grinter et al. 2016). The effect of surface Ni dispersion on activity and coking has been proven; however, one relatively unexplored approach is the subsurface incorporation of the Ni dopant to increase internal strain without the formation of faceted islands and studying the structural effect of the Ni dopant on CZO (Theofanidis, Galvita et al. 2015, Mette, Kühl et al. 2016, Rogers, Mangarella et al. 2016). Alternatively, coke formation is reduced on materials with high oxygen storage capacities (OSC) due to lattice oxygen interactions with adsorbed coke on the surface of the active site. On the other hand, controlling the position of Ni both on the surface and subsurface will offer the chance to study the change in the bulk structure and effects of Ni on the lattice defects of the nanoparticles.
In order to achieve high conversion and maximum catalytic activity in catalysts, Ni is deposited on the surface of certain catalysts (Rezaei, Alavi et al. 2008). The focus of a majority of researchers has been on dispersing the active site homogenously on the surface to avoid Ni clusters for reduced coking rates (Qin and Lapszewicz 1994, Hu and Ruckenstein 1996, Valderrama, Goldwasser et al. 2005, Sierra Gallego, Batiot-Dupeyrat et al. 2008, Lv, Chen et al. 2012). For example, silica supports are frequently used to increase dispersion of Ni on the surface by lowering the coverage of H-bonded SiOHs, which decreases the size of Ni particles and increases dispersion (Lv, Chen et al. 2012). Another direction taken to increase dispersion on the surface is controlling the oxidation state of Ni deposited to increase the metal-support (Liu, Grinter et al. 2016). Ni tends to dissociate the C-H bond better in Ni\(^0\) state and Ce\(_2\)O\(_3\) supports have shown to help stabilize metallic Ni on the surface (Figure 1.8) (Liu, Grinter et al. 2016). Alloying Ni and Pt is another route that has been taken to reduce Ni cluster size and control dispersion on the surface (Pawelec, Damyanova et al. 2007). These methods have all been successful in dispersing active sites on the surface but there have been no reports on being able to control the position of Ni either on the surface or subsurface by modifying the synthetic route. Looking at the synthetic pathways of these
catalysts, they mainly contain a reduction step which leads to segregation of the active site and the support (Xu, Liu et al. 2013). Therefore, alternative synthetic methods that can help stabilize active site position in the bulk to make these less susceptible to segregation and Ni island formation. Additionally, it is believed that these methods will help maximizing the OSC to reduce carbon deposition on the surface of the catalyst.

Figure 1.8. Atomic structure of Ni adsorbed on a) CeO$_2$ and b) Ce$_2$O$_3$. O$_s$ = surface oxygen atoms, O$_{ss}$ = subsurface oxygen atoms, O$_{bulk}$ = bulk oxygen atoms (Liu, Grinter et al. 2016).
To address the coking and sintering challenge in Ni-based catalysts, others have incorporated Ni salts (up to 15 mol%) during the Ce-Zr-O coprecipitation process prior to a high-temperature sintering step, producing Ni cluster sizes of ~12 nm on the catalyst surface (Roh, Potdar et al. 2004). However, with this method it is difficult to spatially control the Ni during incorporation in the bulk of the catalyst (Darapaneni, Moura et al. 2019). On the other hand, a two-step co-precipitation (CP)/molten salt synthesis (MSS) method has been reported which facilitates the incorporation of dopants within complex metal oxides during synthesis (Mao, Park et al. 2005, Dorman, Choi et al. 2012, Dorman, Choi et al. 2012, Pokhrel, Wahid et al. 2016, Pokhrel, Burger et al. 2017). By precipitating the precursors from an aqueous solution in the initial step, M-O-M bonds are formed which then undergo reorganization during the high-temperature treatment to solidify the structure (Park, Lee et al. 1996, Mao, Guo et al. 2009). The formation of the disorganized initial structure results in enhanced phase stability and facilitates the incorporation of a homogeneously distributed dopant (Yoon, Cho et al. 1998, R Bajgiran, Darapaneni et al. 2019).
1.4. Synthesis and Structure

There is a large body of literature on the preparation of CZO NPs using various synthetic methods such as sol-gel (Alifanti, Baps et al. 2003, Dooley, Liu et al. 2013), co-precipitation (Xu and Wang 2005), flame-combustion (Stark, Maciejewski et al. 2003), etc. which yield different oxygen vacancy concentrations despite containing identical compositions (Vlaic, Fornasiero et al. 1997, Nagai, Yamamoto et al. 2002, Di Monte and Kašpar 2004, Aneggi, Boaro et al. 2006). However, to achieve a Ce:Zr ratio of ~2:1 for maximum OSC, the synthetic conditions must be carefully controlled to ensure local and long-range homogeneity due to the different formation rates of the oxides (Roh, Potdar et al. 2004, Laosiripojana and Assabumrungrat 2005, Asencios, Bellido et al. 2011). Additionally, deposition techniques (e.g., strong electrostatic adsorption or incipient wetness impregnation) are often used to activate the catalysts with Ni. However, high temperatures and oxidative/reducing atmospheres can lead to structural changes and reduced OSC (Sanchez-Dominguez, Liotta et al. 2010, Xu, Liu et al. 2013). Specifically, exposure to reducing atmospheres often leads to the formation of segregated CeO₂ and ZrO₂, and non-uniform distribution of Ni (Xu, Liu et al. 2013). This process results in larger Ni clusters that can facilitate dendrite formation and rapid deactivation of the catalyst (Xu and Wang 2005, Xu, Liu et al. 2013). Therefore, alternative methods are needed to synthesize activated nanoparticles that are less susceptible to oxide segregation and Ni island formation. Figure 1.9 demonstrates different morphologies synthesized mixed compounds, for instance, Ce (Metal A) and Zr (Metal B) (He, Ichinose et al. 2003). Specifically, for Ce and Zr two important morphologies are alloy particles (Figure 1.9e) and core-shell particles (Figure 1.9d) which can allow for control of catalytic activity and OSC.
The coprecipitation synthesis has been used to produce catalysts with high coking resistivity that also shows high catalytic activity (Xu and Wang 2005). A problem faced with this method is segregation of Ni particles after the necessary high-temperature sintering. Exploring the optimum Ce:Zr ratio helped control segregation of Ni which reduces coking and improves the activity of the catalysts. Another method that attempted to produce homogeneous catalysts is using a flame-made synthesis resulted in a segregation of the Ni particles after heat treatment of the catalyst in air for 2 h (Figure 1.10) (Stark, Maciejewski et al. 2003). The low-magnification image shows a clear agglomeration of the nanoparticles. It is prominent that the heat treatment of the catalyst during the synthesis causes segregation which can have negative effect on the stability of
the catalyst (Stark, Mädler et al. 2003). Incorporating Ni sites in the lattice of the catalyst can solve this issue by increasing the oxygen mobility of the catalyst.

Figure 1.10. High-resolution electron microscopy images of precipitated Ce$_{0.5}$Zr$_{0.5}$O$_2$ after sintering (900 °C, 2 h in air) (Stark, Maciejewski et al. 2003).
1.5. Scope and Proposed Work

In this work, Ni:CZO NPs are prepared by a two-step CP/MSS synthesis to create a highly dispersed disordered fluorite phase with increased oxygen vacancies. This method allows for production of structure-controlled NPs where the oxygen vacancies can be modified by varying precursor compositions and reaction time. The oxygen vacancy concentration and catalytic activity of the Ni:CZO NPs prepared via CP/MSS were then compared to a more conventional state-of-the-art catalyst prepared via the sol-gel technique. Structural and chemical characterizations were performed on the synthesized NPs to determine the morphology, stoichiometry, and chemical composition prior to any catalytic reaction tests. The percentage of Ni was systematically varied up to 20 mol% (in solution) to identify the optimum Ni content for catalytic activity in dry reforming of methane (DRM) and oxygen vacancy concentration. Thermogravimetric analysis (DSC/TGA), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) were performed to determine the catalytic activity, Ce oxidation state, and oxygen vacancy concentrations of the NPs. The ability to spatially distribute the Ni within the catalyst resulted in a near five-fold increase in activity per surface area, suggesting that subsurface active sites play an important role in catalytic activity of methane reforming reactions.

To further try to improve the catalytic properties of these catalyst, the CP/MSS synthesis was combined with an adsorptive deposition synthesis to generate a core-shell catalyst. The purpose of this is to employ oxygen vacancies from subsurface (core) created via CP/MSS synthesis and the active sites on the surface (shell) that are deposited via adsorptive deposition will promote the C-H breaking which then increases the catalytic activity. To verify the dispersion and Ni surface area on these catalysts, CO chemisorption along with an ICP-OES time-study was performed. X-ray absorption spectroscopy (XAS) was performed to understand the nature of the
surface Ni as the Ni core concentration is modified. This is important when analyzing the XAS data to see if Ni\textsuperscript{0}/NiO (Ni\textsuperscript{2+}) is caused by the deposition of Ni on the surface or by segregation of Ni from the core. The ability to disperse Ni active sites on the surface and provide oxygen vacancies from the core for these catalysts will lead to creating a novel catalyst that is stable with high activity under DRM reaction conditions.
Chapter 2. Experimental Section

This chapter presents the synthesis and characterization of Ni:CZO. First the materials and chemicals that are used in the synthesis are introduced which is followed by the three different synthetic methods of the nanoparticles and finally the characterizations performed on these nanoparticles are showed. The main objective of this research project is to synthesize and characterize (catalytically and structurally) Ni doped CZO nanoparticles to enhance catalytic activity and reduce coking rate of this catalyst by the ability to control the active sites both on the surface and subsurface.

2.1. Materials

Cerium (III) nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O, Stream Chemicals, 99.9%), zirconium oxynitrate hydrate (ZrO(NO$_3$)$_2$·xH$_2$O, Beantown Chemical, 99.9%), nickel chloride hexahydrate (NiCl$_2$·6H$_2$O, Beantown Chemical, 99.0%), 28-30% ammonium hydroxide (NH$_4$OH, VWR Chemicals, ACS grade) and urea (CH$_4$N$_2$O, VWR Chemicals, ACS grade) were used for the synthesis. NaNO$_3$ (high purity grade, VWR Chemicals), and KNO$_3$ (ACS grade, VWR Chemicals) were utilized for the molten salt synthesis. Hydrochloric acid (HCl, 36.5-38%, VWR Chemicals) and nitric acid (HNO$_3$, 68-70%, VWR Chemicals) were used for ICP-OES digestion process.

2.2. Co-precipitation/Molten Salt Synthesis

This segment of the synthesis is divided into two-steps: 1) Co-precipitation synthesis 2) Molten salt synthesis (Dorman, Choi et al. 2012, Dorman, Choi et al. 2012, Pokhrel, Wahid et al. 2016, Pokhrel, Burger et al. 2017, Ofoegbuna, Darapaneni et al. 2019). CeO$_2$-ZrO$_2$ (CZO) nanoparticles have previously been reported to be synthesized via co-precipitation (Xu and Wang 2005), sol-gel (Alifanti, Baps et al. 2003, Dooley, Liu et al. 2013), flame-made (Stark,
Maciejewski et al. 2003), etc. which resulted in segregation of dopants in the structure. Therefore, in order to incorporate the dopant in bulk structure of CZO, Ni was introduced during the two-step synthetic process. In this method, the co-precipitation was performed by dissolving a 2:1 Ce:Zr molar ratio of Ce(NO$_3$)$_3$·6H$_2$O:ZrO(NO$_3$)$_2$·xH$_2$O along with the designated molar percent of NiCl$_2$·6H$_2$O in 400 mL of deionized (DI) water. By precipitating the precursors in the initial solution, the dopant is homogeneously distributed which causes enhanced phase stability (Yoon, Cho et al. 1998). The pH of the solution was adjusted to ~11 by adding 28% NH$_4$OH dropwise to the solution. The solution was stirred for 2 h and the resultant gel-like mixture was collected through filtration and washed with 300 mL of DI water and dried overnight at 100 °C (Tang, Sorensen et al. 1991). The as-prepared powder was ground with a eutectic molar ratio of NaNO$_3$ and KNO$_3$ until a homogeneous powder was collected. The mixture was then transferred to a porcelain crucible and heated at 650 °C for 6 h. During this high-temperature treatment, the preliminary M-O-M bonds undergo reorganization to solidify the structure (Park, Lee et al. 1996, Mao, Guo et al. 2009). The resulting powder was centrifuged and washed 5 times with DI water to completely remove excess salts. The nanoparticles were then collected and dried at 100 °C to produce Ni:CZO.

2.3. Adsorptive deposition

An adsorptive deposition was performed to produce a core-shell structure to enhance the Ni surface composition. The core of the nanoparticles was synthesized via the above CP/MSS synthesis and the shell was added by deposition-precipitation (Dooley, Kalakota et al. 2011, Jiang, Akkullu et al. 2019). The powder collected from section 2.1, along with desired Ni mol% (NiCl$_2$·6H$_2$O) were added to 100 mL of 0.3 M of urea. The solution was stirred and reacted for 24 h under reflux at 90 °C. Urea in this reaction acted as a ligand which will bond Ni on the surface
of CZO core in form of NiO. The resultant powder was washed with DI water and after drying at 100 °C, the sample was reduced in 5% H\textsubscript{2}/95% Ar (300 mL/min) for 6 h at 750 °C with a ramp rate of 10 °C/min.

2.4. X-ray Diffraction (XRD)

Powder X-ray diffraction (XRD) was performed to verify the crystal structure, phase, and homogeneity of the as-synthesized nanoparticles. The powdered sample was prepared and placed on a zero-background sample holder. XRD data was obtained by using PANalytical X-ray diffractometer at 45 kV and 40 mA. The θ-2θ radial scan was performed over the range 5-70º with a step size of 0.04º and dwell time of 60 s, using Cu K\textsubscript{α} (λ=1.54 Å) as radiation source. To further analyze these data, Bragg’s law (nλ = 2d sinθ) and Scherrer equation \(D = \frac{b2\pi}{FWHM(2θ)}\) were employed to calculate the d-spacing, lattice constants, and size of the nanoparticles. λ is the wavelength Cu K\textsubscript{α}, D is the d-spacing of the crystallites, b is a constant for the function used to fit the peaks.

2.5. Brunauer-Emmet-Teller (BET) Surface Analysis

The BET surface area was performed to verify the pore size distribution and surface of the as-synthesized nanoparticles. The powdered sample was prepared by being dried at ~ 300°C and degassed prior to the BET run. The N\textsubscript{2} adsorption (3 points) was performed using a Quantachrome AS-1 porosimeter. The pore size distribution was calculated using the relative pressure of the of N\textsubscript{2} adsorbed on the surface and the surface area was calculated using a linear isotherm model. The pore size distribution was measured using BJH Desorption technique which characterized the pores using the pore diameter.
2.6. Transmission Electron Microscopy and Energy Dispersive X-ray Spectroscopy

The morphology and size of the nanoparticles were determined by high-resolution transmission electron microscopy (HRTEM) using a 200 kV JEOL NEARM electron microscope equipped with double aberration correctors, a dual-energy-loss spectrometer, and a cold FEG source. The powder sample was dispersed in ethanol and drop casted on a 300 mesh, lacey carbon grid prior to imaging. EDX was performed to determine the elemental composition and presence of any impurities in the sample. EDX was executed using a FEI Quanta 3D FIB microscope equipped with an EDAX Apollo XL EDX detector operating at an accelerating voltage of 20 kV and a current of 4 nA. The working distance was maintained at ~10 mm. The samples were dried overnight on silicon tape and then sputtered with Pt for 5 min to limit charging.

2.7. Raman Spectroscopy

The chemical bonding and vibrational modes of the nanoparticles were studied using Raman spectroscopy. Raman spectra were measured using a Renishaw inVia Reflex Raman Spectrometer with a 0.1 mW diode laser at an excitation wavelength of 532 nm, exposure time of 0.5 s, spectral resolution of 1 cm\(^{-1}\) and ~5 μm spot size. After five scans were averaged and the background was subtracted, the peaks were deconvoluted using the OriginPro software (OriginLab Corporation, Northampton, MA, USA) for oxygen vacancy calculation performed.
2.8. X-ray Spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed to verify the oxidation state and oxygen vacancies of the synthesized CZO nanoparticles. XPS measurements were performed using a Scienta Omicron ESCA 2SR equipped with a monochromatic Al Kα (hν=1486.6 eV) X-ray source and a hemispherical analyzer with a 128-channel detector, at 1.3 × 10⁻⁹ torr. The Gaussian width of the photon source was 0.5 eV and a focus voltage of 300 V. The XPS spectra were calibrated to the adventitious C 1s peak at 285.7 eV. All peaks were fit (using CasaXPS software (Fairley 2009)) as Gaussians after Shirley background subtraction.

X-ray absorption spectroscopy (XAS) was performed to verify the nature and coordination of the surface Ni. XAS measurements were performed at VLSPGM beamline located at the Center for Advanced Microstructures and Devices (CAMD). The photon resolution of these measurements is 0.1 eV. The samples are placed in a vacuum chamber of ~ 2 x 10⁻⁹ Torr. The vertical slit width used for Ni L edge spectra was between 50-100 μm. The reported spectra are reported after several scans are averaged. NiO was used as a calibration reference for these samples.

2.9. Catalytic Characterizations

The coking rate and catalytic activity were measured using a Differential Scanning Calorimetry (DSC)/Thermogravimetric Analyzer (TGA) (TA SDT Q600). The catalyst was pretreated in air (100 mL/min) overnight at 750 °C with a 10 °C/min ramp rate. The DRM reaction was performed at 750 °C and 135 mL/min total flow rate under CH₄ + CO₂ (1:1 mixture, 0.25 atm partial pressure of each, with 0.50 atm N₂). The heat flux and change in mass were both measured (when possible), the former being proportional to the heat of the DRM reaction while the latter
being proportional to the coking rate. The reforming rate was extracted from the heat effect using an Aspen HYSYS model of the process.

To scale up the DSC/TGA measurement, selected catalysts were tested in a fixed-bed reactor. The fixed bed reactor is a 1/2” stainless steel reactor tube with α-alumina and 0.25 g of catalyst. The DRM performed in this reactor contains higher partial pressures for CO₂ and CH₄ (~0.65 atm) than the DSC/TGA measurements. The reaction parameters such as temperature, flow rates, and CH₄ + CO₂ ratio were identical to the DSC/TGA runs for comparison purposes.

2.10. CO Chemisorption

CO chemisorption was performed to verify the active site dispersion and nature of the active site (Ni/NiO) on the surface of the catalyst. 500 mg of the catalyst was loaded and pretreated in 5% H₂/95% N₂ overnight to confirm presence of metallic Ni on the surface. CO pulse chemisorption (Micromeritics 2700) at various temperatures (25 °C - 200 °C) was performed on the catalysts after purging the surface with N₂ at the measurement temperature. 10 injections (injection time = 6s) were performed at the desired temperature and once the surface of the catalyst saturated the run was complete. The dispersion of CO on the surface of the catalyst was calculated based on the number of moles of CO adsorbed, weight of the catalyst, weight percent of the active site on the surface, and molecular weight of the active site. This measures how much of the total CO chemisorbed was chemisorbed by the active site on the surface. Different temperatures can be utilized for different oxidation states of a certain active site.
Chapter 3. Ni:CZO Core Structure and Catalytic Performance

Ni:CZO NPs were synthesized using the CP/MSS synthesis, and the catalytic activity and surface area of these NPs were compared to a catalyst that is synthesized via a traditional adsorptive deposition synthesis. To verify the concentration of Ni in the CZO structure, ICP-OES was performed and loss of Ni throughout the synthesis was observed. The structure of (4.6, 6.6, and 9.3 mol% Ni) Ni:CZO was compared to the reference catalyst focusing on the homogeneity of these structures. As the catalytic activity and coking rate of the two different catalysts were compared, the coking rate of the reference catalyst was heavily affected by the segregation of the catalyst during the synthesis. Due to homogeneity and fluorite structure of the Ni:CZO catalyst, a higher oxygen vacancy concentration was observed resulting in an order of magnitude decrease in the coking rate than that of the reference catalyst. In order to test the stability and activity over long period of time, 9.3 mol% Ni:CZO was tested using a fixed bed reactor. Even though 9.3 mol% Ni:CZO catalyst resulted in slightly lower CO\textsubscript{2} conversion, the H\textsubscript{2}/CO ratio was slightly higher than the reference catalyst. Raman Spectroscopy and XPS measurements were performed to verify the presence of oxygen vacancies in Ni:CZO. The 9.3 mol% Ni:CZO was annealed in different environments (vacuum, N\textsubscript{2}, air) to ensure that hydroxyl groups on the surface are not affecting the oxygen vacancy concentration. Finally, it was proven that the crystallinity formed during the CP/MSS helped form oxygen vacancies in the lattice of Ni:CZO which improved the coking rate of this catalyst.

The 2:1 Ce:Zr mixed oxide and a 6.6 mol% Ni:CZO were prepared by CP/MSS with a reaction time of 6 h in air at 650 °C. The diffraction peaks of both powders (Figure 3.1a) were

---

indexed to cubic (Ce$_{0.69}$Zr$_{0.31}$)O$_2$ (ICSD 157416) (Varez, Garcia-Gonzalez et al. 2007) with no Ni or NiO peaks detected. The lattice parameters of the CZO and 6.6 mol% Ni:CZO (starting from 10 mol% Ni in the initial solution) NPs were calculated to be 5.31 Å and 5.34 Å, respectively, and are similar to the literature ($a = 5.33$ Å) (Varez, Garcia-Gonzalez et al. 2007), with slight expansion upon Ni doping. Crystalline sizes (Scherrer equation) were calculated to be 7.5 nm (CZO) and 8.5 nm (6.6 mol% Ni:CZO), showing that incorporation of Ni increases the size of the NPs. The complete XRD results for all samples in Figure 3.2 suggest a homogeneous dispersion of Ni in all samples at the detectability level of XRD. The presence of the signature Ni $L_\alpha$ peak (0.85 keV) from energy dispersive X-ray spectroscopy (EDX) further confirms the presence of Ni in the 6.6 mol% Ni:CZO NPs (Figure 3.1b). As with the XRD measurements, the BF-STEM images of the 6.6 mol% Ni-doped sample show a slight change of the (222) lattice spacing ($d=3$ Å, Figure 3.1c). The size distribution is observed in the inset of Figure 3.1c. The structural characterization indicates that Ni was incorporated into the lattice with no sign of island formation on the surface. As such, different Ni dopant concentrations of up to 20 mol% in solution were employed to study the effect of dopant concentration on the catalytic activity. At higher Ni concentrations a blue effluent was seen suggesting the Ni was in excess of the solid solubility limit (Barrio, Kubacka et al. 2010). To quantify the Ni concentration and verify the stoichiometry of the catalyst, ICP-OES was performed (Table 3.1). A maximum of 9.3 Ni mol% in the catalyst was determined for the initial 20 mol% Ni in solution.
Figure 3.1. a) XRD of CZO and 6.6 mol% Ni:CZO indicating no phase separation for these NPs. b) EDX confirming the presence of Ni in 6.6 mol% Ni:CZO. c) BF-STEM image of Ni:CZO (6.6 mol%) with observed d-spacing of 3.01 Å (d_{222} = 3.05 Å) and HRTEM image in the inset.
Figure 3.2. XRD measurement of 4.6, 6.6, and 9.3% Ni:CZO. The stars represent cubic phase of CZO.

Table 3.1. ICP-OES measurements for 5-20% Ni:CZO ICP-OES that is confirming the stoichiometry of CZO that is extracted from XRD. The stoichiometry reported for Ni is verifying that there is 9.3 mol% content in 20% Ni:CZO.

<table>
<thead>
<tr>
<th>Element</th>
<th>Moles (μM)</th>
<th>Mole percent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% Ni:CZO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.21</td>
<td><strong>9.3</strong></td>
</tr>
<tr>
<td>Ce</td>
<td>1.37</td>
<td>60.4</td>
</tr>
<tr>
<td>Zr</td>
<td>0.69</td>
<td>30.3</td>
</tr>
<tr>
<td>10% Ni:CZO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.29</td>
<td><strong>6.6</strong></td>
</tr>
<tr>
<td>Ce</td>
<td>2.76</td>
<td>62.7</td>
</tr>
<tr>
<td>Zr</td>
<td>1.35</td>
<td>30.7</td>
</tr>
<tr>
<td>5% Ni:CZO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.27</td>
<td><strong>4.6</strong></td>
</tr>
<tr>
<td>Ce</td>
<td>3.76</td>
<td>63.7</td>
</tr>
<tr>
<td>Zr</td>
<td>1.87</td>
<td>31.7</td>
</tr>
</tbody>
</table>
The Ni:CZO catalysts doped with Ni during crystallization were compared to a conventionally prepared sol-gel/urea deposition-precipitation (strong electrostatic adsorption) catalyst containing 5 mol% of Ni (Rossignol, Madier et al. 1999, Dooley, Kalakota et al. 2011, Sukonket, Khan et al. 2011). Unlike the reference catalyst, small/no phase segregation was observed for the 9.3 mol% Ni:CZO (Figure 3.3a), which did not require reducing treatment to drive the Ni dopant into the structure. The catalyst activity (rate of the DRM reaction) and coking rates for the samples run at low conversion in the DSC/TGA are shown in Table 3.2. The heating rate is directly proportional to the DRM reaction rate. The DRM rate on a weight basis can be calculated using a process simulator (Aspen HYSYS) from the heat rate, assuming the rate of reverse water-gas shift reaction (RWGS), which is almost thermoneutral anyway, is negligible. The differential approximation is valid, as indicated by the low CH₄ conversions (Table 3.2). The reference catalyst exhibited a higher reforming rate on a weight basis. While the 4.6 and 6.6 mol% Ni:CZO showed reduced activity compared to the reference, despite similar Ni concentrations to that of the reference catalyst, the 9.3 mol% Ni:CZO catalysts outperformed the reference catalyst slightly in DRM rate. More importantly, the coking rate was 85% less with subsurface Ni inclusion.

Table 3.2. Effect of increased Ni doping (mol%) on particle size, estimated oxygen vacancy concentrations (N) and catalytic activity. The activities are normalized to the surface area.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sizea (nm)</th>
<th>Surface area (m²/g)</th>
<th>Na (cm³)</th>
<th>[Oiv] (%)</th>
<th>Activity (mW/m²)</th>
<th>Coking rate (mg coke/m²·h)</th>
<th>Reforming rate (mmol/m²·h)</th>
<th>CH₄ Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZO</td>
<td>7.9</td>
<td>38</td>
<td>6.3x10⁻⁲¹</td>
<td>5.32</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Reference</td>
<td>5.1</td>
<td>77</td>
<td>7.9x10⁻²¹</td>
<td>-</td>
<td>0.12</td>
<td>1.04x10⁻⁵</td>
<td>1.69</td>
<td>3.4</td>
</tr>
<tr>
<td>4.6% Ni</td>
<td>8.2</td>
<td>38</td>
<td>9.9x10⁻²¹</td>
<td>7.85</td>
<td>0.03</td>
<td>1.76x10⁻⁶</td>
<td>0.87</td>
<td>0.8</td>
</tr>
<tr>
<td>6.6% Ni</td>
<td>8.5</td>
<td>33</td>
<td>1.2x10⁻²²</td>
<td>11.19</td>
<td>0.05</td>
<td>7.27x10⁻⁷</td>
<td>1.64</td>
<td>1.1</td>
</tr>
<tr>
<td>9.3% Ni</td>
<td>9.2</td>
<td>32</td>
<td>3.8x10⁻²²</td>
<td>19.79</td>
<td>0.13</td>
<td>3.75x10⁻⁶</td>
<td>2.56</td>
<td>3</td>
</tr>
<tr>
<td>Core-shell</td>
<td>9.9</td>
<td>15</td>
<td>2.3x10⁻²²</td>
<td>17.36</td>
<td>0.57</td>
<td>3.4x10⁻⁶</td>
<td>8.67</td>
<td>4.2</td>
</tr>
</tbody>
</table>

aExtracted crystalline size from XRD spectra.
bEstimated oxygen vacancy site concentration, details in Calculation 1.

Extracted from deconvoluted O 1s XPS peaks.
Figure 3.3. (a) XRD of 9.3 mol% Ni:CZO and the reference catalyst showing greater phase separation for Ni and ZrO$_2$ in the reference catalyst. (b) Raman spectra showing an increase in the area of the LO band for the 9.3 mol% Ni:CZO compared to the reference catalyst.
To test the activity and stability of the 9.3% CP/MSS catalyst at higher partial pressures and conversions, a long-term (1-5 day period) fixed bed reactor test at 750 °C was performed (Table 3.3). The CH$_4$ conversion×GHSV (an activity metric) of the reference catalyst was ~ 8250 mL/min×g vs. 6800 mL/min×g for the 9.3 mol% Ni:CZO. The ratio of H$_2$/CO of the 9.3 mol% Ni:CZO was 0.44, slightly higher than the reference catalyst (0.42), suggesting a decrease in the rate of RWGS (Jha, Jeong et al. 2015). Incorporation of Ni into the bulk lattice, as would more likely occur with the 9.3 mol% Ni:CZO catalyst, is believed to result in more oxygen vacancies (and higher OSC) due to the difference in the oxidation states of the Ni and Zr (Wang, Shen et al. 2010). The vacancies act as sites where active oxygens can be stored and released, mitigating carbon polymerization. This effect could be responsible for the decreased coking rate of the 9.3 mol% sample. However, the results also suggest that dopant incorporation during crystal growth may not distribute enough Ni at particle surfaces where it is needed to catalyze the DRM reaction.

Table 3.3. Fixed-bed reactor data for the 9.3 mol% Ni:CZO.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>H$_2$/CO ratio</th>
<th>CH$_4$ Conversion×GHSV (mL/min×g)</th>
<th>CO$_2$ Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>0.42</td>
<td>8250</td>
<td>29.2</td>
</tr>
<tr>
<td>9.3% Ni:CZO</td>
<td>0.44</td>
<td>6800</td>
<td>24.4</td>
</tr>
</tbody>
</table>
To better understand the effect of Ni location on the catalysis, Raman spectroscopy was performed on the reference and 9.3 mol% samples (Figure 3.3b). Three characteristic regions of interest, around 228, 470, and 615 cm\(^{-1}\), are attributed to vibrations of Zr-O bonds (symmetrical stretching, \(B_{2g}\) mode), Ce-O bonds (symmetrical stretching, \(F_{2g}\) mode), and a defect-induced (LO) phonon band, respectively (Wang, Mutinda et al. 2013). The blue-shift (474 to 470 cm\(^{-1}\)) in the \(F_{2g}\) band of the 9.3 mol% Ni is attributed to an increase in the bond length of Ce-O caused by Ni incorporation, consistent with its smaller ionic radius compared to Zr\(^{4+}\) (Li, Smith et al. 2001). Additionally, the change in intensities of the \(F_{2g}\) and LO bands are indicative of oxygen vacancy incorporation (Li, Ni et al. 2012). The oxygen vacancy concentrations were estimated using a correlation length model for the \(F_{2g}\) band (Calculation 1) (Kosacki, Petrovsky et al. 2002, Trogadas, Parrondo et al. 2012). The estimated oxygen vacancy concentration \((N)\) for the 9.3 mol% Ni:CZO catalyst is approximately 5 times more than the reference catalyst (Table 3.2), suggesting greater Ni\(^{2+}\) incorporation in the lattice induces more oxygen vacancies. Therefore, it is reasonable to conclude that the reduced coking rates of the CP/MSS catalysts result from the higher oxygen vacancy concentrations characteristic of this synthesis/structure. When comparing two materials of similar Ni concentrations, 4.6 mol% Ni:CZO vs. the reference, the increase in oxygen vacancy concentration is still 25%, suggesting the Ni is preferentially located below the catalyst surface at lower concentrations, as observed in the reactor studies above.
The formation of oxygen vacancies is one of the important characteristics of doped Ni:CZO, with incorporation of Ni within the bulk lattice improving the OSC (Park, Lee et al. 1996, Skorodumova, Simak et al. 2002). It is significant that a single XRD-detectable phase is maintained for Ni:CZO NPs even with a substantial increase in Ni content, implying a uniform dispersion within the particle (Figure 11). Figure 3.4 shows that the area under the LO band at 615 cm\(^{-1}\) increases proportional to the Ni concentration, indicating that more Ni creates more oxygen vacancies within the lattice (Table 3.2). Since oxygen vacancies can play a significant role in enhancing the CO\(_2\) activation step of the DRM reaction (Múnera, Irusta et al. 2007, Kambolis, Matralis et al. 2010, Du, Zhang et al. 2012), it is not surprising that the 9.3 mol% Ni:CZO catalyst shows the highest reforming rate (0.08 mmol/mg*\(\cdot\)h) among the three CP/MSS catalysts. The CZO catalyst by itself contains a certain number of defects, however, incorporation of Ni in the lattice further increases these defects and eventually results in significant surface Ni in any case is needed to activate CH\(_4\). Additionally, post-synthesis migration of Ni\(^{2+}\) (64 pm) into the lattice might be expected to substitute into positions normally occupied by Zr\(^{4+}\) (84 pm) and slightly lower the apparent Ce:Zr(Ni) ratio (Pauling 1947, Park, Lee et al. 1996, Mamontov, Egami et al. 2000). Therefore incorporation of Ni during the CZO crystallization can result in a more stable structure, reducing post-synthetic phase segregation, which was observed for the reference catalyst under reducing environments (Mao, Park et al. 2005). Furthermore, the presence of Ni in place of some Zr in the lattice of the CZO, rather than on the surface, can boost the OSC due to increased stress on the Ce-O bond (Mamontov, Egami et al. 2000, Sugiura 2003, Piumetti, Bensaid et al. 2015).
Figure 3.4. Raman spectra for the CP/MSS particles with increasing Ni contents. The spectra show an increase in the ratio of peak intensities $I_{LO}/I_{F2g}$. 
To observe the change in electronic state of oxygen and cerium at different Ni concentrations, XPS measurements were performed (Figure 3.5). The O 1s spectra showed four peaks: (1) oxygen ions associated with 2-formal charge or oxygen double bonded to carbon (O=C) (O₁) at ~ 528.8 eV, (2) lattice oxygen (O₉) at ~ 530.5 eV, (3) a shoulder peak (O₃) at ~ 531.15 eV indicative of nearby oxygen vacancies, (4) and adsorbed H₂O or O₂ on the surface or dissociated oxygen such as -CO₃ (O₄) at ~ 532.44 eV (Dupin, Gonbeau et al. 2000, Hsieh, Chen et al. 2008, Darapaneni, Kizilkaya et al. 2018). Table 3 shows the calculated percentages of O₃ are 9.9, 17, 24, and 32%, corresponding to CZO, 4.6 mol% Ni:CZO, 6.6 mol% Ni: CZO, and 9.3 mol% Ni: CZO, respectively, denoting an increase in undercoordinated Ce (increased oxygen vacancies), consistent with the Raman measurements (Darapaneni, Kizilkaya et al. 2018, Darapaneni, Moura et al. 2019). To remove the adsorbed species on the surface, air and vacuum annealing (T = 600 °C) was performed on the 9.3% Ni:CZO (Figure 3.6a). Annealing the sample in air decreased the area of O₄ and oxygen vacancy peak area (O₃) by ~5% and 2% respectively (Table 5). This is due to the evaporation of the volatile organic contaminants and surface hydroxyls at 600 °C. Furthermore, the vacuum annealed samples showed an increase in the area under the O₃ peak (by ~ 2%), as expected and also removed the surface contaminants (Table 5) (Lee, Mettlach et al. 2003, Maimaiti, Nolan et al. 2014). To further confirm the intrinsic oxygen vacancies and remove the surface contaminants in the remaining samples, gentle sputtering was performed (Figure 3.6b) with Ar⁺ ion bombardment for 10 min. After sputtering, a decrease in the area under O₃ peak is observed compared to the non-sputtered samples due to the filling of the vacancies by free electrons, along with complete removal of O₁ and O₄ peaks. However, the area under the O₃ peaks follows the same trend of the non-sputtered samples (Table 5). This result is also corroborated by the Ce 3d XPS spectra (Figure 3.5b). V and U shown on the plot are related to the spin-orbit splitting of Ce 3d₅/₂ and Ce 3d₃/₂, respectively. The deconvoluted peaks labeled as U″,
U”, U, V”, V’, V correspond to the 3d\textsuperscript{10}4f\textsuperscript{0} state of Ce\textsuperscript{4+} while U\textsubscript{o}, U’, V\textsubscript{o}, and V’, marked as red, correspond to 3d\textsuperscript{10}4f\textsuperscript{1} state of Ce\textsuperscript{3+} (Liao, Chu et al. 2013). It is evident that with an increase in Ni content the concentration of Ce\textsuperscript{3+} increases, along with an increase in the number oxygen vacancies (Seo, Lee et al. 2004, Nolan, Parker et al. 2005, Wang, Gong et al. 2009). The following calculation was performed to measure the fraction of Ce\textsuperscript{3+} on the surface of the catalysts using Equation 1.1 (Hu, Liu et al. 2016). This calculation shows that 6.6% Ni:CZO and 9.3% Ni:CZO have 8.65% and 16.67% Ce\textsuperscript{3+} oxidation state present in their lattice. The evolution of Ce\textsuperscript{3+}, the increase in the area of O\textsubscript{II} and of the Raman LO peak all confirm that Ni incorporation increases the number of oxygen vacancies in the catalyst.

$$Ce^{3+\%} = \frac{Ce^{3+}}{Ce^{3+} + Ce^{4+}}$$

(1.1)

Figure 3.5. (a) XPS of the O 1s region showing an increase in the area of oxide ions with an increase in Ni doping. (b) Ce 3d XPS spectra of CZO with 4.6, 6.6, and 9.3 mol\% Ni, displaying an increase in the peak areas U\textsubscript{o}, U’, V\textsubscript{o}, and V’, all of which correspond to Ce\textsuperscript{3+}, with respect to Ni content.
Figure 3.6. (a) XPS spectra of 9.3% Ni:CZO annealed in different environments to prove the capability to remove adsorbed OH on the surface. (b) XPS spectra of 9.3% Ni:CZO after gentle sputtering was performed and it is evident that the adsorbed species on the surface is removed.

Table 3.4. $O_{III}$ peak area as the 9.3% Ni:CZO was annealed under different environments. Gentle sputtering decreases the oxygen vacancy concentration because of the Ar$^+$ etching done to the surface which removed surface oxygen vacancies.

<table>
<thead>
<tr>
<th>$[O_{III}]$ (%)</th>
<th>Non-annealed</th>
<th>Air-annealed</th>
<th>Vac-annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>No sputtering</td>
<td>19.79</td>
<td>18.06</td>
<td>24.55</td>
</tr>
<tr>
<td>Gentle sputtering</td>
<td>9.69</td>
<td>9.16</td>
<td>14.82</td>
</tr>
</tbody>
</table>
Based on the above observations, controlling both the oxygen vacancy concentrations and the Ni distribution between surface and bulk can be considered to be important aspects of the synthesis of active, stable DRM catalysts. To further investigate these phenomena, the crystallization (synthesis) time of the 9.3 mol% Ni:CZO was varied to spot any change in the oxygen vacancy concentrations and coking rates of the NPs. The time of the MSS reaction step is a major factor affecting particle agglomeration and crystallization (Mao, Guo et al. 2009) which in turn can affect the location and concentration of oxygen vacancies. As seen in Table 6, three different reaction times of the MSS crystallization (1, 3, and 6 h) were tested. The homogeneity of the NPs was maintained (Figure 3.7). Figure 3.8 displays a red shift in the F$_{2g}$ band of the 9.3 mol% Ni:CZO as the molten salt reaction time is decreased, corresponding to decreased lattice strain (Lewis and Edwards 2001, Sahu, Pandey et al. 2016). Greater lattice strain causes a weakening of the Ce-O bonds in the lattice which is caused by incorporation of Ni in the lattice, (McBride, Hass et al. 1994, Johansson, Luo et al. 2014, Tiwari, Bajpai et al. 2017) this phenomena increases the oxygen vacancy concentration (Table 6). As expected, the coking rate is directly affected, whereas DRM activity is constant with respect to the surface area. However, the trend is the opposite of what might be expected, with higher coking rates associated with the shorter crystallization periods and less lattice strain. This inverse response is attributed to poorer Ni homogeneity and nanocrystal quality at short MSS crystallization times (Fano 1963, Mao, Guo et al. 2009). Specifically, the increase in MSS crystallization time engenders a better Ni rearrangement within the crystal thus causing a lower coking rate for the catalyst (Fano 1963, McBride, Hass et al. 1994). Based on the above results, it is postulated that higher DRM activities can be achieved for these particles if the oxygen vacancy concentration and surface dispersion can be simultaneously controlled.
Figure 3.8. XRD measurements of 20% Ni:CZO after 1, 3, and 6 h synthesis reaction times show only the cubic CZO structure.

![XRD measurements](image)

Figure 3.7. Raman spectra showing a red shift in the F$_{2g}$ peak (boxed area) of the 9.3 mol% Ni:CZO as the synthesis reaction time is reduced.

![Raman spectra](image)

Table 3.5. Effects of MSS reaction time on estimated oxygen vacancy concentration and catalytic activity for the 9.3 mol% Ni:CZO.

<table>
<thead>
<tr>
<th>Molten salt time (h)</th>
<th>Size (nm)</th>
<th>Surface area (m$^2$/mg)</th>
<th>$N$ (cm$^{-3}$)</th>
<th>Catalytic activity (mW/m$^2$)</th>
<th>Coking rate (mg coke/mg cat-h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.8</td>
<td>40</td>
<td>5.2 x 10$^{22}$</td>
<td>0.13</td>
<td>3.0 x 10$^{-4}$</td>
</tr>
<tr>
<td>3</td>
<td>8.7</td>
<td>37</td>
<td>4.8 x 10$^{22}$</td>
<td>0.13</td>
<td>2.8 x 10$^{-4}$</td>
</tr>
<tr>
<td>6</td>
<td>9.2</td>
<td>32</td>
<td>3.8 x 10$^{22}$</td>
<td>0.13</td>
<td>1.2 x 10$^{-4}$</td>
</tr>
</tbody>
</table>
In summary, the oxygen vacancy and catalytic activity of Ni:CZO was studied to understand the effect of the synthesis process on structure of the catalyst. Raman spectroscopy and XPS showed oxygen vacancy are dependent on concentration of Ni in the catalyst of the synthesis. The oxygen vacancy concentration of the 9.3 mol% Ni:CZO MSS samples were five times higher than the reference catalyst which resulted in the same catalytic activity per surface area but an order of magnitude decrease in the coking rate despite no visual detection of active sites on the surface. In addition to the concentration of Ni in the catalyst, it was shown that molten salt time can vary the oxygen vacancy concentration which proved the control of oxygen vacancy concentration in the lattice of the catalyst. Since oxygen vacancy can be controlled, further efforts to control the position of Ni will be discussed in the next chapter to take advantage of the oxygen vacancies present in the lattice of the catalyst and deposit a shell of active sites on the surface.
Chapter 4. Ni:CZO Shell Deposition and Characterization

To control and disperse active sites on 4.6 mol% Ni:CZO, a standard deposition method (adsorptive deposition) was adapted to deposit a shell of active sites on the surface of 4.5 mol% Ni:CZO. After a shell of 2 wt% Ni was deposited on the surface of the MSS 4.6 mol% Ni:CZO catalysts, a boost of 20 times compared to 4.6 mol% Ni:CZO and 5 times compared to 9.3 mol% Ni:CZO in catalytic activity was observed. Shell deposition interrupted the fluorite structure of 4.6 mol% Ni:CZO and a slight segregation of Zr was observed. However, after performing CO chemisorption, highly dispersed Ni was observed and attributed to the high concentration of oxygen vacancy in the lattice of Ni:CZO. Control of dispersion of active sites on the surface was observed by modifying the core Ni concentration. XAS and CO chemisorption showed that presence of high concentration of Ni in the core can cause cluster formation on the surface as the shell is deposited. The control of oxygen vacancy was previously showed and control of active site dispersion which is prominent in this chapter can produce a catalyst that has high catalytic activity with low coking rate.

Ni-doped core (4.6 mol%) was modified by further Ni addition using the Ni-urea adsorptive deposition process. An additional 2 wt% Ni shell was deposited around this core and the resulting material reduced in 5% H2/N2 at 750 °C. While a slight segregation is observed after the reduction treatment (Figure 4.1), the particles are still much more homogeneous than the used reference sample. The core-shell catalyst was run under DRM conditions (Table 3.2) and resulted in a comparable activity on a weight basis compared to the reference catalyst, despite the five-fold smaller surface area. When normalized by surface area, the DRM rate is nearly five times that of the state-of-the-art catalyst prepared by adsorptive deposition. More importantly, the coking rate of the core-shell catalyst is an order of magnitude lower. The increase in performance is attributed
both to the increased number of oxygen vacancies and the absence of large Ni/NiO islands on the surface, both of which facilitate rapid removal of nascent carbon (Li, Feng et al. 2015). While more catalyst optimization is needed, this method clearly demonstrates the important role of surface and subsurface Ni dopant sites in methane reformation.

Subsurface Ni helps mobilize oxygen and mitigate more oxygen vacancies, whereas role of Ni on the surface is breaking down the C-H bond of methane to optimize the syngas ratio (Theofanidis, Galvita et al. 2015). In order to control dispersion and prevent further coking during DRM reaction, 4.6 mol% Ni was used for the core-shell synthesis due to lowest Ni particles on surface which was verified via CO chemisorption (Table 4.1). As seen in Table 4.1, 4.6 mol% Ni shows the smallest dispersion and lowest number of moles of CO adsorbed on the surface, this supports the result that displays a low activity of 4.6 mol% Ni. Higher Ni mol percentages for the core would result in formation of larger Ni aggregates on the surface which is the contrasting point.

Figure 4.1. (a) XRD plot of reference and core-shell catalysts. Less phase separation of Ni and ZrO₂ from cubic CZO is observed for the core-shell catalyst. (b) Raman spectra of the core-shell catalyst shows a higher area under the LO band.
that chapter 3 is trying to prove. This core-shell catalyst employs oxygen vacancies from the core generated from the CP/MSS synthesis and enhances the reforming rate as well as the catalytic activity (Table 3.2) of the catalyst due to the 2 wt% Ni deposited on the surface. Finally, incorporating Ni in the core/support of the catalyst will enhance the reforming rate per surface area by 5 times compared to the reference catalyst with lower Ni composition on the surface (2 wt% Ni vs. 5 wt% Ni). Furthermore, subsurface Ni facilitates more oxygen vacancies which reduces the coking rate per surface area by 3 times compared to the reference catalyst.

Table 4.1. CO chemisorption was performed on the 4.6% Ni:CZO, 6.6% Ni:CZO, and 9.3% Ni:CZO catalysts to measure the dispersion of Ni on the surface as well as the moles of CO adsorbed on the surface of the catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dispersion (%)</th>
<th>CO adsorbed (moles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.6% Ni:CZO</td>
<td>1.03</td>
<td>5.4x10^-7</td>
</tr>
<tr>
<td>6.6% Ni:CZO</td>
<td>1.63</td>
<td>1.2x10^-6</td>
</tr>
<tr>
<td>9.3% Ni:CZO</td>
<td>4.23</td>
<td>2.1x10^-5</td>
</tr>
</tbody>
</table>

To understand the effect of the core on the deposited Ni on the surface, XAS measurements were performed (Figure 4.2). According to the XAS spectra, as Ni concentration increases in the core of the NPs, the NPs exhibit more NiO features due to increase intensity of the e_g peak, suggesting larger clusters on the particle surface. The doublet peak visible in NiO reference corresponds to 3d states (t_{2g}, e_g) of Ni^{2+} ion in an octahedral symmetry (Van der Laan, Zaanen et al. 1986, Van der Laan, Thole et al. 1988, Radtke, Lazar et al. 2006, Darapaneni, Kizilkaya et al. 2018). Increased Ni concentration on the surface increases Ni clusters on the surface which results in poor catalytic activity measurements which does not take into account the change in size and oxidation state of Ni (Pinjari, Delcey et al. 2014, Guo, Sørensen et al. 2016). CO chemisorption measurements show 9.3% Ni:CZO core has higher dispersion than the lower doped samples which
translates into presence of more metallic Ni on the surface (Table 4.2) (Khassin, Yurieva et al. 2001). After the deposition of the NiO shell on the 9.3 mol% Ni:CZO, the spectrum is dominated by NiO, Figure 4.2, peaks spanning 870-872 eV instead of a single metallic peak at ~870 eV (Regan, Ohldag et al. 2001). This would support that the deposited Ni on the surface was not completely reduced due to poor interaction between the support, CZO, and the Ni. The DSC/TGA measurements suggested that due to more metallic nature of Ni for the 4.6% Ni|2%Ni and availability of oxygen vacancies from the core, it is showing the highest coking rate with 1.5 times higher activity than the other core-shell catalysts (Table 3.2). Even though the 6.6% Ni|2%Ni and 9.3% Ni|2% Ni show higher catalytic activity but due to high coking rate of these catalysts, they are not considered the most optimum catalyst. To observe the effect of shell deposition on Ni dispersion, CO chemisorption was done on the core-shell NPs (Table 4.2). The result obtained from XAS measurements is confirmed by CO chemisorption. Metallic Ni adsorbs on the surface at room temperature, however Ni$^{2+}$ adsorbs CO at higher temperature (D'evelyn, Steinrück et al. 1987, Nematollahi, Rezaei et al. 2015). Even though more Ni is positioned on the surface of 9.3% Ni|2%Ni than 4.6% Ni|2%Ni, less CO is adsorbed and lower dispersion is observed at room temperature because of presence large oxide clusters. These results verify that the optimum catalyst synthesized using CP/MS synthesis combined with adsorptive deposition is 4.6% Ni|2%Ni because of higher dispersion and lower coking rate per surface area of this catalyst. The catalytic activities could further be increased if more Ni dispersion is achieved on the surface while maintaining the oxygen vacancies in the core.
Figure 4.2. XAS of the Ni L edge of core-shell NPs showing the transformation of surface Ni as the Ni concentration of the core is increased.

Table 4.2. Effect of modifying the core Ni concentration on catalytic properties as well as active site dispersion of core-shell catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activity (mW/m²)</th>
<th>Coking rate (mgcoke/m²·h)</th>
<th>Dispersion (%)</th>
<th>CO adsorbed (moles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.6 % Ni</td>
<td>2% Ni</td>
<td>0.57</td>
<td>3.4 x 10⁻⁶</td>
<td>1.56</td>
</tr>
<tr>
<td>6.6% Ni</td>
<td>2% Ni</td>
<td>0.67</td>
<td>2.1 x 10⁻⁴</td>
<td>0.46</td>
</tr>
<tr>
<td>9.3% Ni</td>
<td>2%Ni</td>
<td>0.79</td>
<td>6.1 x 10⁻⁴</td>
<td>0.35</td>
</tr>
</tbody>
</table>
In order to completely understand the effect of shell deposition on the structure of Ni:CZO catalyst, CO chemisorption and XAS were performed. XAS showed that Ni clusters are formed as the concentration of Ni increases in the core as 2 wt% Ni shell gets deposited. To achieve maximum dispersion of the shell, the 4.6 mol% Ni:CZO was used as the core to avoid the formation of any Ni clusters and interaction between the shell and the core is maintained. The catalytic activity measurements of the optimum core-shell catalyst were performed, and a 5-fold increase in catalytic activity per surface and an order of magnitude decrease in the coking rate was obtained. The control over oxygen vacancy and active site dispersion of Ni:CZO catalyst showed a significantly increase in overall catalytic activity characteristic of this catalyst compared to a reference state-of-the-art catalyst.
Chapter 5. Conclusions and Future work

In summary, ~20 nm Ni:CZO NPs with Ni doping up to ~10 mol% were synthesized using a two-step CP/MSS method to study the effect of Ni position on structure, oxygen vacancy concentrations, and DRM catalytic activity. This synthesis process produced homogeneous cubic Ce$_{0.69}$Zr$_{0.31}$O$_2$ with Ni concentrations as high as 9.3 mol%. Additionally, Ni inclusion resulted in the formation of oxygen vacancies proportional to the concentration of subsurface Ni dopants. However, increased oxygen vacancies must be accompanied with highly crystalline nanoparticles with homogeneously distributed Ni to achieve the reduced coking rates. The homogenous distribution and enhanced oxygen vacancies are possible due to incorporation of Ni within the CZO crystallization process instead of through a secondary process to drive deposited ions below the surface. This knowledge was used to design a core-shell structure by coupling the MSS method to a Ni-urea adsorptive deposition process to simultaneously engineer greater oxygen vacancy concentration and a better surface-bulk Ni distribution. The core-shell synthetic strategy greatly increased the DRM activity and decreased the coking rate by over an order of magnitude compared to conventionally prepared Ni:CZO catalyst despite a much lower surface area. This ability to control the content of oxygen vacancies in the host lattice and homogeneously disperse Ni sites in the bulk will prove beneficial in designing stable catalysts with higher activity for methane reformation, among other related reactions.

Future work involves studying the relationship between CO chemisorption and XAS in situ. This will help us understand how CO chemisorption will change the Ni coordination on the surface of the NPs. As hypothesized, 9.3% Ni|2% Ni possesses more Ni$^{2+}$ on the surface so temperature dependent CO chemisorption will help us quantify a ratio between Ni$^0$:Ni$^{2+}$ and at what temperature Ni$^{2+}$ will adsorb on the surface. In situ XAS will be performed by flowing CO
into the pressurized XAS chamber and Ni L edge will be monitored to see if CO will change the coordination of Ni. After the chemisorption paired with XAS studies are complete, there will be an effort to optimize the core-shell structure to see if Ni dispersion can be maximized on the surface while keeping the subsurface oxygen vacancies. Utilizing the knowledge about the core and how much Ni is segregating to the surface, it is important to control and maximize the surface-active sites and other methods may be necessary if the absorption-deposition is not sufficient.
Appendix A. Oxygen Vacancy Concentration Calculation

Calculation 1. Defect concentrations were calculated from the correlation length model of Kosacki (Kosacki, Petrovsky et al. 2002). The half-width at half maximum (HWHM) was measured for the gaussian-fitted F2g peaks of the Ni:CZO Raman spectra. The grain size, \( d_g \), was calculated from the correlation (Equation 1). The correlation length, \( L \), was then determined using \( d_g \) and \( \alpha \) (the radius of the CZO structure). Assuming the structure is spherical, the defect concentration \( N \), which is assumed to arise from oxygen vacancies, was calculated using equation 3.

\[
HWHM = 5 + \frac{51.8}{d_g} \quad (1)
\]

\[
L \ (nm) = \sqrt[3]{\frac{\alpha}{2d_g} \left[ \left( \frac{d_g - 2\alpha}{d_g} \right)^2 + 4d_g^2\alpha \right]} \quad (2)
\]

\[
N = \frac{3}{4\pi L^3} \quad (3)
\]
Appendix B. Molten Salt Synthesis Procedure

Purpose: The purpose of this experiment is to synthesize nanoparticles via a wet-chemical method, using a salt solvent under various ambient environments. Safety and exposure details are discussed.

Potential Risks/Hazard: Molten salt chemistry uses relatively high temperature to melt the salt solvent. As a result, there is a tendency for the crucible to shatter inside of the oven due to these extreme temperatures. In such a case, carefully remove the broken parts wash it and throw it in trash. Throw away the spilled salt inside the inorganic waste. Additionally, turn off the switch and pull the wire off from the electrical supply if there is any issue while operating the furnace. In all cases of emergencies, notify the lab supervisor immediately. When performing molten salt experiment under different ambient environments, it is important to note that the tube furnace uses a quartz tube which can handle high vacuum and temperature conditions. If the tube is cracked under one of these conditions it can cause harm. The vacuum pump has an exhaust connection that releases hazardous fumes directly into a ventilation stack. If the flow is blocked, hazardous fumes will accumulate.

Personal Protective Equipment (PPE): Always wear gloves, safety goggles, long pants, and closed toe shoes when operating the vacuum unit. When removing samples from the high temperature oven, always use long tongs and thermal gloves.

Consequences from Deviation from Safe Practices: Improper practice can lead to spillage of the salt mixture onto skin which will cause irritation. High temperature reaction can cause severe burns if not conducted properly.

Procedure:

I. Procedure under Air Ambient:

A. Mix 350 mg of precursor, A(OH)$_3$$\cdot$BO(OH)$_2$$\cdot$nH$_2$O, and 60 mmol of nitrate mixture (NaNO$_3$:KNO$_3$ =1:1) inside a mortar and pestle
B. Hand-grind the mixture created in step 1 for 15 minutes
C. Transfer the grinded mixture into a covered crucible (alumina, porcelain, or nickel)
D. Place the crucible inside the high temperature oven and heat it to the desired temperature at the desired rate (to operate, refer to high temperature oven SOP)
E. After the experiment is completed, take the sample out of the high temperature furnace and immerse the product in deionized water for ~6-12 hours to dissolve out the salt solvent
F. Centrifuge the precipitate with ~ 200 mL of deionized water several times
G. Place the washed sample into the low temperature oven (to operate, refer to low temp oven SOP) to dry overnight
H. Final product is ready for further characterization
Appendix C. Different Annealing Methods

Purpose: The purpose of this equipment is for performing experiments/drying under oxygen deficient environments. Safety and exposure details are discussed.

Potential Risks/Hazard: The tube furnace uses a quartz tube which can handle high vacuum and temperature conditions. If the tube is cracked under one of these conditions it can cause harm. The vacuum pump has an exhaust connection that releases hazardous fumes directly into a ventilation stack. If the flow is blocked, hazardous fumes will accumulate.

Personal Protective Equipment (PPE): Always wear gloves, safety goggles, long pants, and closed toe shoes when operating the vacuum unit.

Consequences from Deviation from Safe Practices: Improper inspection of glassware for use in the vacuum unit may cause bodily harm. Shards of glass can be flown into all exposed body parts.

Procedure:

I. Heating using the Tube Furnace:

A. Thoroughly inspect tube for cracks (i.e. star crack, etc.) before use. If a crack is spotted put the tube into a box and properly label the box for disposal.
B. Place sample into a crucible boat and slide sample/crucible set to the center of the tube.
C. Place alumina foam insulation blocks into the tube so only half of the block is visible
D. Turn the power switch ON (green button)
E. Adjust the temperature using the up/down arrows. The tube furnace uses a fixed ramp rate to reach the set point temperature.

I. Heating under Vacuum using the Tube Furnace:

A. Thoroughly inspect tube for cracks before use.
B. Follow steps 1-3 for placing sample into the tube furnace
C. Place vacuum attachments (O-ring and stainless-steel clamps) onto the tube and screw them securely in place
D. Check to make sure the valve for the oven is closed and the valve for the tube furnace is open.
E. Connect the pump to the power and let warm up for 1-2 min
F. Open the valve (directly on top of the vacuum pump) to start pulling air out of the tube furnace. Keep the valve open until the pressure reaches 1 torr.
G. Close the valve to tighten/check the vacuum connections
H. Open the valve a second time to pump down to the pressure of interest.
I. Once the pressure is reached begin the heating step by following steps 4-5
J. After the experiment is completed, open the valve on the tube to let air into the tube furnace. This will cause the pressure to increase.
K. Once the pressure reaches atmospheric conditions (760 torr), close the vacuum pump valve and unplug the pump.
Appendix D. Characterization Procedures (XRD, Raman, DSC/TGA, XPS, XAS)

Standard Procedure for X-ray Diffraction

Purpose: The purpose of this equipment is to determine the crystal structure of synthesized materials (thin films, powders, etc.) using X-rays. Safety and exposure details are discussed.

Potential Risks/Hazard: The XRD instruments generates electrons by applying a bias to a Cu foil. The bias creates an X-ray that if exposed to a user can cause cancer, genetic, or hereditary effects. Another serious hazard from the instrument is electrical shock.

Personal Protective Equipment (PPE): Always wear gloves, safety goggles, long pants, and closed toe shoes when operating the vacuum unit. Always wear radiation badge for monitoring level of radiation exposure.

Consequences from Deviation from Safe Practices: Improper operation of the XRD may result in damaging the instrument and warning/dismissal from the facility.

I. Start-up procedure
   A. Check to see if the radiation is on and wear your radiation badge when you enter the XRD room.
   B. Turn on the lights inside the diffractometer chamber by pressing the on/off button.
   C. Check to see if the five important components are in place before you place the sample.
   D. The left and right side soller slits should be in place such that the 0.04 rad written on it is facing towards you.
   E. The mask which is in golden color (left side) should be checked to see if the size written on it suits our sample. Typically, we use 10 mm mask for our samples.
   F. The 2º fixed slit is placed such that the words FAST are facing the detector.
   G. On the right side behind the soller slit, check whether the Nickel β filter is in position.
   H. Finally, take a look at the level of the detector, sample stage and the soller slits to check if there is any offset.
   I. Open the Data Collector program on the computer and log in with the following credentials.
      Username: User-1
      Password: galaxy
   J. Click on measurement located at the top menu tab, and select connect to sync the computer with the device
   K. Select Reflection Transmission Spinner (RTS)

II. Instrument settings
   A. Click on the first menu bar option in the right panel: instrument settings
   B. Click on X-rays option in the top menu of the opened window and change the current to 40 mA, wait five minutes.
C. Click on sample stage in the top menu and uncheck the lift-up box, click apply, and wait until the rotation of the cursor stops. Then press the unlock button on the chamber and place the sample holder on the stage.
D. Close the chamber door and, on the computer, check the box next to lift-up
E. Next, click on the offset and change the values of 2(Theta), Omega offset, Omega, Phi to zero and then hit Apply→OK.
F. In the instrument settings section, recheck to see if the offset angles are all equal to zero.

III. Incident beam optics
A. Click on the second menu bar option in the right panel: incident beam optics
B. Double click on any of the parameters that are displayed.
C. The PreFix Module should read Program divergent slit with anti-scattering slit.
D. The divergent slit should be checked automatic and the anti-scattering slit is a fixed slit-2º.
E. The soller slits are 0.04 rad and no filter should be selected for the incident beam side.

IV. Diffracted beam optics
A. Click on the third menu bar option in the right panel: diffracted beam optics
B. The anti-scattering slit should read scattering line detector (1D).
C. The PreFix module option should read PixCel with programmable anti-scattering slit is chosen. Ensure that the default offset is 0º and the total offset is also 0º.
D. The irradiated length is chosen based on the length of the sample (for example: for a 7 mm sample, the irradiated length is chosen to be 6 mm)
E. There is no receiving slit, collimator, beam attenuator and mirror used.
F. The filter is opened to see if the Large Ni β filter is selected and the soller slits as 0.04 rad is checked.
G. The detector used is Pixcel-3D detector [2] and select the usage as Scanning line detector [1D]. In the usage, the active length 2Theta: 3.3473, Active channels: 255 and the radiation is K-Alpha-1. Select the Pulse Height Discrimination (PHD) level option. For non-magnetic samples the lower level is set as 25% and upper level is set as 100 % and then hit on OK. For magnetic samples, the lower level is set as 45% and the upper level is set as 70% and then hit on OK.
H. After making the above changes hit Apply→OK.

V. Measuring the diffraction pattern
A. Recheck to make sure all the offset angles are zero in the instrument settings section
B. Recheck inputs for incident beam and diffracted beam parameters
C. The program is run by selecting the measurement option from the top menu bar→Program→Browse→Dr.Dorman→Pragathi→20160622→rts 5-70: 8mm file→→Enter sample name→Dr.Dorman→Pragathi→20160622→Sample name.
D. The diffracted pattern is saved in a folder (in the name of the date→Pragathi→Dr. Dorman→XRD data) by the sample name.
E. The lift up box is unchecked and the sample is taken out by unlocking the doors and carefully taking it out from the sample stage.
F. Check the lift up box and reset all the offset parameters and angles to zero.
G. Finally, Hit OK close all the windows.

VI. Converting XRD data
A. The obtained diffracted data is converted to XRMDL, CSV, RTS or C-C CSV formats which are convenient for plotting and analyzing
B. Open the High Score program on the computer and clicking file → open → XRD data → Dr. Dorman → Pragathi → 20160622 → Sample name.
C. The default option at the bottom left of the window is clicked in order to convert automatic slit data to fixed slit data.
D. The converted file is saved by selecting file → save as → sample name. c.xrmdl.
E. Select the Data Viewer program from the start menu in the computer. Open the xrdml file by clicking on file → open → sample name → file → convert all → Close the window.
F. Open the OS (C:\) → XRD data → Dr. Dorman → Pragathi → 20160622 → Email all the files
G. The saved files are in the csv format which can be analyzed using any plotting software.

VII. Shut-down Procedure
A. Click on the instrument setting section, reset the current to 20 mA and click on the sample stage, check the lift-up box, and change the value of 2(Theta), Omega offset, Omega, Phi to zero and then hit Apply → OK.
B. Click on the diffraction beam optics section, reset the PHD level to 25/100
C. Close the programs (Data Collector, High Score, and Data Viewer)
D. Turn off the lights inside the diffractometer chamber by pressing the on/off button.
Standard Procedure for Raman Spectrometer

Potential Risk/Hazard:
In all cases of emergencies, notify the Lab supervisor (Dr. Cao) immediately.
1. Forgetting to turn the lasers off
2. Leaving the shutter/door of the equipment open while running a measurement
3. Spillage of the sample on the microscope lens

Safe Practices:
In all cases of emergencies, notify the Lab supervisor (Dr. Cao) immediately.
1. Make sure that you are always equipped with PPE when performing this characterization.
2. Lasers should be turned on at least 20 minutes before the start of experiment and turned off immediately after done with the experiments
3. Ensure that the shutter/door of the equipment is locked when starting a run

Personal Protective Equipment (PPE):
1. Goggles, gloves, pants, and closed toed shoes

Consequences of Deviation from Safe Practices:
In all cases of emergencies, notify the Lab supervisor (Dr. Cao) immediately.
1. Spillage of sample on your skin might cause irritation if you’re not equipped with proper PPE.
2. Laser lifetime is limited and if the lasers are left on for a long time will damage and drain the lifetime of the lasers.
3. If the shutter is not closed and a run has started the user might get exposed to a high power laser.

Procedure:
Part 1: Sample Preparation
1. Shake your scintillation vial and open the cap
2. Tap the cap on the sample holder so very tiny amount of your sample is transferred on to the sample holder.
3. Using a second sample holder collect all your sample in the middle of the sample holder.
4. With the second sample holder press on your sample and make sure that it is uniform and in the center of the sample holder.

Part 2: Equipment Startup and Run
1. Turn all three lasers (532 nm, 633 nm, and 720 nm) on 30 minutes before the start of the experiment
2. The program, WiRE 4.4, should be on. If not, open
3. Unlock the equipment door and mount your sample holder under the microscope
4. Make sure the magnification is x5.
5. Through the eyepiece lens look at your sample
6. Adjust the magnification and focus with a knob that is below to the right of where your sample is placed
7. After you have focused on your sample and it looks clear change the magnification to x20
8. Repeat step 6 (It will be a little harder since it is more magnification).
9. After you have focused on your sample and it looks clear change the magnification to **x50 L**

10. Close the equipment door (locks automatically)

11. On the software under magnification, choose **x50 L**

12. By Clicking on the video camera and the flashlight button your sample should be visible on the right screen

13. Adjust the focus on your sample with F-stop, hexagonal shape will come up

14. You can control the power of the laser exposed to your sample by changing the power percentage (**10%** is normally fine)

15. Using the knob, focus on your sample. Inner coarse of the knob will help you move the spot and the outer coarse will help you focus

16. To start your measurement, click on measurement → New → Spectral acquisition

17. Make sure your grating scan type is **Static**

18. Set your Spectrum range by changing the Centre position to 1000 Raman shift/cm$^{-1}$, this will give you a range of 0-1800 Raman shift/cm$^{-1}$

19. Then choose Acquisition → Exposure time: 0.5 /s → Laser power: **10%** → Accumulations: 100

20. Then click Apply and then OK

21. By clicking you will start your measurement

---

**Part 3: Saving spectrum of your sample**

1. Click on File → Save file as → Give it a name and save it as .wdf

2. Repeat step one but save it as .txt

---

**Part 4: Aborting a measurement**

1. To abort a measurement, you have to click on the red square next to the start measurement button

2. The software will ask if you are sure and click yes

---

**Part 5: Equipment Shutdown**

1. Turn off all of the lasers

2. If any sample spilled clean the area

3. **DO NOT** exit out of the software
Standard Procedure for DSC/TGA

Purpose: is a method of thermal analysis in which the mass of a sample is measured over time as the temperature changes.

Potential Risks/Hazard: High temperature, Chemical exposure

Personal Protective Equipment (PPE): Always wear gloves, safety goggles, and closed toe shoes.

Consequences from Deviation from Safe Practices: Improper operation may cause burn on the skin. Improper cooling may cause overheat.

Sample loading
A. Open the “TA - 2960 SDT” op. software. Click on “experiment view” in the tool bar. Be certain the mode selected is DSC-TGA. SDT Standard.
B. Before starting the measurement, make sure N₂ valve is open.
C. Hit “furnace” on TA, then be sure crucibles clean and properly loaded. Hit “furnace” to close the furnace. Then “tare”, wait until it shows near 0 mg.
D. Open the furnace again, load sample to the FRONT crucible. Fill the crucible to 3/4 at most (12mg or more). Use swing out pan under crucible when loading. Clean the swing out pan if you spill it.
E. Hit “furnace“ to close. Make sure there’s sufficient gas flowing (at least 75 mL/min total flow).

Setting up
A. Go to “summary” - set up all sample parameters, or load a method or procedure file (they are the same, the extension is .prc). When you load a procedure file, click on “procedure” to have the new procedure show in the window.
B. Set up sample name, etc. It prompts you for the storage directory later.
C. To pretreat the sample with hydrogen, make sure open the H₂ valve. After pretreatment, close H₂ valve and open CH₄/CO₂ valve for reforming reaction.
D. If running a “procedure”, get your procedure file.
E. Start by hitting green button. See if the little man turns green and runs.
F. Even if not using Gas 1, don’t close the N₂ valve. Because it automatically switches back to Gas 1 at the end of the run during the cooling period.

Data transfer
A. Before starting another run, you must remember to “Transfer” your data. This is under “Tools”. Set up the path to your directory and your file name (which may or may not be the same as the sample name). You always get an error message here but ignore it. Start the transfer. Wait until it stops transferring before closing the window,
B. To analyze - use WIN UA. At least go look at the graph to be sure the data transferred, even if you will analyze later.
C. When you look at the graph, it may not show “heat flow” on the Y-axis. To show the heat flow, click on the 7th icon from the left side (the “hand”) and you can set Y2 to show heat flow in W/g. You can change any axis you want here.
D. To save data - export to text file. File - Export Data File - File Signals Only - ASCII data file - Finish
Standard Procedure for X-ray Photoelectron Spectroscopy

Purpose: The purpose of this experiment is to measure the elemental composition at the parts per thousand range, empirical formula, chemical state and electronic state of the elements that exist within a material. Safety and exposure details are discussed.

Potential Risks/Hazard: Chemical Exposure, High vacuum chamber, X-ray exposure

Personal Protective Equipment (PPE): Always wear gloves, safety goggles, and closed toe shoes.

Consequences from Deviation from Safe Practices: Improper operation may cause X-ray exposure and health issues. Also, it may break the vacuum chamber.

Start instrument:
A. Turn 5 power supply switches all the time. The 5 switches are 3 orange switches and 2 black switches (charge neutralizer and ion source).
B. Always turn on the electronics first and then open the program.

Software:
A. Stage control > connect > toggle enable > click on the dropdown menu (inverse triangle) > select faraday cup > Go to
B. Open StCam software
C. Open Faraday cup (FC) and move cursor center of analyzer position
D. Adjust y (y-) to go to your sample.
E. Change z to around 2.24 mm (if sample on silicon wafer, z=1.7mm)
F. Adjust x to see the cursor in the middle.
G. Open Matrix v4.1.1: (ignore if any pop box shows up).
H. Click the middle one (a “c” in a square)
I. Tools > result file preference > select folder > my computers > data (: D) > data > Pragathi > choose (use daily folders)
J. Custom folder’s name
K. Ixps > data set > custom sample name > save
L. Turn on x-ray source
M. Wait until power is 600W, high voltage is 15 kV
N. Click on Spectra
O. Make sure big yellow tag unchecked so that the unwanted sequence doesn’t run.
P. Click on Group and drag into loop
Q. Drag sweep inside blue of group (click on periodic table to add elements)
R. Double check on survey scan (start: 1200 eV, end: 0 eV, step: -0.5, CAE: 50, Dwell time:0.1, transition: survey)
S. Double click periodic table > C 1s> create sweep node
T. Loop under C 1s
U. Drag sweep C 1s inside blue bar of 1x
V. Change 1x to 2x by double clicking
W. Edit C 1s range – double click (start: 298, end: 278, Step: -0.05, CAE: 30, Dwell time: 0.5)
X. Click of 2x sweep C 1s and drag until it goes into the blue tag of yellow group
Y. Duplicate make it O 1s 2x
Z. For all detailed scans, set step size: 0.05, dwell time: 0.5
AA. In live tools, change Binding energy to 532 eV, click live region (CAE: 150, Dwell Time: 0.1) shift – 0.5 eV (537 peak position)
BB. Change Binding energies accordingly
CC. Optimize Z based on maximizing the counts
DD. Check yellow sequence (green)
EE. Execute

Charge neutralizer
A. Connect two lights STC and analysis. Change neutralizer – vernissage. Click on the U button on the right low corner to change neutralizer to make sure beam energy = 2 eV, focus voltage = 300 V, exit voltage = 15 V, emission = 250 µA
B. When O peak isn’t seen separate focus, turn on U to change neutralizer. Reduce beam energy to 1 eV to center the position of peak.
C. under spectra group drag change neutralizer (F54OA) > adjust parameters > double dwell time for spectra (1s)

CasaXPS analysis procedure:
A. Click on File to open the .vms file gathered from XPS instrument.
B. To fit the peaks, click on one the quantify bottom to open the quantification parameter window. If there is a green background and some unknown lines, click on and to delete them.
C. Click one “create” bottom in the quantification parameter window to create a new background. Change the BG Type to “Shirley”. Then drag the two green vertical lines in the diagram to identify the peak region you want to fit.
D. If there are multiple peaks, create a background for each peak area. Then create a background for the whole diagram, make sure it starts at the left edge of the left peak region and ends at the right edge of the right peak region. Set the BG Type as “Skip”.
E. Go to components tag in the quantification parameters window. Click on create to create as many peaks as you need to fit the diagram. All the line shapes should be “GL(30)”. Click on fit components for a few times until the parameters don’t change anymore. (you can rename the peaks here).
F. Click on the Tile Annotation bottom, then choose Components tag in Annotation window. Check the terms you want to exclude then click on Apply.
G. Click on the figure, go to file then choose “save picture” to save the fitted diagrams. Click on “save comps TAB ASCII to Clipboard” bottom to save the data as .txt file.
H. The exported data can then be plotted in any plotting software such as Origin for better understanding of the peaks.
Standard Procedure for X-ray Adsorption Spectroscopy

Purpose: The purpose of these beamlines is to measure the X-ray absorption spectra of the elements present in our materials (thin films, powders, etc.)

Potential Risks/Hazard: Do not measure anything on the beamline if you are not a radiation user. Always wear radiation safety badge while you are in CAMD.

Personal Protective Equipment (PPE): Always wear gloves, safety goggles, and closed toe shoes.

Consequences from Deviation from Safe Practices: Improper operation of the beamlines may result in damage of the CAMD ring and permanent dismissal from the facility.

Procedure:

I. Operation of Soft X-Ray beam line:
   The Variable Line Spacing-Plane Grating Monochromator (VLS-PGM) beam line is used for the elements with lower edge energies around 200-1000 eV. As soft X-rays have low energy, the air absorbs UV-light in the X-rays. Therefore, the samples are placed in vacuum for these measurements. The K edges for lower atomic number elements and L and M edges for higher atomic number elements are measured. There are two types of gratings present in the monochromator. One for lower energy which ranges from 200-500 eV and the other one from 500-1000 eV. For our samples of TiO$_2$-Ni, a higher monochromator grating is employed for all the measurements on this beam line.

Sample Preparation:
A. For powders sample, the double sided carbon tape is cut into four small squares and it is stuck on both the sides of the circular sample holder.
B. Very little amount of sample is taken with a spatula and then it is spread uniformly on the tape with the help of a brush and excess sample is slowly pushed off the sample holder without contaminating the other sample.
C. In the case of thin films, we can mount one substrate on one side of the sample holder at a time. The thin film is attached to the glue of the carbon tape and it is made sure that it does not move.

Equipment Description:
D. The vacuum chamber has an inlet pump which is not connected to the chamber but an extension through which the samples can be taken out or placed inside without disturbing the vacuum inside the chamber.
E. An entrance slit near the beam ring and an exit slit near the sample are present in the beam line which will determine the resolution of the measurement.
F. The pump inlet to the vacuum chamber is closed and the green valve near the load lock chamber is slowly opened.
G. The screws of the load lock chamber are unscrewed and the sample holder is carefully placed inside it with the help of tweezers.
H. The load lock valve is then closed and the screws are finger tightened and the valve is opened while closing the blue valve.
I. Now the pressure is monitored and the valve is opened once the vacuum inside is at high pressure.
J. It takes around 90 minutes for the chamber to be pumped out of air and after that the beam is turned on, which takes about 10 min for warming up.

Sample Measurement:
A. All the shutters are closed till the beam is near the slit and it takes about 10 min to warm up.
B. The shutters are slowly opened except for the Gate valve 5. The entrance slit is kept at 100 μm (144) and the exit slit is increased to 150 μm (300).
C. The lab view software is opened on the first computer and VLS mirror software is opened on the second one. In the first computer, Utilities is selected. Then hit on go white light and then one single click on white light. We can see the monochromator moving as the energy is changing to white energy.
D. The sample inside the chamber is adjusted along the X, Y and Z axes by turning the respective knobs and it is ensured that the white light beam hits the center of the sample.
E. Now the exit slit is turned again to 100 μm (121) and on the software Go back to main button is clicked.
F. In the main utilities window, Go to energy is clicked and the energy for our specific element of interest is entered manually. This value is usually greater than the edge energy value.
G. When the monochromator stops rotating, the Gate valve is opened by pressing on the monitor screen and the input values for our scan are given. For O K edge spectra, the values would be something like this:
   Energy Range - min 525 eV max 565 eV
   Step size – 0.2 eV
   Trigonometric count – 1
   Grating – 2
   Sample name - TiO2 thin film, O K edge
   Notes - Beam current = 70 mA

H. Now the optimize I, is selected and the Z position and pitch are made sure that they are non-zero five digit numbers. The increment value is given as 100 and hit on go to see if the current in the Keithley meter is increasing or not. We can go in the opposite direction too by decreasing the values to maximize the current.
I. The window on the first computer is closed by hitting on back to main and the go button is clicked next to the Grating value to begin the scan.
J. After the scan is completed, it directs you to a path and we can create a new folder in the Dataparti (:C) drive with the date and name.
K. Copy a log.txt file from any of the other folders and save it in your folder by clearing the text in it.
L. The sample scan is now saved by its name and then log.txt file is selected.
M. To begin another scan of the same sample but for another element, change the energy range and optimize the current for every new scan and also change the slit widths if necessary.
N. For rotating the sample holder to measure samples on the other side, close the gate valve 5 and then rotate the black long knob in clock-wise direction and again adjust the position such that the white light beam will fall on the center of the sample.
O. After finishing all the measurements, close the gate valve 5 and all the shutters are closed one by one from right to left. They are opened in the reverse order.
The data collected can be processed in Athena simultaneously while performing the scans and the change in the absorption edges is observed.
Chapter 6. Bibliography


Li, X., et al. (2012). "Development of attapulgite/Ce1− xZrxO2 nanocomposite as catalyst for the degradation of methylene blue." Applied Catalysis B: Environmental 117: 118-124.


Vita

Education


Publications and Presentations


Finally, I would like to thank my family, friends, Dr. Dorman, and Dr. Dorman’s lab members who helped me throughout my Masters program at Louisiana State University. It has been a pleasure to study and perform research at Louisiana State University. I plan on receiving my M.S. in Chemical Engineering in August of 2020.