REACTIVITY AND MECHANISM OF CATALYTIC METHANE CONVERSION OVER CERIA-ZIRCONIA SUPPORTED METAL/METAL OXIDE CATALYSTS

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# TABLE OF CONTENTS

## ACKNOWLEDGEMENTS

## LIST OF TABLES

## LIST OF FIGURES

## LIST OF SYMBOLS AND ABBREVIATIONS

## SUMMARY

## CHAPTER 1. Introduction

1.1 Supply and Issues of Methane  
1.2 Catalytic Conversion of Methane  
1.3 Ceria Supported Metal/Metal Oxides as Catalysts for Methane Conversion  
1.4 Understanding Methane Activation using *operando* FTIR Spectroscopy  
1.5 Objectives and Organization

## CHAPTER 2. Nickel Speciation and Methane Dry Reforming Performance of Ni/Ce₅Zr₁₋ₓO₂ Prepared by Different Synthesis Methods

2.1 Backgrounds  
2.2 Experimental  
  2.2.1 Materials  
  2.2.2 Catalyst synthesis  
  2.2.3 Physicochemical Characterization  
  2.2.4 Reactivity tests  
  2.2.5 Spent catalyst characterization  
2.3 Results  
  2.3.1 Physiochemical Properties of Catalysts  
  2.3.2 Reactivity tests for methane dry reforming  
  2.3.3 Spent catalysts analysis  
2.4 Discussion  
  2.4.1 The effect of synthesis methods on Ni speciation and redox properties  
  2.4.2 The effect of varying Ni content for CP and CS catalysts on Ni speciation and redox properties  
  2.4.3 The relationship between catalyst structure and performance in dry reforming of methane  
  2.4.4 The relationship between catalyst structures and deactivation mechanism  
  2.4.5 Insight regarding catalyst design  
2.5 Conclusions

## CHAPTER 3. *In-situ* FTIR Spectroscopy Study of Surface Reactions during Methane Activation over NiO/Ce₀.₈₂Zr₀.₁₈O₂ Catalysts

3.1 Introduction
List of Tables

Table 2.1 – Physiochemical properties of ceria zirconia (CZ), 2 wt% Ni/CZ synthesized by dry impregnation (2DI), 2 wt% Ni/CZ synthesized by strong electronic adsorption (2SEA), 2, 4, 6, and 10 wt% Ni in CZ synthesized by co-precipitation (2CP, 4CP, 6CP, 10CP), and 2, 4, 6, and 10 wt% Ni in CZ produced by combustion synthesis (2CS, 4CS, 6CS, 10CS). ................................................................. 22

Table 2.2 – Total H₂ consumption from TPR experiments, the Ni species composition from linear combination fitting the XANES spectra, coordination number of 1st Ni-O shell and 2nd Ni-Ni shell from EXAFS fitting and the estimated particle size of NiO from EXAFS fitting. ..................................................................................... 28

Table 2.3 – Initial and steady state H:CO ratio and conversions of CH₄ and CO₂, and time until the loss of half initial CH₄ conversion................................................................................................................................. 36

Table 2.4 – Surface area, pore volume, and pore width of the spent catalysts measured by N₂ physisorption, the loss of weight during TGA of the spent catalysts, and Ni particle size in the spent sample from XRD. .............................................................................................. 39

Table 3.1 – Physiochemical properties of CZ, 2NiO/CZ and 10NiO/CZ. ....................... 70

Table 3.2 – Optimized peak parameters for IR spectra from methane activation over 2NiO/CZ at 200 °C and peak assignments. ................................................................................................................................. 76

Table 4.1 – Physiochemical properties of the catalysts. ................................................. 95

Table 4.2 – Steady state CO₂ yield, methanol yield and selectivity over different catalysts. (Temperature at 250 °C, WHVS at 30.2 h⁻¹ with 30% of steam, 1% of oxygen, 20% methane and a balance of nitrogen). ................................................................. 105

Table A.1 – EXAFS fitted parameters for fresh samples. ................................................. 123

Table A.2 – Peak deconvolution and assignment of TPR profiles. ................................. 125

Table B.1 – Peak parameters and assignments from peak fitting TPR profiles. ............ 136

Table B.2 – Peak position and area of pyridine adsorbed on Lewis acid sites at different thermoevacuation temperature for catalysts and the CZ support............................. 138

Table B.3 – Optimized peak parameters for IR spectra from methane activation over 10NiO/CZ at 200 °C and peak assignments. ................................................................................................................................. 141

Table B.4 – Optimized peak parameters for IR spectra from methane activation over 2NiO/CZ at 300 °C and peak assignments. ................................................................................................................................. 142

Table B.5 – Optimized peak parameters for IR spectra from methane activation over 10NiO/CZ at 300 °C and peak assignments. ................................................................................................................................. 143

Table C.1 – Peak parameters for peak at 1444 cm⁻¹ from peak fitting of IR spectra from during pyridine thermoevacuation at 150, 250, 350, and 450 °C for the CZ support and the samples. ................................................................................. 148

Table C.2 – Peak parameters for XPS peak fitting of all samples................................. 151

Table C.3 – Peak position of C-H stretching vibrations and variance of the basis set of peaks representing surface species. ................................................................................................................................. 154

Table C.4 – Peak areas of different surface species from methane activation over different catalysts. ........................................................................................................................................... 157

Table C.5 – Total weight loss and weight loss from carbon deposit from each sample after 8 h on stream........................................................................................................................................ 158
Table C.6 – Total weight loss and weight loss from carbon deposit from each sample after 100 minutes on stream.
LIST OF FIGURES

Figure 1.1 – The possible upgrading routes converting methane to fuels and chemicals... 2
Figure 1.2 – Mechanism for methane activation.1.84 .............................................. 7
Figure 2.1 – a) X-ray diffraction spectra of CZ, 2DI, 2SEA, 2CP, 4CP, 6CP, 10CP, 2CS, 4CS, 6CS and 10CS catalyst samples. b) XRD diffraction peaks of NiO on the 10CP catalyst sample. Vertical dashed lines indicate diffraction angles for CZ solid solutions.24
Figure 2.2 – XANES spectra of unreduced catalysts and a NiO standard as reference. a) Catalysts with 2 wt%. nickel content; b) CP catalysts; c) CS catalysts. EXAFS for unreduced catalysts and a NiO standard as reference. d) Catalysts with 2 wt%. nickel content; e) CP catalysts; f) CS catalysts. ................................................................. 26
Figure 2.3 – a) Different Ni and Ce species in NiO/CZ catalysts and TPR profiles of catalysts: b) catalysts with 2 wt% nickel loading and the CZ support; c) co-precipitation catalysts and d) combustion synthesis catalysts. ................................................................. 33
Figure 2.4 – Conversion of a) CO2 and b) CH4 after 0, 400 min, and 800 minutes on stream and at steady state for reactions with diluted catalysts. For 4CP, 6CP, and 10CP samples reaction were terminated before steady state was established. ........................................ 35
Figure 2.5 – XANES and EXAFS spectra of spent catalysts and a Ni foil standard as reference. a) XANES spectra of catalysts with 2 wt% nickel content; b) XANES spectra of CP catalysts; c) XANES spectra of CS catalysts. ................................................................. 40
Figure 2.6 – XRD patterns of spent catalysts: a) 2 wt% samples b) CP samples and c) CS samples. .............................................................................................................................................. 41
Figure 2.7 – SEM images of 2 wt% Ni spent samples and spent samples with carbon nanotubes a) 2DI, b) 2SEA, c) 2CP, d) 4CP, e) 6CP, f) 10CP, g) 2CS and h) 10CS. ...... 42
Figure 2.8 – Relationship between the initial methane conversion and the surface Ni concentration on different catalysts, defined as species that showed a reduction temperature of less than 285 °C for bulk synthesis techniques and less than 235 °C for the surface synthesis techniques. .................................................................................. 48
Figure 2.9 – Correlation between the amount of coke formed vs. the surface oxygen concentration. ............................................................. 53
Figure 3.1 – TPR profiles for CZ, 2NiO/CZ, and 10NiO/CZ................................................. 72
Figure 3.2 – a) Pyridine adsorption over CZ, 2NiO/CZ and 10NiO/CZ at 150 °C followed by FTIR spectroscopy. b) Thermoevacuation of pyridine at 250 °C, 350 °C, and 450 °C. .................................................................................. 73
Figure 3.3 – IR spectra of methane activation over a) 2NiO/CZ at 200 °C, b) 10NiO/CZ at 200 °C, c) 2NiO/CZ at 300 °C, d) 10NiO/CZ at 300 °C. ................................................................. 77
Figure 3.4 – Evolution of surface species over time during methane activation over a) 2NiO/CZ at 200 °C, b) 10NiO/CZ at 200 °C, c) 2NiO/CZ at 300 °C, and d) 10NiO/CZ at 300 °C. ................................................................. 79
Figure 3.5 – Comparison of the evolution of different species over 2NiO/CZ and 10NiO/CZ at 200 and 300 °C: a) formates, b) carbonates, c) aromatics, and d) alkoxy species. .................................................................................. 81
Figure 3.6 – Reaction pathways during methane activation over NiO/CZ catalysts. [O]$^1$ refers to the adsorbed active oxygen species, and [O]$^2$ is the active oxygen species that can selectively oxidize methyl to methoxy species. ......................................................... 84
Figure 3.7 – The normalized relative intensity of alkoxy species compared to the sum of other species in experiment over a) 2NiO/CZ at 200 °C, b) 10NiO/CZ at 200 °C, c) 2NiO/CZ at 300 °C, d) 10NiO/CZ at 300 °C. e) The relative intensity of alkoxy species compared to the sum of other species in different experiments......................................................... 86
Figure 4.1 – TPR profiles for the CZ support, FeO/CZ, CuO/CZ, NiO/CZ, NiCuO/CZ, and NiFeO/CZ catalysts.................................................................................................................. 96
Figure 4.2 – NH$_3$-TPD profiles for the CZ support, FeO/CZ, CuO/CZ, NiO/CZ, NiCuO/CZ, and NiFeO/CZ catalysts............................................................ 98
Figure 4.3 – a) IR spectra taken after pyridine adsorption over the CZ support and catalysts at 150 °C; b) Lewis acid sites concentration measured by pyridine adsorption after desorption at 150, 250, 350, and 450 °C in vacuum......................................................... 100
Figure 4.4 – a) Methane activation over different catalysts measured by operando FTIR spectroscopy. b) Peak area of different surface species (calculated as the sum of area of the symmetric and asymmetric contributions) from methane activation................. 103
Figure 4.5 – Reactivity of a) NiO/CZ, b) NiCuO/CZ, c) NiFeO/CZ, d) CuO/CZ and e) FeO/CZ for selective oxidation of methane to methanol at 250 °C. (Temperature at 250 °C; WHVS at 30.2 h$^{-1}$ with 30% of steam, 1% of oxygen, 20% methane and a balance of nitrogen).) .................................................................................................................. 104
Figure 4.6 – a) Correlation between methanol selectivity and methoxy peak areas from methane activation over different catalysts. b) Correlation between methoxy peak areas from methane activation and concentration of strong Lewis acid sites for different catalysts........................................................................................................ 110
Figure 4.7 – Correlation between methane conversion (%) and the selectivity (%) towards methanol..................................................................................... 113
Figure A.1 – Adsorption/desorption isotherms for the CZ support and DI, SEA, CP and CS catalysts from N$_2$ physisorption measurements. (Open points: adsorption isotherm curves. Solid points: desorption isotherm curves.) ...................................................... 119
Figure A.2 – Accumulative pore volume and pore size distribution for the CZ support and DI, SEA, CP and CS catalysts from N$_2$ physisorption measurements. (Open points: accumulative pore volume as a function of pore width. Solid points: pore size distribution curve.) ........................................................................................................ 120
Figure A.3 – Linear combination fitting of the XANES spectra for fresh catalysts...... 121
Figure A.4 – The standards used for the non-linear combination fitting of XANES data, including NiO standard, NiO 1$^{\text{st}}$ shell standard and LaNiO$_3$ standard. .................. 122
Figure A.5 – EXAFS fits of unreduced catalysts............................................................ 124
Figure A.6 – TPR patterns and peak fittings for different catalysts. ............................... 127
Figure A.7 – Reactivity performance for different catalysts with dilution. (Catalyst diluted with SiC, normalized to 0.2wt% Ni content, 700 °C, 1 atm, 46300 h$^{-1}$ GHSV, 35% CH$_4$, 35% CO$_2$ and 30% N$_2$)......................................................................................... 128
Figure A.8 – SEM images of spent samples........................................................................ 129
Figure A.9 – Adsorption/desorption isotherms for the spent catalysts from N$_2$ physisorption measurements. (Open points: adsorption isotherm curves. Solid points: desorption isotherm curves.)...................................................... 130
Figure C.14 – Correlation between logarithms of MeOH selectivity and CH₄ conversion over Ni-containing catalysts. .......................................................... 162
LIST OF SYMBOLS AND ABBREVIATIONS

CZ  ceria-zirconia
FTIR  Fourier-transform infrared
RWGS  Reverse-water gas shift reaction
DI water  De-ionized water
DI  Dry impregnation
SEA  Strong Electrostatic Adsorption
CP  Co-precipitation
CS  Combustion synthesis
PIXE  Proton induced X-ray emission
XRD  Powder X-ray diffraction
TPR  Temperature programmed reduction
XPS  X-ray photoelectron spectroscopy
XAS  X-ray adsorption spectroscopy
EXAFS  Extended X-ray absorption fine structure
TGA  Thermogravimetric analysis
SEM  Scanning electron microscopy
\( \mu \)  Peak position
\( \sigma \)  Peak width
LPy  Pyridine adsorbed to Lewis acid sites
LAS  Lewis acid sites
NH\(_3\)-TPD  Ammonium temperature programmed desorption
WHHSV  Weight hourly space velocity
SUMMARY

Methane is the major component of natural gas and is vastly available on Earth. However, the transportation of remote natural gas resources requires the construction of pipelines or the production of liquefied natural gas. Both methods significantly increase the cost of natural gas for consumers. Natural gas and by-products are often vented or flared on site, which is not just a waste of resource, but also raises significant environmental concerns. Therefore, the development of chemical processes converting methane to fuels and chemicals is of high importance. The traditional industrial methane conversion to fuels and chemicals involves the production of syngas through steam reforming as an intermediate step. Steam reforming itself requires high temperature, high pressure operation, which is quite energy consuming. Further upgrading of syngas to chemical and fuels often requires purification or separation of the syngas feed stream. Hence, large scales of operation are necessary for the traditional steam reforming-based methane conversion processes to be economically feasible. Therefore, the development of alternative one-step methane valorization routes to value-added products has drawn significant interests.

CZ supported metal oxides catalysts combine Lewis acidity with redox activities and are excellent materials for the catalytic methane conversion. Methane can be activated over Lewis acidic metal oxides through the heterolytically splitting of the C-H bond. The redox active support can promote the oxidant activation, facilitate coke removal and stabilize the small and well-dispersed metal/metal oxides species. Various methane valorization pathways, including the partial oxidation to oxygenates, steam and dry
reforming, and non-oxidative aromatization or alkylation, are catalyzed by the CZ supported metal/metal oxides catalysts.

In Chapter 2, the synthesis-structure relationships for Ni/Ce\textsubscript{2}Zr\textsubscript{1-x}O\textsubscript{2} materials are demonstrated through the thorough characterization of catalysts synthesized differently. The nickel speciation and reducibility of the materials are revealed by N\textsubscript{2} physisorption, XRD, XAS, XPS and H\textsubscript{2}-TPR experiments. The structural properties are further related to methane dry reforming performances. All catalysts are active for methane dry reforming and retain partial activity at a steady state. The conversion of both CH\textsubscript{4} and CO\textsubscript{2} correlates linearly with the concentration of accessible Ni, which indicates that methane activation primarily occurs on Ni and is the rate-limiting step of the reaction. The major challenge for industrial applications of methane dry reforming using Ni-based catalysts is the deactivation of the catalyst. The Ni particle growth during reactions can be suppressed by introducing SMSI, avoiding isolated Ni precursor species with insufficient ability to anchor on the support, and encapsulating the Ni particles. The concentration of active surface oxygen is a good descriptor for coke resistance. The dominant deactivation mechanism for CS catalysts appears to be the encapsulation of Ni particles by the support. The support capsules likely allow some reagents to access the Ni particles in the core because the catalysts retained partial activity. In summary, I decoupled complex interplay between the three deactivation mechanisms over catalysts from different synthesis methods, which provides important insights for the rational design of methane dry reforming catalysts.

While understanding the synthesis-structure relationship allows controlling the physiochemical properties of active sites, rational catalyst design requires a fundamental understanding of how active sites facilitate reaction chemistries. In Chapter 3, methane
activation over NiO/CZ catalysts is investigated using *in-situ* FTIR spectroscopy. The NiO/CZ catalysts are active for methane activation and produces various carbonaceous surface intermediates. A large variety of surface species, including formates, carbonates, aromatics, aldehydes and alkoxy intermediates are formed during methane activation and generate complex features in the IR band. A novel data analysis algorithm is developed to deconvolute the contribution from different surface species based on non-linear regression fitting. By comparing methane activation over different NiO/CZ catalysts at different temperatures, it is concluded that the formation of CO$_2$ precursor such as formates and carbonates are driven the concentration of the adsorbed surface oxygen in the catalyst, and the production of aromatic and alkoxy intermediates are catalyzed by the NiO sites. The selectivity towards alkoxy intermediates, which is precursors to alcohol production, is maximized with a controlled balance of the active oxygen species and the accessible NiO active sites.

The observation of surface alkoxy intermediates during methane activation over NiO/CZ catalysts suggests it is possible to achieve the direct selective oxidation of methane to methanol. In Chapter 4, I demonstrate the selective oxidation of methane to methanol over MO$_x$/CZ (M= Ni, Cu, Fe) catalysts. The Lewis acidity and redox properties of the catalysts are assessed using XRD, XAS, H$_2$-TPR, NH$_3$-TPD and pyridine adsorption followed by FTIR spectroscopy. The quantity of methoxy intermediates formed during methane activation is evaluated using *in-situ* transmission FTIR spectroscopy. With the addition of oxygen and steam, methane can be directly converted to methanol at steady state with CO$_2$ and coke as the other products. The concentration of strong Lewis acid sites is a good descriptor for the quantity of methoxy intermediates formed during methane
activation, which in turn governs the selectivity towards methanol. The methane conversion inversely relates to the methanol selectivity, suggesting the possibility of enhancing the methanol selectivity by reaction engineering approaches.
CHAPTER 1. INTRODUCTION

1.1 Supply and Issues of Methane

Methane is the most abundant form of fossil carbon on Earth appearing as the main component of natural gas. Recent discoveries of shale gas reserves significantly increased the availability of methane.\textsuperscript{1-3} However, due difficulties in the transport of methane, a large portion of the natural gas resources is considered economically ‘stranded’. The low energy density by volume of methane requires the transportation of natural gas resources through pipelines.\textsuperscript{4} As the pipeline construction is very costly, if a resource too remote from a market for natural gas, then there is no economical drive for the pipeline construction, leaving the resource stranded.\textsuperscript{5} Another way for transportation of natural gas is through liquefied natural gas (LNG). However, methane itself is a gas under standard conditions with a boiling point at 111.6 K. The production of liquefied natural gas (LNG) requires expensive downstream separation process to remove impurities. Additionally, cryogenic storage is required for the entire LNG transportation process. Both factors significantly increase the production cost of LNG.\textsuperscript{6}

Hence, the development of chemical process using methane as a platform molecule is of high importance.\textsuperscript{4} Traditionally, industrial methane conversion to fuels and chemicals involves two steps: 1) methane is converted to syngas through steam reforming and 2) the syngas is further converted to higher hydrocarbons by Fischer-Tropsch synthesis or used for methanol synthesis.\textsuperscript{7, 8} The two-step high temperature, high pressure process requires large scale operations for economic feasibility.\textsuperscript{4} In particular, this prohibits effective use of the stranded natural gas resources, which accounts for a large portion of the world
reserves. Therefore, the development of alternative one-step methane valorization routes to value-added products has drawn significant interests.\textsuperscript{9-12} Considering the vast availability of natural gas resources, the development of such processes has the potential for revolutionizing the chemical supply chain.

1.2 Catalytic Conversion of Methane

Over the years, many efforts have been put into the task of developing efficient methods for upgrading methane into other value-added products.\textsuperscript{9-14} Potential methane valorization pathways include the partial oxidation to oxygenates, such as methanol, formaldehyde and formic acid, oxidative coupling to ethane, ethylene or propylene, and aromatization or alkylation (Figure 1.1).

![Figure 1.1 – The possible upgrading routes converting methane to fuels and chemicals.](image)

Non-oxidative alkylation and aromatization are endothermic. Hence thermodynamics require these reactions to be operate at high temperatures to achieve decent methane.\textsuperscript{9, 14, 15} At high temperatures, the formation of coke is thermodynamically favored, hence catalysts for these reaction pathways often deactivates from coke formation.
Guo et al reports catalysts with single Fe sites confined by SiO$_2$ or SiC lattice that can steadily convert methane to ethylene, benzene and naphthalene at 1000 °C quite selectively without much coke formation. A previous study from our group showed that well-dispersed NiO clusters supported by ceria-zirconia (CZ) can convert methane to ethane, ethylene and aromatics close the thermodynamic limits at 350 – 500 °C.

The introduction of oxidants to the reaction systems remediates the thermodynamic limit in non-oxidative alkylation and aromatization reactions. Unfortunately, the presence of O$_2$ can also cause the overoxidation of methane to CO$_2$ and H$_2$O. The pioneering work by Keller and Bhasin tested a wide range of metals supported by alumina for the oxidative coupling of methane to ethylene and acetylene at 800 °C. Since then, numerous materials have been studied for the improvement of the selectivity towards C2 hydrocarbons. Catalysts based on strong basic oxides, such as MgO and La$_2$O$_3$ are active for direct oxidative coupling of methane. The inevitable formation CO and CO$_2$ significantly reduces the selectivity towards C2 products especially at high conversion. As the reaction is favorable at high temperature (>700°C), catalysts often suffer from stability issues.

Both dry and steam reforming of methane produce syngas. Similar to the non-oxidative alkylation and aromatization reactions, methane reforming is highly endothermic and is limited by thermodynamics. The reaction requires high temperature (>800 °C) even with the presence of catalysts. Group VIII transition metals comprise most catalysts for steam reforming. In industry, the reforming reactions are typically carried out in a heated furnace in the presence of a nickel catalyst. Noble metals such as Ru, Rh, Pd, Ir, and Pt are also active, but these metals are normally too expensive for industrial applications.
The formation of coke is thermodynamically favored at high temperature, which can cause rapid deactivation of the catalyst.

The direct selective oxidation of methane to methanol is considered as the ‘holy grail’ in C1 chemistry. In industry, methanol is synthesized from syngas at elevated pressure (50 to 100 bar) and temperature (200 to 300 °C) over Cu/ZnO/Al₂O₃ catalysts. Over the years, many efforts have been made to develop efficient methods for direct conversion of methane into methanol. Studies have shown that it is possible to convert methane to methanol directly using more selective oxidants such as H₂O₂ and N₂O. The selective oxidation of methane to methanol is also possible using photocatalysis or plasma reactions. Methane monooxygenase enzymes with iron or copper active centers showed great selectivity for converting methane to methanol under ambient conditions. Inspired by these enzymes, extensive studies on copper-containing zeolites have shown the possibility of converting methane directly into methanol using O₂ as the oxidant via chemical looping processes. Such processes are usually composed of three steps: the activation of catalysts under O₂ at high temperature; the activation of methane at moderate temperatures; and the introduction of steam to release the methanol formed. Since chemical looping processes for this reaction have been shown to be uneconomical, the development of steady state systems is critical.

All the routes discussed above have certain drawbacks and room for improvement. With the large reserve of methane available, it provides enough motivation for developing more effective upgrading routes that converts methane into more valuable products.

1.3 Ceria Supported Metal/Metal Oxides as Catalysts for Methane Conversion
Transition metal complexes can serve as active sites for methane activation at rather mild temperatures,\textsuperscript{1,40-43} and promote different mechanisms of methane activation.\textsuperscript{1,44} Over Lewis acidic metal oxides, methane can be activated through heterolytic splitting of the C-H bond, leading to the formation of methyl and hydroxyl species.\textsuperscript{40,45} The activation of methane is also affected by the presence of other species. Studies have shown that when the catalyst is in contact with steam, the formation of metal hydroxides will promote selective oxidation of methane over Ni, Cu and Fe complexes.\textsuperscript{46-50} Our group have performed a screening of metal oxides for methane activation capability using transmission FTIR spectroscopy, where NiO is found the most capable not just in activating methane through heterolytically splitting of the C-H bond, but also in coupling activated methyl species to produce higher alkyl species.\textsuperscript{15}

Redox-active ceria and ceria-based mixed oxides, such as CZ, are promising catalyst support materials for bifunctional supported metal oxides catalysts for catalytic methane conversion. The oxidation state of cerium can shift between Ce(III) and Ce(IV), which allows for easy oxygen storage and removal.\textsuperscript{51} Because of this property, cerium-based oxides are widely used for applications in automotive exhaust converters, hydrocarbon reforming, and water gas shift reactions.\textsuperscript{52-55} By doping zirconia into the ceria support, a CZ solid solution is formed, which greatly enhances thermal stability and oxygen storage capacity and increases the accessibility of bulk lattice oxygen.\textsuperscript{56-58} Finally, the use of CZ introduces a strong metal-support interaction, which stabilizes small metal/metal oxide clusters on its surface.\textsuperscript{15,59,60}

CZ supported metal oxides catalysts combine Lewis acidity and redox activity, which are materials with great performance for methane conversion. A recent surface science
study showed that NiO/CZ can catalyze the selective oxidation of methane to methanol.\textsuperscript{50} Zuo et. al. developed an inverse CeO\textsubscript{2}/CuO catalyst that is also capable of converting methane to methanol.\textsuperscript{46, 49} Ni/CZ catalysts are extensively studied for steam, dry and autothermal reforming of methane.\textsuperscript{61-73} A previous study from our group showed NiO/CZ can catalytically convert methane to ethane, ethylene and aromatics through non-oxidative coupling.\textsuperscript{15} The materials can also catalyze the partial/complete oxidation of methane to CO or CO\textsubscript{2}.\textsuperscript{65, 74-83}

1.4 Understanding Methane Activation using \textit{operando} FTIR Spectroscopy

The main challenge in utilizing methane as a platform chemical lies in methane activation, i.e., the cleavage of the 1\textsuperscript{st} C-H bond in methane.\textsuperscript{1, 84-86} Methane is smallest hydrocarbon molecule and is the least active. It is a symmetric molecule with a stable tetrahedral structure and has an extremely high C-H bond energy at 439 kJ/mol.\textsuperscript{1-4} Three major methane activation mechanisms, namely Lewis acid/base pair or σ-bond metathesis, oxidative addition and electrophilic substitution, have been proposed in both heterogenous and homogeneous metal-based catalytic systems (Figure 1.2).\textsuperscript{1, 40, 87-89} Coperet et al. proposed the activation of methane over Lewis acidic γ-alumina through the Lewis acid/base pair activation, where methane is activated by the heterolytically splitting of the C-H bond.\textsuperscript{90} The oxidative insertion, where a hydrate and a methyl group are bonded to the metal species through activation, are more commonly observed for late transition metals.\textsuperscript{87, 91} The Shilov system uses high oxidation, electron-deficient, and coordinatively unsaturated species, such as Pt\textsuperscript{IV} salts, to activate methane through electrophilic substitution in homogeneous catalytic systems.\textsuperscript{92}
Figure 1.2 – Mechanism for methane activation.\textsuperscript{1,84}

Fundamental understandings of reaction mechanisms are essential for the development of more productive catalytic processes and are often hindered by challenges in understanding the catalyst surface as well as unravelling the complex surface reaction networks.\textsuperscript{93} Fortunately, the activation of methane produces various surface carbonaceous species, which vibrate at different frequencies, making Fourier-transform infrared (FTIR) spectroscopy a perfect tool for understanding the methane activation mechanism over catalyst surfaces.\textsuperscript{94} The Beer-Lambert Law grants a linear response between the concentration of surface species and the peak area from transmission FTIR spectroscopy allowing the quantitative analysis of the evolution of surface species over time. The Ribeiro Group demonstrated a sophisticated design of an \textit{operando} transmission IR cell, which enables the monitoring of catalytic surfaces using FTIR spectroscopy under reaction conditions.\textsuperscript{95}

In summary, \textit{operando} FTIR spectroscopy is powerful tool for unravel the methane activation as well as the subsequent surface reaction networks during methane activation. Understanding methane activation mechanisms can provide important insights for the better design of CZ supported metal oxide catalysts converting methane to value-added products.
1.5 Objectives and Organization

The overall objective of this work is to conduct a systematic investigation of CZ supported metal/metal oxide catalysts to provide design principles for catalytic methane conversions.

First, I will demonstrate the synthesis-structure relationship through thorough characterization of NiO/CZ catalysts synthesized differently. Specifically, the impact of synthesis on the nickel speciation and the reducibility of catalysts are discussed in detail. The structural properties are further related to methane dry reforming performances, suggesting that the Ni morphology and the oxygen storage capacity are the key factors shaping the deactivation behavior.

While understanding the synthesis-structure relationship allows for controlling the physiochemical properties of active sites, rational catalyst design requires a fundamental understanding of how active sites facilitate reaction chemistries. Next, I will go through the investigation of methane activation over NiO/CZ catalysts using operando FTIR spectroscopy. Using a novel data analysis algorithm based on non-linear regression fitting, the evolution of different surface species is deconvoluted to elucidate the surface reaction pathways during methane activation, showing that different reactivity can be achieved by fine tuning the nature of active sites and reaction conditions.

The observation of surface alkoxy intermediates during methane activation suggests it is possible to achieve direct selective oxidation of methane to methanol over NiO/CZ catalysts. Finally, I will demonstrate the selective oxidation of methane to methanol over MOₓ/CZ (M=Ni, Cu, Fe) catalysts. By carefully balancing the accessible LAS and the
active oxygen species, continuous conversion of methane to methanol is realized. The strong LAS concentration controls the formation of methoxy intermediates during methane activation, which in turn governs the selectivity towards methanol. Together, these three studies lay a solid foundation for the rational design of catalysts for methane upgrading reactions.
CHAPTER 2. NICKEL SPECIATION AND METHANE DRY REFORMING PERFORMANCE OF Ni/CEₓZr₁₋ₓO₂ PREPARED BY DIFFERENT SYNTHESIS METHODS

2.1 Backgrounds

Methane dry reforming with carbon dioxide (Reaction 2.1) has drawn much attention as it utilizes these two greenhouses gases at the same time. The reaction produces syngas, which is an essential building block in the production of value-added products, such as oxygenated \(^{96}\) and long-chain hydrocarbons \(^{97}\). Compared to syngas produced from methane steam reforming, syngas produced from dry reforming has a lower H\(_2\) to CO ratio of approximately 1:1, which makes it useful for Fischer-Tropsch synthesis of long-chain hydrocarbons. \(^{8}\)

\[
\text{CO}_2 + \text{CH}_4 \rightarrow 2\text{CO} + 2\text{H}_2 \quad \Delta H^\circ = +276 \text{ kJ/mol} \quad \text{(Reaction 2.1)}
\]

Although dry reforming of methane is advantageous for utilizing and eliminating greenhouse gases, the concept is not yet economically feasible for industrial applications. Noble metal-based catalysts, such as Rh, Ru, and Pt, have shown steady conversion and decent resistance to coke formation but are often found to be uneconomical. \(^{98,99}\)

Ni-based catalysts are applied in industrial processes for steam reforming of methane and have comparable activities to noble metals for dry reforming. \(^{73,100-103}\) However, such catalysts often suffer from rapid deactivation under reaction conditions. Carbon deposition leads to severe deactivation of the catalysts and an increased pressure
drop over the catalyst bed.\textsuperscript{104-106} Methane decomposition (Reaction 2.2) and CO disproportionation (Boudouard reaction, Reaction 2.3) contribute to the majority of coke formed during the reaction. Additionally, since the reaction operates at high temperatures (>1000 K), agglomeration of active nickel species is another key deactivation mechanism of the catalyst.\textsuperscript{107, 108} The encapsulation and decoration of the active Ni particles by certain supports, such as alumina and ceria,\textsuperscript{59, 109, 110} were reported in multiple studies, which also led to the loss of activity. Sophisticated catalyst design is required to resolve the fast and severe deactivation of Ni-based catalysts before the reaction can be implemented industrially. Fortunately, studies have shown that the catalyst durability can be improved by tuning various design parameters, including the choice of the support, and the size of nickel particles.\textsuperscript{111, 112}

\begin{equation}
\text{CH}_4 \rightarrow \text{C}_{\text{solid}} + 2\text{H}_2 \quad \Delta H^\circ = +17.9 \text{ kJ/mol} \quad \text{(Reaction 2.2)}
\end{equation}

\begin{equation}
2\text{CO} \rightarrow \text{C}_{\text{solid}} + \text{CO}_2 \quad \Delta H^\circ = -41.2 \text{ kJ/mol} \quad \text{(Reaction 2.3)}
\end{equation}

Basic\textsuperscript{113, 114}, acidic\textsuperscript{101, 115}, inert\textsuperscript{116, 117} and redox active supports\textsuperscript{64} have been studied to improve the activity of nickel-based catalysts for methane dry reforming. Redox active ceria and ceria-based mixed oxides are of particular interest because the interconversion of Ce(III) and Ce(IV) allows for facile oxygen storage and removal.\textsuperscript{51} Because of this property, cerium-based oxides are widely used for applications in automotive exhaust converters, hydrocarbon reforming, and water gas shift reactions.\textsuperscript{52-55} By doping zirconia into the ceria support, a CeO\textsubscript{2}-ZrO\textsubscript{2} solid solution is formed (CZ), which greatly enhances thermal stability and oxygen storage capacity and increases the accessibility of bulk lattice oxygen.\textsuperscript{56-58} Using ceria as a support for methane dry reforming reaction increases the
conversion, lowers the carbon formation, and enhances the reverse-water gas shift reaction (RWGS). The surface oxygen vacancies of the CZ support promote the activation of CO$_2$ during reaction. Mobile oxygen species stored in the CZ support facilitate the removal of deposited coke, and thus these species extend catalyst lifetime. Additionally, CZ supports interact strongly with the Ni metal, which stabilizes small surface nickel particles.

Catalyst synthesis and composition strongly affect the physicochemical properties, including metal dispersion, strength of the metal-support interactions and oxygen storage capacity. Strong electrostatic adsorption uses Coulomb forces to deposit dissolved charged precursor metal complexes onto the support, which results in a better dispersion of the metal. These forces are controlled through the pH of the synthesis solution. Co-precipitation produces solid oxide solutions of Ni with Ce and Zr. The Ni is incorporated into the ceria-zirconia support with stronger metal-support interactions. Combustion synthesis combines a fuel, such as citric acid, with a catalyst precursor solution. The solution is evaporated, and a polymeric resin is formed, which is burned quickly. The resulting catalytic material has nanostructured particles. The fast combustion of the polymeric resin traps the mixed metal oxides in kinetically-formed (non-thermodynamically equilibrated) crystal structures and introduces more defect sites and oxygen vacancies to the catalyst.

The major challenge in the industrial application of dry reforming using Ni-based catalyst lies in the deactivation issue. Studies on single synthesis method often observed a combination of multiple deactivation pathways and hence could only draw qualitative structure-performance relationships.
synthesis methods provided information on the synthesis-structure relationship, but focused less on the deactivation of the catalyst. This lack of systematic insight into the synthesis-structure-performance relationships limits the design of catalysts with better performance.

Herein, I report the effect of catalyst synthesis method and nickel content on the structure, activity and stability of Ni/CZ catalysts during methane dry reforming and provide novel insights on the design of better catalysts. Ni/Ce0.83Zr0.17O2 (Ni/CZ) catalysts prepared by dry impregnation, strong electrostatic adsorption, co-precipitation and combustion synthesis are thoroughly characterized and their performance is evaluated.

2.2 Experimental

2.2.1 Materials

Ni(NO3)2·6H2O (99.999% trace metals basis), Ce(NO3)3·6H2O (99.999% trace metals basis), ZrO(NO3)2·xH2O (99.999% trace metals basis), ammonium hydroxide solution (ACS reagent, 28.0-30.8 NH3 basis), sodium hydroxide (ACS reagent, ≥ 97%, pellet) and citric acid (ACS reagent, 99.5% purity) were purchased from Sigma Aldrich. Gases used for reactivity tests, CO chemisorption experiments, and temperature programmed reduction (TPR) experiments were obtained from Airgas and included methane (research grade), nitrogen (ultra-high purity, UHP), CO2 (UHP), argon (UHP), 10% Hz/Ar (UHP), helium (UHP), and 10% O2/He (UHP).

2.2.2 Catalyst synthesis

2.2.2.1 Ceria-Zirconia Support
The CZ support was synthesized following procedure described in previous study by the group. Cerium and zirconium nitrates were dissolved in DI water. The pH of the precursor solution was adjusted to 3.0 by further diluting the solution with deionized water (DI water). The solution was then added dropwise to an ammonium hydroxide solution at a pH of 11.9. An excess amount of ammonium hydroxide solution was used to ensure instantaneous and complete precipitation of the metal cations. The suspension was filtered, and the collected precipitate was dried in an oven at 110 °C overnight. The cerium-zirconium precipitate was then calcined at 450 °C for 4 hours under air flow.

2.2.2.2 Synthesis of Dry Impregnation (DI) Catalysts

The synthesis procedure for the DI sample was adapted from previous studies by the group. The pore volume of the CZ support was measured with N\textsubscript{2} physisorption. To form the precursor solution, nickel nitrate was dissolved in a volume of DI water equal to the pore volume of the CZ support used in the synthesis. The precursor solution was added dropwise to the support and the mixture was vigorously agitated after each drop was added. To ensure pore saturation of the support after the entire solution was added, the mixture was further agitated for 10 minutes using a vortex mixer. The catalyst was then dried in an oven at 110 °C overnight and calcined at 450 °C for 4 hours under air flow. The collected powder was ground and sieved to a particle size between 38 and 75 µm. This catalyst is denoted as 2DI.

2.2.2.3 Synthesis of Strong Electrostatic Adsorption (SEA) Catalysts

The SEA catalyst was synthesized following procedures described in literature. The CZ support was suspended in ammonium hydroxide solution such that the surface area
available in the solution was 1000 m$^2$/L. Nickel nitrate was then added to the mixture and constant stirring. The pH of the solution was monitored every 5 minutes and additional ammonium hydroxide solution was added to maintain a constant pH of 10.5. The deposition of nickel cations onto the support was considered complete once the pH remained constant for 5 consecutive measurements. The catalyst was filtered and dried in an oven at 110 °C overnight. Then, it was calcined at 450 °C for 4 hours under air flow. The collected powder was ground and sieved to a particle size between 38 and 75 µm. This catalyst is denoted as 2SEA.

2.2.2.4 Co-precipitation (CP) Catalysts

The CP samples were synthesized following procedures described in literature. Nitrate precursors of nickel, cerium, and zirconium were dissolved in DI water. The amount of each precursor used was calculated to achieve the desired final catalysts composition (2, 4, 6, and 10 wt% Ni/Ce$_{0.83}$Zr$_{0.17}$). The solution was then added dropwise into a NaOH solution at pH 13. An excess of NaOH solution was used to ensure complete precipitation of the nickel cations. The precipitated catalyst was filtered, fully washed, and then placed in an oven at 110 °C to dry overnight. After calcination at 450 °C for 4 hours under air flow, the catalyst was ground and sieved to a particle size between 38 and 75 µm. These catalysts are denoted as 2CP, 4CP, 6CP and 10CP for 2, 4, 6, and 10 wt% Ni content, respectively.

2.2.2.5 Combustion Synthesis (CS) Catalysts

The CS samples were synthesized following procedures described in literature. Nitrate precursors of nickel, cerium and zirconium and citric acid were dissolved in 40 ml
of DI water. The amount of each precursor used was calculated to obtain catalysts with the desired Ni, Ce and Zr content. The amount of citric acid added was 1/3 the concentration of nitrate ions in the solution to achieve a stoichiometric combustion. The solution was then heated to evaporate the water. Once the water was fully evaporated, the citric acid formed a polymeric resin. Further heating of the resin to 156 °C liquified the resin and led to fast and vigorous combustion of the mixture, fully consuming the resin. The resulting powder catalysts were denoted as 2CS, 4CS, 6CS and 10 CS for 2, 4, 6, and 10 wt% Ni content, respectively.

2.2.3 Physicochemical Characterization

2.2.3.1 Composition and morphology

The composition of each catalyst was measured utilizing Proton Induced X-ray Emission (PIXE) at Elemental Analysis Incorporated.

\[ N_2 \] physisorption measurements were performed using a Micromeritics ASAP 2020 instrument. Approximately 50 mg of sample was used in each measurement. Samples were degassed at 400 °C for 4 h prior to analysis. Reported surface areas were calculated using the BET method.\textsuperscript{133} The pore volume and pore size were calculated using the BJH method applied to the desorption branch of the isotherm.\textsuperscript{134}

Powder X-ray diffraction (XRD) patterns for both unreduced and spent catalysts were measured on a X’Pert PRO Alpha-1 diffractometer equipped with an X’celerator module. Diffractograms for unreduced catalysts were obtained with Cu K\( \alpha \) radiation for 2\( \theta \) =10−80° with a step size of 0.0167°. Diffractograms for spent samples were collect with
Cu Kα radiation for 2θ =35−65° with a step size of 0.0167°. The crystal sizes within the CZ support were calculated using Scherer’s equation.

2.2.3.2 CO chemisorption and temperature programmed reduction (TPR)

CO chemisorption and TPR experiments were carried out on a Micromeritics AutoChem II 2920 instrument equipped with a cold trap and a TCD detector. For each CO chemisorption experiment, approximately 100 mg of sample was used. The sample was first degassed in flowing helium at 450 °C for 1 hour. Then, a reductive pretreatment was performed by flowing 30 cm³/min of 10% H₂ in helium over the sample. The sample was heated to 600 °C at 5 °C/min and then held at 600 °C for 2 h under the H₂ flow, which simulated conditions analogous to those of the reactivity tests. The sample was then cooled to 40 °C under 40 cm³/min helium flow and held at 40 °C for 1 h. The CO chemisorption was carried out by injecting finite quantities of CO in pulses until no further CO uptake was observed. The chemisorbed CO was then desorbed during a temperature programmed desorption by heating the sample under 40 cm³/min helium flow to 450 °C at 5 °C/min and holding the sample at 450 °C for 30 minutes.

For the TPR experiments, approximately 40 mg of each sample was loaded to the instrument. The catalysts were pre-oxidized to establish a well-defined, fully oxidized state for the subsequent TPR analysis. The pre-oxidation was carried out by flowing 30 cm³/min of 10% O₂ in He over the sample at 450 °C for 2 hours. The catalysts were then cooled to 50 °C in helium flow. The TPR analyses were carried out by flowing 10% H₂ in helium at 30 cm³/min over the sample while heating to 900 °C with a 10 °C/min ramp rate. A cold
trap in a dry ice-acetone bath was used during the experiment to eliminate the interference from water in the TCD detector.

2.2.3.3 X-ray photoelectron spectroscopy (XPS) measurements

The XPS experiments were carried out using a Thermo K-α XPS instrument. The X-ray source of the instrument was a monochromatic small-spot aluminum anode (Al Kα, hv = 1486.6 eV). The measurements were carried out with a background pressure of 4.3 × 10⁻⁸ bar. The sample stage, which contains copper, was used as internal calibration standard for binding energies. The peak fittings for Ni were performed over the range of 850 – 870 eV. The signals above 870 eV were not included in the fits due to a strong overlap with Ce 3d peaks.

2.2.3.4 X-ray adsorption spectroscopy (XAS) measurements

Ex-situ XAS data for all unreduced and spent catalysts were collected at the 8-ID beamline at the Brookhaven National Lab. Samples were pressed into self-supported wafers. The beam energy was internally calibrated with a metallic Ni reference foil and spectra were collected in fluorescence mode. Each sample was measured multiple times at the Ni K-edge. Standard samples of nickel oxide, metallic nickel foil, NiAl₂O₄, and NiLaO₃ were also measured at the beamline for reference.

An average of three spectra collected for each sample was used for further analysis. The averaged spectra were normalized using Athena software. The edge energy, E₀, was identified as the maximum of the first derivative of the X-ray absorption near edge structure (XANES) spectrum. A linear combination fit using NiO, Ni foil and NiLaO₃ standards to
each spectrum was performed to determine the composition of the nickel species in each sample.

Extended X-ray absorption fine structure (EXAFS) data were converted to k space with $k^2$ weighting. The Fourier transform of the $k^2$ weighted EXAFS oscillation ($\Delta k = 3−13$) converted the data from k space to R space to obtain a radial distribution function. For unreduced catalysts, the first two shells in R space were fitted to the Ni-O shell and Ni-Ni shell of NiO calculated from FEFF using Arthemis package.\textsuperscript{135} The amplitude reduction factor ($S_0^2$) was determined from the reference NiO spectrum. The coordination number from the fit was used to estimate the particle size using relationships by Kuzmin et al.\textsuperscript{136}

2.2.4 Reactivity tests

Reactivity tests of all catalysts were carried out under atmospheric pressure in a laboratory scale reactor. Brooks mass flow controllers (Model 4850) were used to control the flowrates of gases (N$_2$, CO$_2$ and CH$_4$) fed into the reactor. A quartz tube reactor with an inner diameter of 10.5 mm was placed vertically inside a tube furnace (Lindberg Minimite furnace). A mixture of catalysts and silicon carbide was loaded on a quartz frit in the middle of the reactor. The effluent was analyzed using an online GC (Bruker 450 RGA) equipped with 2 TCD detectors and an FID detector. The effluent stream was sampled every 20 min. Hydrogen, carbon dioxide, nitrogen, methane and carbon monoxide were quantified with the two TCD detectors, and methane quantification was confirmed with the FID detector. A Hayesep Q column and a Molsieve 5A column were used in series to isolate the hydrogen for analysis in the first TCD. The second TCD was used for
permanent gas analysis with a Hayese T column, a Hayesep Q column and a Molsieve 13x column in series. The FID channel was connected to a BR-1 column.

Calibrations for H$_2$, CO$_2$, CH$_4$, CO, and N$_2$ were carried out by feeding various concentrations of each species through an empty reactor under ambient pressure. Linear responses between the peak intensity and concentration of each species were observed.

The catalysts were reduced via a pretreatment step prior to the reaction. The samples were heated to 600 °C at 5 °C/min and held for 2 h in a 20% H$_2$/N$_2$ gas mixture. After the pretreatment, samples were heated to 700 °C for the reactivity tests. Catalysts were diluted with silicon carbide to normalize the same nickel content to 0.2 wt% within the catalyst/SiC bed. For each experiment, 200 mg of the diluted catalysts was used equivalent to a weight hour space velocity ( WHSV) of 19,700 h$^{-1}$ with respect to the nickel content. The feed consisted of 35% CH$_4$, 35% CO$_2$ and 30% N$_2$ with a total flow rate of 100 mL/min. The reactions were run until a steady state was achieved.

2.2.5 Spent catalyst characterization

Thermogravimetric analysis (TGA) was carried out using a TA Instruments SDT Q600 Thermogravimetric Analyzer to determine the amount of carbon deposit on spent catalysts. For 2DI, 2SEA and 2CP samples, approximately 5-10 mg were used. For the 2CS samples, 2 mg was loaded due to their low density. The samples were first heated to 30 °C and held at that temperature for 15 minutes to establish a stable baseline. Then, they were heated to 150 °C at 10 °C/min ramp rate and was held at 150°C for 30 mins under N$_2$ flow. Finally, the sample was heated to 900 °C at a rate of 10 °C/min under air flow.
Scanning electron microscopy (SEM) images were obtained on a Hitachi 8230. The samples were pressed onto a copper base, and images were collected at an energy level of 1 keV.

2.3 Results

2.3.1 Physiochemical Properties of Catalysts

2.3.1.1 Composition and morphology

According to PIXE analysis, all catalysts had similar Ce/Zr ratios, and the nickel fractions were within the expected 10% error of the targeted values (Table 2.1).

Comparison of the nitrogen physisorption isotherms of 2DI and 2SEA with the CZ support showed that Ni deposition onto the support reduced the surface area and pore volume by 17%, and 25%, respectively (Table 2.1, Figure A1 and A2). The 2DI, 2SEA, 2CP and 2CS catalysts had comparable surface areas (varying from 55 to 75 m²/g), and 2CP had the largest surface area. Contrarily, the 2CP catalysts had significantly lower pore volumes compared to catalysts made by other synthesis techniques indicating the presence of smaller pores. In general, bulk synthesis techniques (CS and CP) exhibited narrower pore widths compared to surface synthesis techniques (DI and SEA).

Among the CP samples, 10CP had the lowest surface area and pore volume along with the largest pore width. The surface area, pore volume and pore width for 2CP, 4CP, and 6CP were similar. The surface area and pore volume decreased with increasing nickel loading for the CS samples. 10CS had 30% less surface area and 40% less pore volume
than 2CS. However, the pore width for the CS samples were relatively constant and independent of nickel loading.

Table 2.1 – Physiochemical properties of ceria zirconia (CZ), 2 wt% Ni/CZ synthesized by dry impregnation (2DI), 2 wt% Ni/CZ synthesized by strong electronic adsorption (2SEA), 2, 4, 6, and 10 wt% Ni in CZ synthesized by co-precipitation (2CP, 4CP, 6CP, 10CP), and 2, 4, 6, and 10 wt% Ni in CZ produced by combustion synthesis (2CS, 4CS, 6CS, 10CS).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CZ</th>
<th>2DI</th>
<th>2SEA</th>
<th>2CP</th>
<th>4CP</th>
<th>6CP</th>
<th>10CP</th>
<th>2CS</th>
<th>4CS</th>
<th>6CS</th>
<th>10CS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel content (wt. %)</td>
<td>N/A</td>
<td>2.08</td>
<td>2.11</td>
<td>2.23</td>
<td>3.62</td>
<td>5.95</td>
<td>9.77</td>
<td>2.06</td>
<td>4.30</td>
<td>6.55</td>
<td>9.74</td>
</tr>
<tr>
<td>Surface nickel content (wt. %)</td>
<td>2.73</td>
<td>2.92</td>
<td>1.58</td>
<td>4.80</td>
<td>5.92</td>
<td>14.7</td>
<td>1.98</td>
<td>3.53</td>
<td>5.27</td>
<td>8.67</td>
<td></td>
</tr>
<tr>
<td>BET surface area (m²/g)</td>
<td>80.5</td>
<td>66.2</td>
<td>67.4</td>
<td>73.5</td>
<td>77.3</td>
<td>83.3</td>
<td>28.2</td>
<td>54.7</td>
<td>37.8</td>
<td>43.5</td>
<td>38.7</td>
</tr>
<tr>
<td>Pore volume (cm³/g)</td>
<td>0.14</td>
<td>0.109</td>
<td>0.108</td>
<td>0.049</td>
<td>0.052</td>
<td>0.047</td>
<td>0.037</td>
<td>0.108</td>
<td>0.081</td>
<td>0.087</td>
<td>0.060</td>
</tr>
<tr>
<td>Pore width (nm)</td>
<td>9.83</td>
<td>8.29</td>
<td>7.88</td>
<td>4.07</td>
<td>3.72</td>
<td>3.43</td>
<td>4.52</td>
<td>5.17</td>
<td>5.45</td>
<td>5.36</td>
<td>5.33</td>
</tr>
<tr>
<td>Metal dispersion (%)</td>
<td>N/A</td>
<td>9.3</td>
<td>16.2</td>
<td>4.37</td>
<td>8.32</td>
<td>6.85</td>
<td>0.77</td>
<td>15.3</td>
<td>7.55</td>
<td>5.84</td>
<td>2.12</td>
</tr>
<tr>
<td>Ce₉ZrₓO₂ crystalline size (nm)</td>
<td>7.31</td>
<td>7.47</td>
<td>7.70</td>
<td>5.42</td>
<td>6.22</td>
<td>7.94</td>
<td>6.08</td>
<td>4.99</td>
<td>4.71</td>
<td>4.87</td>
<td>4.50</td>
</tr>
</tbody>
</table>

* From PIXE analysis
* From XPS analysis
* From desorption isotherms measured by N₂ physisorption using the BET method
* From desorption isotherms measured by N₂ physisorption using the BJH method
* From CO chemisorption after a 2-hour reduction in 10% H₂ at 600 °C, assuming a 1:1 CO to Ni stoichiometric ratio
* From XRD using Scherrer equation for the Ce₉ZrₓO₂ (111) peak at 28.5°

2.3.1.2 X-ray Diffraction (XRD)

The diffraction peaks at 28.8°, 33.4°, 47.9°, 56.9°, 70.1° and 78° in the diffractograms of the CZ support were consistent with those of ceria-zirconia solid solutions (Figure 2.1). All samples lacked the characteristic diffraction peaks for pure ceria and pure zirconia, indicating that the CZ supports were homogeneous solid solutions without any significant phase separation. In unreduced catalysts, characteristic
diffraction peaks for NiO were only observed for 10CP, indicating that the small NiO crystal sizes in the other samples were below the detection limit of XRD (Table 2.1). The lattice constant for the Ce$_{0.83}$Zr$_{0.17}$O$_2$ (111) plane was constant at 3.1 Å for all catalysts regardless of synthesis method and Ni content. Thus, potential incorporation of Ni into crystalline CZ domains did not significantly change the lattice constant relative to the lattice contraction that was caused by the incorporation of Zr$^{4+}$ ions.\textsuperscript{139, 140} However, the unchanged lattice constant across samples does not rule out the possibility of incorporation of Ni into the CZ lattice.\textsuperscript{140}

The crystal sizes for the 2CP, 4CP and 6CP samples increased with the nickel content, but 10CP possessed crystals smaller than those of 6CP and 4CP. All CS catalysts had similar crystal sizes, which were smaller than those in the 2DI and 2SEA samples. The relatively small crystal sizes of the CS catalysts indicate that the rapid combustion procedure restricted crystal growth.
Figure 2.1 – a) X-ray diffraction spectra of CZ, 2DI, 2SEA, 2CP, 4CP, 6CP, 10CP, 2CS, 4CS, 6CS and 10CS catalyst samples. b) XRD diffraction peaks of NiO on the 10CP catalyst sample. Vertical dashed lines indicate diffraction angles for CZ solid solutions.

2.3.1.3 CO Chemisorption

The dispersion of nickel species after reduction of the catalysts was determined by CO chemisorption (Table 2.1). 2SEA had a higher dispersion than 2DI, which indicates that the Coulomb force introduced through SEA synthesis stabilized small well-dispersed Ni clusters. The surface deposition synthesis techniques (i.e., DI and SEA) produced catalysts with greater apparent nickel dispersions compared to most of those made using
bulk synthesis techniques. This result was expected since a fraction of the Ni species is incorporated into the support during the bulk synthesis techniques and hence should be inaccessible for CO chemisorption. However, 2CS showed an apparent Ni dispersion comparable to 2SEA and greater than 2DI, indicating that the combustion synthesis method produced well-dispersed and accessible nickel species on the surface of the catalyst. Among the catalysts prepared by bulk synthesis techniques, the CP samples showed lower apparent dispersion than the CS samples. The apparent dispersion of Ni in both CP and CS samples decreased with increasing nickel loading.

2.3.1.4 X-ray Adsorption Spectroscopy (XAS)

The oxidation state of Ni and the abundance of different Ni species in each unreduced sample was analyzed by XAS (Figure 2.2 and Table 2.2). Among the catalysts with 2 wt% nickel, the CP and CS samples had positive energy shifts of slightly above 1 eV for the Ni K-edge position relative to the NiO standard, while the shift for the 2DI and 2SEA was only 0.3 eV. The positive energy shift is an indication of higher oxidation states of the Ni atoms in the samples.\textsuperscript{135, 141, 142} The LaNiO\textsubscript{3} standard, a common standard used to identify Ni\textsuperscript{3+} species, showed a positive shift of 2.98 eV, which further supports the presence of Ni species with a higher oxidation state in the bulk synthesis materials. The 2DI and 2SEA samples had the first local minimum after the white line around 8362 eV. This feature was absent from the spectra of 2CS and 2CP, which indicates the presence of very small and under-coordinated NiO species.\textsuperscript{110, 143} As the nickel content increased in both CP and CS samples, the white line position approached that of NiO. The CS samples had a larger edge shift than the CP samples with the same nickel content.
Figure 2.2 – XANES spectra of unreduced catalysts and a NiO standard as reference. a) Catalysts with 2 wt%. nickel content; b) CP catalysts; c) CS catalysts. EXAFS for unreduced catalysts and a NiO standard as reference. d) Catalysts with 2 wt%. nickel content; e) CP catalysts; f) CS catalysts.

The distribution of Ni species was determined by linear combination fitting using standard spectra of NiO, NiO 1st shell and NiLaO₃ (Figure A.3). NiO is the most common form of nickel in oxides and adopts a rock salt structure, where the Ni²⁺ ion has 6 oxygen atoms as nearest neighbors.¹⁴⁴ The ‘1st shell NiO’ notation refers to a simulated XANES spectrum adopted from the work from Preda et al.¹⁴³, where they simulated a NiO cluster containing the contributions of only the first coordination shells around Ni (6 oxygen atoms at 2.07 Å). This simulated spectrum is a good representation of very small NiO clusters on the catalyst surface or Ni²⁺ incorporated into the CZ support. The key difference between NiO and NiO 1st shell standards is that the NiO standard has a local minimum around 8362 eV, while such feature is missing in the NiO 1st shell standard (Figure A.4). Finally, I used NiLaO₃ as a representative of the Ni³⁺ species.¹⁴⁵
Nickel species in both 2DI and 2SEA were all in Ni\(^{2+}\) form, with comparable contributions from bulk NiO and 1\(^{st}\) shell NiO (Table 2.2). 2SEA had a larger contribution from 1\(^{st}\) shell NiO than 2DI, indicating a better dispersion of the nickel oxide clusters induced by a stronger metal-support interaction. For bulk synthesis methods (2CP and 2CS), a larger fraction of Ni species was affected by the CZ support. Only 30% of the nickel atoms in these two catalysts were represented by the NiO standard. The remaining nickel was strongly influenced by the CZ support, either by forming almost atomically dispersed NiO clusters or by incorporation into the fluorite-structured CZ support. In 2CP, about half of such nickel retained a 2+ oxidation state, i.e. were represented by the 1\(^{st}\) shell NiO standard, while the other half was in the Ni\(^{3+}\) form. The 2CS catalyst contained more Ni\(^{3+}\) compared to 2CP. Further evidence for the presence of Ni\(^{3+}\) species in these samples was that the average Ni-O bond length estimated from the EXAFS fitting (Table 2.2) was much shorter for the 2CS and 2CP samples compared to those of the 2DI and 2SEA samples. The bulk synthesis methods produced samples with a Ni-O bond length of 2.01 Å (2CS) and 1.96 Å (2CP), which were very close to the typical bond length of Ni\(^{3+}\)-O species around 1.95 – 1.98 Å.\(^{146}\) For the surface synthesis methods, 2DI and 2SEA samples both had a Ni-O bond length of 2.06 Å, which is a typical bond length for the Ni\(^{2+}\)-O species (2.05 – 2.09 Å).\(^{146}\)

The fraction of the bulk NiO species in the CP catalysts increased as the nickel loading increased to 6 wt%, and the 6CP and 10CP sample had approximately the same relative amount of bulk NiO at around 67% of all Ni species. The relative abundance of Ni\(^{3+}\) species decreased with increasing nickel content, and the 6CP and 10CP samples had no such species. The fraction of 1\(^{st}\) shell NiO species was around 30% for all CP samples.
The large fraction of NiO in 6CP and 10CP indicates the presence of a separate NiO phase. A similar trend was observed for the CS samples as with the CP samples. However, Ni$^{3+}$ species were present in all CS samples except when the Ni content was 10 wt%. The contribution from 1st shell NiO species was around 20% for the CS samples, indicating that a greater fraction of nickel was in a higher oxidation state than the CP samples.

**Table 2.2 – Total H$_2$ consumption from TPR experiments, the Ni species composition from linear combination fitting the XANES spectra, coordination number of 1st Ni-O shell and 2nd Ni-Ni shell from EXAFS fitting and the estimated particle size of NiO from EXAFS fitting.**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>2DI</th>
<th>2SEA</th>
<th>2CP</th>
<th>4CP</th>
<th>6CP</th>
<th>10CP</th>
<th>2CS</th>
<th>4CS</th>
<th>6CS</th>
<th>10CS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total H$_2$ uptake (mmol/gcat)$^a$</td>
<td>0.56</td>
<td>0.54</td>
<td>0.69</td>
<td>1.19</td>
<td>1.55</td>
<td>2.51</td>
<td>0.90</td>
<td>1.15</td>
<td>1.40</td>
<td>1.93</td>
</tr>
<tr>
<td>Energy shift in edge position (eV)$^b$</td>
<td>0.3</td>
<td>0.35</td>
<td>1.01</td>
<td>0.75</td>
<td>0.12</td>
<td>0</td>
<td>1.14</td>
<td>0.69</td>
<td>0.42</td>
<td>0.05</td>
</tr>
<tr>
<td>Fraction of NiO (%)$^c$</td>
<td>52.9</td>
<td>46.0</td>
<td>30.8</td>
<td>46.4</td>
<td>67.2</td>
<td>67.7</td>
<td>35.1</td>
<td>59.1</td>
<td>65.0</td>
<td>73.1</td>
</tr>
<tr>
<td>Fraction of Ni$^{3+}$ (%)$^c$</td>
<td>0.0</td>
<td>0.0</td>
<td>35.4</td>
<td>16.3</td>
<td>0.0</td>
<td>0.0</td>
<td>43.7</td>
<td>25.4</td>
<td>17.3</td>
<td>0.0</td>
</tr>
<tr>
<td>Fraction of 1st shell NiO(%)$^c$</td>
<td>47.1</td>
<td>54.0</td>
<td>33.8</td>
<td>37.3</td>
<td>32.8</td>
<td>32.3</td>
<td>21.2</td>
<td>15.5</td>
<td>17.7</td>
<td>26.9</td>
</tr>
<tr>
<td>Coordination number (Ni-O)$^d$</td>
<td>4.84</td>
<td>5.28</td>
<td>6.22</td>
<td>4.82</td>
<td>6</td>
<td>6</td>
<td>5.21</td>
<td>5.36</td>
<td>4.3</td>
<td>5.35</td>
</tr>
<tr>
<td>Coordination number (Ni-Ni)$^d$</td>
<td>9.68</td>
<td>10.57</td>
<td>4.1</td>
<td>9.63</td>
<td>12</td>
<td>12</td>
<td>0.54</td>
<td>1.62</td>
<td>8.6</td>
<td>10.7</td>
</tr>
<tr>
<td>Ni-O bond length (Å)$^d$</td>
<td>2.06</td>
<td>2.06</td>
<td>1.96</td>
<td>2.06</td>
<td>2.07</td>
<td>2.07</td>
<td>2.01</td>
<td>2.03</td>
<td>2.04</td>
<td>2.06</td>
</tr>
<tr>
<td>Particle size (nm)$^e$</td>
<td>0.54</td>
<td>0.65</td>
<td>≤0.4</td>
<td>0.54</td>
<td>≥7</td>
<td>≥7</td>
<td>≤0.4</td>
<td>≤0.4</td>
<td>0.46</td>
<td>0.68</td>
</tr>
</tbody>
</table>

*a* The total H$_2$ consumption from TPR experiments  
*b* The shift of the Ni K-edge position for each catalyst compared to the edge position of the NiO standard  
*c* The Ni species composition from linear combination fitting the XANES spectra.  
*d* Coordination number of the 1st Ni-O shell and the 2nd Ni-Ni shell and the bond length of the Ni-O from EXAFS fittings.  
*e* Estimated particle size of NiO from coordination number of the 2nd Ni-Ni shell from EXAFS fittings.
EXAFS analysis showed that 2DI and 2SEA contained very small NiO clusters with an average nickel particle sizes of approximately 0.5 nm (Figure A.5, Table A.1). The second Ni-Ni shell (peak around 2.6 Å) for NiO was absent for 2CP and 2CS samples, indicating that a large portion of nickel atoms were almost atomically dispersed NiO clusters. The NiO particle sizes of the CP catalysts increased with increasing Ni content. EXAFS analysis of the 4CP catalyst showed a particle size around 0.5 nm, which was comparable to the 2DI and 2SEA samples. The CS catalysts also displayed small NiO clusters. Both 2CS and 4CS were missing the second Ni-Ni shell in the EXAFS spectra, indicating that these two catalysts also had isolated Ni species. The NiO particle size increased with increasing nickel content. Unlike the CP catalysts, the NiO particles in the CS catalysts remained small (~0.7 nm) at 10% nickel.

2.3.1.5 X-ray photoelectron spectroscopy (XPS)

The XPS analysis showed that the Ni contents near the surface of 2DI and 2SEA were slightly higher than the nominal loading of 2 wt% as it would be expected for a surface deposition technique (Table 2.1). For most of the samples prepared by bulk synthesis methods, the Ni content near the surface was lower than the nominal value, which is attributed to integration of Ni into mixed bulk phases. 4CP and 10CP were exceptions to this trend indicating that phase segregation during the co-precipitation process can lead to gradients in the composition of the sample.

The surface chemical state of Ni was determined through peak fitting (Figure A.6, Figure A.7, and Table A.2). Peaks at 854.1 eV and 860.2 eV were assigned to the main and satellite 2p\(^{3/2}\) peaks of Ni\(^{2+}\), and peaks at 855.6 and 863 eV were assigned to the main
and satellite $2p^{1/2}$ peaks of Ni$^{3+}$. At 2 wt% Ni content, Ni on the surface were present in Ni$^{2+}$ from surface synthesis techniques (2DI and 2SEA). Samples prepared by surface synthesis techniques (2DI and 2 SEA) contained Ni only as Ni$^{2+}$. The presence of surface Ni$^{3+}$ was observed in the samples made by bulk synthesis techniques with low Ni contents of 2-4 wt%. For both CS and CP samples, the contribution from Ni$^{3+}$ decreased with increasing Ni content and dropped to 0 with 6 wt% Ni. The presence of Ni$^{3+}$ and trend of the Ni$^{3+}$ fraction with increasing Ni content were in line with XAS results. The discrepancy that Ni$^{3+}$ in 6CS was present from XAS but absent from XPS could be due to differences between surface and bulk compositions of these samples or the ambiguity of the XPS fittings.

2.3.1.6 Temperature Programmed Reduction (TPR)

The TPR profiles of all samples were de-convoluted to multiple peaks for detailed analysis of the Ni and CZ species (Figure 2.3, Table A.3 and Figure A.8). The deconvolution analysis assumed constant reduction temperatures of the same species across different samples and a symmetric reduction peak for a certain species. These assumptions were verified following the analysis provided by Caballero et al. The addition of Ni to the CZ support through either bulk incorporation or surface deposition enhances the reducibility of the CZ support. The earliest peak below 205°C is assigned to the removal of the adsorbed oxygen species on the CZ support. The reduction peaks around 310 to 390 °C were assigned to surface reduction of the CZ support, whereas the reduction of bulk CZ happens above 500 °C.
Peaks between 200 °C and 350 °C are attributed to the reduction of different Ni species. For 2DI and 2SEA that contain small and well-dispersed NiO species, the peak around 230 °C was assigned to the reduction of free surface NiO (Figure 2.3a). The next peak around 255 °C to 270 °C was assigned to the reduction of NiO strongly bound to the CZ support, or interfacial NiO. For the bulk synthesis methods (CP and CS), stronger metal-support interactions are expected compared to the surface methods. Hence, the reduction of various Ni species occurred at higher temperature. The reduction of the free surface NiO occurred between 220 °C to 275 °C and was highly dependent on the NiO nanoparticle size because the intensity of metal-support interactions varied and affected the reduction temperature over a wider range. The next peak between 255 °C to 275 °C was assigned to the reduction of Ni$^{3+}$ to Ni$^{2+}$. Peaks between 280 °C and 320 °C were attributed to incorporated Ni$^{2+}$ or surface Ni$^{2+}$ species strongly interacting with the support for the bulk synthesis techniques. Finally, the peaks around 345 °C were assigned to the reduction of bulk NiO species, which were only present when the Ni content reached 10 wt%.

The samples with 2 wt% nickel showed total H$_2$ consumption between 0.54 and 0.90 mmol/g$_\text{cat}$ (Table 2.2). Bulk synthesis catalysts (CP and CS) had total H$_2$ consumptions higher than that of the surface synthesis catalysts (DI and SEA). The H$_2$ consumption assigned to Ni species in the bulk synthesis samples were around 0.4 mmol/g, which was slightly higher than the 0.344 mmol of Ni in 2 wt% Ni samples. The additional H$_2$ consumption by Ni species was due to the reduction of Ni$^{3+}$. The H$_2$ consumption assigned to CZ were also higher in bulk synthesis samples (Table A.3). It is suggested that the incorporation of nickel into the CZ support introduced defects into the CZ lattice, which
increased the oxygen storage capacity of the support and thus the H₂ consumption during temperature-programmed reduction.\textsuperscript{160} For both bulk synthesis techniques (CP and CS), the total H₂ consumption increased with increasing nickel content.

At 2 wt\% Ni content, the bulk synthesis produced more surface oxygen species compared to the surface synthesis methods, and CS sample had the highest surface oxygen concentration. The Ni species in bulk synthesis methods had higher H₂ consumption than surface synthesis methods from peak deconvolution (Table A.3), which provides additional evidence for the presence of Ni\textsuperscript{3+} in these samples. Comparing the two surface synthesis methods, 2DI had less interfacial NiO and more free surface NiO than 2SEA. The reduction temperature of Ni species in 2CP was higher than in 2CS, which is attributed to stronger interactions with CZ.
Figure 2.3 – a) Different Ni and Ce species in NiO/CZ catalysts and TPR profiles of catalysts: b) catalysts with 2 wt% nickel loading and the CZ support; c) co-precipitation catalysts and d) combustion synthesis catalysts.

At higher Ni content, the surface oxygen concentration decreased for CP and CS samples. The CP catalysts had lower surface oxygen concentrations at the same Ni content.
compared to the CS samples. The surface oxygen concentration dropped to 0 for the 10CP sample, while the 10CS sample retained some surface oxygen. The concentration of Ni$^{3+}$ species decreased to zero at 6 wt% Ni loading for the CP catalysts., while for the CS samples, the concentration of Ni$^{3+}$ species dropped to zero at 10 wt% Ni loading. Both 10CP and 10CS samples had bulk NiO species.

2.3.2 Reactivity tests for methane dry reforming

Dry reforming reactions at 700 °C were performed with catalyst beds containing 0.2 wt% Ni and SiC as a diluent to keep the conversion well below the thermodynamic equilibrium of 78% CH$_4$ conversion and 86% CO$_2$ conversion (Figure A.9).$^{105}$ SiC was inactive for dry reforming under the reaction conditions described above. All catalysts experienced initial deactivation before reaching a steady state conversion. The extent of deactivation was related to the conversion of CH$_4$ and CO$_2$ at different times during the run and to the time required for each catalyst to lose half of the initial methane (Figure 2.4, Table 2.3).

Among the catalysts with 2 wt% nickel, 2SEA demonstrated the best initial activity for methane conversion, while the other three catalysts showed comparable initial methane conversion. 2CS had an initial CO$_2$ conversion similar to that of the 2SEA catalyst and better than both the 2CP and 2DI catalysts. A steady state was considered achieved when the methane conversion remains unchanged, or slightly decreased (less than 5%) over 2 hours. The steady state methane conversion for all 2 wt% nickel catalysts was similar, while the 2CS catalyst had the highest CO$_2$ conversion at steady state. As for the time to steady state conversion, 2CP reached steady state conversion after 40 h, while 2CS, 2SEA
and 2DI reached steady state conversion after only 20, 18, and 10 h, respectively (Figure A.9).

Figure 2.4 – Conversion of a) CO\textsubscript{2} and b) CH\textsubscript{4} after 0, 400 min, and 800 minutes on stream and at steady state for reactions with diluted catalysts. For 4CP, 6CP, and 10CP samples reaction were terminated before steady state was established.
Table 2.3 – Initial and steady state H$_2$:CO ratio and conversions of CH$_4$ and CO$_2$, and time until the loss of half initial CH$_4$ conversion.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO$_2$ conv. (%)</th>
<th>CH$_4$ conv. (%)</th>
<th>H$_2$:CO</th>
<th>CO$_2$ conv. (%)</th>
<th>CH$_4$ conv. (%)</th>
<th>H$_2$:CO conversion (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2DI</td>
<td>21.4</td>
<td>13.0</td>
<td>0.43</td>
<td>2.25</td>
<td>0.66</td>
<td>0.07</td>
</tr>
<tr>
<td>2SEA</td>
<td>31.0</td>
<td>19.3</td>
<td>0.49</td>
<td>2.90</td>
<td>1.42</td>
<td>0.06</td>
</tr>
<tr>
<td>2CP</td>
<td>25.6</td>
<td>14.3</td>
<td>0.38</td>
<td>2.70</td>
<td>1.28</td>
<td>0.05</td>
</tr>
<tr>
<td>4CP</td>
<td>34.4</td>
<td>23.3</td>
<td>0.60</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>6CP</td>
<td>34.5</td>
<td>22.0</td>
<td>0.59</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>10CP</td>
<td>20.1</td>
<td>13.3</td>
<td>0.49</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>2CS</td>
<td>29.0</td>
<td>15.5</td>
<td>0.39</td>
<td>4.77</td>
<td>1.92</td>
<td>0.07</td>
</tr>
<tr>
<td>4CS</td>
<td>36.1</td>
<td>23.4</td>
<td>0.64</td>
<td>3.01</td>
<td>1.13</td>
<td>0.06</td>
</tr>
<tr>
<td>6CS</td>
<td>41.9</td>
<td>26.9</td>
<td>0.57</td>
<td>4.11</td>
<td>1.60</td>
<td>0.09</td>
</tr>
<tr>
<td>10CS</td>
<td>40.1</td>
<td>25.7</td>
<td>0.60</td>
<td>1.54</td>
<td>0.69</td>
<td>0.06</td>
</tr>
</tbody>
</table>

4CP and 6CP exhibited similar initial conversion, which was higher than that over 2CP and 10CP. A comparison of the time until the loss of half of the initial methane conversion showed that the deactivation rates decreased with increasing nickel loading. As a consequence, a steady state was not reached for 4CP, 6CP and 10CP during the experiments.

The initial CH$_4$ and CO$_2$ conversions over CS catalysts increased with increasing nickel content up to 6CS and remained similar for 10CS. The CS catalysts showed a faster deactivation rates compared to CP catalysts, and the time needed to establish a steady state was approximately 20 h regardless of the nickel content. While the deactivation rate was
independent of the nickel content, the steady-state CH₄ and CO₂ conversion were significantly lower for 10CS compared to the other CS samples.

At 2 wt% Ni content, the 2SEA sample had the highest H₂:CO ratio at the start of the reaction compared to the other catalysts with 2 wt% Ni (Table 2.3). At higher nickel content, both CP and CS catalysts showed greater initial H₂:CO ratio compared to the 2 wt% Ni samples. The initial H₂:CO ratios were maximal at 4 wt% Ni for both CP and CS catalysts. The final H₂:CO ratios were much lower compared to the initial values and were around 0.06 for all catalysts. The 6CS sample was an exception with a final H₂:CO ratio of 0.09. These low values indicate that significant amounts of water were formed by reverse water gas shift.

2.3.3 Spent catalysts analysis

2.3.3.1 N₂ Physisorption

2SEA and 2DI lost ~60% and 70% of their surface areas, respectively (Table 2.4, and Figure A.10, A.11). The loss in surface area for the CP catalysts increased with decreasing nickel content except for 10CP. The 10CP sample had the lowest surface area after reaction, which is consistent with its initial lowest surface area. The surface areas of the CS catalysts decreased by less than 40% after the reaction. The 2DI, 2SEA and CS catalysts showed an increase in pore volume and pore width. The pore volume for the CP catalysts did not change much after the reaction.
2.3.3.2 TGA

TGA of the spent catalysts was carried out to characterize the carbon deposits formed (Table 2.4 and Figure A.12). Among the 2 wt% Ni samples, 2SEA showed the highest weight loss (17%) followed by 2CP (8%). Spent 2DI and 2CS lost less than 2% of their weight. For 2DI, analysis of the first derivative of weight with respect to temperature (DTG) showed two peaks at 438 °C and 596 °C, corresponding to amorphous carbon and carbon nanotubes. 2SEA had a major peak at 659 °C, which is attributed to the presence of whisker type structures or carbon nanotubes as most abundant deposits. The 2CS had a single peak around 400 °C, which indicates that the limited amount of coke formed on these samples was amorphous carbon. As for 2CP, besides a whisker type carbon peak at 545 °C, an additional amorphous carbon peak at 467 °C was observed.

With increasing Ni content, the CP samples produced heavier coke. The CP samples all showed a major peak for carbon nanotubes in the range of 550-660 °C. Both 4CP and 6CP had a shoulder at the low temperature edge of the major peak at 450 °C, which was assigned to amorphous carbon. An additional peak at 799 °C was observed for spent 10CP, which implies the presence of graphitic coke. As for the CS samples, only 10CS had significant coke formation, while others produced limited coke (< 2 wt% loss). 2CS, 4CS and 6CS had a single peak around 400 °C to 470 °C, which indicates the limited amount of coke formed on these samples was amorphous carbon. Spent 10CS showed a weight loss of 12% and a peak around 488 °C, indicating the formation of whisker type carbon during the reaction.
Table 2.4 – Surface area, pore volume, and pore width of the spent catalysts measured by N\textsubscript{2} physisorption, the loss of weight during TGA of the spent catalysts, and Ni particle size in the spent sample from XRD.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>2DI</th>
<th>2SEA</th>
<th>2CP</th>
<th>4CP</th>
<th>6CP</th>
<th>10CP</th>
<th>2CS</th>
<th>4CS</th>
<th>6CS</th>
<th>10CS</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area (m\textsuperscript{2}/g)\textsuperscript{a}</td>
<td>23.8</td>
<td>34.9</td>
<td>8.3</td>
<td>27.8</td>
<td>31.7</td>
<td>9.9</td>
<td>34.2</td>
<td>40.7</td>
<td>39.0</td>
<td>23.1</td>
</tr>
<tr>
<td>Pore volume (cm\textsuperscript{3}/g)\textsuperscript{b}</td>
<td>0.094</td>
<td>0.134</td>
<td>0.074</td>
<td>0.079</td>
<td>0.138</td>
<td>0.026</td>
<td>0.119</td>
<td>0.091</td>
<td>0.095</td>
<td>0.086</td>
</tr>
<tr>
<td>Pore width (nm)\textsuperscript{b}</td>
<td>14.0</td>
<td>12.0</td>
<td>15.7</td>
<td>11.4</td>
<td>12.6</td>
<td>11.6</td>
<td>11.0</td>
<td>11.5</td>
<td>11.4</td>
<td>10.5</td>
</tr>
<tr>
<td>Weight loss (%)\textsuperscript{c}</td>
<td>2.0</td>
<td>17.0</td>
<td>8.4</td>
<td>21.4</td>
<td>17.4</td>
<td>20.0</td>
<td>0.75</td>
<td>0.78</td>
<td>1.9</td>
<td>13.5</td>
</tr>
<tr>
<td>Ni particle size (nm)\textsuperscript{d}</td>
<td>96.7</td>
<td>28.6</td>
<td>85.3</td>
<td>84.6</td>
<td>20.3</td>
<td>22.9</td>
<td>9.04</td>
<td>11.05</td>
<td>8.61</td>
<td>9.07</td>
</tr>
</tbody>
</table>

\textsuperscript{a}From adsorption/desorption isotherms measured by N\textsubscript{2} physisorption using BET method
\textsuperscript{b}From adsorption/desorption isotherms measured by N\textsubscript{2} physisorption using BJH method
\textsuperscript{c}From TGA
\textsuperscript{d}From XRD data using the Scherrer equation for Ni(111) peak at 44.6°

1. X-ray Adsorption Spectroscopy (XAS)

In the spent catalysts, Ni was almost fully reduced except for the 2DI sample (Figure 2.5). The spent catalysts were exposed to air prior to the XAS measurements. Hence, exposed Ni was subjected passivation from oxygen in air, which was observed in 2DI. The fact that the nickel remained in a reduced state indicates that it was protected from atmospheric oxygen, possibly through encapsulation by either the support or carbon deposits formed during the reaction.
2.3.3.3 X-ray Diffraction (XRD)

The X-ray diffractograms of all spent catalysts contained a characteristic peak for Ni(111) at 44.6 (Figure 2.6).\textsuperscript{161} Significant growth in Ni particle size was observed for all samples. Among the samples with 2 wt% Ni, 2DI and 2CP had larger Ni particles above 80 nm, while the 2SEA and 2CS samples had Ni particles with an average size of less than 30 nm. In particular, the Ni particle size of spent 2CS was less than 10 nm. Spent 2CP had relatively large Ni particles compared to the other synthesis methods. Spent 2CP and 4CP had Ni particles of around 85 nm, while a sudden decrease in the size of Ni particles was observed once the nickel content was greater than 6 wt%. Both 6CP and 10CP had Ni particles of size around 20 nm. The CS sample had the smallest Ni particles with size around 10 nm. The Ni particle size in the spent CS samples seemed to be independent of the nickel content.
Figure 2.6 – XRD patterns of spent catalysts: a) 2 wt% samples b) CP samples and c) CS samples.

2.3.3.4 Scanning Electron Microscopy (SEM)

SEM images were collected for all spent catalysts (Figure A.13), but only images for samples with significant coke formation are shown in Figure A.7. Carbon nanotubes
were observed on the surface of 4CP, 6CP, 10CP, 2SEA and 10CS. Carbon nanotubes covered the surface of spent 4CP fully and that of 2SEA, 6CP and 10CP partially.

Figure 2.7 – SEM images of 2 wt% Ni spent samples and spent samples with carbon nanotubes a) 2DI, b) 2SEA, c) 2CP, d) 4CP, e) 6CP, f) 10CP, g) 2CS and h) 10CS.

2.4 Discussion

2.4.1 The effect of synthesis methods on Ni speciation and redox properties

Catalysts containing nickel on ceria or ceria-zirconia supports can be prepared by various synthesis techniques that results in samples with different structures and thus different catalytic performance.\textsuperscript{130, 162-164} In SEA, strong electronic forces bind metal precursors to the support and this interaction is believed to introduce a stronger metal support interaction (SMSI) that persist during subsequent calcination and reduction steps.\textsuperscript{120, 165} Bulk synthesis methods incorporate Ni atoms into the CZ lattice to form a mixed metal oxide and also induce stronger metal support interactions.\textsuperscript{83, 121, 122, 166}
XANES, XPS and TPR fitting (Table 2, S2, and Figure S3, S6) showed that the Ni species in both of the surface synthesis catalysts (2DI and 2SEA) were in the 2+ oxidation state, either in free NiO or well-dispersed interfacial NiO clusters (1st shell NiO), whereas Ni\(^{3+}\) species were absent. Both synthesis techniques provided sufficiently strong metal support interactions to obtain small NiO clusters with particle sizes around 0.5 nm in the unreduced catalysts. However, TPR, XANES and CO chemisorption (Table 2.1) indicated that 2DI had more free surface NiO species than the 2SEA. These results indicate that electronic adsorption of the Ni precursors onto the support during synthesis generated stronger metal-support interactions and better dispersion compared to those generated by DI.

By applying bulk synthesis methods, the apparent NiO dispersion derived from CO chemisorption decreased, yet the EXAFS analysis (Table 2.2, A.1, and Figure 2.2, A.5) indicated almost isolated Ni species. These results imply that a large fraction of the Ni formed atomically dispersed NiO clusters or was incorporated into the CZ lattice to form a mixed metal oxide. The incorporation of Ni cations into the mixed metal oxides altered the local electronic structure of the Ni species and formed Ni\(^{3+}\) species. Both incorporated Ni\(^{3+}\) cations and the atomically dispersed NiO are less stable than bulk NiO species and require strong interactions with the CZ support for stabilization. Although the presence of Ni\(^{3+}\) species in NiO/CZ catalysts were confirmed by other researchers,\(^{167,168}\) such species were often ignored in catalysis research.

Different synthesis methods and nickel contents altered not only the nickel speciation but also the properties of the support. It was previously shown that decreasing the size of CZ crystallites improves the reducibility of the support.\(^{131}\) The SMSI between
Ni and the CZ support in surface synthesized catalysts and the incorporation of Ni cations into the CZ matrix also improved the reducibility of the CZ support.\textsuperscript{15, 76} Our group previously performed in-situ XANES measurements of methane activation over the 2DI catalyst at 450 °C, and the results showed a synergistic effect between the NiO and CZ support with respect to oxygen transfer where the CZ support supplied the small and well-dispersed NiO with oxygen and kept NiO at the 2+ oxidation state until the active surface oxygen was depleted.\textsuperscript{15} The reducibility of CZ solution allows the formation of oxygen vacancies at high temperature upon inert/reducing conditions.\textsuperscript{51} Such vacancies are filled at room temperature upon exposure to air forming the active oxygen species. Hence the active surface oxygen concentration, which is probed by TPR, is a good indicator for the ability to form oxygen vacancy and closely related to oxygen vacancy concentrations reported in other studies.\textsuperscript{169, 170}

The 2CP catalyst had a smaller crystallite size than 2DI and 2SEA and was more reducible (Table 2.1 and 2.2). The CZ supports for the 2DI and 2SEA catalysts were prepared by co-precipitation on Ce and Zr precursors in a similar way to the synthesis of the CP catalysts. Thus, the difference in crystal sizes is attributed to reduced crystallization due to the addition of Ni to the CZ matrix as well as the difference in pH during synthesis. Specifically, the synthesis of 2CP catalyst was carried out at pH of 13, while the synthesis of the CZ support for the 2DI and 2SEA was at pH of 11. The lower pH allowed the CZ grains to form larger crystals. The combustion process during the synthesis of the CS catalysts limited the time for the CZ crystal structure to equilibrate to a thermodynamically stable phase, which limited the growth of the crystal grains and yielded smaller, most reducible crystals.
The bulk synthesis methods provided mixed metal oxides that contained oxygen vacancies to achieve charge neutrality.\textsuperscript{171, 172} Compared with the liquid precipitation conditions at high pH during the co-precipitation synthesis, the chelation of the metal cations by citric acid and impeded annealing during combustion synthesis favored the formation of mixed metal oxides, which contained more incorporated Ni\textsuperscript{2+}/Ni\textsuperscript{3+} and hence more reducible CZ.\textsuperscript{173} Therefore, The CS samples had more Ni cations incorporated into the support than the CP samples at the same Ni content. The fast combustion process that occurs during the synthesis of CS samples inhibited annealing of the catalysts to the thermodynamically favored state and created more defects and oxygen vacancies compared to other synthesis methods, which led to the highest surface oxygen concentration.

2.4.2 The effect of varying Ni content for CP and CS catalysts on Ni speciation and redox properties

In NiO/CZ systems, Ni can migrate between a mixed metal oxide phase and a separate NiO/Ni phase.\textsuperscript{159, 174} Ni incorporation into the CZ phase often requires a bulk synthesis method or high temperatures for solid state diffusion. Many researchers have studied bulk synthesized NiO/CZ catalysts at Ni content well above 2 wt\% and suggest that NiO and CeO\textsubscript{2} can form solid solution but that the addition of zirconium to the ceria support significantly lowers the fraction of dissolved Ni.\textsuperscript{66, 75, 83, 152, 159, 175} Barrio et. al. found a limit of 10–12\% for NiO in CeO\textsubscript{2} to form Ni\textsubscript{x}Ce\textsubscript{1-x}O\textsubscript{2-}\textsubscript{y} mixed metal oxides.\textsuperscript{159} Larimi et. al. observed XRD-detectable NiO crystals at 5 wt\% Ni content in a co-precipitated NiO/Ce\textsubscript{x}Zr\textsubscript{1-x}O\textsubscript{2} system.\textsuperscript{75} Safavania et. al. produced homogeneous Ni-Ce-Zr mix oxides with Ni concentrations up to 9.3 mol\% without phase separation.\textsuperscript{172}
Increasing the Ni content in both CP and CS catalysts resulted in: 1) an increase in the fraction of Ni present as a separate NiO phase and a decrease in the Ni$^{3+}$ concentration, 2) a decrease in the concentration of adsorbed surface oxygen species on the CZ support, and 3) no discernable trend with respect to changes in the surface area and pore volume. Given that the solubility of NiO in CeO$_2$ is limited, NiO is expected to segregate from the CZ support and form a separate phase at greater Ni content. With less fraction of Ni dissolved in the CZ lattice, the fraction of Ni$^{3+}$ dropped with increasing Ni content. The CS catalysts had comparable surface oxygen concentration at 2-6 wt% Ni content with 6CS being the highest (Table A.3), which indicates possible saturation of incorporated Ni cations in the CZ was reached at 6 wt% Ni for CS samples. As for the 10CS sample, the surface oxygen concentration dropped by ~70% compared to 2CS due to a separation of NiO phase from the mixed metal oxide (Table A.3). The presence of NiO characteristic peaks in the XRD and the abnormally high surface Ni content from XPS uniquely observed in 10CP evidenced the formation of a separate NiO phase, which occupied the surface. The 10CP sample had no adsorbed surface oxygen species, probably because these species were consumed by the formation of NiO particles. In addition, the formation of larger NiO clusters in 10CP likely blocked accessibility to adsorbed surface oxygen. With respect to surface area and pore volume, the 10CP sample was an ‘outlier’ compared to other CP catalysts. It had significantly lower surface area and pore volume and was almost entirely mesoporous, which suggests that the larger NiO clusters in 10CP reduced microporosity. For CZ supports, larger crystalline size often yields a lower surface area. As the 10CP had a lower crystalline size than 6CP, the loss of surface area and pore volume is probably
due to pore structure collapse or blockage of pores from the formation of larger NiO particles.

2.4.3 The relationship between catalyst structure and performance in dry reforming of methane

Nickel is well-known as the active site for activating methane, which is the rate limiting step in most dry reforming reactions. The well dispersed Ni species in Ni/CZ catalysts allow for better accessibility of the active sites and high initial activity. In this work, I define a surface Ni species as the Ni that reduced below 235 °C for surface synthesis methods and below 285 °C for bulk synthesis methods during TPR. Since the Ni species were more strongly bound to the support or even incorporated into mixed oxide phases with bulk synthesis techniques, a higher reduction temperature for surface nickel species is not surprising. The initial rate of methane conversion increased linearly with increased surface nickel concentration (Figure 2.8), and the initial CO$_2$ conversion followed the same trend (Figure A.14). This linear relation demonstrated that the conversion is directly related to the accessible surface nickel species during the first 20 minutes of reaction. Since it is commonly proposed that CO$_2$ activation occurs on the CZ support rather than the Ni particles, the similar trends in both CO$_2$ and CH$_4$ conversion with respect to the accessible Ni sites indicates that the rate of the reaction at high conversion is strongly controlled by methane activation on Ni particles. In contrast, activated CO$_2$ appears to be abundantly available on the catalyst. The apparent dispersion of Ni measured by CO chemisorption was not a good descriptor for accessibility of Ni after reduction. This is probably because Ni species strongly interacting with CZ remain partially oxidized after the reducing treatment and did not chemisorb CO but are active for methane activation.
After 20 minutes, the conversion over all catalysts decreased (Figure 2.4), and possible deactivation mechanisms are discussed in the next section.

The initial H$_2$:CO ratios over all catalysts were well below unity (Table 2.3), indicating that RWGS occurred to a significant extent during dry reforming of methane. Multiple researchers proposed a bifunctional mechanism where the redox active CZ support is capable of activating CO$_2$, which further reacts with hydrogen produced from methane activation, and contributes to the RWGS activity.$^{105, 156, 179}$ In line with this interpretation, catalysts with 2 wt% Ni made by bulk synthesis methods had lower initial H$_2$:CO ratios because they showed high reducibility of the CZ support along with fewer accessible Ni sites. These effects were reversed at higher Ni content, as the reducibility of the CZ support decreased and the more Ni became accessible, hence the initial H$_2$:CO ratio increased from ~0.4 to 0.6.

![Figure 2.8](image.png)

**Figure 2.8 – Relationship between the initial methane conversion and the surface Ni concentration on different catalysts, defined as species that showed a reduction temperature of less than 285 °C for bulk synthesis techniques and less than 235 °C for the surface synthesis techniques.**

In experiments where a steady state conversion was reached, all catalysts showed a nonzero steady state conversion. Although these catalysts all retained some activity, the product distribution changed significantly throughout the reaction due to increasing
selectivity to the RWGS. Thus, it is suggested that the redox active sites on CZ deactivate at a slower rate compared to the Ni sites required to activate methane.

2.4.4 The relationship between catalyst structures and deactivation mechanism

The deactivation of Ni on supported metal oxides catalysts during methane dry reforming is the major challenge for its industrial application and has been studied by multiple researchers. Two well-recognized deactivation paths include Ni particle growth and coke formation. In addition to these, the encapsulation and decoration of Ni particles by the support under reduction and reaction conditions has been observed in catalysts where strong metal-support interactions are present. However, a systematic understanding of the relationship between structure of catalysts and their sensitivity to specific deactivation paths has yet to be established. So far, many discussions were limited to samples prepared by the same synthesis method and with similar Ni contents. Herein, I discuss how the deactivation pathways are affected by the synthesis procedure and provide new insights on the structure-performance relationships for Ni/CZ catalysts.

2.4.4.1 Ni particle growth

Post-reaction characterization of the catalysts showed that all catalysts, regardless of synthesis method, initial particle size, or Ni content, underwent Ni particle growth, which likely contributed to the deactivation (Table 2.4). Crystal migration, atom migration and vapor transport are three common mechanisms of particle growth. However, vapor transport for Ni is only favored at temperature below 425 °C and at high CO partial pressure.
through the formation of Ni(CO)$_4$.$^{185}$ As the test conditions do not match these criteria, the formation of Ni(CO)$_4$ will not be discussed here.

The extent of the Ni particle growth varied among the different synthesis methods. While 2DI and 2SEA initially contained Ni particles around 0.6 nm in size, spent 2DI and 2SEA contained Ni particles around 100 and 30 nm, respectively. This illustrates that the strong electrostatic surface interactions utilized during the Ni precursor deposition at least partially persist to stabilize the supported Ni particles during dry reforming at 700 °C. However, the present results do not allow for correlating this trend to a specific growth mechanism.

Previous studies mainly focused on Ni/CZ catalysts with higher nickel contents above 5 wt% or using surface deposition synthesis methods, where the NiO particles size in fresh catalysts are generally well above the isolated clusters found in some of the present samples. For such catalysts, there is a general consensus that strong metal-support interactions stabilize the better-dispersed Ni nanoparticles well enough to prevent Ni particle growth during reforming.$^{64, 69, 71, 127, 186}$ Interestingly, in this study, the Ni particles in the spent 2CP sample (85 nm) were roughly 9 times larger than those in the spent 2CS sample (9 nm) and 3 times larger than those in the 2SEA sample, and the higher reduction temperature of Ni species exhibited in 2CP compared to 2SEA and 2DI from TPR clearly demonstrated a stronger interference from CZ (Figure 2.3 and Table A.3). As mentioned previously, a large fraction of Ni in 2CP catalyst was dissolved in the CZ matrix, forming a mixed metal oxide. Ni cations incorporated in the CZ support are thermally unstable under reducing conditions. The exsolution of Ni cations during reduction or the dry reforming reaction generated highly mobile Ni species that were free to migrate until a
more stable cluster was formed.\textsuperscript{187} Due to this thermodynamic driving force and high Ni mobility, 2CP suffered the most pronounced particle growth during the reaction.

More significant Ni particle growth was observed in the CP samples when the Ni content was lower than 4 wt\% and the initial NiO particles were much smaller (Table 2.2). In unreduced 2CP and 4CP, dissolved Ni\textsuperscript{2+}/Ni\textsuperscript{3+} cations were the dominant Ni species (Table 2), which are subjected to exsolution from the CZ lattice and form Ni atoms with higher mobility. Hence, the Ni particle growth was more pronounced in samples that contains such species. On the other hand, the Ni\textsuperscript{3+} species was missing in the unreduced 6CP and 10CP samples and a large fraction of the Ni was present as larger (>7 nm) more stable NiO particles that likely formed stable Ni clusters during the reductive pre-treatment. Thus, their concentration of rapidly sintering species is reduced. In conclusion, by improving the Ni dispersion to isolated cations, the Ni particle growth mechanism switched from crystal migration to atom migration, which led to higher degrees of particle growth.

While CS samples with 2-6 wt\% Ni contained a substantial fraction of Ni\textsuperscript{3+} species (Table 2.2), particle growth was much less severe regardless of Ni content. This is attributed to encapsulation of Ni by the CZ support, which is uniquely significant for the CS samples (section 2.4.4.3).

2.4.4.2 Coke formation

Different types of carbon deposits can be formed under dry reforming reaction conditions including adsorbed surface carbon atoms, amorphous carbon; carbon nanofibers; and graphitic carbon.\textsuperscript{188} It is generally accepted that larger nickel particles favor coke formation and thus are not desirable for methane dry reforming.\textsuperscript{181, 182, 189} Small, nano-
sized nickel species have shown better activity due to suppressed coking.\textsuperscript{116,190} Kim et al. established that a 7 nm minimum threshold for the nickel particle size is required for the generation of filamentous carbon.\textsuperscript{181} Ceria supports effectively lower carbon formation and enhance RWGS activity.\textsuperscript{71} Incorporation of Ni into the ceria support introduces more oxygen vacancies and is believed to improve the coke resistance.\textsuperscript{70}

Figure 2.9 correlates the concentration of active surface oxygen measured in the unreduced catalysts to the amount and type of coke formed. The inverse relationship indicates that the active surface oxygen species are effectively preventing excessive accumulation of surface carbon intermediates, regardless of the quantity and nature of the supported Ni species. It is likely that these oxygen species oxidize the surface carbides into CO and are then replenished through CO\textsubscript{2} activation on the support. Hence, I conclude that the concentration of active surface oxygen is a key property of the catalyst that facilitates the removal of coke during dry reforming reactions.\textsuperscript{191}

The 2DI catalyst was the only exception to the inverse relationship between active surface oxygen and coke formation, as it had low surface oxygen concentration and yet produced little coke (Table 2.4 and A.2). This phenomenon was likely due to the severe sintering (particle size increased by a factor of 180) of Ni in 2DI that occurred within 10 h on stream as shown by XRD (Figure 2.6). Considering that this catalyst lost over 50% of its activity within the first hour on stream, it is suggested that it deactivated by sintering before significant amounts of coke could form. Once the reaction reached the low conversion regime (i.e., 3.3%), the rate of methane activation and subsequent coke formation became too slow for significant accumulation (>2 wt%), even though the sintered Ni particles were large enough to favor coke formation.
Figure 2.9 – Correlation between the amount of coke formed vs. the surface oxygen concentration.

The deactivation rate over different types of catalysts did not consistently correlate with the amount of coke formed or the type of coke formed. In the case of 2DI, fast and severe Ni particles growth even limited the coke formation. Hence, the dominating deactivation mechanism for 2DI is Ni particle growth. For the CP samples, the Ni particle growth became less significant with increasing Ni content, which was in line with the deactivation rate. Therefore, the dominating deactivation pathway was also Ni particle growth for the CP samples. However, the contribution from coke formation should not be neglected, especially for the 10CP sample, where the formation of graphitic coke was observed. The 2SEA sample experienced less from Ni particle growth but more coke formed compared to the 2CP sample, and the deactivation of 2SEA was faster compared to 2CP. Hence, coke formation plays a significant role in the deactivation of 2SEA, while Ni particle growth likely has a compounding effect.
2.4.4.3 The encapsulation of Ni by the CZ support on CS samples

In contrast to the SEA and CP catalysts, the CS samples showed little to no coke formation after approximately 1 day on stream. In addition, XANES analysis of the spent samples showed that the spent CS samples remained reduced even after exposure to air, indicating that the Ni particles were protected from atmospheric oxygen. Compared to the CP samples, especially at low Ni content (2CP and 4CP), sintering of Ni was significantly less dramatic. Yet, the deactivation of the CS catalysts was faster than that of the CP samples. Thus, the most plausible explanation is that the Ni particles are encapsulated by the support.

Ni encapsulation by the support within the CS catalysts can be attributed to the unique porous structures formed during synthesis and annealing of the CZ crystallites. During the combustion synthesis procedure, the citric acid polymerized, and the resulting resin formed a porous 3D structure, which was inherited by the catalyst through the subsequent combustion process.\textsuperscript{132} As the maximum temperature during the combustion process could reach above 1000 °C,\textsuperscript{132} such structure could be stable under reaction conditions (i.e., 700 °C). However, the difference between the oxidizing synthesis conditions and the reducing conditions during dry reforming cannot be neglected. Additionally, the fast and vigorous combustion process prevented the annealing of the Ni/CZ system to a thermodynamically stable form and produced smaller CZ crystallites in the unreduced sample. Hence, the sintering of the CZ support was more severe under reduction/reaction conditions compared to the materials produced using the other synthesis methods. Together, the limited mobility of the Ni atoms and the crystal growth of the CZ support introduced the unique environment where the Ni particles are buried by the
support. A similar behavior of Ni/CeO$_2$ CS samples during H$_2$ reduction treatment was reported DelaCruz et al. The encapsulation of Ni particles by the support fixed the Ni particles in place and prevented further sintering. Hence, even though the 2CS sample had a similar Ni speciation to that of the 2CP sample, and both 4CS and 6CS had a considerable fraction of Ni$^{3+}$ species, these catalysts were the most resistant to Ni sintering and had the smallest Ni particles in the spent samples.

Other observations unique to the CS samples were that the deactivation rates were almost independent of the nickel content and that the Ni particles in the spent samples were of the same size (~10 nm) (Table 2.3 and 2.4). Hence it is expected that the rate of Ni encapsulation and the mobility of Ni were balanced in a way that favors the formation of Ni particles around 10 nm. These observations combined with the small quantities of coke formed suggest that Ni encapsulation by the CZ support was the primary mechanism in the deactivation behavior of these materials. This implies that the rate of Ni particle encapsulation by the CZ support was much faster than the rate of Ni atom migration and particle growth and thus controlled the catalyst deactivation and the final Ni particle size. XANES analysis of the spent CS samples revealed that the Ni remained reduced (Figure 2.5), which implies that the encapsulation of Ni by the support occurred to an extent that most of Ni was not re-oxidized upon handling in air. However, the CS catalysts retained 0.7 to 1.9% CH$_4$ conversion at steady state, which suggested that at least some of the capsules may possess holes or were flexible enough under reaction conditions to allow reactants to reach the Ni particles in their core to a limited extent.$^{110,166}$
2.4.5 *Insight regarding catalyst design*

By comparing the synthesis-structure-performance relationships, trade-offs between the different deactivation pathways were observed and new insights regarding the design of better catalysts can be gained. Ni particle growth is not entirely avoidable when starting with well dispersed precursors. Fortunately, limited Ni mobility under reaction conditions could be realized by 1) introducing stronger metal support interaction, 2) avoiding isolated Ni precursor species with insufficient ability to anchor on the support, and 3) encapsulating the Ni particles. Having larger Ni particles limited the Ostwald ripening of Ni atoms but in-turn facilitates the formation of coke. The spent CS samples had Ni particle size around 10 nm and showed limited coke formation, which suggests that the threshold for significant coke formation could be around a Ni particle size of 10 nm. Encapsulating the Ni particles could limit the accessibility of active Ni sites, hence producing stable, active but useless Ni particles. Coke resistance is an important feature for methane dry reforming catalysts. The surface oxygen concentration after pre-oxidation in 10% O\textsubscript{2} in He at 450 °C for 2 h was found to be a good descriptor for the coke resistance. The incorporation of Ni into the CZ lattice introduces more defect sites and better oxygen storage capacity, and hence makes the catalyst more resistant to coke formation. Promoters that are stable in an oxidation state of 3+ like La and Y could also introduce additional defects and form mixed oxide solutions with CeO\textsubscript{2}. Inclusion of such promoters to the CZ solution could be a valid approach enhancing the coke resistance by optimizing redox properties.\textsuperscript{32} The CS samples were more resistant to both Ni particle growth and coke formation but suffered from Ni encapsulation by the support. Surrounding the active Ni sites with CZ support enhances the coke resistance and limits the mobility of Ni species.
Hence, materials in which Ni is protected by penetrable layers of redox active material be
catalysts that are resistant to both coke formation and Ni particle growth. However, the
challenge in this approach lies in preventing the excessive accumulation of the protective
layer over the active Ni sites, which could eventually prevent the access of reactants to the
Ni core.

2.5 Conclusions

By varying synthetic conditions, a series of Ni/Ce$_{0.83}$Zr$_{0.17}$O$_2$ (Ni/CZ) catalysts was
synthesized and characterized. The SEA method produces NiO clusters with better
dispersion and a stronger metal-support interaction compared to the DI method. Samples
prepared by bulk synthesis methods contain Ni cations incorporated into the CZ lattice with
Ni$^{3+}$ species at low Ni content. The formation of mixed metal oxides further increases the
reducibility of CZ and increases the abundance of active surface oxygen.

All NiO/CZ catalysts are active for methane dry reforming and retained partial
activity at steady state. The abundance of surface Ni species, which reduce below 285 °C
for bulk synthesis techniques and 235 °C for the surface synthesis techniques, is a good
descriptor for the accessible nickel during the initial stage of the reaction. The conversion
of both CH$_4$ and CO$_2$ correlates linearly to the concentration of accessible Ni, which is
evidence that methane activation primarily occurs on Ni and is the rate limiting step of the
reaction.

The major challenge for industrial applications of methane dry reforming using Ni
on supported metal oxides catalysts is the deactivation of the catalysts. In the case of
methane dry reforming over Ni/CZ, deactivation can follow different paths, and their
relative significance strongly depends on the physiochemical properties that are in turn
determined by the synthesis methods. Regardless of the synthesis route, larger Ni particles
are formed under reaction conditions. Introducing stronger metal support interactions
during surface deposition synthesis decelerates but does not prevent the growth of Ni
particles. The ex-solution of Ni cations inside the mixed metal oxide phase yields highly
mobile Ni species upon reduction/reaction and larger Ni particles in the spent samples.
Hence, dispersing Ni to atomic levels alters the Ni particle growth mechanism and
negatively affects the resistance to Ni particle growth. The concentration of active surface
oxygen is a good descriptor for resistance to coking. For catalysts prepared by CS, the
deactivation rates are independent of the Ni content. The dominant deactivation mechanism
for CS catalysts appears to be the encapsulation of Ni particles by the support. The support
capsules likely allow some reagents to access the Ni particles in the core since the catalysts
retained partial activity. In summary, I decoupled complex interplay between the three
deactivation mechanisms over catalysts from different synthesis methods, which provides
important insights into rational design of methane dry reforming catalysts.
CHAPTER 3.  *IN-SITU* FTIR SPECTROSCOPY STUDY OF SURFACE REACTIONS DURING METHANE ACTIVATION OVER NIO/CE$_{0.82}$ZR$_{0.18}$O$_2$ CATALYSTS

3.1 Introduction

The main challenge in utilizing methane as a chemical feedstock lies in methane activation, i.e., the selective cleavage of the 1st C-H bond in methane.\textsuperscript{1, 84-86} Methane is the smallest hydrocarbon molecule with a stable symmetric tetrahedral structure and an extremely high C-H bond energy at 439 kJ/mol.\textsuperscript{1, 4} Three major methane activation mechanisms, namely Lewis acid/base pair or σ-bond metathesis, oxidative addition and electrophilic substitution, have been proposed in both heterogenous and homogeneous metal-based catalytic systems.\textsuperscript{1, 40, 87-89} Coperet et al. proposed the activation of methane over Lewis acidic γ-alumina through the Lewis acid/base pair activation, where methane is activated by the heterolytically splitting of the C-H bond.\textsuperscript{90} The oxidative insertion, where a hydrate and a methyl group are bonded to the metal species through activation, are more commonly observed for late transition metals.\textsuperscript{87, 91} The Shilov system uses high oxidation, electron-deficient, and coordinatively unsaturated species, such as Pt$^{IV}$ salts, to activate methane through electrophilic substitution in homogeneous catalytic systems.\textsuperscript{92}

The activation of methane produces various carbonaceous surface species, which vibrate at different frequencies, making infrared (IR) spectroscopy a perfect tool for identifying and quantifying carbonaceous surface species.\textsuperscript{94} Analyzing the time resolved evolution of surface species under reaction conditions provides important mechanistic and
kinetic insights. The Ribeiro Group demonstrated a sophisticated design of an operando transmission IR cell, which enables monitoring catalytic surfaces using FTIR spectroscopy under reaction conditions. However, the overlapping nature of IR adsorption peaks requires applying advanced analysis, such as curve fitting, linear combination fitting, or chemometrics analysis, to decompose the IR band in order to fully understand the contribution from different species. Curve fitting the IR spectra is widely applied and has proved effective in revealing structural information of proteins. In surface chemistry studies where adsorption of simple molecules, such as CO, CO₂, or NH₃ over surfaces are probed by FTIR, curve fitting is often applied to differentiate surface sites. When examining changes in IR spectra with time, the identification and separation of all possible peaks over the IR bands over time becomes the major challenge. Often times, the relative quantities of species over time are expressed through the integrated area beneath certain peaks, which is only valid when the interference from other species are minimal. Keles et. al. demonstrated non-linear curve fitting routines to fit series of IR spectra, where they used local maxima in the 1ˢᵗ IR spectrum of each time series as indicators for existing peaks, which is insufficient to capture all features over time.

Here, we present a time-resolved investigation on the surface reaction pathways of methane activation using in-situ IR spectroscopy. A novel non-linear regression curve fitting algorithm is developed and applied to reveal the evolution of different surface species. Rather than analyzing desorbed reaction products, this study provides mechanistic and kinetic insights of key surface intermediates to enable a more rational design of catalysts for methane valorization.
3.2 Experiment and Method

3.2.1 Materials

Citric acid (ACS reagent, 99.5% purity) and catalyst precursors including Ni(NO$_3$)$_2$·6H$_2$O (99.999% trace metals basis), Ce(NO$_3$)$_3$·6H$_2$O (99.999% trace metals basis), and ZrO(NO$_3$)$_2$·xH$_2$O (99.999% trace metals basis) were purchased from Sigma Aldrich. Gases used for methane activation and temperature programmed reduction (TPR) experiments including methane (research grade), nitrogen (ultra-high purity, UHP), a10% H$_2$/Ar (UHP), helium (UHP), and 10% O$_2$/He (UHP) were purchased from Airgas.

3.2.2 Catalyst Synthesis

The combustion synthesis method described in our previous study$^{60}$ was applied for the synthesis of materials.$^{132}$ A solution of nickel, cerium and zirconium nitrate precursors and citric acid was prepared with deionized water and was heated continuously. Desired amounts of precursors were added to achieve target compositions (2 wt% or 10 wt% Ni in NiO/Ce$_{0.83}$Zr$_{0.17}$O$_2$). The amount of citric acid added was set to achieve a stoichiometric combustion with nitrate ions. Upon heating, water evaporated, and the remaining citric acid polymerized into a resin. The resin liquified at 156 °C and then underwent a fast combustion, where the citric acid resin and the nitrate ions were consumed and resulted in porous mixed metal oxide catalysts. The samples synthesized were Ce$_{0.82}$Zr$_{0.18}$O$_2$ (CZ), 2 wt% NiO/Ce$_{0.82}$Zr$_{0.18}$O$_2$ (2NiO/CZ) and 10 wt% NiO/Ce$_{0.82}$Zr$_{0.18}$O$_2$ (10NiO/CZ).
3.2.3 Physicochemical Characterization

3.2.3.1 Composition and Morphology

The composition of the samples was analyzed by proton induced X-ray emission (PIXE) at Elemental Analysis Incorporated.

A Micromeritics ASAP 2020 instrument was used for N$_2$ physisorption measurements. Approximately 50 mg of sample was loaded and degassed at 400 °C for 4 h prior to analysis. The pore volume and pore size were determined by using the BJH method applied to the desorption branch of the isotherm$^{133}$, and the surface areas were calculated using the BET method.$^{134}$

Powder XRD patterns were measured on a X’Pert PRO Alpha-1 diffractometer equipped with an X’celerator module. Diffractograms were collected with Cu K$_\alpha$ radiation for 2θ =10–90° with a step size of 0.0167°. The crystal sizes within the CZ mixed oxide were estimated using the Scherrer’s equation.

3.2.3.2 Temperature Programmed Reduction (TPR)

TPR measurements were performed on a Micromeritics AutoChem II 2920 instrument equipped with a cold trap and a TCD detector. Approximately 40 mg of the sample was loaded and was pretreated under 10% O$_2$ in He at 450 °C for 2 h to establish a fully oxidized state. After cooling the sample to 50 °C under helium flow, 10% H$_2$ in helium was flowed over the sample while heating to 900 °C with a 10 °C/min ramp rate. A cold trap was applied to avoid any interference from water in the TCD detector. Curve fitting of the TPR profiles were performed by assuming the reduction of each individual
species produces a symmetric Gaussian profile. The validity of the assumption is confirmed in our previous study using the methods proposed by Malet et. al.$^{60,149}$

3.2.4 **FTIR Spectroscopy**

3.2.4.1 **Pyridine Adsorption followed FTIR Spectroscopy**

Pyridine adsorption followed by FTIR spectroscopy was carried out using a Nicolet iS10 FTIR spectrometer equipped with an MCT/A detector. Catalyst samples were pressed into self-supported wafer and were loaded into a vacuum transmission FTIR spectroscopy cell. Samples were activated at 450 °C for 1 h under high vacuum (~$1 \times 10^{-6}$ mbar) to remove moisture and other deposits. The catalyst wafer was exposed small amount of pyridine repeatedly at 150 °C, until the pyridine adsorption reached equilibrium at 0.1 mbar. To ensure only chemisorbed pyridine on the surface was recorded, the excess pyridine vapor and physiosorbed pyridine were removed by evacuation under high vacuum for 1 h. The thermoevacuation of the adsorbed pyridine was then carried out by heating the cell to 250 °C, 350 °C, and 450 °C and held for 30 minutes under vacuum. For each of the thermoevacuation temperatures, a spectrum was taken when the cell temperature was brought back to 150 °C. A 6.35 mm diameter disc of the wafer was weighed for calculating the density of the wafer. Assuming a 1:1 pyridine to acid site adsorption ratio, the concentration of Lewis and Brønsted acid sites were determined from the peak area of the peaks at 1445 cm$^{-1}$ and 1540 cm$^{-1}$, respectively, using extinction coefficients reported by Datka et. al.$^{206}$
3.2.4.2 High-Vacuum Transmission FTIR Spectroscopy

Approximately 20 mg of the 2NiO/CZ sample was pressed into a self-supported vapor and was pretreated under high vacuum (~$1 \times 10^{-6}$ mbar) at 450 °C for 1 h. The sample was then cooled to 50 °C and a background of the clean catalyst surface was taken with 64 scans at a resolution of 4 cm$^{-1}$. The sample was exposed to small quantity of probe molecule vapor, including methanol, formaldehyde, formic acid and benzene, repeatedly until an equilibrium state was established at 0.5 mbar. The chamber was then evacuated, and a spectrum of the species on the catalyst surface was recorded.

3.2.4.3 Methane Activation using in-situ FTIR Spectroscopy

Methane activation experiments were carried out using an in-situ IR cell based on the design by Ribeiro et. al.$^{95}$ that was placed in a Nicolet 8700 FTIR spectrometer equipped with an MCT/A detector. Approximately 120 mg of the catalyst was pressed into a self-supported wafer. The catalyst wafer was then loaded to the cell and activated at 450 °C for 2 h under 50 sccm of N$_2$ flow. A background of the activated catalyst was collected once the cell was cooled to the reaction temperature (200 or 300 °C). Methane activation over the sample was carried out by subsequently flowing of 20 sccm of methane over the catalyst for 12 h. Every 30 sec, a spectrum was collected with 64 scans at a resolution of 4 cm$^{-1}$ over the course of 12 h of the experiment. The effluent stream of the in-situ IR cell was monitored using an in-line MS. The absorbance of surface species on different samples was normalized to the amount of sample used in each experiment allowing for quantitative comparison between experiments.
3.2.5  *Data Analysis Procedure*

Time-resolved series of IR spectra of surface species formed by methane activation were collected during each experiment. Following the data analysis procedure described below, the evolution of various surface species during methane activation was revealed.

3.2.5.1  *Pretreatment of the Data Set*

3.2.5.1.1  Subtraction of Gaseous Methane Signal

Gaseous methane vibrations superimposed by rotational modes created features overlapping with the features around 2800 – 3000 cm$^{-1}$ and 1300 cm$^{-1}$ from methane activation. The removal of the gaseous methane features was achieved by subtracting the spectrum of gaseous methane collected in an empty cell at the same temperature from each of the spectra collected during the experiment. A response factor was calculated based on the ratio of the peak height of the peak at 3012 cm$^{-1}$ for methane in the empty cell data and during a surface reaction.

3.2.5.1.2  Splitting Spectra to Three Regions

Features from carbonaceous species from methane activation reside in several regions in the IR band. For better analysis of weaker features and reducing the computational cost, spectra over the entire IR band were split to three regions and other regions without significant IR features were discarded for further analysis. Specifically, the three regions of interest are: 1) the 2800-3000 cm$^{-1}$ region with the characteristic peaks from the C-H stretching modes; 2) the 1300 - 1700 cm$^{-1}$ region with complex features from surface species like formates, carbonates, aromatics, and aldehydes; 3) the 1000 - 1150 cm$^{-1}$
with features from alkoxy species or alcohols. Baseline correction of the spectra was carried out based on the method developed by He et. al. as needed.  

3.2.5.2 Revealing the Evolution of the Surface Species  

We developed a novel curve fitting algorithm that consists of three steps as described below based on non-linear regression fitting to reveal the evolution of the surface species. The non-linear regression fitting is carried out using the *lmfit* package and the *Scipy.optimize* package.  

3.2.5.2.1 Step 1: Identification of All Characteristic Peaks  

The identification of peaks was carried out by analyzing the 1st and 2nd derivatives of the IR curves. Additionally, the analysis of the difference between spectra at adjacent times (referred to as ‘the difference spectra’) allows for the detection of features arising at later times, especially if they are shadowed by the larger peaks that rise earlier. Given a specific number of peaks and reasonable initial guesses of peak parameters, a model IR spectrum can be described mathematically as:

\[ y_{\text{model},i} = \sum_j a_j F(\mu_j, \sigma_j) \]

where \( i \) is the time index, and \( j \) is the peak index; \( a \) is the amplitude of the peak; and \( F \) refers to the peak profile. The peak parameters were then optimized using non-linear regression fitting by minimizing the difference between the model and the actual data over all time:
\[ l(\tilde{a}, \tilde{\mu}, \tilde{\sigma}) = \sum_l \| y_l - y_{\text{model},l} \| \]

The peak shape of each peak, defined by the peak profile (Gaussian or Voigt), the position (\( \mu \)) and the peak width (\( \sigma \)), were held constant over time, or at least over a certain period of time, as changes in the peak position or width is an indication of changes in the chemical properties of the surface species.

3.2.5.2.2 Step 2: Construction of Vector Basis for All Surface Species

In this step, a vector basis was constructed by categorizing peaks that belong to the same species together into vectors. Such assignment was guided by examining 1) the correlation matrix of relative intensity of peaks over time, as peaks that are highly correlated likely belong to the same species; 2) peak assignments based on literature; and 3) reference experiments carried out by dosing probe molecules over the same surface. By grouping peaks from the same species into a vector, each surface species was described as a set of peaks with known chemical assignment. If there were more than one peaks in a vector, i.e., the surface species had more than one characteristic peak, the ratio of integrals between these peaks were fixed within the vector. Mathematically, each surface species \( S_j \), with \( k \) characteristic peaks can be expressed as:

\[ S_j = \sum_k a_{jk} F(\mu_{jk}, \sigma_{jk}) \]

where \( j \) is the surface species index, and \( k \) is the peak index within each species. Different from Step 1, the amplitudes of peaks within a surface species vector were restrained by both
the ratio of peak amplitudes between peaks from the same vector and the integral of the vector, which was set to 1.

By categorizing all the peaks identified in Step 1 to vectors representing surface species, a vector space that contains all the surface species in the IR band of interest was established.

\[ X = \{ S_0, S_1, S_2 \ldots \} \]

**3.2.5.2.3 Step 3: Analysis of the Evolution of Surface Species**

With the vector basis established, the model IR spectra can be expressed as:

\[ y_{model,i} = \omega \overrightarrow{X} + b \]

, where \( b \) is the intercept and \( \omega \) are the coefficients of each surface species in the vector space. It should be noted that since the integral of each vector was normalized to 1, hence, the coefficient \( \omega \) actually represented the relative concentration of each surface species.

The optimization of the coefficients \( \omega \) together with the hyperparameters: \( a, \mu \) and \( \sigma \), was carried out using non-linear regression fitting by minimizing the loss function:

\[ l(\omega, a, \mu, \sigma) = \sum_i \|y_i - y_{model,i}\| = \sum_i \left( y_i - \sum_j \omega_j \sum_k a_{jk} F(\mu_{jk}, \sigma_{jk}) - b_i \right)^2 \]

Finally, the optimized \( \omega \) reflected the evolution of quantities of different surface species over time.
3.2.6 **Spent Sample Characterization**

Thermogravimetric analysis (TGA) of spent samples was performed using a TA Instruments SDT Q600 Thermogravimetric Analyzer. Approximately 10 mg of each sample were loaded and was heated to 150 °C at 10 °C/min ramp rate under N₂ flow. The sample was held at 150°C for 60 mins to remove moisture and other deposits. The sample was then heated to 900 °C at a rate of 10 °C/min under air flow.

3.3 **Results**

3.3.1 **Physiochemical Properties**

PIXE results showed that the elemental composition of the samples was close to target values. The surface area, pore volume and pore width of the CZ support and 2NiO/CZ were almost identical. By increasing the Ni content to 10 wt%, the surface area dropped by 24%, and the pore volume dropped by 17% compared to 2NiO/CZ. The pore width remained almost constant across all three samples.

In the X-ray diffractograms of all samples, only the characteristic diffraction peaks of the CZ solid solution at 28.8°, 33.4°, 47.9°, 56.9°, 70.1° and 78° were observed (Figure B1). The lack of characteristic diffraction peaks for either pure ceria or pure zirconia suggested no significant phase separation in the CZ mixed metal oxides. Additionally, no characteristic peaks for NiO were observed in any sample either. The lattice constant for the CZ (111) plane appeared to be constant with varying Ni contents (Table 3.1). However, this did not exclude the possibility that Ni was incorporated into the
The crystalline size of the mixed oxides for 10NiO/CZ was 11% higher than for 2NiO/CZ.

Table 3.1 – Physiochemical properties of CZ, 2NiO/CZ and 10NiO/CZ.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CZ</th>
<th>2NiO/CZ</th>
<th>10NiO/CZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel content (wt. %)(a)</td>
<td>N/A</td>
<td>1.9</td>
<td>9.6</td>
</tr>
<tr>
<td>Ce:Zr ratio(a)</td>
<td>81:19</td>
<td>81:19</td>
<td>82:18</td>
</tr>
<tr>
<td>BET surface area (m(^2)/g)(b)</td>
<td>52</td>
<td>56</td>
<td>43</td>
</tr>
<tr>
<td>Pore volume (cm(^3)/g)(c)</td>
<td>0.11</td>
<td>0.12</td>
<td>0.1</td>
</tr>
<tr>
<td>Pore width (nm)(c)</td>
<td>5.4</td>
<td>5.3</td>
<td>5.2</td>
</tr>
<tr>
<td>Ce(<em>x)Zr(</em>{1-x})O(_2) crystalline size (nm)(d)</td>
<td>4.1</td>
<td>4.1</td>
<td>4.7</td>
</tr>
<tr>
<td>Lattice constant for CZ (111) plane (Å)(e)</td>
<td>3.09</td>
<td>3.09</td>
<td>3.09</td>
</tr>
<tr>
<td>Total H(_2) uptake (mmol/g)(f)</td>
<td>0.54</td>
<td>0.94</td>
<td>1.87</td>
</tr>
<tr>
<td>H(_2) uptake by adsorbed surface O(_2) (mmol/g)(f)</td>
<td>N/A</td>
<td>0.13</td>
<td>0.12</td>
</tr>
<tr>
<td>H(_2) uptake by surface CZ or interfacial CZ associated with Ni (mmol/g)(f)</td>
<td>0.34</td>
<td>0.16</td>
<td>0.22</td>
</tr>
<tr>
<td>Lewis acid site concentration (μmol/g)(g)</td>
<td>51</td>
<td>74</td>
<td>102</td>
</tr>
</tbody>
</table>

\(a\) From elemental analysis.  
\(b\) From desorption isotherms measured by N\(_2\) Physisorption using the BET method.  
\(c\) From desorption isotherms measured by N\(_2\) physisorption using the BJH method.  
\(d\) From XRD using Scherrer equation for the Ce\(_x\)Zr\(_{1-x}\)O\(_2\) (111) peak at 28.8°.  
\(e\) From XRD using Bragg’s Law for the Ce\(_x\)Zr\(_{1-x}\)O\(_2\) (111) peak at 28.8°.  
\(f\) From TPR experiments.  
\(g\) From pyridine adsorption followed FTIR spectroscopy experiments.

3.3.2 TPR

The reducibility of the samples and the support were assessed by TPR. Peak fitting of the TPR profiles were performed for better estimation of reduction temperatures and quantitative analysis of the data (Figure B.2, Table 3.1, Table B.1). Three major reduction peaks were observed for the CZ support (Figure 3.1). Reduction features at 455 °C and 536 °C were assigned to the successive reduction of the surface and bulk CZ.\(^{209}\) The earliest peak at 349 °C was discussed with speculative assignments according to literature,\(^{131,153}\) either from the dissociative adsorption of H\(_2\) or the non-stoichiometric reduction of the surface CZ.\(^{131,209}\) The addition of NiO significantly enhanced the reducibility of CZ judging by the shift of reduction peaks from 460 °C to 370 °C for the surface CZ and from
605 °C to 420-460 °C for the bulk CZ. Hence, for the catalyst samples, the earlier peaks at 
~ 370 °C were assigned to the interfacial CZ associated with Ni and the later peaks at 420-
460 °C were assigned to the bulk CZ associated with Ni. Additionally, the earliest peak at
177 and 196 °C were attributed to the consumption of the adsorbed surface oxygen
species.15, 76, 83, 150-152 The peaks at around 250 °C and 310 °C were assigned to the
successive reduction of NiO species on the catalyst surface and buried inside the bulk of
the catalysts.83, 159 Both peaks corresponding to the reduction of NiO species became much
stronger when the Ni content was increased from 2 to 10 wt%. The adsorbed surface
oxygen concentrations in the two samples were similar. However, 10NiO/CZ showed more
H₂ uptake from interfacial CZ associated with Ni and less H₂ uptake from bulk CZ
associated with Ni compared to 2NiO/CZ (Table 3.1).

3.3.3 Pyridine Adsorption followed by FTIR Spectroscopy

The acidity of the samples was characterized by the pyridine adsorption followed
by FTIR spectroscopy. The peak around 1443 cm⁻¹ is attributed to the vibrational mode
19a of pyridine adsorbed to Lewis acid sites (LPy) and it was observed for all samples.206,
210, 211 The ring vibrational mode 19b for pyridinium ions formed on Brønsted acid sites
gives rise to the peak at 1535-1540 cm⁻¹,211, 212 which was missing in all cases, indicating
the surfaces were free of Brønsted acid sites. The CZ support itself contains some Lewis
acidity (Table 3.1). Both 2NiO/CZ and 10NiO/CZ had higher Lewis acid site (LAS)
concentrations compared to the bare CZ, and the LAS concentration increased with higher
Ni content. The difference between the LAS concentration of the catalyst and the support
can be attributed to the LAS from NiO species. Though, it should be noted that the presence
of NiO could block or alter some LAS of the CZ support. LAS concentrations from NiO
species (22.4 μmol/g for 2NiO/CZ and 50.9 μmol/g for 10NiO/CZ) were much lower than the Ni concentrations (341 μmol/g for 2NiO/CZ and 1704 μmol/g for 10NiO/CZ). The apparent dispersion of NiO, defined by the pyridine uptake by NiO at 150 °C divided by the Ni concentration, was 6.5% for 2NiO/CZ and 3.0% for 10NiO/CZ.

Figure 3.1 – TPR profiles for CZ, 2NiO/CZ, and 10NiO/CZ.
Figure 3.2 – a) Pyridine adsorption over CZ, 2NiO/CZ and 10NiO/CZ at 150 °C followed by FTIR spectroscopy. b) Thermoevacuation of pyridine at 250 °C, 350 °C, and 450 °C.

During thermoevacuation, the LPy peak area decreased in all cases, indicating the desorption of pyridine from LAS (Figure B.3). A peak around 1437 cm$^{-1}$ overlapped with the LPy peak. It is assigned to carbonate species that formed from the decomposition of adsorbed pyridine with active oxygen from the samples.\textsuperscript{210,213} That peak became stronger at higher temperatures for both catalysts. Peak fitting was required to quantify the contribution of the LPy band (Figure B.4, Table B.2). The difference between LAS in the
2NiO/CZ sample and the CZ support remained almost constant across temperature, indicating the LAS from NiO were much stronger and were capable of retaining pyridine even at 450 °C. The 10NiO/CZ sample also showed a higher concentration of strong LAS compared to the CZ support. However, the LAS concentration for the two catalysts were almost identical at 350 °C and 450 °C, indicating the increase in Ni content did not alter the concentration of strong LAS in the two samples.

3.3.4 Methane activation over NiO/CZ catalysts

Methane activation over NiO/CZ catalysts was analyzed using in-situ FTIR spectroscopy at 200 °C and 300 °C. Methane was activated in all cases producing various surface species as indicated by the complex features in the IR spectrum (Figure 3.3). An in-line MS was used to monitor the effluent stream of cell. However, only small quantities of CO₂ were detected by the MS (Figure B.5), suggesting limited desorption of the surface species formed during methane activation. The peak assignments are discussed for the surface species formed on 2NiO/CZ at 200 °C (Table 3.2), but the same species were observed in other experiments (Table S6.2, S6.4 and S6.6). The broad features above 3000 cm⁻¹ were ascribed to the surface hydroxyl groups subjected to hydrogen bonding.¹³¹ By dosing formic acid over the 2NiO/CZ, we observed a broad peak in the 2800-3000 cm⁻¹ region, which are in close proximity with the four peaks observed here (Figure B.6). Combined with literature, these peaks were assigned to the C-H stretching of formates and methyl species formed from methane activation.²⁰³, ²¹⁴⁻²¹⁸ Peaks around 1600 cm⁻¹ were assigned to the C=O stretching mode of carbonyl species from aldehydes,²¹⁹ in agreement with the spectrum after formaldehyde adsorption on 2NiO/CZ at 50 °C (Figure B.7). Two peaks around 1540 cm⁻¹ were recognized as characteristic peaks from the carbonate
species. The sharp peak around 1540 cm\(^{-1}\) was assigned to the O-C-O stretching from carbonates\(^{214-218}\), and the broader peak was assigned to the C=O stretching.\(^{41,214-218}\) These two peaks were also observed in spectrum of adsorbed formic acid on 2NiO/CZ (Figure B.6). The peaks around 1500, 1450, and 1380 cm\(^{-1}\) were assigned to ring vibrations from aromatic species.\(^{220-226}\) These peaks were in general very broad, indicating the presence of various poly-aromatics, which probably constitute the precursors of the carbon deposit detected by TGA of the spent catalyst (Figure B.8). One additional piece of evidence supporting the assignment is that these broad peaks from aromatics were observed from adsorption of benzene over 2NiO/CZ at 200 °C (Figure B.7). Even the absolute absorbance of benzene was weaker than the C1 oxygenates (Figure B.6), the presence of features in the 1300-1600 cm\(^{-1}\) region indicates the activation of benzene C-H bond\(^{224}\) and the formation of poly-aromatic precursors. The peak around 1350 cm\(^{-1}\) was assigned to O-C-O stretching of formates, while the peak around 1370 cm\(^{-1}\) was assigned to the in-plane scissoring O-C-H vibration of formates.\(^{214-218}\) These peaks were also observed after dosing formic acid on 2NiO/CZ at 50 °C. The peaks around 1080 and 1030 cm\(^{-1}\) were assigned to the C-O stretching modes from alkoxy species formed after methane activation, potentially on different sites.\(^{227-232}\) The same peaks were formed in this region when methanol was dosed onto the 2NiO/CZ surface (Figure B.6).

The evolution of surface species from methane activation over NiO/CZ catalysts can be divided into three stages for all cases. In the initial stage (i.e., the first 30 min) of the experiment with 2NiO/CZ at 200 °C, fast growths of all species were observed (Figure 3.4a). In the middle stage, between 30 min to 120 min, the growth of formates and carbonates, and aromatics slowed down, while the growth of aldehydes and alkoxy species
continued at the same rate as in the initial stage. In the final stage, formates and carbonates,
and aromatics continued to grow at a slower rate, while aldehydes and alkoxy species
slightly decreased in intensity over the final 10 h of the experiment.

Table 3.2 – Optimized peak parameters for IR spectra from methane activation over 2NiO/CZ at 200 °C and peak assignments.

<table>
<thead>
<tr>
<th>Species</th>
<th>Vibrational Modes</th>
<th>Stage</th>
<th>Type</th>
<th>Position (cm⁻¹)</th>
<th>Variance (cm⁻¹)</th>
<th>Relative Amplitude</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formates</td>
<td>v_sym(C-H)</td>
<td>All period</td>
<td>Voigt</td>
<td>2855.3</td>
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<td>1</td>
<td>203, 214</td>
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<td></td>
<td>v_Ca(C-H)</td>
<td>All period</td>
<td>Voigt</td>
<td>2934.3</td>
<td>2.9</td>
<td>1.18</td>
<td>203, 214</td>
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<td>All period</td>
<td>Voigt</td>
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<td>218</td>
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<td></td>
<td>v_Ca(C-H)</td>
<td>All period</td>
<td>Voigt</td>
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<td>Aldehydes</td>
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<td>Voigt</td>
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<td>1</td>
<td>41, 219</td>
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<tr>
<td></td>
<td></td>
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<td>Voigt</td>
<td>1605</td>
<td>18</td>
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<td></td>
<td></td>
<td>Final</td>
<td>Voigt</td>
<td>1610</td>
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<td>1</td>
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<td>Carbonates</td>
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<td></td>
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Figure 3.3 – IR spectra of methane activation over a) 2NiO/CZ at 200 °C, b) 10NiO/CZ at 200 °C, c) 2NiO/CZ at 300 °C, d) 10NiO/CZ at 300 °C.

For the experiment over 10NiO/CZ at 200 °C, the initial stage lasted for 10 min, where accumulation of all species was observed. In the middle stage, between 10 mins to
60 mins, formates and carbonates decreased in intensity and aromatics continued to accumulate at a slower rate, while the formation of aldehydes and alkoxy species continued at the same rate as in the initial stage. In the final stage, i.e., after 60 mins, formates, carbonates, and aromatics formed at slower rates, while aldehydes and alkoxy species either ceased to form or were consumed to some extent over the final 11 h of the experiment.

For the experiment over 2NiO/CZ at 300 °C (Figure 3.4c), the initial stage was much shorter lasting only 5 min. Again, fast formation of all species was observed. In the middle stage, between 5 min and 20 min, the peaks of formates and carbonates, as well as aromatics decreased slightly, while the accumulation of aldehydes and alkoxy species continued at the same rate as in the initial stage. In the final stage (i.e., after 20 min) the concentration of formates and carbonates stayed constant while aromatics were formed at a slightly slower rate, and the intensity of aldehydes and alkoxy species either stayed constant or slightly decreased.

Finally, for 10NiO/CZ at 300 °C (Figure 3.4d), the initial stage lasted for only 1 minute. Fast formation of all species was observed. In the middle stage, between 1 min to 10 min, the peaks of formates and carbonate decreased by 40%; while the rate of formation of aromatics, aldehydes and alkoxy species remained constant. In the final stage, i.e., after 10 mins, all species formed at a slower rate.
Figure 3.4 – Evolution of surface species over time during methane activation over a) 2NiO/CZ at 200 °C, b) 10NiO/CZ at 200 °C, c) 2NiO/CZ at 300 °C, and d) 10NiO/CZ at 300 °C.
3.4 Discussion

3.4.1 Reducibility and Acidity of the Catalysts

Combustion synthesis is a bulk synthesis which embeds a fraction of the Ni species inside the CZ lattice. Our previous study showed that such incorporation has two impacts: 1) the local electronic structure of the Ni species is strongly altered, producing some Ni$^{3+}$ species, which are stronger Lewis acid sites if accessible; and 2) more defect sites inside the CZ are created, enhancing the reducibility of the CZ support.

Our previous study showed that, for samples synthesized similarly, Ni species in the 2NiO/CZ sample were almost atomically dispersed, while the average NiO particle size in the 10NiO/CZ sample was 0.68 nm. The apparent dispersion of NiO (i.e., fraction of accessible Ni cations) was 6.5% for 2NiO/CZ and 3.0% for 10NiO/CZ, indicating a large fraction of the Ni was inaccessible because it was incorporated into the CZ lattice or NiO clusters encapsulated by the support. However, the limited quantity of accessible NiO on the surface demonstrated strong Lewis acidity as a significant portion of these NiO species (72% from 2NiO/CZ and 33% from 10NiO/CZ) were able to adsorb pyridine even at 450 °C. Such strong Lewis acidity may originate from Ni$^{3+}$ species on the surface that were detected by XAS and XPS. The relatively weaker LAS that are also associated with NiO are likely from the NiO nanoclusters, whose local electronic environment is less influenced by the support. However, our previous study showed these weaker LAS are still capable of activating methane as long as they can adsorb pyridine at 150 °C.

The fast combustion step during the synthesis assures rapid quenching of the mixed metal oxides and prevents the material from equilibrating to the thermodynamically most
stable form. Thus, it generates catalysts with more defect sites in the mixed metal oxide lattice and enhanced reducibility.\textsuperscript{132} The inclusion of NiO to the CZ support produces a significant quantity of surface defects evidenced by the adsorbed surface oxygen species in both catalysts probed by TPR. As shown by the shift in reduction temperature, a higher Ni content creates more interfacial CZ associated with Ni, and these species are easier to reduce than the surface CZ on the pure CZ support.

3.4.2 *Mechanistic Insights on Methane Activation*

Lewis acidic metal oxides are capable of activating methane through heterolytic splitting of the C-H bond producing a surface methyl and hydroxyl group.\textsuperscript{40} The subsequent conversion of the activated methyl species can produce key intermediates towards value-added products.\textsuperscript{1} Here, we compare the methane activation over different catalysts at different temperatures to develop a better understanding of the methane activation mechanisms over NiO/CZ catalysts.

![Figure 3.5 – Comparison of the evolution of different species over 2NiO/CZ and 10NiO/CZ at 200 and 300 °C: a) formates, b) carbonates, c) aromatics, and d) alkoxy species.](image)

81
The integral of formates and carbonates at 12 h of experiment were almost constant across experiments and were independent of temperature or samples. In the case of the 2NiO/CZ at 200 °C, though the quantity of carbonate and formate at 12 h was slightly lower than other experiments, the system had not reached steady state judging by the increasing trend in the formate and carbonate curves at the end of 12 h of experiment, indicating there was still room for the accumulation of such species. The formation of formate and carbonate requires an oxygen source, which could only be the oxygen species stored in the catalysts. The adsorbed surface oxygen is the most active oxygen species in the system as it reduced the earliest in TPR. Additionally, the concentration of adsorbed surface oxygen in both samples were quite comparable (Table 3.1). Hence, it is likely that the adsorbed surface oxygen concentration controls the surface reaction pathways to CO\textsubscript{2} precursors such as formates and carbonates. Except during the experiment over 2NiO/CZ at 200 °C, a decrease in the quantity of formate and carbonate was observed during the middle stage of the experiment, indicating that the consumption rate was faster compared to the accumulation rate of these species. Considering both formate and carbonate are CO\textsubscript{2} precursors, and the fact that a pulse of CO\textsubscript{2} signal observed by in-line MS in these experiments (Figure B.5), the decrease can be explained by the conversion of intermediate formate and carbonate to CO\textsubscript{2} became faster than the formation of these intermediates once the highly active oxygen species were consumed.

The formation of aromatic species was clearly favored at higher temperature and at higher Ni content. The non-oxidative aromatization of methane is endothermic, hence is thermodynamically favored at higher temperature. Higher temperature also facilitated faster methane activation to produce methyl species, which can further couple with each
other and produce aromatics. Increases in the quantity of aromatics at higher Ni content suggests NiO was the active site for the formation of aromatics. The presence of larger NiO clusters in 10NiO/CZ also facilitated the formation of aromatics, which could be related to their ability to effectively co-adsorb multiple intermediates for the aromatization reaction. The accumulation rate of aromatic species in the final stage gradually decreased, especially for the 10NiO/CZ sample, suggesting an increasing coverage of the active NiO sites with aromatic deposits over the course of the experiment.

The formation of alkoxy species was also favored at higher Ni content but was suppressed at higher temperature. The Ni content dependence suggests that NiO were also the active site for forming alkoxy intermediates. At the higher temperature, the formation of aromatics was favored and became faster in the initial stage. Hence, more NiO sites were covered at earlier times during the experiment, which lowers the yield towards alkoxy intermediates on the surface. The oxygen source for the formation alkoxy intermediate could be the oxygen species originating from the interfacial CZ associated with Ni (Table 3.1), as the H₂ uptake from TPR of such species correlated with quantity of alkoxy species formed between samples. The differentiation of active oxygen species in the system is extremely challenging and not possible based on the current data set. However, there probably exists specific oxygen species, likely ones from the interfacial CZ associated with Ni, that can selectively oxidize the activated methyl groups to alkoxy intermediates.

Based on discussion above, we propose the following surface reaction pathways for methane activation over NiO/CZ catalysts (Figure 3.6). Methane was first activated through the Lewis/acid pair mechanism over the catalyst surface, producing a methyl and hydroxyl group. If the formation of formate and carbonate intermediates was driven by the
adsorbed oxygen species, it is likely that the methane activated by the CZ support underwent the pathway of producing CO$_2$ precursors, such as formates and carbonates (Pathway 1). When the highly active adsorbed O$_2$ species were highly available on the surface, usually during the initial stage, methyl intermediates formed on NiO could also access these oxygen species and produce formates and carbonates.

Pathway 1: \( \text{CH}_4 \xrightarrow{\text{CeZrO}_2} \text{CH}_3^* + \text{OH}^* \xrightarrow{[\text{O}]} \text{HCOO}^* \)

Pathway 2: \( \text{CH}_4 \xrightarrow{\text{NiO}} \text{CH}_3^* + \text{OH}^* \xrightarrow{[\text{O}]^2} \text{H}_3\text{CO}^* \)

Pathway 3: \( \text{CH}_4 \xrightarrow{\text{NiO}} \text{CH}_3^* + \text{OH}^* \xrightarrow{\text{CH}_2^*} \text{C}_2\text{H}_y^* \rightarrow \text{Aromatics} \)

**Figure 3.6 – Reaction pathways during methane activation over NiO/CZ catalysts.** [O]$^1$ refers to the adsorbed active oxygen species, and [O]$^2$ is the active oxygen species that can selectively oxidize methyl to methoxy species.

NiO was the major active site for the formation of alkoxy and aromatic species. Methyl species formed from the methane activation over NiO sites can react with certain active oxygen species to form alkoxy intermediates (Pathway 2). The exact nature of such active oxygen species remains unknown, but they are tentatively attributed to interfacial CZ associated with Ni and were denoted as [O]$^2$ in the Scheme 2. The synergy between the isolated Ni species and the interfacial CZ associated with Ni possibly facilitated the formation of alkoxy species. Isolated Ni species were strongly interfered by the CZ lattice and were in higher oxidation state, such as Ni$^{3+}$. Hence, they were stronger Lewis acid and were more effective in methane activation. The isolated Ni species could also incorporate into the CZ lattice creating defect sites and oxygen vacancies, which can possibly generate
[O]² species. With better methane activation capability and access to [O]² species, isolated Ni sites could more selectively produce alkoxy intermediates.

The methyl species can also couple with each other to produce C2 species, and upon further coupling of the C2 species, aromatics can be produced (Pathway 3). This pathway is presumably more favored over larger NiO clusters, which can co-adsorb multiple intermediates for the aromatization reaction. However, judging by the fact that aromatics were also formed over 2NiO/CZ, the isolated Ni species could also produce aromatics.

3.4.3 Strategies for Improving Selectivity towards Alkoxy Intermediates

Alkoxy intermediates are the key precursors to the production alcohols. Improving the selectivity to alkoxy intermediates during methane activation is crucial for the development of catalytic processes for the direct selective oxidation of methane to alcohols. One way of semi-quantitatively analysis of the selectivity towards alkoxy species is to plot the peak area of their IR bands relative to the sum of the peak areas of other species over time (Figure 6). For all cases, the maximum selectivity towards alkoxy species was achieved in the middle stage of the methane activation experiment. Two factors appear to control the formation of alkoxy intermediates: 1) the concentration and the morphology of accessible NiO active sites, and 2) the availability of the ‘right’ oxygen species. During the middle stage of the experiment, the most active adsorbed oxygen has been mostly consumed allowing the somewhat less reactive oxygen species from the interfacial CZ associated with Ni to participate the surface reactions. Additionally, at lower temperature, the accumulation of aromatics was not very significant, leaving more NiO active site
uncovered from aromatics. Hence, maximum selectivity towards alkoxy intermediates was achieved in this period.

Figure 3.7 – The normalized relative intensity of alkoxy species compared to the sum of other species in experiment over a) 2NiO/CZ at 200 °C, b) 10NiO/CZ at 200 °C, c) 2NiO/CZ at 300 °C, d) 10NiO/CZ at 300 °C. e) The relative intensity of alkoxy species compared to the sum of other species in different experiments.

The heterolytic splitting of the C-H bond over Lewis acidic NiO sites has been identified as the first step for the formation of both aromatics and alkoxy intermediates (Figure 3.6). \(^1,^{40,41}\) Aromatic species covering the active site is one of causes for decrease in the selectivity towards alkoxy intermediates. Thus, the competition between Pathway 2 and Pathway 3 controls the selectivity towards alkoxy and aromatic intermediates. Large NiO clusters favor the formation of aromatic/poly-aromatic surface species.\(^{15,237}\) Hence, one strategy to improve the alkoxy intermediates selectivity is to create higher
concentration of small and well-dispersed of NiO species. Such species not only enhance the concentration of LAS, but also suppress the formation of aromatics. Another strategy is to operate at lower temperature, as it limits the formation of aromatics both kinetically and thermodynamically.

Selectivity to alkoxy also depends on the availability of the ‘right’ active oxygen species.\(^{238}\) The adsorbed surface oxygen species had been identified as the driving force for the formation of formates and carbonates. Therefore, it could be beneficial to apply a reduction pretreatment step to remove some of the over-active oxygen species for enhancing the selectivity towards alkoxy intermediates. However, the pretreatment agent and condition should be chosen carefully to avoid over reduction of the catalyst producing reduced Ni species.

### 3.5 Conclusion

Methane activation over NiO/CZ catalysts is investigated using \textit{in-situ} FTIR spectroscopy. Complex IR features are observed from methane activation and are attributed to the formation of surface alkyl/alkoxy, aldehyde, formate/carbonate, and aromatic species. A novel data analysis algorithm based on non-linear regression fitting is developed to evaluate the evolution of different surface species over time. The formation of formate and carbonate species are driven by the adsorbed surface oxygen and the formation of aromatics and alkoxy intermediates are controlled by NiO. The selectivity towards alkoxy intermediates can be improved by 1) increasing the dispersion of NiO, 2) operating at a lower temperature, and 3) applying a reduction pretreatment step.
CHAPTER 4. SELECTIVE OXIDATION OF METHANE TO METHANOL OVER CERIA-ZIRCONIA SUPPORTED MONO AND BIMETALLIC TRANSITION METAL OXIDE CATALYSTS

4.1 Background

Methanol is an ideal platform for methane valorization, as it is a liquid chemical of high demand. In industry, methanol is synthesized from syngas at elevated pressure (50 to 100 bar) and temperature (200 to 300 °C) over Cu/ZnO/Al₂O₃ catalysts. Over the years, many efforts have been made to develop efficient methods for upgrading methane into methanol. Studies have shown that it is possible to convert methane to methanol directly using more selective oxidants such as H₂O₂ and N₂O. The selective oxidation of methane to methanol is also possible using photocatalysis or plasma reactions. Methane monooxygenase enzymes with iron or copper active centers showed great selectivity for converting methane to methanol under ambient conditions. Inspired by these enzymes, extensive studies on copper-containing zeolites have shown the possibility of converting methane directly into methanol using O₂ as the oxidant via chemical looping processes. Such processes are usually composed of three steps: the activation of catalysts under O₂ at high temperature; the activation of methane at moderate temperatures; and the introduction of steam to release the methanol formed. Since chemical looping processes for this reaction have been shown to be uneconomical, the development of steady state systems is critical.
In this study, I synthesized a series of CZ supported mono- and bi-metallic transition metal oxides catalysts. Reactivity tests showed that the catalysts are capable of continuous direct conversion of methane to methanol at moderate temperatures using O₂ as the oxidant and steam to release the methanol. Such steady state activity has been shown in few other cases. Synergistic effects in supported bimetallic metal oxides are elucidated.

4.2 Experimental

4.2.1 Materials and Catalyst Synthesis

Metal precursors, including Ni(NO₃)₂·6H₂O (99.999% trace metals basis), Fe(NO₃)₃·9H₂O (99.999% trace metals basis), Cu(NO₃)₂·3H₂O (99.999% trace metals basis), Ce(NO₃)₃·6H₂O (99.999% trace metals basis), and ZrO(NO₃)₂·xH₂O (99.999% trace metals basis) and ammonia hydroxide solution (ACS reagent, 28.0-30.8 NH₃ basis) were purchased from Sigma Aldrich. Gases for reactivity studies were purchased from Airgas, including methane (research grade), nitrogen (UHP grade), and oxygen (UHP grade). Gases used for TPR and ammonium temperature programmed desorption (NH₃-TPD) experiments were all UHP grade and were also from Airgas, including 2000 ppm NH₃/He, argon, 10% H₂/Ar, helium, and 10% O₂/He.

The catalysts were synthesized by dry impregnation of the CZ support similarly to previous study. The CZ support was synthesized by co-precipitation of the cerium and zirconium nitrate precursors at a Ce:Zr ratio of 3:1. Cerium and zirconium precursors were dissolved in the DI water, and the pH of the precursor solution was adjusted to 3.0. The solution was then dropwise added to excess amount of ammonia hydroxide solution at
pH of 11.9 to ensure the precipitation of the precursors under constant conditions. The obtained suspension was filtered and then dried in an oven at 110 °C overnight. Finally, the support was calcinated at 450 °C for 4 hours under air flow.

Three monometallic catalysts were synthesized with 2 wt% metal in the form of NiO, CuO, or FeO\textsubscript{x} clusters on CZ. Two bimetallic samples were synthesized containing 2 wt% of Ni and 1 wt% of Fe or Cu. To prepare these catalysts, the pore volume of the CZ support was measured by \textit{N}_2 physisorption. Metal nitrate precursors were dissolved in a volume of DI water that was equal to the pore volume of the CZ support used. The precursor solution was added dropwise to the support during agitation. After drying at 110 °C overnight, the collected powder was calcined at 450 °C in air for 4 hours. The calcined catalysts were ground and sieved to a particle size between 38 and 75 µm. The monometallic catalysts were denoted as NiO/CZ, CuO/CZ, and FeO/CZ and the bimetallic catalysts were denoted as NiFeO/CZ, and NiCuO/CZ.

4.2.2 \textit{Catalyst Characterization}

PIXE analysis was carried out to examine the elemental composition of the catalysts at Elemental Analysis Incorporated.

\textit{N}_2 physisorption measurements were carried out in a Micromeritics ASAP 2020 instrument. Approximately 150 mg of sample was degassed at 400 °C for 4 h prior to analysis. Surface areas were calculated using the BET method applied to the desorption branch of the isotherm, and the pore volume and pore size were calculated using the BJH method applied to the desorption branch of the isotherm, respectively.\textsuperscript{133,134}
Powder XRD patterns were measured using a X’Pert PRO Alpha-1 diffraction system equipped with an X’celerator module. Diffractograms were obtained with Cu Kα1 radiation for 2θ between 10° and 80° with a step size of 0.0167°. The Scherrer equation was applied for calculation of the crystalline size of the CZ support.

TPR experiments were performed on a Micromeritics AutoChem II 2920 instrument equipped with a TCD detector and a cold trap. Approximately 40 mg of the sample was loaded to the instrument. Before the reduction, the catalysts were oxidized with 10% O2 in He at 450 °C for 2 h to establish a well-defined fully oxidized state. After cooling in He to 50 °C, the TPR analysis was carried out by flowing 30 cm3/min 10% H2 in helium over the sample while heating to 900 °C at a ramp rate of 10 °C/min. A cold trap in a dry ice-acetone bath was used to avoid the interference from water to the TCD detector. A calibration curve for H2 was established by measuring standard H2 in Ar at different concentration to determine the H2 uptake.

NH3-TPD experiments were also performed on a Micromeritics Autochem II 2920 instrument. Approximately 40 mg of the catalyst was loaded. The sample was heated to 500 °C and held for 1 h under 25 sccm He flow to ensure the desorption of any previously absorbed molecules. Then, the reactor was cooled to 100 °C, and 25 sccm 2000 ppm NH3 in He was dosed over the sample at 100 °C for 2 h. After the exposure, 25 sccm of He was flowed through the sample for 1 h. Once a stable baseline was established, the TPD was carried out by heating the sample to 700 °C at 10 °C/min under 25 sccm of He flow. The signal above the activation temperature 500 °C was excluded when counting the total uptake because it is attributed to the release of water by dehydration of the sample. The dispersion of the metal oxides was calculated by assuming a 1:1 ratio of NH3 on Lewis acid
sites of the supported metal oxide clusters and excluding the NH₃ adsorption on the CZ support.

Pyridine adsorption followed by FTIR spectroscopy was performed using a Nicolet iS10 FTIR spectrometer equipped with an MCT/A detector. Each spectrum was recorded with 64 scans at a resolution of 4 cm⁻¹. A self-supported wafer of each sample was loaded into a vacuum FTIR transmission cell and was activated at 450 °C for 1 h under high vacuum (~1·10⁻⁶ mbar) and then cooled to 150 °C. Small quantities of pyridine were dosed into the cell repeatedly, until adsorption equilibrium of pyridine at 0.1 mbar was reached. The excess pyridine vapor and physiosorbed pyridine were removed by evacuation under high vacuum for 1 h before the spectrum representing pyridine on all acid sites was taken. Then, the sample was heated to 250, 350, and 450 °C, respectively, under vacuum for 30 min. After heating to each of these temperatures, the cell was brought back to 150 °C and a spectrum was taken. The density of the wafer was determined by measuring the weight of a 6.35 mm diameter disc of the wafer. Using the Beer-Lambert law, the concentration of Lewis and Brønsted acid sites were calculated from the integral of the peaks at 1444 cm⁻¹ and 1540 cm⁻¹, respectively. Extinction coefficients were used as reported by Datka et al.²⁰⁶

XPS experiments were carried out using a Thermo K α XPS instrument equipped with a monochromatic small-spot aluminum anode (Al Kα, hν = 1486.6 eV) as the X-ray source. A background pressure of 3.8 × 10⁻⁸ bar was maintained during the measurement. The internal calibration standard used for binding energies was copper from the sample stage.
4.2.3 Methane Activation by In-situ FTIR Spectroscopy

The methane activation on each sample was monitored using in-situ FTIR spectroscopy. The experiments were carried out on a Nicolet 8700 IR spectrometer with a MCT/A detector using an operando IR cell built based on a design reported by the Ribeiro Group. Approximately 150 mg of the catalysts was pressed into a self-supported wafer and was loaded to the cell. The catalyst was activated at 450 °C for 1 h under 50 sccm of N2 flow. The cell was then cooled to 250 °C, and the activated catalyst was measured as the background. A flow of 20 sccm of methane was sent over the catalyst at 250 °C. The methane flow was stopped after 30 mins of exposure, and a spectrum, with surface species from methane activation, was taken after residual gaseous methane was swept from the cell with an N2 stream. The spectrum was collected with 64 scans at a resolution of 4 cm⁻¹. The absorbance of surface species on different samples was normalized to the amount of sample used in each experiment allowing quantitative comparison between samples.

4.2.4 Reactivity Tests

Reactivity tests were carried out in a laboratory scale reactor under atmospheric pressure. A detailed description of the reactor setup can be found in Chapter 2. Approximately 200 mg of the sample was loaded and then activated at 450 °C under 100 sccm of N2 flow for 1 h. The sample was further pre-treated under 20% of methane in N2 at a total of 100 sccm for 2 h. After the sample was cooled to 250 °C, the reaction was started by feeding 30% of steam and 1% of O2 together with 20% methane in balancing N2. The weight hourly space velocity (WHSV) of the reaction was set to 30.2 h⁻¹. The
composition of the effluent stream was analyzed by an in-line MS. Calibration curves for \( \text{CH}_4, \text{O}_2, \text{H}_2\text{O}, \text{CH}_3\text{OH}, \) and \( \text{CO}_2 \) were collected by measuring the MS response to gas mixtures with known composition.

4.3 Results

4.3.1 Physicochemical properties

Elemental analysis by PIXE showed that the metal loadings for NiO/CZ and the bimetallic samples (NiCuO/CZ and NiFeO/CZ) were close to the desired values (Table 4.1). The BET surface areas for all catalysts varied around 66-76 m\(^2\)/gcat, which were slightly lower than that of the CZ support (Table 4.1, and Figure A.1). All catalysts had less pore volume and smaller pore widths than the CZ support. XRD patterns of all samples were similar to the CZ support and showed diffraction peaks at 28.8°, 33.4°, 47.9°, 56.9°, 70.1° and 78° (Figure C.2). The peaks were consistent with those of ceria-zirconia solid solutions.\(^{131, 137, 138, 240}\) No characteristic peaks for nickel oxides, iron oxides or copper oxides were observed for any catalyst. The crystallite sizes within the CZ support were similar for all catalysts and were between 7.5 and 7.9 nm. The Ni K-edge XANES of the fresh bimetallic samples (Figure C.3a) resembled that of the fresh Ni/CZ sample without a local minimum around 8362 eV.

4.3.2 TPR

The CZ support showed three major reduction peaks (Figure 4.1). Peaks at 454 °C and 660 °C were recognized as the successive reduction of the surface and bulk CZ.\(^{209}\) The peak at 321°C was observed by other researchers as well, but the assignment was
speculative.\textsuperscript{131, 153, 209} It is believed to be related to the dissociative adsorption of H\textsubscript{2} or the non-stoichiometric reduction of the surface CZ.\textsuperscript{131, 209}

Table 4.1 – Physiochemical properties of the catalysts.

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<th>CZ</th>
<th>NiO/CZ</th>
<th>NiCuO/CZ</th>
<th>NiFeO/CZ</th>
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<td>Total H\textsubscript{2} uptake (mmol/g)\textsuperscript{e}</td>
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<td>Calculated H\textsubscript{2} uptake from the CZ support (mmol/g)\textsuperscript{g}</td>
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<tr>
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</table>

\textsuperscript{a} From PIXE analysis.
\textsuperscript{b} Surface areas calculated using the BET method applied to the desorption branch of the N\textsubscript{2} physisorption isotherm.\textsuperscript{134}
\textsuperscript{c} Pore volume and pore size calculated using the BJH method applied to the desorption branch of the isotherm.\textsuperscript{133}
\textsuperscript{d} From XRD using the Scherrer Equation.
\textsuperscript{e} From H\textsubscript{2}-TPR.
\textsuperscript{f} Theoretical calculation assuming catalysts contain Ni(II), Fe(III) and Cu(II) oxides at targeted concentrations.
\textsuperscript{g} Calculated as the difference between the experimental total H\textsubscript{2} uptake and theoretical H\textsubscript{2} uptake from metal oxides.
\textsuperscript{h} Measured by pyridine adsorption followed by FTIR spectroscopy at 150 °C, assuming a 1:1 pyridine on LAS adsorption ratio.
\textsuperscript{i} From NH\textsubscript{3}-TPD, assuming a 1:1 NH\textsubscript{3} on metal oxides adsorption ratio and excluding the NH\textsubscript{3} adsorption from the CZ support.
Figure 4.1 – TPR profiles for the CZ support, FeO/CZ, CuO/CZ, NiO/CZ, NiCuO/CZ, and NiFeO/CZ catalysts.

The presence of supported metal oxide cluster resulted in additional reduction peaks. Specifically, the first peaks in the H$_2$-TPR profiles for the catalyst samples, such as the peak at 164 °C for the NiO/CZ, and the peak at 110 °C for the CuO/CZ, were assigned to the consumption of the adsorbed oxygen species on the support.\textsuperscript{15, 60, 76, 83, 150-152} The concentration of the adsorbed surface oxygen was less in samples with Fe than the others. The peak at 233 °C in the NiO/CZ sample was assigned to the reduction of NiO clusters.\textsuperscript{154, 155} Such peaks were also present in the TPR profiles of the two bimetallic samples and therefore were assigned to the same species. The peaks at 125 °C and 132 °C in the CuO/CZ and NiCuO/CZ samples, respectively, were assigned to the reduction of copper oxide species.\textsuperscript{241} Two additional peaks at 245 and 275 °C in the FeO/CZ sample were assigned
to the successive reduction of Fe(III) oxide and Fe(II) oxide species.\textsuperscript{242, 243} The later peak overlapped with a contribution from the surface reduction of CZ at 318 °C (vide infra) and was not obvious in the TPR profile of the NiFeO/CZ sample.

In contrast to the bare CZ support, the reduction peaks for surface CZ were much smaller for all catalysts with supported metal oxide clusters, while the reduction features around 320 °C were more intense and overlapped with the reduction peaks from metal oxides that were observed at lower temperature. This is probably because the reduced metal on the surface facilitated the H\textsubscript{2} activation during TPR and led to an earlier reduction of the surface CZ. It is known that the addition of metal oxides to the support introduces metal-support interactions and more defects in the CZ support, especially on the surface.\textsuperscript{15, 76, 83, 150, 151} This domain might be reduced at significantly lower temperature than bare CZ.

4.3.3 Temperature Programmed Desorption of Ammonia (NH\textsubscript{3}-TPD)

The acidity of the catalysts and the support was measured by NH\textsubscript{3}-TPD (Table 4.1, and Figure 4.2). CZ-supported metal oxides catalysts are generally free of Brønsted acid sites.\textsuperscript{244} As the sample activation was carried out at 500 °C, insignificant signals above 500 °C were likely from dehydration of the sample and hence were not included for total NH\textsubscript{3} uptake calculations.\textsuperscript{245}
Figure 4.2 – NH$_3$-TPD profiles for the CZ support, FeO/CZ, CuO/CZ, NiO/CZ, NiCuO/CZ, and NiFeO/CZ catalysts.

The CZ support contained some Lewis acid sites (LAS) as indicated by the release of the adsorbed NH$_3$. The addition of 2-3 wt% of metal oxide clusters to the CZ support increased the LAS concentration by 80 – 220% as indicated by the greater NH$_3$ uptake (Table 4.1). A comparison of the mono-metallic samples showed that CuO/CZ and FeO/CZ had greater metal oxide dispersion than NiO/CZ as defined by the fraction of Cu, Fe or Ni atoms capable of adsorbing NH$_3$. The addition of 1 wt% Fe or Cu oxides to the NiO/CZ increased the overall metal dispersion in the bimetallic samples. It should be noted that the metal oxide dispersion was calculated by excluding the NH$_3$ uptake contribution from the
CZ support. Such calculations ignore the possibility that metal oxides could block or convert LAS of the support. Thus, the reported dispersions represent a lower limit of the actual metal oxide dispersion.

While NH$_3$-TPD provides information on the acidity of the samples, it cannot differentiate between Lewis and Brønsted acid sites, and the estimation of acid strength from desorption temperatures is affected by the specific analysis instrument.

4.3.4 *Pyridine adsorption followed by FTIR spectroscopy*

In addition to NH$_3$-TPD, the acidity of the samples and the CZ support was assessed by pyridine adsorption followed by FTIR spectroscopy (Figure 4.3). A peak around 1444 cm$^{-1}$ was observed for all samples and is attributed vibrational mode 19a of pyridine adsorbed to Lewis acid cites (LPy). The ring vibrational modes 8a and 19b for pyridinium ions formed on Brønsted acid sites (BPy) typically give rise to peaks at 1535-1550 cm$^{-1}$ and about 1640 cm$^{-1}$, respectively. As both BPy peaks were absent, it is inferred that the concentrations of Brønsted acid sites were fairly low for all samples and the support.

The addition of NiO to the CZ support increased the LAS concentration by ~110%, and LAS concentrations on CZ and NiO containing samples determined by pyridine adsorption were comparable to the NH$_3$ uptake from NH$_3$-TPD (Table 4.1). The CuO/CZ and FeO/CZ samples showed a much lower increase in pyridine uptake of 16% compared to the CZ support but a more significant difference for NH$_3$-TPD. Considering that NH$_3$ is a smaller and more basic molecule compared to pyridine, the significant inconsistency in the LAS concentrations between two analytical methods can be explained by the limited
number of LAS on CuO and FeO clusters that were not strong enough to hold pyridine at 150 °C in high vacuum, while they were strong enough to adsorb NH$_3$ at 100 °C. Adding a second metal oxide to NiO/CZ further increased the LAS concentration. The LAS concentration of NiCuO/CZ was higher compared to NiFeO/CZ and was very close to the NH$_3$ uptake from NH$_3$-TPD.

![IR spectra and Lewis acid sites concentration](image)

**Figure 4.3** – a) IR spectra taken after pyridine adsorption over the CZ support and catalysts at 150 °C; b) Lewis acid sites concentration measured by pyridine adsorption after desorption at 150, 250, 350, and 450 °C in vacuum.

The LPy peak areas decreased in all cases when the samples were evacuated at increasing temperatures (Figure 4.3b, Figure C.4), indicating the desorption of pyridine
from LAS upon heating. A peak next to the LPy peak at around 1437 cm$^{-1}$ that was observed at higher temperatures is assigned to the carbonate species formed from the decomposition of adsorbed pyridine at higher temperature (Figure C.4). While this peak was not of significance for the acidity analysis, its overlap with the LPy peak requires deconvolution to reveal the peak area of the LPy peak (Figure C.5, Table C.1). Among mono-metallic samples, pyridine desorption was relatively linear in the temperature range 150 – 450 °C, and NiO/CZ showed a steeper slope compared to CuO/CZ and FeO/CZ. A more gradual decline of the amount of adsorbed pyridine with increasing temperature was observed for CuO/CZ and FeO/CZ, and the concentration of LAS strong enough to retain pyridine at 350 °C was higher for these samples compared to NiO/CZ. The LAS concentration profiles of NiFeO/CZ overlapped with NiO/CZ above 250 °C, suggesting a similar LAS strength distribution for the two samples. Compared to the other samples with Ni, a higher fraction of pyridine remained adsorbed on the NiCuO/CZ sample at 250 °C.

4.3.5 X-ray Photoelectron Spectroscopy

The surface chemical state of transition metals was examined by XPS (Figures C.6 and C.7, Table C.2). For samples with Ni, peaks at 855.5 and 861.7 eV were assigned to the main and satellite 2p$^{3/2}$ peaks of Ni$^{2+}$, respectively. For NiCuO/CZ, the main Ni2p$^{3/2}$ peak showed a ~0.3 eV positive shift compared to the NiFeO/CZ and NiO/CZ. For samples with Cu, peaks at 933.5 and 943.0 eV were assigned to the main and satellite 2p$^{3/2}$ peaks of Cu$^{2+}$, respectively. The main Cu2p$^{3/2}$ peak showed a ~0.3 eV negative shift in the NiCuO/CZ compared to the CuO/CZ. For samples with Fe, peaks at 711.4 and 716.6 eV were assigned to main and satellite 2p$^{3/2}$ peaks of Fe$^{3+}$, respectively. Peak fitting showed
that the peak positions for the main and satellite Fe2p\(^{3/2}\) peaks were almost identical for FeO/CZ and NiFeO/CZ, indicating similar chemical states of the Fe in two samples.

4.3.6 Methane activation by in-situ FTIR spectroscopy

Surface species formed during methane activation at 250 °C were monitored by in-situ FTIR spectroscopy (Figure 4.4a and Figure C.10). The activated methane produced features that were characteristic of O-H stretching vibration from surface hydroxyl groups and C-H stretching vibrations from various carbonaceous surface species, respectively. Peaks at 2960 cm\(^{-1}\), 2950 cm\(^{-1}\) and 2932 cm\(^{-1}\) were assigned to the asymmetric C-H stretching from methoxy groups, methyl groups, and alkyl groups, respectively.\(^{41,248}\) The symmetric vibration of these species were at 2870 cm\(^{-1}\), 2858 cm\(^{-1}\) and 2845 cm\(^{-1}\), respectively (Figure 4.4a). The features around 2739 cm\(^{-1}\) and 2723 cm\(^{-1}\) are characteristic adsorption peaks for aldehyde C-H stretches.\(^{219}\) The presence of -CH\(_2\) species was evidence for the coupling of the activated methyl groups. Detailed peak deconvolution and linear regression fittings were applied to identify and quantify the surface carbonaceous species formed (Table C.3, Figure 4.8 and 4.9). The ratio between peak areas of -CH\(_3\) and -CH\(_2\) species was around 0.4 among all catalysts (Table C.4). The relative peak areas of the methoxy groups on the bimetallic samples were larger than their mono-metallic counterparts (Figure 4.4b).
Figure 4.4 – a) Methane activation over different catalysts measured by operando FTIR spectroscopy. b) Peak area of different surface species (calculated as the sum of area of the symmetric and asymmetric contributions) from methane activation.

4.3.7 Reactivity Tests

The performance of each catalyst for selective oxidation of methane to methanol was tested at 250 °C (Figure 4.5, and Table 4.2). Over all catalysts, continuous direct conversion of methane to methanol was achieved, with CO₂ as the major product. In the initial stage of reaction, the yields of CO₂ decreased, and the selectivity towards methanol increased with time on stream. A steady state conversion was observed after about 100 min on stream for all samples.

Samples with Ni showed higher steady-state CO₂ and methanol yields than CuO/CZ and FeO/CZ, as well as a higher methanol selectivity. The bimetallic samples had higher CO₂ and methanol yields compared to NiO/CZ. The NiFeO/CZ sample had the
highest methanol yield among all catalysts. The highest methanol selectivity appeared to occur over NiCuO/CZ, but there was an estimated uncertainty of about 15% (Appendix C.9). Carbon deposit formation was observed over all catalysts by TGA (Figure C.11, C.12, Table C.5, C.6). NiO/CZ formed the highest amount of carbon deposit at 2.4 wt%, while the other samples showed limited carbon deposition below 1.2 wt%. The majority of the carbon deposit (>90%) was formed in the first 100 min on stream over all catalysts (Figure C.12, Table C.6).

Figure 4.5 – Reactivity of a) NiO/CZ, b) NiCuO/CZ, c) NiFeO/CZ, d) CuO/CZ and e) FeO/CZ for selective oxidation of methane to methanol at 250 °C. (Temperature at 250 °C; WHVS at 30.2 h⁻¹ with 30% of steam, 1% of oxygen, 20% methane and a balance of nitrogen).
Table 4.2 – Steady state CO₂ yield, methanol yield and selectivity over different catalysts. (Temperature at 250 °C; WHVS at 30.2 h⁻¹ with 30% of steam, 1% of oxygen, 20% methane and a balance of nitrogen).

<table>
<thead>
<tr>
<th></th>
<th>NiO/CZ</th>
<th>NiCuO/CZ</th>
<th>NiFeO/CZ</th>
<th>CuO/CZ</th>
<th>FeO/CZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ yield (%)</td>
<td>0.069</td>
<td>0.079</td>
<td>0.095</td>
<td>0.042</td>
<td>0.041</td>
</tr>
<tr>
<td>Methanol yield (μmol/h/g_cat)</td>
<td>2.32</td>
<td>2.84</td>
<td>3.20</td>
<td>0.57</td>
<td>0.52</td>
</tr>
<tr>
<td>Methanol yield (%)</td>
<td>8.6×10⁻⁴</td>
<td>1.1×10⁻³</td>
<td>1.2×10⁻³</td>
<td>2.2×10⁻⁴</td>
<td>2.2×10⁻⁴</td>
</tr>
<tr>
<td>Methanol selectivity (%)</td>
<td>1.25</td>
<td>1.44</td>
<td>1.27</td>
<td>0.52</td>
<td>0.53</td>
</tr>
</tbody>
</table>

4.4 Discussion

4.4.1 Synthesis of Well-Dispersed Metal Oxide Clusters and Their Impact on Acidity and Reducibility

The redox active sites on CZ supports induce a SMSI, which can stabilize well-dispersed metal oxide clusters or metal cations.¹⁵, ¹⁰⁰, ²⁴⁹ These well-dispersed clusters generate interfacial defect sites, which in turn enhance the reducibility of the CZ support.¹⁵, ⁷⁶ Such catalysts often demonstrate superior catalytic activities. Chagas et. al. showed that the synergetic interaction between finely dispersed copper species and oxygen vacancies created via the incorporation of Ni into ceria significantly increased the CO oxidation activity of CuO-NiO/CeO₂.²⁵⁰ Zhang et. al. showed that NiO nanoclusters supported on CeO₂ are better dispersed than on SiO₂ and that NiO/CeO₂ had high activity for the complete oxidation of CH₄ in the temperature range of 350–600 °C.²⁵¹

The present work aimed to leverage these SMSI by creating Lewis acid sites in close proximity to the redox sites of CZ. The absence of peaks from NiO, FeOₓ and CuO
phases or mixtures thereof in the XRD patterns (Figure C.2) showed that the size of the clusters was below the XRD detection limit. This is in agreement with our earlier analysis of a NiO cluster size below ~2-3 nm based on EDX mapping analysis of a similar NiO/CZ catalyst. EXAFS analysis of the NiO/CZ catalyst also showed the presence of small clusters with an average NiO particle size of 0.46 nm. The missing local minimum around 8362 eV in the Ni K-edge XANES of freshly calcined NiO-CZ and the bimetallic samples indicates the presence of well-dispersed NiO clusters.

The impact of the highly dispersed metal oxide clusters manifests itself in the significant fraction of the metal atoms in these clusters that act as LAS; while other factors, such as the choice of metals, and the formation of mixed metal oxides could also affect the Lewis acidity. While the CZ support itself demonstrated Lewis acidity, the contribution of the supported metal oxide clusters was dominant, since the addition of 2-3 wt% of metal as metal oxides led to an 80 – 220% increase in the NH$_3$ uptake (Table 4.1 and Figure 4.2). The same results were obtained by pyridine adsorption followed by FTIR for all samples with Ni. Certain discrepancies seemed to emerge for CuO/CZ and FeO/CZ samples when examining acidity using NH$_3$ and pyridine as probe molecules, as only a 16% increase in the LAS concentration was observed by pyridine adsorption in contrast to the 200% increase in the total NH$_3$ uptake. Considering ammonia is a smaller molecule and a stronger base compared to pyridine$^{211}$ and the difference in adsorption temperature (NH$_3$ at 100 °C and pyridine at 150 °C), such a ‘discrepancy’ actually is an indication that the majority of CuO and FeO$_x$ clusters on CZ contained weaker LAS compared to NiO and were not strong enough to adsorb pyridine readily at 150 °C.
FeO\textsubscript{x} and CuO cluster were more dispersed than monometallic NiO. The addition of a second metal oxide (FeO\textsubscript{x}/CuO) to the NiO-CZ increased the metal oxide dispersion compared to NiO/CZ. However, even though CuO/CZ showed about 40% higher dispersion than FeO/CZ, the dispersion for bimetallic sample NiCuO/CZ was slightly lower than NiFeO/CZ, which suggests that the CuO and NiO clusters had stronger interactions and probably formed mixed metal oxide clusters. Additionally, XPS showed a positive 0.3 eV shift of the main Ni2p\textsuperscript{3/2} peak and a negative 0.3 eV shift of the main Cu2p\textsuperscript{3/2} peak in the NiCuO/CZ sample compared to its mono-metallic counterparts. A higher binding energy in XPS is an indication for a higher oxidation state.\textsuperscript{252} Hence, more positively charged Ni and less positively charged Cu were observed in NiCuO/CZ compared to NiO/CZ and CuO/CZ suggesting electron transfers between NiO and CuO, which is likely a result of the formation of mixed metal oxide domains. It is recognized that the experimental conditions of XPS measurements and catalytic reactions were different, but it should be possible to extrapolate the direction of the electron transfer. This synergy between NiO and CuO also enhanced the strength of LAS as evidenced by the ability of NiCuO/CZ to retain pyridine at elevated temperature (Figure 4.3).\textsuperscript{253} On the other hand, the addition of FeO\textsubscript{x} to NiO/CZ had little impact on the Lewis acid strength, as the amount of retained pyridine on NiFeO/CZ and NiO/CZ at elevated temperatures almost overlapped. This is likely due to the limited mixing of the NiO and FeO\textsubscript{x} as the dispersion of NiFeO/CZ was almost equal to the weighted sum of the dispersion of mono-metallic samples.\textsuperscript{254} The similarities in Ni2p and Fe2p XPS spectra from NiFeO/CZ and its mono-metallic counterparts also support the hypothesis.
The reduction temperatures of the supported metal oxide clusters was much lower compared to the corresponding bulk metal oxides, indicating the presence of well-dispersed metal oxide clusters. The reduction of the metal oxides produced reduced metal clusters, which facilitate the reduction of surface CZ at lower temperature. The amount of the adsorbed oxygen species in samples with Fe was lower than other samples, likely because iron is more oxyphilic than the other metals so that some of the adsorbed oxygen species should be bound to the catalysts more strongly. The H₂ consumption by the CZ support was slightly higher in the pure CZ, which is probably because the metal oxides blocked or altered the surface of the support. The H₂-TPR profiles of the bimetallic samples showed distinct reduction peaks of NiO, FeOₓ, and CuO, that seemed unaffected by the addition of a second metal oxide. This could point to segregation of the transition metal clusters upon excessive reduction, which would reduce the synergy between the constituents.

4.4.2 Methane Activation and Formation of Methoxy Species over CZ Supported Transition Metal Oxides

Lewis acidic metal oxides are capable of activating methane through heterolytic splitting of the C-H bond. In this study, the well-dispersed Lewis acidic transition metal oxide clusters were found capable of activating methane as indicated by the C-H stretching modes from various carbonaceous surface species after the exposure of methane to the catalysts at 250 °C. The presence of surface -CH₃ species and hydroxyl groups suggest that the methane was activated through heterolytic splitting of the C-H bond, forming surface methyl and hydroxyl groups. The activated methyl groups could further react with oxygen species from the catalyst forming
oxygenates, such as methoxy, formate, carboxylate species or surface aldehydes (Figure 4.4 and C.10). Alternatively, the activated methyl groups could couple with each other and form long chain hydrocarbons, evidenced by the presence of -CH₂ species.

Further analysis of the quantity of different carbonaceous species formed over different catalysts provided insights into the reaction mechanism. The similar ratio between the areas of CH₃ and CH₂ species among all samples implies that the coupling of the activated methyl groups to higher alkyl groups was independent of the transition metals. However, the peak area of the bands from the methoxy groups (the sum of peak areas of asymmetric and symmetric methoxy stretching bands) showed an apparent linear correlation with the methanol selectivity at steady state (Figure 4.6a), indicating the surface methoxy group is a key intermediate for the conversion of methane to methanol. It is generally expected that methanol formation involves the hydrolysis of the surface methoxy species. However, this correlation also implies that these methoxy groups can be hydrolyzed fairly selectively rather than being converted to other oxidation products.

During the in-situ IR spectroscopy experiments, the only source of oxygen was that stored within the catalysts. Our previous study revealed that the NiO clusters remained oxidized upon exposure to methane at 450 °C while there was active oxygen in the CZ support indicating that the latter oxygen species play the key role in oxidation reactions. Therefore, the formation of methoxy groups is probably related to the reducibility of the CZ support. However, the H₂ uptake by CZ did not correlate to the amount of methoxy species formed. This could be explained by the presence of different types on active oxygen species in CZ.
Figure 4.6 – a) Correlation between methanol selectivity and methoxy peak areas from methane activation over different catalysts. b) Correlation between methoxy peak areas from methane activation and concentration of strong Lewis acid sites for different catalysts.

There was a strong correlation between the formation of methoxy species and the concentration of strong LAS of the catalysts (Figure 4.6b, defined as the amount of pyridine uptake at 150 °C as shown in Table 1). While mono-metallic FeOₓ/CZ and CuO/CZ catalysts were also Lewis acidic and showed higher NH₃ uptake than the NiO/CZ sample (Table 4.1), they contained a smaller number of LAS with sufficient strength to form methoxy intermediates during methane activation over these samples. Considering that methane activation on a LAS occurs through heterolytic splitting of a C-H bond and formation of a metal-carbon bond,¹,⁴⁰,⁴¹ it is reasonable to suggest that a stronger LAS will generate a more positively charged methyl groups. The positive partial charge should increase the affinity of the methyl group to nucleophilic active oxygen species, which tend
to produce methoxy groups – the key intermediate to methanol.\textsuperscript{260, 261} Hence, the monometallic samples with the strongest LAS, NiO/CZ, produced the most surface methoxy groups during methane activation. The addition of FeO\textsubscript{x} or CuO improved the methane activation capability judging from the increase in the quantity of the activated surface species. This is expected as both FeO\textsubscript{x} and CuO were Lewis acidic and hence were capable of activating methane. The likely formation of NiO-CuO mixed oxides introduced synergy between the two metal oxides and improved the Lewis acidity; hence NiCuO/CZ generated the most methoxy species during methane activation. The synergistic effect is probably due to the alternation of local electronic environments as indicated by XPS, which resulted in an increase in the strength of Lewis acid sites.\textsuperscript{262-265}

4.4.3 The Conversion of Methane to Methanol

Based on the observation that surface methoxy/alkyl groups were formed during methane activation and a thermodynamic analysis that indicated that an oxidant like O\textsubscript{2} is needed for methanol production,\textsuperscript{3} we hypothesized that the direct conversion from methane to methanol can be achieved by feeding steam and oxygen together with methane. Under the reaction conditions reported, continuous direct conversion from methane to methanol was achieved for all catalysts. A methane pre-treatment step at 450 °C was performed to remove highly active adsorbed surface oxygen species that promote the formation of CO\textsubscript{2}.\textsuperscript{60} Using a weak reducing agent, methane, avoids the over-reduction of NiO to Ni, as indicated by the in-situ XAS experiment performed in our previous study.\textsuperscript{15} The CO\textsubscript{2} yield decreased with time on stream by more than 85% over all catalysts, while the yield towards methanol increased (Figure 4.4), indicating that the conversion of methane to CO\textsubscript{2} and methanol was achieved over different active sites or involved different active oxygen species from the
CZ support. Considering the fact that at least 90% of the coke were formed during first 100 min on stream (Table C.3 and C.4), it is likely that coke formation covered certain larger metal oxide clusters.\textsuperscript{15} However, it is also possible that a change in the speciation of active oxygen species could affect the performance of the catalyst.\textsuperscript{238} Multiple researcher have shown that the small transition metal/metal oxides, such as di-copper sites in Cu-zeolites, were active sites for the selective conversion of methane to methanol.\textsuperscript{30, 36, 266, 267} Thus, it is proposed that the more selective active sites were the small well-dispersed NiO clusters and that these clusters are less impacted by coke due to steric effects or the fact that they experience stronger interactions from the CZ support.

As the methane molecule has the highest C-H bond among all hydrocarbons,\textsuperscript{1, 84-86} the intermediate species formed from methane activation are often subject to complete oxidation and produce CO\textsubscript{2}. However, it may be possible to create environments in which such series reactions are largely suppressed. In this study, the methane conversion (calculated by the sum of CO\textsubscript{2} yield and methanol yield) was inversely related to the methanol selectivity, and the presence of Ni increased the selectivity relative to Ni-free catalysts (Figure 4.7). The inverse relationship implies that a further reduction in methane conversion could eventually lead to a methanol selectivity close to unity. Extrapolation of the curve indicates that a methanol selectivity around unity could be expected for a methane conversion below approximately 0.002\% for the Ni-containing samples (Figure C.14). It is expected that extrapolation of a log-log plot is subjected to relatively large uncertainty in the estimated value. Nevertheless, such an extrapolation shows that reaction engineering approaches could have the potential for enhancing the methanol selectivity during the selective oxidation of methane to a high level.
Figure 4.7 – Correlation between methane conversion (%) and the selectivity (%) towards methanol.

4.5 Conclusion

The deposition of mono or bi-metallic transition metal oxide clusters (i.e., NiO, CuO, FeO, NiCuO and NiFeO) on a ceria-zirconia (CZ) support creates catalysts that combine Lewis acidity and redox activity. All of the metal oxides are well-dispersed due to strong metal support interactions. The addition of CuO to the supported NiO clusters increases the strength of Lewis acid sites which improved selectivity to methanol. All catalysts are capable of activating methane at 250 °C to produce surface methyl, methoxy, and alkyl groups. Samples containing Ni show a greater activity for methane activation due their stronger Lewis acidity. By co-feeding CH₄, O₂, and steam together, continuous conversion of methane to methanol is achieved albeit with low selectivity. The conversion of methane to methanol at steady state is an important step towards economically viable valorization of methane in limited quantities. The concentration of strong Lewis acid sites is found to be a key descriptor for the formation of methoxy species, which is a key intermediate towards the formation of methanol. The methane conversion inversely relates
to the methanol selectivity, suggesting the possibility of enhancing the methanol selectivity by reaction engineering approaches.
CHAPTER 5. FINAL CONCLUSIONS AND RECOMMENDATIONS

The purpose of the dissertation is to demonstrate a systematic investigation of the CZ supported metal oxide materials for the rational design of catalysts for methane conversion. The vast natural gas resources available on Earth and the unsatisfactory performance of current industrial processes utilizing methane ensure that the development of catalytic process for methane conversion will remain of interest in the near future. The search for highly active and selective catalysts requires a strong understanding of the surface reaction mechanisms and the functions of active sites at a fundamental level. Additionally, the evaluation of the impact of synthesis on the physiochemical properties of materials is also crucial for the realization the desired active site morphologies.

In Chapter 2, by comparing the synthesis-structure-performance relationships, trade-offs between the different deactivation pathways are observed and new insights regarding the design of better catalysts are gained. Three deactivation mechanisms: Ni particle growth, coke formation and encapsulation of Ni by CZ, are identified and their complex interplays are decoupled. The Ni particle growth can be refrained by limiting the Ni mobility under reaction conditions. The concentration of the adsorbed surface oxygen is a good descriptor for coke resistance. The encapsulation of the active Ni site by the redox active CZ confines the mobile Ni species under reaction conditions but also enhances the reducibility of the material. Hence, such design greatly suppresses both Ni particle growth and coke formation during methane dry reforming. However, when the encapsulating CZ layer grows too thick, the highly active Ni species becomes inaccessible and therefore
useless. Nevertheless, the design strategy provides a potential solution for methane dry reforming over Ni-based catalysts. Hence, it is worthwhile to further investigate the mechanism of the encapsulation of Ni particles by CZ, especially for the CS catalysts. A combination of in-situ XRD and XAS could reveal the morphology changes in both Ni and CZ under reduction/reaction conditions. Analyzing the changes in both Ni and CZ under different conditions could hopefully provide information on the encapsulation mechanism and synthesis strategies controlling the encapsulation can be developed. Eventually, the goal would be to synthesize highly stable, coke resistance methane reforming catalysts with Ni particles confined by a thin layer of CZ, which immobilizes the Ni particles while allowing the penetration of reactants through the layer to access the Ni core.

In Chapter 3, the methane activation over NiO/CZ catalysts is investigated and surface reaction networks are unraveled. A novel data analysis algorithm is developed for the effective evaluation of the evolution of different surface species over time. The adsorbed surface oxygen is the driving force for the formation of formate and carbonate intermediates. NiO clusters are found active for the production of both alkoxy and aromatic intermediates. The selectivity towards alkoxy, which is a key intermediate for the production of alcohols, can be improved by increasing the concentration of well-dispersed NiO species and adjusting the reducibility of CZ. While methane activation is often the most challenging step in the catalytic conversion of methane, understanding of the complete catalytic cycle is also of high importance. Hence, I recommend that for future work, the functionalization of the activated methyl species and desorption of the products for different methane conversion chemistry should also be investigated using operando FTIR spectroscopy. Studying the response of surface species to pulses of reactant feed,
such as methane, oxygen and steam, at transient state can provide fruitful information on surface chemistry mechanisms. As mentioned previously, in addition to the complexity in the surface reaction networks, understanding of the nature of the catalyst surface is another key challenge in surface chemistry. In-situ/operando XAS allows probing changes in the catalysts during reaction. Combined with operando FTIR spectroscopy, the full picture of surface chemistry for methane conversion over NiO/CZ catalysts can be revealed. Other techniques, such as near ambient-pressure XPS, could also provide information on the catalyst surface under reaction conditions. Finally, upon fundamental understanding of the surface chemistry, i.e., a comprehensive analysis of the surface reaction pathway networks together with thorough understanding of the catalyst surface and functions of active sites, the kinetics of surface reactions can be evaluated by applying advanced computational tools, such as protocols developed by the Medford group.  

In Chapter 4, the selective oxidation of methane to methanol is achieved over CZ supported mono and bi-metallic oxides catalysts by feeding methane with oxygen and steam. The Lewis acidity of the metal oxides is found to be a key descriptor for the quantity of surface methoxy species formed during methane activation, which is the key intermediate towards methanol production. Adding CuO to CZ supported NiO catalysts produces mixed metal oxides, which further enhances the Lewis acidity and yields the best methanol selectivity. An inverse relationship between methane conversion and the methanol yield is observed, suggesting the possibility of enhancing the methanol selectivity by reaction engineering approaches. However, the nature of the active oxygen species and the surface reaction that produces methoxy species are still unclear. Therefore, for future works, I recommend the investigation of the active oxygen species, both its nature and its
function during selective oxidation of methane. A recent review paper by our group has listed the possible analytical instruments for probing surface oxygen species. For understanding the nature of active oxygen species, I suggest comparative study of catalyst surfaces exposed to different oxidants, such as $\text{O}_2$, $\text{H}_2\text{O}$, and $\text{CO}_2$. Then, investigations of changes in the oxygen species during sequential dosing of methane and then different oxidants to the catalyst surface could potentially reveal the function of the different oxygen species.

In conclusion, there is great potential in using CZ supported metal oxides catalysts for the conversion of methane to value-added fuels and chemicals. I hope that this dissertation lays the foundation for future work in development of more efficient catalysts for methane conversion.
Figure A.1 – Adsorption/desorption isotherms for the CZ support and DI, SEA, CP and CS catalysts from N\textsubscript{2} physisorption measurements. (Open points: adsorption isotherm curves. Solid points: desorption isotherm curves.)
Figure A.2 – Accumulative pore volume and pore size distribution for the CZ support and DI, SEA, CP and CS catalysts from N₂ physisorption measurements. (Open points: accumulative pore volume as a function of pore width. Solid points: pore size distribution curve.)
Figure A.3 – Linear combination fitting of the XANES spectra for fresh catalysts.
Figure A.4 – The standards used for the non-linear combination fitting of XANES data, including NiO standard, NiO 1st shell standard and LaNiO₃ standard.
Table A.1 – EXAFS fitted parameters for fresh samples.

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Figure A.5 – EXAFS fits of unreduced catalysts.
Table A.2 – Peak deconvolution and assignment of TPR profiles.

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Figure A.6 – TPR patterns and peak fittings for different catalysts.
Figure A.7 – Reactivity performance for different catalysts with dilution. (catalyst
diluted with SiC, normalized to 0.2wt% Ni content, 700 °C, 1 atm, 46300 h⁻¹ GHSV,
35% CH₄, 35% CO₂ and 30% N₂).
Figure A.8 – SEM images of spent samples.
Figure A.9 – Adsorption/desorption isotherms for the spent catalysts from N₂ physisorption measurements. (Open points: adsorption isotherm curves. Solid points: desorption isotherm curves.)
Figure A.10 – Accumulative pore volume and pore size distribution for the spent catalysts from N₂ physisorption measurements. (Open points: accumulative pore volume as a function of pore width. Solid points: pore size distribution curve.)
Figure A.11 – TGA of spent catalysts for reaction with pure catalyst.
Figure A.12 – Relationship between the initial CO$_2$ conversion and the surface Ni concentration on different catalysts, defined as species that showed a reduction temperature of less than 285 °C for bulk synthesis techniques and less than 235 °C for the surface synthesis techniques.
Figure B.1 – XRD diffractograms of 10NiO/CZ, 2NiO/CZ and CZ.
Figure B.2 – Peak fitting of TPR profiles for a) CZ, b) 2NiO/CZ, c) 10NiO/CZ.
Table B.1 – Peak parameters and assignments from peak fitting TPR profiles.

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<th>Peak Assignment</th>
<th>H$_2$ Uptake (mmol/g)</th>
<th>Peak Position (cm$^{-1}$)</th>
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Figure B.3 – Pyridine adsorption followed by FTIR spectroscopy upon thermoevacuation at 250 °C, 350 °C, and 450 °C for a) CZ, b) 2NiO/CZ and c) 10NiO/CZ.
Table B.2 – Peak position and area of pyridine adsorbed on Lewis acid sites at different thermoevacuation temperature for catalysts and the CZ support.

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Figure B.4 – Separation of peaks at 1443 cm⁻¹ for LPy, and 1437 cm⁻¹ for carbonates for a) CZ, b) 2NiO/CZ and c) 10NiO/CZ.
Figure B.5 – MS response from methane activation experiments using a) 2NiO/CZ at 200 °C, b) 10NiO/CZ at 200 °C, c) 2NiO/CZ at 300 °C, and d) 10NiO/CZ at 300 °C.
Figure B.6 – Adsorption of 0.1 mbar methanol, formaldehyde and formic acid over 2NiO/CZ at 50 °C.

Figure B.7 – Adsorption of 0.1 mbar benzene over 2NiO/CZ at 50 °C and 200 °C.
Table B.3 – Optimized peak parameters for IR spectra from methane activation over 10NiO/CZ at 200 °C and peak assignments.

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Table B.4 – Optimized peak parameters for IR spectra from methane activation over 2NiO/CZ at 300 °C and peak assignments.

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Table B.5 – Optimized peak parameters for IR spectra from methane activation over 10NiO/CZ at 300 °C and peak assignments.

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<td>1356.7</td>
<td>2.9</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>(v(C-O))</td>
<td>Initial</td>
<td>Gaussian</td>
<td>1370.6</td>
<td>3.5</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Middle</td>
<td>Gaussian</td>
<td>1370.9</td>
<td>3.5</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Final</td>
<td>Gaussian</td>
<td>1370.4</td>
<td>3.5</td>
<td>0.58</td>
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<tr>
<td>Alkoxy</td>
<td>(v(C-O))</td>
<td>All period</td>
<td>Voigt</td>
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<td>7</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>(v(C-O))</td>
<td>All period</td>
<td>Voigt</td>
<td>1076.4</td>
<td>10.5</td>
<td>2.04</td>
</tr>
</tbody>
</table>
Figure B.8 – TGA and DTG curve of spent sample from methane activation over a) 2NiO/CZ at 200 °C, b) 10NiO/CZ at 200 °C, c) 2NiO/CZ at 300 °C, and d) 10NiO/CZ at 300 °C.
APPENDIX C. SUPPLEMENTARY INFORMATION FOR

CHAPTER 4

Figure C.1 – The adsorption/desorption isotherm from N₂ physisorption for the CZ support and catalysts with supported metal oxide clusters.
Figure C.2 – XRD patterns of the CZ support and catalysts with supported metal oxide clusters.
Figure C.3 – a) Ni K-edge XANES spectra of NiO/CZ, NiFeO/CZ, NiCuO/CZ and a NiO standard. b) EXAFS spectra of NiO/CZ and a NiO standard.
Table C.1 – Peak parameters for peak at 1444 cm\(^{-1}\) from peak fitting of IR spectra from during pyridine thermoevacuation at 150, 250, 350, and 450 °C for the CZ support and the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>150</th>
<th>250</th>
<th>350</th>
<th>450</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pos (cm(^{-1}))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CZ</td>
<td></td>
<td>1443</td>
<td>1443.8</td>
<td>1444.5</td>
<td>1443.3</td>
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<tr>
<td></td>
<td></td>
<td>Area (a.u.)</td>
<td>2.45</td>
<td>1.73</td>
<td>0.85</td>
</tr>
<tr>
<td>NiO/CZ</td>
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<td>1443.5</td>
<td>1444.9</td>
<td>1444.8</td>
<td>1444.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Area (a.u.)</td>
<td>3.55</td>
<td>2.06</td>
<td>0.85</td>
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<td>FeO/CZ</td>
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<td>1444.5</td>
<td>1444.4</td>
<td>1443.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Area (a.u.)</td>
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<td>1.07</td>
<td>0.94</td>
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<tr>
<td>CuO/CZ</td>
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<td>1443.5</td>
<td>1443.5</td>
<td>1443.5</td>
<td>1443.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Area (a.u.)</td>
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<td>0.85</td>
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<tr>
<td>NiFeO/CZ</td>
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<td>1445.1</td>
<td>1446</td>
<td>1445.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Area (a.u.)</td>
<td>2.84</td>
<td>1.49</td>
<td>0.55</td>
</tr>
<tr>
<td>NiCuO/CZ</td>
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<td>1444</td>
<td>1444.6</td>
<td>1444.7</td>
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<tr>
<td></td>
<td></td>
<td>Area (a.u.)</td>
<td>4.2</td>
<td>3.08</td>
<td>0.83</td>
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</table>
Figure C.4 – FTIR spectra during pyridine thermoevacuation at 150, 250, 350, and 450 °C for a) CZ, b) NiO/CZ, c) FeO/CZ, d) CuO/CZ, e) NiFeO/CZ, and f) NiCuO/CZ.
Figure C.5 – Separation of peaks at 1444, and 1437 cm\(^{-1}\) during pyridine thermoevacuation at 150, 250, 350, and 450 °C for a) CZ, b) NiO/CZ, c) FeO/CZ, d) CuO/CZ, e) NiFeO/CZ, and f) NiCuO/CZ.
Table C.2 – Peak parameters for XPS peak fitting of all samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni(II)2p3/2</th>
<th>Satellite</th>
<th>Ni(II)2p1/2</th>
<th>Satellite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amp (a.u.)</td>
<td>Cen (eV)</td>
<td>Amp (a.u.)</td>
<td>Cen (eV)</td>
</tr>
<tr>
<td>NiO/CZ</td>
<td>4095.2</td>
<td>855.51</td>
<td>6524.8</td>
<td>861.81</td>
</tr>
<tr>
<td></td>
<td>2164.5</td>
<td>872.92</td>
<td>3725.5</td>
<td>878.06</td>
</tr>
<tr>
<td>NiCuO/CZ</td>
<td>6087.9</td>
<td>855.82</td>
<td>8780.7</td>
<td>861.84</td>
</tr>
<tr>
<td></td>
<td>7011.4</td>
<td>872.05</td>
<td>3858.7</td>
<td>873.6</td>
</tr>
<tr>
<td>NiFeO/CZ</td>
<td>5976.3</td>
<td>855.57</td>
<td>5948.1</td>
<td>861.86</td>
</tr>
<tr>
<td></td>
<td>1661.3</td>
<td>872.81</td>
<td>3624.8</td>
<td>875.53</td>
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</table>

<table>
<thead>
<tr>
<th>Cu(II)2p3/2</th>
<th>Satellite</th>
<th>Cu(II)2p1/2</th>
<th>Satellite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amp (a.u.)</td>
<td>Cen (eV)</td>
<td>Amp (a.u.)</td>
</tr>
<tr>
<td>NiCuO/CZ</td>
<td>8013.3</td>
<td>933.23</td>
<td>4075.6</td>
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<td></td>
<td></td>
<td>1985.6</td>
</tr>
<tr>
<td>CuO/CZ</td>
<td>10259.7</td>
<td>933.54</td>
<td>6494.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3819.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fe(III)2p3/2</th>
<th>Satellite</th>
<th>Fe(III)2p1/2</th>
<th>Satellite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amp (a.u.)</td>
<td>Cen (eV)</td>
<td>Amp (a.u.)</td>
</tr>
<tr>
<td>NiFeO/CZ</td>
<td>3980.8</td>
<td>711.37</td>
<td>716.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>724.89</td>
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<tr>
<td></td>
<td>731.33</td>
<td></td>
<td>731.33</td>
</tr>
<tr>
<td>FeO/CZ</td>
<td>9154.1</td>
<td>711.29</td>
<td>25955.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5730.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>731.25</td>
</tr>
</tbody>
</table>
Figure C.6 – XPS spectra for all catalysts: a) Ni 2p region, b) Cu 2p region, and c) Fe 2p region.
Figure C.7 – Fitting spectra of XPS fitting for all samples: a) Ni 2p region, b) Cu 2p region, and c) Fe 2p region.
Methane activation by operando FTIR spectroscopy

To identify the different species formed on the catalyst surface during methane activation, IR spectra were deconvoluted to multiple peaks. A common basis set of peaks representing different species was established, with the peak positions and variances shown in Table C.3. Linear regression fits were performed using the basis set to quantify the relative quantity of surface species formed through methane activation over different catalysts (Figure C.8). The peak area of different species from each fit is listed in Table C.4.

Table C.3 – Peak position of C-H stretching vibrations and variance of the basis set of peaks representing surface species.

<table>
<thead>
<tr>
<th>Peak position (cm(^{-1}))</th>
<th>Variance</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2960.4</td>
<td>10.96</td>
<td>asymmetric (O)-CH(_3)</td>
</tr>
<tr>
<td>2950.2</td>
<td>4.83</td>
<td>asymmetric -CH(_3)</td>
</tr>
<tr>
<td>2932.0</td>
<td>6.32</td>
<td>asymmetric -CH(_2)</td>
</tr>
<tr>
<td>2870.3</td>
<td>10.30</td>
<td>symmetric (O)-CH(_3)</td>
</tr>
<tr>
<td>2858.5</td>
<td>5.17</td>
<td>symmetric -CH(_3)</td>
</tr>
<tr>
<td>2844.9</td>
<td>8.51</td>
<td>symmetric -CH(_2)</td>
</tr>
<tr>
<td>2723.5</td>
<td>2.74</td>
<td></td>
</tr>
<tr>
<td>2739.3</td>
<td>7.99</td>
<td>aldehyde C-H</td>
</tr>
<tr>
<td>2701.1</td>
<td>9.13</td>
<td></td>
</tr>
</tbody>
</table>
Figure C.8 – Linear regression fit of IR spectra after methane activation at 250 °C on a) NiO/CZ, b) CuO/CZ, c) FeO/CZ, d) NiCuO/CZ and e) NiFeO/CZ.
The $R^2$ score of each fit was recorded to examine the quality of the fit (Figure C.9a). All fits showed a $R^2$ score higher than 0.9, indicating the fits were of decent quality. The ratio of peak areas of asymmetric and symmetric stretching modes from the same species (i.e. -CH3, -CH2, and methoxy groups) was taken to verify the reliability of the fits (Figure C.9b). Provided that similar nature of the activated carbonaceous species on the catalyst surface, the ratio of the asymmetric and symmetric peak areas of each species should be constant. The mean value of all the ratios calculated was 0.35 with the standard deviation of 0.06. The standard deviation counts towards 17% of the mean, which implies all the ratios were rather consistent. Hence the fitting in general described the carbonaceous species present on the catalyst surface.

**Figure C.9** – a) The $R^2$ score for each fit and b) the ratio of asymmetric and symmetric vibration from different species.
Table C.4 – Peak areas of different surface species from methane activation over different catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Asym methoxy</th>
<th>Asym -CH$_3$</th>
<th>Asym -CH$_2$</th>
<th>Sym methoxy</th>
<th>Sym -CH$_3$</th>
<th>Sym -CH$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCuO/CZ</td>
<td>0.15</td>
<td>0.08</td>
<td>0.29</td>
<td>0.56</td>
<td>0.21</td>
<td>0.72</td>
</tr>
<tr>
<td>NiFeO/CZ</td>
<td>0.16</td>
<td>0.05</td>
<td>0.21</td>
<td>0.45</td>
<td>0.13</td>
<td>0.56</td>
</tr>
<tr>
<td>NiO/CZ</td>
<td>0.14</td>
<td>0.04</td>
<td>0.28</td>
<td>0.42</td>
<td>0.13</td>
<td>0.64</td>
</tr>
<tr>
<td>CuO/CZ</td>
<td>0.05</td>
<td>0.04</td>
<td>0.25</td>
<td>0.18</td>
<td>0.17</td>
<td>0.56</td>
</tr>
<tr>
<td>FeO/CZ</td>
<td>0.09</td>
<td>0.02</td>
<td>0.07</td>
<td>0.20</td>
<td>0.06</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Figure C.10a shows the IR spectra between 3000 cm$^{-1}$ to 4000 cm$^{-1}$ for methane activation over different catalysts. The peaks observed around 3700 cm$^{-1}$ and 3500 cm$^{-1}$ confirm the formation of hydroxyl groups from methane activation.

![Figure C.10a](image)

Figure C.10 – Methane activation over different catalysts measured by operando FTIR spectroscopy in a) 3000 – 4000 cm$^{-1}$ region b) 1000-1700 cm$^{-1}$ region.
TGA

TGA of the spent Ni-containing catalysts were carried out to determine the coke formation. All catalysts showed some weight loss during the TGA. The DTG plots showed the weight loss occurred in two regions: the first was a peak below 180 °C, which could be assigned to loss of adsorbed water, the second was a broad shoulder between 200 °C to 500 °C, which was assigned to combustion of the carbon deposition. Judging from the DTG curve, it is assumed the weight loss above 200 °C are from carbon deposit. The NiO/CZ sample showed the highest weight loss among the three catalysts.

Comparing the weight loss from carbon deposit from samples after 1 h and 8 h on stream, it was concluded that the majority of the carbon deposit (>90%) formed during the 8 h experiment period was formed in the 1st hour on stream.

Table C.5 – Total weight loss and weight loss from carbon deposit from each sample after 8 h on stream.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NiO/CZ</th>
<th>FeO/CZ</th>
<th>CuO/CZ</th>
<th>NiFeO/CZ</th>
<th>NiCuO/CZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total weight loss (%)</td>
<td>5.14</td>
<td>3.33</td>
<td>4.45</td>
<td>2.38</td>
<td>3.15</td>
</tr>
<tr>
<td>Weight loss from carbon deposit (%)</td>
<td>2.36</td>
<td>1.18</td>
<td>0.87</td>
<td>0.72</td>
<td>0.87</td>
</tr>
</tbody>
</table>

Table C.6 – Total weight loss and weight loss from carbon deposit from each sample after 100 minutes on stream.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NiO/CZ</th>
<th>FeO/CZ</th>
<th>CuO/CZ</th>
<th>NiFeO/CZ</th>
<th>NiCuO/CZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total weight loss (%)</td>
<td>2.72</td>
<td>2.07</td>
<td>2.44</td>
<td>1.56</td>
<td>2.27</td>
</tr>
<tr>
<td>Weight loss from carbon deposit (%)</td>
<td>2.22</td>
<td>0.93</td>
<td>0.89</td>
<td>0.72</td>
<td>0.80</td>
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</table>
Figure C.11 – TGA and DTG curves for spent samples after 8 h on stream.

Figure C.12 – TGA and DTG curves for spent samples after 100 minutes on stream.
Reactivity tests and error analysis

Calibration curves of all reactants and products were measured using the MS. Correlation between the MS response for a specific m/z signal and the feed concentration was established. Linear responses were observed for all compounds of interest. The MS m/z = 44 signal was used to quantify the CO₂ yield, and the MS m/z = 31 signal was used to quantify methanol. The results are shown in Figure C.13.

Two sources of uncertainty were identified in the error analysis of the reactivity data. The first was from data collection, the introduction of steam caused fluctuation in the stream composition, which resulted in 10% uncertainty in the data collected. The second error source was from the calibration curve reported above. The uncertainty in the calibration for methanol was 1.55% and for CO₂ was 0.79%. The uncertainties in the calibration for CH₄ was 2.5%, which was already an order of magnitude higher than the total yield at steady state. Calculation of conversion of methane gave statistically

Figure C.13 – Calibration curves for methane, oxygen, CO₂, methanol and steam.

Two sources of uncertainty were identified in the error analysis of the reactivity data. The first was from data collection, the introduction of steam caused fluctuation in the stream composition, which resulted in 10% uncertainty in the data collected. The second error source was from the calibration curve reported above. The uncertainty in the calibration for methanol was 1.55% and for CO₂ was 0.79%. The uncertainties in the calibration for CH₄ was 2.5%, which was already an order of magnitude higher than the total yield at steady state. Calculation of conversion of methane gave statistically
insignificant random noise fluctuate around the zero. Hence, the conversions were not reported here.

The uncertainties in the reported yield and selectivity for both CO\(_2\) and methanol were calculated through error propagation. The uncertainty in the yield was calculated as:

\[
\sigma_{\text{yield}} = \sqrt{\sigma_{\text{dat}}^2 + \sigma_{\text{cal}}^2} = 10.1\% \ (MeOH) \ or \ 10.03\% \ (CO_2)
\]

The uncertainty of the MeOH selectivity was calculated as:

\[
\sigma_{\text{Sel.}} = \sqrt{\sigma_{\text{MeOH}}^2 + \sigma_{\text{CO}_2}^2} = 14.2\%
\]
**Extrapolation of the selectivity-conversion relationship**

By taking the logarithm of both methane conversion and methanol selectivity a linear correlation was observed (Figure C.14). Extrapolation shows that a selectivity of 100% would be achieved for a methane conversion of 0.002%.

![Correlation between logarithms of MeOH selectivity and CH₄ conversion over Ni-containing catalysts.](image)

**Figure C.14** – Correlation between logarithms of MeOH selectivity and CH₄ conversion over Ni-containing catalysts.
REFERENCES


95. Wang, J.; Kipersky, V. F.; Delgass, W. N.; Ribeiro, F. H., Determination of the Au active site and surface active species via operando transmission FTIR and isotopic


