HYDROGEN PRODUCTION BY WATER GAS SHIFT REACTION FOLLOWING DRY
REFORMING OF BIOGAS METHANE IN MEMBRANE AND PACKED BED
TUBULAR REACTORS

A Thesis
Submitted to the Faculty of Graduate Studies and Research
In Partial Fulfillment of the Requirements
For the Degree of
Master of Applied Science
In
Process Systems Engineering
University of Regina

By
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Regina, Saskatchewan
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Ishioma Judith Oluku, candidate for the degree of Master of Applied Science in Process Systems Engineering, has presented a thesis titled, *Hydrogen Production by Water Gas Shift Reaction Following Dry Reforming of Biogas Methane in Membrane and Packed Bed Tubular Reactors*, in an oral examination held on November 12, 2013. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

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*Not present at defense*
ABSTRACT

The goal of this study was to develop a high performance catalyst for the water gas shift reaction of reformate gas obtained from the dry reforming of biogas methane, in order to produce bio-renewable hydrogen suitable for feed to a fuel cell. Accordingly, three phases of the study were executed involving the identification and optimization of the catalyst, application in a membrane reactor and kinetic studies of the water gas shift reaction. A portfolio of ternary oxide catalysts with a nominal composition of 3Ni5Cu/CeZrM (where M = La, Mg, Y, Gd, Ca) were developed and prepared by surfactant assisted route. A binary oxide catalyst was also prepared to serve as a benchmark for comparing the effect of incorporating a promoter element.

The catalysts were screened for the water gas shift reaction at 500°C at atmospheric pressure in a packed bed tubular reactor using 30% CO/balance N₂ gas and the catalyst with Ca promoter element showed the best performance. This catalyst was further tested using reformate gas comprising of 46.2%CO, 8.5% CH₄, 7.2% CO₂ and 38.1 % H₂ to simulate a realistic product stream from a biogas dry reformer. Again, the Ca catalyst fared well even under such conditions without any deactivation, making it a potential candidate for possible commercialization.

To optimize the catalyst preparation method, the method of impregnation was varied using atmospheric pressure or vacuum conditions; the amount of surfactant used and calcination temperature were also varied. Subsequently, the operating conditions were also varied including reaction temperature, steam/CO ratio and reactor pressure. An extended TOS stability test was performed for 12 hours to evaluate the continuous performance of the catalyst over extended time duration. Several characterization
techniques were also employed to investigate the correlation between the catalyst structure and the performance exhibited. The techniques employed include TPR, TPO, XRD, ICP-MS, N2 Physisorption, and H2 Chemisorption. Several statistical methods including Analysis of Variance (ANOVA) and two level factorial design of experiment (DOE) analysis were used to determine the main effects and interacting effects contributing to the observed activity based on the catalyst structure and operating conditions. The catalyst developed was further tested in a membrane reactor in order to investigate the possibility of reducing the number of units usually required in a conventional water gas shift process.

The results from the membrane tests showed a better performance compared to the conventional packed bed reactor whilst allowing for the production of 100% pure hydrogen. As part of the membrane studies, permeation tests were performed to correlate the amount of hydrogen recovered through the membrane with pressure and temperature. Furthermore, kinetic studies were performed on the packed bed tubular reactor operating at atmospheric pressure and high pressure (200 psi) in addition to the membrane reactor. The parameters varied were temperature ranging between 400 – 500°C and W/F_A0 ranging from 1.1 to 1.6 g-cat.hr/mol. An empirical power law model was used to correlate the resulting experimental data giving orders with respect to CO of 1.27, 1.78, 0.24 and activation energies of 137.2 kJ/mol, 190.3 kJ/mol and 99.8 kJ/mol for the packed bed (atmospheric), packed bed (high pressure) and membrane reactors, respectively. These kinetic results re-emphasized the benefit of incorporating a membrane reactor into the water gas shift reaction process.
ACKNOWLEDGEMENTS

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PBTR  Packed Bed Tubular Reactor
pH    Negative logarithm of hydrogen ion concentration
ppm   Parts Per Million
PV    Pore volume
Pt    Platinum
Pd    Palladium
psi   Pound per square inch (pressure unit)
Rh    Rhodium
SA    Specific surface area
SAR   Structure activity relationship
sccm  Standard cubic centimetre per minute
SiO₂  Silica
S/M   Surfactant/metal ratio
S/CO  Steam/CO
Sr    Strontium
Tₘₐₓ  Temperature at maximum peak
TCD   Thermal conductivity detector
TGA   Thermo gravimetric analysis
TOS   Time on stream
TPO   Temperature programmed oxidation
TPR   Temperature programmed reduction
UHP   Ultra high purity
Vol.  Volume
W/Fₐ₀ Weight time
WGSR  Water-gas-shift
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CHAPTER 1

INTRODUCTION

There has been an ever increasing consumption of energy worldwide over the past few decades. This trend is expected to continue far into the future. Much of the world energy is typically derived from fossil fuels resulting in a corresponding increase in greenhouse gas (GHG) emissions blamed for global warming and climate change issues (Gawade et al., 2010). There is extensive research worldwide aimed at developing methods and strategies to mitigate GHG emissions. Such strategies include either the development of CO$_2$ capture technologies or by the development and utilization of clean renewable energy. One key source of clean and renewable energy is hydrogen which can be used as a feed to a fuel cell – a device that converts chemical energy to electrical energy (Naidja et al., 2003). Amongst the fuel cells, the polymer electrolyte membrane fuel cell (PEMFC) is the most attractive because of its characteristic low temperature requirement (80–100° C), high amount of current produced per unit volume, quick start-up, suitability for alternating operation and compactness (Marcello et al., 2011).

The use of hydrogen as a potential source of clean energy has been known for about two centuries since 1805 when Isaac de Rivaz built the first combustion energy fueled with hydrogen (Abdollahi M. 2011). Hydrogen used as a fuel burns clean to produce water without any carbon emission according to the equation;

\[
2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 572\text{kJ} \quad \Delta H = -286\text{kJ/mol} \quad \text{(1.1)}
\]

Hydrogen, though abundant in the atmosphere, does not exist in its elemental form and therefore has to be formed either by electrolysis of water or by the reforming of hydrocarbons mainly, fossil fuels (natural gas, coal, petroleum products) and biofuels
(Mendes et al., 2010). However, due to the uneconomical nature of electrolysis, hydrocarbon reforming is a major means of producing hydrogen. Hydrogen can also be produced by biological processes such as fermentation and photolysis (Levin et al., 2004).

1.1 HYDROGEN PRODUCTION METHODS

1.1.1 Hydrocarbon reforming

The reforming reaction is a gas phase process which can produce hydrogen cost-effectively and efficiently at the point of application, thereby meeting the requirements of a hydrogen fuel cell (Idem et al., 2010). Partial oxidation, auto thermal reforming and steam reforming are the three major methods of producing hydrogen from hydrocarbons for fuel cell application. In addition, dry reforming, involving the reaction between hydrocarbon and carbon dioxide can also be used in the production of hydrogen. Partial oxidation involves the combustion of the fuel at high temperatures using a limited supply of oxygen. On the other hand, steam reforming involves the reaction of the hydrocarbon fuel with steam whereas auto thermal reforming is the combination of both steam and partial oxidation reforming to produce hydrogen and carbon monoxide (Pastore et al., 2010). The applicable chemical reactions are as follows:

**Steam Reforming**

\[ C_nH_m + mH_2O \rightleftharpoons mCO + (m+\frac{1}{2}n)H_2 \] .............................. (1.2)

**Auto thermal Reforming**

\[ C_nH_m + \frac{1}{4}mO_2 + \frac{1}{2}mH_2O \rightarrow mCO + (\frac{1}{2}m+\frac{1}{2}n)H_2 \] ................. (1.3)
**Partial Oxidation Reforming**

\[ C_{m}H_{n} + \frac{1}{2}mO_{2} \rightarrow mCO + \frac{1}{2}H_{2} \] ....................................................... (1.4)

**Dry Reforming**

\[ C_{m}H_{n} + mCO_{2} \rightarrow 2mCO + \frac{1}{2}H_{2} \] ....................................................... (1.5)

The steam reforming process alone produces 90% of hydrogen used commercially. Typical hydrocarbons and oxygenated hydrocarbons that have been used for the reforming process include methane (natural gas), methanol, ethanol, diesel, glycerol and mixtures of the oxygenated hydrocarbon. It has been reported that methane is the most common commercial raw material for hydrogen production by steam reforming (Lee et al., 2012). Another potential raw material for producing hydrogen is biogas produced by the anaerobic digestion of biodegradable waste because it is cheap, readily available and serves as a waste-clean up process since biogas is produced mainly from landfills, in addition, its two key components – CH\(_4\) and CO\(_2\) – can be readily used as raw materials for the dry reforming of methane to produce hydrogen (Saha, 2011). According to Nauman and Myren (1995), the high CO\(_2\) content of biogas enables it to be used directly for the production of hydrogen by the dry reforming reaction and the subsequent reduction of the CO level to an acceptable composition by the water gas shift reaction for use in a fuel cell. The electrical efficiency obtained by using biogas is comparable to that obtained when natural gas is used, thus making it a viable source of energy.
1.1.2 Gasification Process

Gasification is a process that involves the conversion of carbonaceous materials at high temperature (700°C) into a gaseous product containing CO, CO$_2$ and H$_2$ in the presence of controlled amounts of oxygen and/or steam without complete combustion taking place. Gasification is typically carried out on coal or biomass under high pressures. Biomass is derived from forest residues, agricultural products, municipal and industrial wastes while coal can be obtained from natural reserves. Gasification thus has the potential to reduce CO$_2$ emissions and produce clean energy. The carbon dioxide generated while producing hydrogen can be sequestered at the source of production and is not released into the environment.

The hydrogen and carbon monoxide mixture accompanied by carbon dioxide which is produced from reforming and gasification processes, typically known as syngas can be used as the raw material for producing synthetic fuels according to the Fischer-Tropsch (GTL) synthesis process or can be further processed by the water gas shift reaction to produce pure H$_2$ and CO$_2$ so as to get a higher yield of hydrogen (Bharadwaj and Schmidt, 1995) or to increase the ratio of H$_2$ to CO to make the syngas suitable for the Fischer-Tropsch (GTL) synthesis process.
1.2 WATER GAS SHIFT REACTION

The reforming reaction produces carbon monoxide (CO) alongside the hydrogen which needs to be separated in order to obtain pure hydrogen feed with less than 10 – 20 ppm CO suitable for the PEMFC to avoid corrosion of the anode and enhance the fuel cell efficiency. The water gas shift reaction (WGSR) is one of the several methods used in purifying the hydrogen produced from hydrocarbon reforming and so far, has proven to be the most technologically feasible purification method (Barbieri et al., 2008). The water gas shift reaction occurs downstream of the reformer and involves the reaction between carbon monoxide (CO) and steam (H$_2$O) to form hydrogen and carbon dioxide according to the following equation:

$$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2 \quad \Delta H = -41 \text{ kJ/mol} \quad \text{.......................... (1.6)}$$

The water gas shift reaction is kinetically and thermodynamically limited because it is both a reversible and exothermic reaction. As an exothermic reaction, it requires low temperature to promote the forward reaction; however, as a reversible reaction it also requires a high temperature to favour its kinetics. Thus the reaction is conventionally carried out in two reactors operating at high temperature (300-500°C) and low temperature (200-300°C) utilizing Fe-Cr and Cu-ZnO- Al$_2$O$_3$ catalysts, respectively (Wade, 2004). The product stream from this conventional system contains a mixture of H$_2$ and CO$_2$ which is then separated downstream using methods such as methanation, preferential oxidation (PROX), pressure swing adsorption (PSA), absorption with physical solvents (Rectisol and Selexol) or chemicals such as MDEA.
1.3 KNOWLEDGE GAP AND PROBLEM IDENTIFICATION

Certain problems associated with the production and utilization of hydrogen need to be addressed before it can replace fossil fuels. These include lack of infrastructure for distribution and efficient storage (Elghawi et al., 2008). In the mean time, on board hydrogen production can serve as a short term solution (Chekatamarla et al., 2008). However, this on-board production also has its setbacks such as the need for compactness of process units and the performance of catalysts used. With respect to catalysts, typical high temperature shift catalysts are not active at temperatures lower than 300 °C, while Cu-ZnO-Al₂O₃ catalysts which are used for low temperature shift degenerate above 250 °C. Furthermore, there are certain factors that make the commercial WGS catalysts unsuitable for on board fuel processors. For instance, the catalysts need to be activated by reduction. These catalysts can be pyrophoric in the reduced state which could lead to sintering and subsequent deactivation of the catalyst. Also, in the course of shutting down, these catalysts may reoxidize due to exposure to condensing steam. Therefore, the catalyst could be prone to poor mechanical stability as a result of its exposure to frequent start-ups and shutdowns. In addition, the conventional catalysts are designed exclusively to catalyze the WGSR with the feed being CO and H₂O. However, in reformate gas (the products of dry reforming or gasification), for which WGSR would be their realistic clean-up process, the feed would consist of CO₂, H₂ or CH₄ in addition to CO and H₂O. It has been reported that the conventional catalysts perform poorly (Kumar and Idem, 2007) if there is any variation of the typical WGSR feed. Moreover, Chromium (Cr) which is present in high temperature shift (HTS) catalyst is hazardous to the environment and its utilization should be kept at a minimum.
(Newsome et al., 1980). Therefore the challenges involved with this process over the past years include developing a suitable catalyst with high activity and stability (Naidja et al., 2003) for WGSR process involving reformate gas.

Moreover, the conventional process for the water gas shift reaction involves two shift reactors and several purification units downstream resulting in significant energy and equipment requirements in order to meet the desired purity of hydrogen. This leads to a reduced plant efficiency and hydrogen recovery (Zou et al., 2007; Marcello et al., 2011). Several efforts have been made to simplify the conventional water gas shift process such as the cyclic water gas shift reaction (Galvita and Sundmacher, 2007) and sorption enhanced water gas shift reaction (Stevens et al., 2010). However, with the recent development of membrane reactors which combine the reaction and separation step in one unit, the traditional process can be redesigned in order to achieve more compact plant size and improved yield (Mendes et al., 2010). Again, these membrane reactors have specific requirements in the type of catalyst employed and so far, there has not been any significant catalyst development suitable for use in membrane reactors as more effort has been tailored to optimize membrane manufacture methods (Basile et al., 1995), membrane material selection (Basile et al., 1996) and theoretical modeling (Bracht et al., 1996).

Furthermore, kinetic studies and performance tests on water gas shift reaction of reformate gas from dry reforming of biogas in a membrane reactor using similar catalyst formulation has never been attempted in the literature, to the best of our knowledge, thus making this current work unique.
1.4 RESEARCH OBJECTIVES AND SCOPE

Although there are several sources of syngas as identified above that could be used as feed to the water gas shift reaction, the focus of this study was to use reformate gas from dry reforming of biogas as the feed material for the water gas shift reaction. The main objectives of this work were (i) to develop a catalyst suitable for the water gas shift reaction using reformate gas, (ii) to study the effect of using a membrane reactor for the water gas shift reaction, (iii) to develop intrinsic kinetics of the water gas shift reaction in both the packed bed and membrane reactors. These objectives were mapped into three phases.

1.4.1 Phase 1: Development of Catalyst

a) Evaluate the performance of a portfolio of catalysts for the water gas shift reaction using pure CO as feed.

b) Test the best catalyst using a simulated reformate gas (from biogas dry reforming) feed for the water gas shift reaction at atmospheric pressure in a packed bed tubular reactor (PBTR).

c) Optimise the catalyst preparation method and reaction operating conditions.

d) Characterize the catalysts using bulk and surface techniques like temperature programmed reduction (TPR), N\textsubscript{2} physisorption, H\textsubscript{2} chemisorption, X-ray Diffraction (XRD), Thermo-gravimetric analysis, Inductively Coupled Plasma (ICP) techniques.

e) Relate the structure and characteristics to the catalyst performance using structure-activity relationships (SAR) for possible catalyst refinements and improvements.
1.4.2 Phase 2: Membrane Reactor Studies

a) Characterize the membrane reactor using different hydrogen compositions and operating conditions.

b) Test the novel catalyst in the membrane reactor at high pressures.

c) Perform the WGSR in the packed bed tubular reactor at high pressures to compare with the membrane performance.

d) Vary operating parameters such as flow rate, catalyst weight, and steam/CO ratio.

1.4.3 Phase 3: Kinetic Modelling

a) Perform kinetic studies on the three systems identified above: PBTR at atmospheric pressure, PBTR at high pressures and Membrane reactor at high pressures.

b) Derivation of power law rate model for the three systems above.

c) Parameter estimation and validation of the power law model.

The thesis is organized as follows:

Chapter 2 gives an extensive survey of the literature addressing the catalysts that have been developed to date for the water gas shift reaction, kinetic studies and the application of membrane reactors to the water gas shift reaction. Chapter 3 outlines the experimental methods used in this research including the catalyst preparation method and characterization techniques employed as well as the operating conditions, equipment and performance evaluation criteria used in determining the activity of the developed catalyst. Chapter 4 presents the results of this study obtained from each phase outlined
above alongside the justification of the results while chapter 5 gives the conclusions and recommendations.
CHAPTER 2
LITERATURE REVIEW

2.1 Synopsis

In this section, extensive literature survey is presented that represents the core areas covered in this work in order to put the research in perspective. This includes the catalyst materials employed, catalyst preparation and characterization techniques used, feed composition, reactor type and operating conditions employed. Studies on the kinetics of the water gas shift reaction will be presented as well. Since the catalyst developed in this work is suited for high temperature water gas shift, the review will focus on high temperature shift catalysts (>300°C) that have been studied in literature.

2.2 Catalysts for Water Gas Shift Reaction

In addition to other conditions such as operating conditions and reactor type, the catalyst composition and the preparation method also exert considerable influence on the activity of the catalyst (Azzam et al., 2007). There are two important side reactions that may occur during the water gas shift reaction. These are given as follows:

\[
\begin{align*}
\text{CO} + 3\text{H}_2 & \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \quad \text{(Methanation)} \\
\text{CO}_2 + 4\text{H}_2 & \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \quad \text{(Methanation)} \\
2\text{CO} & \rightleftharpoons \text{C} + \text{CO}_2 \quad \text{(Boudouard Reaction)}
\end{align*}
\]

Methanation reduces the amount of hydrogen produced and can damage the catalyst due to the exothermicity of the methanation reaction whereas the Boudouard reaction leaves carbon deposits on the catalyst causing the catalyst to deactivate. Several researchers have developed catalysts used for the water gas shift reaction in a fuel processor aimed at avoiding the above side reactions. Some authors have focused on avoiding Cr in the
catalyst (Gawade et al., 2010), while others have focused on developing sulphur resistant catalysts for the WGSR occurring downstream a reformer whose feed contains sulphur such as off gas from a coal gasifier or even a natural gas reformer. These catalysts are known as Sour Shift Catalysts (SSC).

Storch and Pinkel (1937) reported that a mixture of cobalt carbonate and small amounts (5 - 25%) of copper oxide heated rapidly (in 3 minutes) from room temperature to about 1100°C yield a catalyst with good activity and mechanical stability. They tested the catalyst with reformate gas from natural gas steam reforming having a composition of 68%H₂, 23%CO, 1.5%CO₂, 5%N₂, 2% CH₄, 0.5%O₂ at 310°C for over 100 hours using a high steam ratio of 4 and noticed a stable activity. However they observed that the catalyst produced by rapid heating was sintered, while that produced from slower heating was unsuitable. Also the catalyst deactivated in the presence of hydrogen sulphide but could be regenerated in the presence of air. Co/Mn and CoCr₂O₄ WGS catalysts which demonstrated 90% conversion with minimal methane formation have also been used (Gottschalk et al., 1988; Mellor et al., 1997). More recently, Park et al. (2000), Hla et al. (2011) and Osa et al. (2011) amongst others, have developed Mo and Co based catalysts supported on Al₂O₃ with only slight variation from each group. For instance, Park et al. (2000) and Laniecki et al. (2000) added nickel (Ni) to the active metal and support respectively, and this was found to enhance the catalytic activity whereas Nickolov et al. (2000) observed that the addition of potassium (K) improved the activity and texture which was confirmed by activity test at 400°C under atmospheric pressure and N₂ physisorption test for BET surface area, respectively.
Other catalysts proposed for the water gas shift reaction include Ir/TiO\(_2\) and Ru/Fe\(_2\)O\(_3\) (Erdohelyi et al., 1996, Basinska and Domka, 1999). In the latter case, the support was doped with Samarium (Sm), Lanthanum (La) or Cerium (Ce). It was observed that Sm and La doped supports performed better at low temperatures whereas Ce doped support performed better at a higher temperature of 350ºC. Hua et al. (2005) proposed the use of MgAl\(_2\)O\(_4\) spinel support due to its thermal and mechanical stability and impregnated this with \(\gamma\)-Fe\(_2\)O\(_3\) while using Ru and La as promoters. This catalyst gave a good conversion of 89% at 400ºC with a low steam to gas ratio of 0.6.

Recently, the focus has moved to the use of supported noble metals such as Pt, Pd, Rh, and Au as active metals which provide resistance to coking and offer high activity and stability. For catalyst supports, ceria based supports are being explored for the water gas shift reaction due to its oxygen storage property. However, the structure of ceria has been found to be a contributing factor to the activity it exhibits. High activity is favoured at low calcination temperatures were the crystallite size is small and is easily reducible (Bunluesin et al., 1998; Thormann, 2008). In a similar study, Gorte and Zhao (2005) observed that the effect of adding promoters was to improve the WGS activity for ceria supported precious metals of Pt and Pd, and found out that the addition of Fe drastically increased the catalyst activity. They also observed that the addition of Tb\(^{3+}\), Gd\(^{3+}\), Y\(^{3+}\), Sm\(^{3+}\), Pr\(^{3+}\), Eu\(^{3+}\), and Bi\(^{3+}\) to ceria had no effect whereas the addition of Mo reduced the activity. Gold has also been proposed by Karpenko et al. (2007) to promote the WGS activity. However, according to Luengnaruemitchai et al. (2003), Pt/ceria had a better catalytic activity over Au/ceria. These noble metal catalysts show a better performance than the conventional ones but are very expensive. Meanwhile Liu et al.
(2005) reported that Pt/CeO$_2$ deactivates under the frequent start ups and shutdown experienced in a fuel cell due to the irreversible deposition on the catalyst surface of carbonates from the reformate gas used. An in situ regeneration of the poisoned catalyst with reformate is impossible but is possible with air. Again, in line with ceria development, Zerva and Philippopoulos (2006) studied the effect of preparation method on the activity of WGS catalysts (Cu-CeO$_2$, Cu/CeO$_2$-La$_2$O$_3$) using impregnation with aqueous and organic solutions, as well as coprecipitation methods. They observed that those prepared by the coprecipitation method gave the highest activity while those prepared by impregnation gave the highest surface area. Also, amongst the impregnated catalysts, those prepared with aqueous solution gave better activity over those prepared with organic solutions.

It is more cost effective to develop cheap nickel-based catalysts which yield similar performance to those of noble metal catalysts. Iwamoto et al. (1983) examined a variety of metal ion exchanged zeolites for the water gas shift reaction at temperatures up to 773K (500°C) using Mn, Co, Ni, Cu, Zn, Fe in the zeolites. They observed that amongst the portfolio of metal ions tested, Cu and Ni showed the best performance and related their performance to the electro negativities of the metal ions. Li et al. (2000) studied the activity of Cu and Ni loaded cerium oxide prepared by co-precipitation-gelation method using La as a structural stabilizer for ceria. They observed that Cu and Ni increased the reducibility of ceria and though the catalyst did not require activation, yet it retained high activity and stability up to 600°C. Hilaire et al. (2004) observed that Ni/ceria had similar performance with Pd/ceria and were more active than Co/ceria and Fe/ceria. Similarly, Huang et al. (2006) reported that increasing the Cu and Ni loading in
a Ni-Cu catalyst supported on Sm doped ceria increased the rate of the water gas shift reaction over methanation reaction and performed better than $\alpha$-Al$_2$O$_3$. Ni/Fe based catalysts have also been used (Watanabe et al., 2009) in which it was reported that the addition of Fe reduced methanation whilst Lee et al. (2011) doped the Ni-Fe catalyst with Cs using reformate from methane steam reforming and assuming 100% methane conversion.

The problem associated with using this type of catalyst (nickel based) is its easy deactivation due to coking which stems from carbon deposition and sintering of the nickel. Choudhary et al. (2002) proposed that composite oxides with perovskite structure like LaNiO$_3$, La$_{0.8}$Ca(or Sr)$_{0.2}$NiO$_3$, and LaNi$_{1-x}$Co$_x$O$_3$ (where $x = 0.2–1$) were coke resistant. Also, Bolt et al. (1995) reported that NiAl$_2$O$_4$ catalyst offers less sintering of the nickel as a result of its discontinuous interfacial layers. Methanation has been reported to be minimized in a nickel based catalyst when Fe is added to a Ni-Al catalyst. Redox supports like cerium oxide based solid solutions have been found to prevent catalyst coking as a result of its ability to disperse the active component – Nickel. Ceria-zirconia in particular are more advantageous when compared to other redox supports because of their better redox characteristics (e.g. high oxygen storage capacity (OSC) and oxygen buffer/transport capacity (OBC/OTC). On the other hand, zirconia (Zr) offers good thermal stability to the catalyst (Idem et al., 2010; Khan et al., 2012). Ceria has also been reported to increase the surface area and pore volume of the catalyst as well as decrease the reduction temperature (Lilong et al., 2008) according to the BET and TPR tests conducted.
Using these characteristics, Kumar and Idem (2007) developed a high temperature Ni-Cu/CeO$_2$-ZrO$_2$ catalyst for the WGSR which could be used at temperatures up to 700°C in a packed bed tubular reactor. The addition of Copper (Cu) improves the selectivity to hydrogen. The metals were dispersed on the support by wetness impregnation technique while the supports were prepared by surfactant templating method because this method of preparation yields a mesoporous and thermally stable catalyst. When this support is combined with suitable loadings of Ni and/or Cu it results in high performance water gas shift catalysts. They also reported that the mixed bimetal oxides in the support overcome methanation problems and both Ni and Cu were used due to their respective properties of conversion and selectivity. Thus this catalyst was suitable for use downstream of a natural gas dry reformer because it worked well in the presence of reformate gas. Flytzani et al. (2004) also used CeO$_2$ support with Cu as the active metal for the WGSR at temperatures below 450°C. They however used urea as the surfactant to synthesize their support, whereas according to Idem et al. (2010), cetyl-trimethyl-ammonium-bromate (CTAB) offers better activity than urea. Other preparation routes used for WGS catalysts include flame synthesis (Pati et al., 2009), deposition-precipitation (Lenite et al., 2011), mechano-chemical activation (Andreeva et al., 2010), hard template and solution combustion synthesis (Galletti et al., 2011), solution spray plasma technique which gave high dispersion of the active phase – Ni (Watanabe et al., 2009). In some cases, sintering occurred or a large amount of methane was formed due to the preparation method. Galletti et al. (2011) had used a simulated reformate gas comprising of 5%CO, 20%H$_2$O, 11%CO$_2$ and 40% H$_2$. 
However, the problem with the ceria-zirconia support is that it deactivates in the presence of steam as discussed by Khan et al. (2012), in the dry reforming of methane due to the inherent hydrophilic nature of the ceria-zirconia support which increases the affinity of the support to water inhibition of active sites, which deactivates the catalyst. The addition of foreign or dopant cations can be used to adjust the catalytic activity including its hydrophilicity/hydrophobicity. In conjunction with this, Khan et al. (2012) used several aliovalent and isovalent cations (Al, Y, La, Pr, Sm, Tb, Ca, Sr, Ba, Hf), to form ternary oxide supports of the general formula Ce$_{0.5}$Zr$_{0.33}$-M$_{0.17}$O$_{2.5}$ using the surfactant (CTAB) - assisted route. The catalyst activity was tested for CO$_2$ reforming of CH$_4$ at 800°C with addition of steam, and was compared to the performance of the binary support catalyst. They also performed low-temperature (500°C) and long term (100 hours) tests for the CO$_2$ reforming of CH$_4$ including steam in order to test for possible membrane reactor application. Ternary oxide catalysts with the promoter elements Ca, La and Y, showed exceptional activity and tolerance to steam. This is concurrent with other literature reports in which Lanthanum (La) and Yittrium (Y) have been added as promoters (Tabakova et al., 2007; Yusheng et al., 2009). Magnesium and Gadolinium have also been reported to improve the Ce-Zr support in reforming applications (Sengupta et al., 2012; Haryanto et al., 2009) although Mg gave higher activity and has also been used to dope alumina support (Yixin et al., 2009, Saha, 2011) towards improvement of the overall catalytic activity. Following this review and the cognizance of the need for a novel catalyst for the WGSR at high temperatures, a portfolio of ceria based ternary oxide supported catalysts were developed and tested for the WGSR using some of the promoter elements identified above.
2.3 Membrane Reactor application in the Water Gas Shift Reaction

In all the literature cited above, the reactions were performed at atmospheric pressure and in a fixed bed reactor. Membrane reactors have been widely studied over the years for hydrogen production because they have been observed to enhance the hydrogen yield and reactant conversion either as a reforming unit or a water gas shift reactor. Kikuchi et al. (1989) reported a conversion of 100% using a palladium based membrane reactor at a pressure of 5 atm and temperature of 400°C in the presence of a Fe-Cr high temperature catalyst. Seok and Hwang (1990) also performed WGSR in a porous vycor glass membrane coated with ruthenium chloride serving as the catalyst, from which they obtained a conversion of 85% less than the equilibrium conversion of 99% at 430K (157°C). The membrane reactor typically comprises of a membrane enclosed inside a reactor shell which is selectively permeable to one of the reaction products, in most cases hydrogen, and a catalytic bed outside the membrane tube. The reaction takes place on the catalyst in the retentate side and the hydrogen produced is transferred to the permeate side, thus the continual removal of a product, according to Le Chatelier’s principle promotes the forward reaction (Kim et al., 2012). The rate of permeation of the species across the membrane is dependent on temperature and trans-membrane pressure acting as the driving force (Bracht et al., 1996). The trans-membrane pressure is achieved by operating at a high pressure on the retentate side while the permeate side is kept at atmospheric pressure in the presence or absence of an inert sweep gas.

According to Mendes et al. (2010), it is better to apply a membrane reactor as a water gas shift reactor rather than as a reforming unit because when used as a reforming
unit, the membrane metal may be damaged due to the formation of hotspots in addition to reducing the overall hydrocarbon conversion; for instance, high pressure increases the yield of hydrogen as a result of increasing permeation; however, the number of moles in the forward steam reforming reaction is increased thereby enhancing the reverse reaction rate and reducing the hydrocarbon conversion depending on the operating conditions. Consequently, the use of membranes for the hydrogen recovery enhancement through the WGS reaction yields a better process efficiency.

It has also been reported that the incorporation of a membrane reactor reduces the amount of catalyst required (Brunetti et al., 2007). In a similar study, Barbieri et al. (2008), used CuO/CeO$_2$ in a Pd-alloy MR working at 280°C and 1000 kPa (9.9 atm) to reach 90% of the equilibrium conversion with a reduced catalyst volume of 25% of that used in a conventional reactor. The use of membrane reactors in the WGSR thus offers the following advantages:

- It allows the use of high temperatures to achieve higher CO conversion thus overcoming the thermodynamic equilibrium restriction (Ciocco et al., 2003)
- It reduces the steam-to-CO ratio requirement of the WGSR from 9:1 for conventional WGS reactors to 2:1 thereby reducing energy requirement (Basile et al., 2001),
- It integrates chemical reaction with product separation into a single unit, eliminating the need for additional purification equipment and reducing capital costs (Munera et al., 2003),
- It yields higher hydrogen recovery and purity by utilization of a completely hydrogen selective membrane (Mendes et al., 2010),
- It allows for lower amount of catalyst required to achieve equivalent conversion in a conventional reactor (Enick et al., 2002),
- It also allows the utilization of higher pressure to enhance the permeation of hydrogen gas through the membrane (Enrico et al., 2011).

Although the membrane reactor reduces the amount of steam required for the WGSR, low steam/CO ratio results in certain side reactions producing unwanted products like carbon and methane. The degree to which these side reactions proceed depends on the catalyst, reaction operating conditions and reaction kinetics. It is therefore important that the catalyst chosen has a high activity and selectivity for the WGSR (Xue et al., 1996).

In line with this phenomenon, the authors tested commercial Fe-Cr and Cu-Zn, including laboratory prepared Co-Cr, Pt/ZrO₂ catalysts at a steam/CO ratio of 1.33 in quartz tubular reactor at 150 – 450°C and observed that Pt/ZrO₂ catalyst gave the best conversion of 72% and selectivity at high temperature of 350°C with minimal carbon and methane formation even when the ratio of steam/CO was reduced to 0.33. According to Cornaglia et al., (2011), the catalyst for the WGS reaction in a membrane reactor application should;

(i) Operate above 680 K (407°C) to limit the poisoning effect of CO on the Pd alloy membrane

(ii) Be considerably more active than commercial high temperature formulations

(iii) Be very stable and should not form carbonaceous residues even with low H₂O/CO ratios because carbon has a great affinity for Pd, and it rapidly destroys the membrane.
Furthermore, Gosiewski et al., (2010) recommended that a catalyst suitable for a membrane reactor should be able to withstand a wide operating temperature range from 200 – 550°C while maintaining a high CO conversion in the presence of low steam/CO ratio based on his simulation of WGS membrane reactor for gas from coal gasification.

Majority of the studies on membrane reactors have focused on improvement of the membrane material, manufacturing methods and modelling studies. Several materials have been used for manufacturing the membrane reactor for WGSR including silica, zeolites, palladium and its alloys of Cu & Ag but Pd based membranes have been proven to be better because of its high selectivity to hydrogen (Munera et al., 2003). Majority of these studies employed commercially available catalysts (Fe/Cr and Cu/Zn/Al$_2$O$_3$) and artificial feeds that do not represent an industrial scenario (Bi et al., 2009). For instance, Basile et al. (1996) studied several membrane preparation methods using commercial low temperature catalyst. Also, Tosti et al. (2000) used a commercial catalyst to study the effect of membrane preparation method and membrane composition on the water gas shift reaction. In a similar study, Criscuoli et al. (2000) studied the effect of feed composition (amongst which was reformate gas from methane steam reforming) when using ceramic mesoporous membrane as compared to a palladium membrane. Basile et al. (2001) and Arstad et al. (2006) used commercial low temperature shift catalysts and focused on preparation method and membrane properties. Conversely, Iyoha et al. (2007) studied the feasibility of performing the WGSR in Pd based membrane without additional heterogeneous catalysts at a very high temperature of 1173K (900°C), although they obtained high conversion due to the combination of temperature, catalytic membrane surface and high rate of H$_2$ permeation, they observed pinholes after
prolonged usage which they related to the extreme temperatures used and recommended the use of additional catalyst particles.

There are only a few literature reports on catalyst development for WGS in a membrane reactor. In some cases, the catalyst developed is only tested in a traditional fixed bed reactor under potential membrane conditions. For instance, Khan et al. (2008) developed modified nano-crystalline ferrites catalyst of the form Fe$_{1.82}$M$_{0.18}$O$_3$ for the high temperature WGS membrane reactor using either first row transition metals atoms (M = Cr, Mn, Co, Ni, Cu), the non transition atom (M = Zn), or the inner-transition atom (M = Ce) prepared by coprecipitation method. Characterization techniques such as XRD, TPR, N$_2$ physisorption were performed. The activity tests were performed at atmospheric pressure in a fixed bed reactor at 350 – 550°C with steam/CO ratios in the range of 1 – 7. They observed that there was no carbide nor methane formation with all the dopants except in Fe-Mn. Fe-Ce was reported to be the most promising for a membrane reactor application which was attributed to the improved oxygen storage capacity, reducibility and redox charge transfer between Fe III $\Leftrightarrow$ Fe II and Ce IV $\Leftrightarrow$ Ce III. In a follow up study by the same group, Tang et al. (2010) tested the Fe-Ce catalyst in a zeolite membrane reactor with a feed inlet pressure close to atmospheric (1.5 atm) and observed an improved conversion of 81.7% which was well over the equilibrium conversion in a packed bed reactor. However, they proposed that an improvement in the membrane material and a higher pressure will improve the permeability and hence the conversion. Flytzani-Stephanopoulos et al. (2004) used Cu-Ce (30%La)-O$_x$ in a 10μm Pd-Cu membrane at 350°C and obtained a conversion of 94% which exceeded the equilibrium conversion of 93%. This catalyst may not be suitable to withstand higher temperature
since there is no additive such as Zr that will give it thermal stability in addition to the presence of only Cu as the active metal which will deactivate at higher temperature. Bi et al. (2009) reported that CO inhibits H₂ transport through Pd and Pd alloy membranes below 350°C, and thus, it is more efficient to carry out the WGS reaction at higher temperatures in Pd membrane reactors. They used Pt/CeO₂-ZrO₂ (similar to Xue et al., 1996 mentioned earlier) and attained a CO conversion above 70% but H₂ recovery decreased significantly upon increasing the feed rate. Thus, they concluded that, in addition to high temperature, there is need to develop a catalyst with faster kinetics because at a high temperature in the range of 327–477°C, the reaction rate is the limiting factor rather than the permeance of the Pd membrane. The authors also suggested that in order to optimise the WGSR in a membrane reactor, it is more beneficial to improve the catalyst rather than focusing on the state of the art Pd membrane material. They used feed composition typical of reformate from autothermal reforming of natural gas (1.1% CH₄, 45.3% H₂, 11.8% CO, and 7.4% CO₂) and a total pressure of 1.2MPa (11.8 atm). In 2010, Abdollahi et al. (2010) used a commercial sulfur tolerant Co/Mo/Al₂O₃ catalyst for the WGSR using typical coal gasification off gas composition containing 39.5% H₂, 15.2% CO, 32.4% CO₂, 12.2% CH₄ and 0.7% H₂S in a carbon molecular sieve membrane. They obtained stable conversion and permeance at 250 – 300°C over a period of 1 month which was better than their packed bed experiments. Cornaglia et al. (2011) developed an active, non-carbon forming and stable catalyst for the WGSR (Rh/La₂O₃-SiO₂) suitable for use in a membrane reactor; however, their activity test was performed in a fixed bed tubular reactor (non-membrane) and pure CO gas was used as feed.
In some other cases, catalytic membrane materials are used in which the membrane itself catalyses the water gas shift reaction without separate catalyst particles. Still, in other cases, the membrane is wash coated with the catalytic material to prevent direct contamination of the membrane (Romero and Wilhite, 2012). An example of a catalytic membrane material is found in the work by Li et al. (2009), in which they prepared NiO–SrCeO₃₋δ mechanical support for a membrane made from SrCe₀.₉Eu₀.₁O₃₋δ where NiO also served as a WGS catalyst. They obtained a H₂ yield of 92% with recovery of 32% and an increase in conversion by 46% as compared to the conventional system using a steam/CO ratio of 1 - 2. These researchers suggested that the catalytic membrane material can be used at high temperatures > 640°C which is a cheaper alternative to palladium membrane. This is similar to the findings by Hwang et al. (2011) who proposed that Ni modified with potassium (K) is more active and selective for the WGSR with no carbon deposition over a period of 20 hours at 350°C and that this could be applied as a catalytic membrane material, although they performed their activity tests in a packed bed reactor. Garcia-Garcia et al. (2010) prepared a Pd catalytic hollow fibre membrane reactor impregnated with 30%CuO/CeO₂ catalyst and attributed the observed high conversion and hydrogen yield to a greater availability of catalyst surface area to volume ratio, improved heat and mass transfer as well as mixing of the gases, which was not the case in the absence of the membrane.

It can be seen that there is a need to develop highly stable and active catalyst for the water gas shift reaction (WGSR) that can withstand high temperatures and can be used in the presence of other components which typically make up reformate gas (from dry reforming of biogas methane or from gasification) such as CO₂, CH₄ and H₂. In this
study, a novel catalyst was developed that can withstand the conditions required in a Pd-based membrane reactor operating at high temperature and pressure. Characterization techniques were performed using several techniques in order to understand the relationship between the inherent physico-chemical properties of the catalyst and its performance.

2.4 High Pressure Water Gas Shift Reaction

The water gas shift reaction has equal number of moles of reactants and products according to stoichiometry so that its equilibrium and hence the composition of the product gas is not affected greatly by an increase in pressure except when a system that removes one of the products is employed. As a result, majority of the studies and even commercial operations are performed at atmospheric pressure. However, several studies have shown that the rate of the water gas shift reaction increases with pressure to some extent (Atwood et al., 1950).

Padovani and Lotteri (1937) reported an increase in catalyst activity with increasing pressure up to 20 atmospheres using a commercial high temperature shift catalyst; however, further increase in the pressure caused a decrease in the activity. Atwood et al. (1950) investigated the effect of pressure on the WGSR within the range of 1 – 30 atm and 346 - 404°C using a steam/gas ratio of 1.02 – 1.13. They observed that the activity of the catalyst doubled, up to a pressure of 10 atm. A further increase in pressure caused only a slight increase in activity. They used a feed composition of 25%CO and balance of H₂. Similarly, Chinchen et al. (1984), using a feed composition of 10%CO, 10%CO₂ and 80%H₂, reported a linear dependence of WGS reaction rate on
total pressure up to 30 bar (30 atm) but becomes independent of pressure beyond this point. Fott (1979) and Zhao (1999) also observed similar trends with WGS reaction rate increasing with total pressure following a downward convex curve. On the other hand, Bohlbro (1962) and Rhodes and Hutchings (2003) observed a totally linear dependence of the rate on reaction total pressure. Conversely, Bustamante et al. (2005) reported a negligible effect of high pressure (15.8 atm) condition on the WGS reaction rate as compared to the low pressure condition (1 atm).

More recently, Hla et al. (2009) reported a linear relationship between total pressure (1 – 11 atm) and the CO conversion rate using a sour shift catalyst, Co-Mo and Fe-Cr with a simulated coal derived syngas as feed with very high CO amount of 65%. In the current work being reported, high pressures were applied to the WGSR in a packed bed system without a membrane so as to compare the catalyst activity at high pressures in similar conditions in the presence and absence of a membrane.

2.5 Kinetic Studies on Water gas shift Reaction

Several studies have been carried out on the kinetics of the WGSR. In this section more focus will be directed to studies on high temperature kinetics. The study of the WGS reaction kinetics is important so as to appropriately design a reforming process, in particular, the water gas shift reactor, and optimise the operating conditions. Previous studies on kinetics of WGSR resulted in different kinetic parameters owing to the different catalysts and reaction conditions used. Thus, it is necessary to determine the kinetics for the novel catalyst developed in the current study. This will not only help in reactor design, but will also help in understanding the characteristics of the catalyst in
terms of the possible reaction mechanisms, nature of deactivation and its active sites (Kumar et al., 2008).

There are basically two reaction mechanisms that have been proposed in the literature namely; regenerative redox mechanism and associative mechanism. The redox mechanism is such that water molecules dissociate on the active site of the catalyst releasing hydrogen and simultaneously creating an oxidised surface which is then reduced by the absorption of carbon monoxide, thus producing carbon dioxide. In the associative mechanism, an intermediate is formed, typically formate, surface carbonates and carboxyl species, as a result of the reaction between CO and H₂O, which then dissociates to form the products, H₂ and CO₂ (Lin et al., 2011). Several researchers have studied the presence and type of intermediate formed using several techniques including differential reflectance infrared fourier transform spectroscopy (DRIFTS) isotope labeling, fourier transform infrared spectroscopy (FTIR), and steady state isotopic transient kinetic analysis (SSITKA) (Phatak et al., 2007; Olympiou et al., 2007). Based on the regenerative and associative mechanisms, rate expressions have been developed based on the Langmuir-Hinshelwood (LH) and Eley-Rideal mechanism. A simple empirical power law rate model which is not representative of any particular mechanism has also been used for the high temperature shift kinetic studies by several authors (Bustamante et al., 2005; Kumar et al., 2008).

In 1981, Grenoble et al. (1981) studied the pressure dependency of the WGS reactants on several alumina supported catalysts using Cu, Re, Co, Ru, Ni, Pt, Os, Au, Fe, Pd, Rh and Ir at 300°C and fitted the kinetic data using the power law expression. They observed that the reaction order over CO for most of the metals was close to zero.
while that with respect to H₂O was about 0.5. In particular, for the Ni and Cu catalysts, the orders were -0.14 and 0.30 for CO and 0.62 and 0.38 for H₂O respectively. They also proposed a mechanism including formic acid as an intermediate. They reported activation energies to be in the range of 47.3 – 98.8 kJ/mol and pre-exponential factor in the range of 9.46 x 10² – 7.38 x 10⁷ moles/sec/metal site. Chinchen et al. (1984) obtained activation energy of 129.4 kJ/mol over a Fe-Cr catalyst at a total pressure of 31.6atm and temperature of 350°C.

Campbell et al. (1992) studied the kinetics and mechanism of the WGSR over cesium (Cs) promoted copper catalysts and proposed the redox mechanism as the underlying reaction pathway. An activation energy of 46.05 kJ/mol for the Cs/Cu was reported which was slightly higher than the 41.9 kJ/mol for the non-promoted Cu, with an order of 0.5 in CO and zero-order for H₂O, however at a higher partial pressure of CO > 100 Torr (0.13 atm), the order changed such that CO approached zero order while that of H₂O became 0.5 for the Cs/Cu at 250°C. In support of the redox mechanism, Li et al. (2000) used a power law model that depended only on the partial pressures of CO and H₂O, to study the kinetics of Ni/Ce-La over a temperature range of 250 – 300°C and obtained an activation energy of 38.2 kJ/mol. Ma and Lund (2003) developed a microkinetic model also supporting the redox mechanism for the high temperature WGSR on ferrochrome (Fe-Cr) catalyst within a temperature range of 327 – 477°C, this kinetic model was further used to simulate the performance of a Pd based membrane reactor. They obtained a pre-exponential factor of 10⁶atm⁻¹s⁻¹ and activation energy of 72.5 kJ/mol.
Previously, most kinetic studies were performed on pure CO and H₂O without considering the effect of the products, CO₂ and H₂ which are usually present in the feed under realistic reforming conditions. In line with this observation, Koryabkina et al. (2003) studied the effect of CO₂ and H₂ on the rate of WGSR and reported that the presence of the products in the feed material tends to inhibit the forward reaction with orders of 0.8, 0.8, -0.7, -0.8 with respect to CO, H₂O, CO₂ and H₂ respectively using a feed composition of 7% CO, 8.5% CO₂, 22% H₂O, 37% H₂ on Cu based catalysts with ceria and alumina as supports. They reported activation energies in the range of 32 – 79 kJ/mol. In 2005, Bustamante et al., studied the kinetics of WGSR at high temperature (797 – 861°C) and both low (1 atm) and high pressure (15.8 atm) conditions using a reactor composed of a catalytic (Ni-Cr) wall. They reported a chain reaction mechanism and employed the power law model which was characterized by orders of 0.5 and 1 for CO and H₂O respectively and activation energy of 288.3 kJ/mol and pre-exponential factor of 7.4 x 10^{11} at high pressure condition which was quite different from the results at atmospheric pressure. Azzam et al. (2008) studied the reaction mechanism of the WGSR using transient kinetic studies and in situ FTIR spectroscopy. They proposed an associative formate mechanism coupled with regenerative redox route over a Pt-Re/TiO₂ catalyst. Using the power law model, they reported activation energy of 31 kJ/mol and observed that the rate of the reaction was independent of CO (especially at high CO concentrations) and CO₂ but had a first order dependence on H₂O and -0.5 order with respect to H₂.

For ceria based catalyst with Pt as the active metal, Meunier et al. (2008) studied the kinetics of the WGSR and observed that increasing the partial pressure of CO caused
a decrease in the reaction rate leading to a negative order with respect to CO which they explained to result from the competitive adsorption between reactant molecules during the reaction. Similarly, Yablonsky et al. (2010) reported an increase in activation energy with increasing partial pressure of CO at low temperatures < 300°C and atmospheric pressure. Kumar et al. (2008) studied the kinetics of the WGSR at high temperatures in the range of 400 – 600°C, testing four models based on Langmuir Hinshelwood (LH) and redox mechanisms as well as the power law rate expression. The LH model gave the best prediction amongst the mechanistic models of their experimental rates supporting the associative formate mechanism, however the power law model gave a better fitting of the experimental data with an activation energy of 48.2kJ/mol and a pre-exponential factor of 3.9 x 10^4. The orders with respect to CO, H₂O, CO₂ and H₂ were reported as 0.34, 0.39, -0.09 and -0.25 respectively.

In a bid to determine the effect of high pressure on high temperature WGSR, Hla et al. (2009) reported that the reaction order obtained from a power law expression at atmospheric pressure can be used at high pressures up to 11 atm over a Fe-Cr and Co-Mo catalyst using coal gasification off gas as feed at 450°C. Similarly, Abdollahi et al. (2010) used the power law model for the reaction at 1 – 5 atm at 300°C for similar catalyst and feed but including CH₄ in both packed bed and membrane reactors, and obtained pre-exponential factor of 16.63 and activation energy of 33.28 kJ/mol. For membrane reactor modelling, both the Langmuir Hinshelwood (Cornaglia et al., 2013) and power law model have been used. Also, Osa et al. (2011) compared 3 LH models based on associative and redox mechanisms to describe the kinetics of the WGSR at 350 – 500°C and pressure at 19 atm using coal derived syngas and Co-Mo catalyst in a
packed bed reactor. The redox mechanism was found to best describe the kinetic data giving activation energy of 84.7 kJ/mol and pre-exponential factor of 452.6 mmolg⁻¹s⁻¹bar⁻¹. Using Ce-Cu-Ni and Ce-Cu-Fe, Shinde and Madras (2012) obtained activation energy of 32 and 37 kJ/mol respectively supporting the redox mechanism in a fixed bed tubular reactor. Gokaliler et al. (2013) used Au-CeO₂ catalyst at 280 – 325°C to perform kinetic studies on WGSR proposing the power law rate expression with activation energy of 29.4 kJ/mol and order of 0.75, 2.0, -0.34 and -0.6 with respect to CO, H₂O, CO₂ and H₂ partial pressures respectively. As can be seen, different kinetic parameters are obtained with different catalysts and operating conditions and various mechanisms can be proposed based on the type of kinetic data obtained.

In this work however, we set to determine the activation energy and the dependency of the reaction rate on the partial pressures/moles of CO that are obtained from the novel catalyst under different operating conditions for the WGSR.
CHAPTER 3

EXPERIMENTAL SECTION

In this section, the chemicals, gases and instruments used in the course of this research are reported. The details of experimental methods employed in preparing the catalysts, activity evaluation tests, performance evaluation parameters, characterization techniques as well as safety precautions observed in the lab are also given.

3.1 SAFETY PRECAUTIONS

1. Personal Protective Equipment comprising lab coat, safety goggles, hand gloves and suitable shoes were always employed during experimental runs in the lab.

2. Liquid chemicals such as ammonium hydroxide were handled in the fume hood to prevent diffusion of toxic fumes.

3. Flammable chemicals were stored in appropriate cabinets for flammable materials.

4. Gas cylinders were properly clamped to sturdy supports and were transported in suitable carts when being replaced.

5. Chemical wastes were properly contained, labelled and disposed using standard procedures.

6. Gas monitor installed for CO detection was regularly checked to ensure the permissible limit was not exceeded.

7. Good housekeeping of the lab apparatus was ensured and spills properly cleaned up.
3.2 CATALYST PREPARATION

3.2.1 Chemicals used for catalyst preparation

1. Nickel (II) nitrate hexahydrate, Ni(NO$_3$)$_2$.6H$_2$O, 99.99%; Aldrich
2. Copper (II) nitrate hydrate, Cu(NO$_3$)$_2$.xH$_2$O, 99.99%; Aldrich
3. Cerium (III) nitrate hexahydrate, Ce(NO$_3$)$_2$.6H$_2$O, 99%; Aldrich
4. Zirconium (IV) oxynitrate hydrate, ZrO(NO$_3$)$_2$.xH$_2$O, 99.99%; Aldrich
5. Calcium (II) nitrate tetrahydrate, Ca(NO$_3$)$_2$.4H$_2$O, 99%; Aldrich
6. Gadolinium (III) nitrate hydrate, Gd(NO$_3$)$_3$.xH$_2$O, 99.99%; Alfa Aesar
7. Lanthanum (III) nitrate hexahydrate, La(NO$_3$)$_3$.6H$_2$O, 99.99%; Aldrich
8. Magnesium nitrate, Mg(NO$_3$)$_2$.6H$_2$O, 98%; Sigma
9. Yttrium (III) nitrate hexahydrate, Y(NO$_3$)$_3$.6H$_2$O, 99.99%; Aldrich
10. Ammonium hydroxide reagent ACS-Pure: Fisher (30 volume %)
11. Hexadecyltrimethylammonium bromide (CTAB), C$_{19}$H$_{42}$NBr: Sigma

3.2.2 Equipment used for catalyst preparation

1. Isotemp Muffle furnace, Model 550-126, Fisher Scientific Company
2. Hydraulic Press, model 3912, Carver
3. Magnetic Stirrer hot plate, Gyratherm IIa, VWR Scientific Inc.
4. Rotary Evaporator, Buchi Corporation
5. U.S.A standard test sieve, ASTM, E-11 specification, Fisher Scientific
6. Weighing Balance
3.2.3 Preparation of Ternary Oxide Support

Ternary oxide supports with a composition of $\text{Ce}_{0.5}\text{Zr}_{0.33}\text{M}_{0.17}$ were prepared using CTAB as the surfactant under basic conditions, where M is a promoter element and is either a transition metal, non-transition metal or inner transition metal. This procedure is similar to previous studies in our group (Sengupta, 2011; Sukonket et al., 2011). In this study, the promoter elements used were Ca, Mg, Y, Gd and La which were obtained from their nitrate precursors. The molar ratio of $[\text{CTAB}]/[\text{Ce+Zr+M}]$ was kept constant at 1.25. Typically, pre-determined amounts of the nitrate precursors were each dissolved in 500ml of deionised water. The surfactant - cetyltrimethyl ammonium bromide (CTAB) was also dissolved in 1000 ml of deionized water and added to the previous solution. Ammonium hydroxide was then slowly added to the above solution over a period of 120 min until the pH was increased to 12 while stirring. The pH was confirmed by use of standard pH paper. This caused the precipitation of a gelatinous yellow-brown slurry. After precipitation, the slurry was then sealed in pyrex glass bottles and aged hydrothermally in an oven maintained at $90^\circ \text{C}$ for 5 days. The mixture was then cooled to room temperature and the precipitate filtered and washed with warm deionised water to remove the free surfactant not incorporated within the oxide. The resulting residue was dried overnight at $120^\circ \text{C}$, crushed and calcined at $650^\circ \text{C}$ for 3 hours in the muffle furnace to remove the surfactant and obtain oxides. In order to optimise the catalyst preparation method, the surfactant to metal ratio was varied between 0, 0.2, 0.5 and 1.25. For the surfactant to metal ratio of zero, the $\text{Ce}_{0.5}\text{Zr}_{0.33}\text{M}_{0.17}$ with support M=Ca was prepared by co-precipitation route. In this method, no surfactant was added and the amount of aqueous ammonium hydroxide required to precipitate the solution of nitrates
was less than in the surfactant route. The subsequent ageing, washing, filtration, drying and calcination steps were similar to the previous method.

### 3.2.4 Preparation of Binary Oxide Support

The binary oxide supported catalyst was used as a benchmark to show the effect of the promoter element in the ternary oxide supported catalyst. The catalyst support was prepared using surfactant-assisted route and comprised of two metal oxides (CeO$_2$/ZrO$_2$) having a composition of 50wt% each, similar to previous report by our group (Kumar and Idem, 2007). Certain amounts of Ce(NO$_3$)$_3$.6H$_2$O and ZrOCl$_3$.XH$_2$O were each dissolved in 500 ml of deionised water. The surfactant (CTAB) was also dissolved in 1000 ml of deionized water and mixed with the previous solution (molar ratio of CTAB/Ce+Zr = 1.25) under rigorous stirring. Aqueous NH$_4$OH was then slowly added until the pH was increased to 12. The resulting colloidal slurry was then sealed in glass vessels and aged in an oven maintained at 90$^\circ$C for 5 days under autogenous pressure. The mixture was then cooled to room temperature and the precipitate filtered and washed with warm deionised water to remove the free surfactant not incorporated within the oxide. The resulting residue was dried overnight at 90$^\circ$C, crushed and calcined at 450$^\circ$C for 4 hours to remove the surfactant and obtain oxides.

### 3.2.5 Preparation of Supported Bimetallic Catalysts

The ternary oxide supports were simultaneously impregnated with both Nickel (3wt%) and Copper (5wt%) using their nitrate precursors through the wet impregnation method. These compositions were selected based on a previous study by Kumar and Idem (2007). In a typical run, 4.6g of oxide support was immersed in 25.55ml of 0.1M
Ni(NO$_3$)$_2$.6H$_2$O and 39.31ml of 0.1M Cu(NO$_3$)$_2$.xH$_2$O solutions and slowly dried via two routes. The first method involved continuous stirring of the solution in a hot silicon oil bath (85$^0$C) exposed to the atmosphere while the second method which yielded better impregnation/metal dispersion involved the use of a vacuum controlled rotary evaporator comprising of a hot water bath (85$^0$C). In both cases, the resultant dry powders were calcined at 650$^0$C for 3 hours. Afterwards, the calcined catalyst powders were pressed into tablets using the hydraulic press and sieved into sizes of 0.8mm for use in the reactor. The calcination temperature was later varied between 650 and 425$^0$C to optimise the catalyst preparation method. All the catalysts used in the present work were prepared by similar procedures to allow for direct comparison of their performance and properties.
Table 3.1 Portfolio of catalysts prepared

<table>
<thead>
<tr>
<th>Types of Impregnation</th>
<th>Name of the Catalysts (CTAB=1.25)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet Impregnation (3Ni-5Cu)</td>
<td>Ni-Cu/CeO$_2$-ZrO$_2$</td>
</tr>
<tr>
<td></td>
<td>Ni-Cu/CeO$_2$-ZrO$_2$-GdO$_x$</td>
</tr>
<tr>
<td></td>
<td>Ni-Cu/CeO$_2$-ZrO$_2$-MgO$_x$</td>
</tr>
<tr>
<td></td>
<td>Ni-Cu/CeO$_2$-ZrO$_2$-CaO$_x$</td>
</tr>
<tr>
<td></td>
<td>Ni-Cu/CeO$_2$-ZrO$_2$-YO$_x$</td>
</tr>
<tr>
<td></td>
<td>Ni-Cu/CeO$_2$-ZrO$_2$-LaO$_x$</td>
</tr>
</tbody>
</table>
3.3 CATALYST CHARACTERIZATION

The prepared catalysts and supports were characterized using several bulk/surface techniques to identify the inherent properties of the materials that are responsible for the catalytic activity observed. Both fresh and used catalysts were characterized by the following methods which can be classified according to bulk (>3nm) or surface (<3nm) techniques depending on the sampling depth from catalyst surface employed during characterization. This classification is shown in Table 3.2 and the details described below.

3.3.1 Instruments used for characterization

1. Micromeritics ASAP 2010: N₂ physisorption and H₂ chemisorption
2. Shimadzu TGA-50: TGA and TPO
3. ChemBET 3000 Quantachrome: TPR
4. Bruker Discover Diffractometer: XRD
### Table 3.2 Classification of catalyst characterization techniques

<table>
<thead>
<tr>
<th>Bulk Technique</th>
<th>Surface Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray diffraction (XRD)</td>
<td>H$_2$ chemisorption</td>
</tr>
<tr>
<td>Temperature programmed reduction (TPR)</td>
<td>N$_2$ physisorption</td>
</tr>
<tr>
<td>Thermo-gravimetric Analysis (TGA)</td>
<td></td>
</tr>
<tr>
<td>Inductively coupled plasma-mass spectrometry (ICP-MS)</td>
<td></td>
</tr>
<tr>
<td>Temperature Programmed Oxidation (TPO)</td>
<td></td>
</tr>
</tbody>
</table>
3.3.2 N\textsubscript{2} Physisorption

The catalysts and supports were analysed for their BET surface area, pore volume, pore size and pore size distribution by N\textsubscript{2} physisorption. The analysis was conducted at liquid N\textsubscript{2} temperature using a Micromeritics ASAP 2010 apparatus. Before the actual analysis, all the samples were evacuated for 4 hours at 180 °C under vacuum. The desorption branch of the N\textsubscript{2}-isotherm were used to analyze the pore size distribution and average pore volume.

3.3.3 H\textsubscript{2} chemisorption

H\textsubscript{2} chemisorption was used to determine the metallic surface area and dispersion of the active metal phase (Ni-Cu) in the catalyst samples. The analysis was performed at 35 °C using a Micromeritics ASAP 2010 instrument. The catalyst samples were first dried at 120 °C and then reduced in situ in flowing H\textsubscript{2} gas (UHP grade) at 500-650 °C for 3h. This was done so as to mimic the reduced state of the catalyst as in the case of a typical run. Thereafter the catalyst was evacuated at 500-650 °C for 1 h and then cooled down to 35 °C before performing actual measurements. In a typical volumetric H\textsubscript{2} chemisorption measurement, known amounts of hydrogen are dosed and subsequently adsorbed at different partial pressures, resulting in a chemisorption isotherm. The weakly adsorbed hydrogen molecules are then removed in an evacuation step and the isothermal measurement repeated. The difference between the two isotherms is used to calculate the active metal surface area and represents the chemically bonded reactive gas. A combination of this information with information on metal loading is then used to calculate the metal dispersion. The metallic surface area (S\textsubscript{Ni}) was calculated by
considering the adsorption stoichiometry as 2 surface nickel and copper atoms per hydrogen molecule. The metal dispersion ($D\%$) was then calculated as the percentage of surface metal atoms with respect to total metal atoms in the catalysts.

### 3.3.4 X-ray Diffraction (XRD) Measurements

Powder XRD measurements of the catalysts and supports were performed in order to verify the chemical components present and also determine the degree of crystallinity. The XRD patterns were recorded on a Bruker Discover diffractometer using Ni-filtered Cu Kα (0.154056 nm) as the radiation source. The intensity data were collected over a 2θ range of $10^0 - 90^0$ with a step size of $0.02^0$ using a counting time of 1 s per point and crystalline phases were identified. For reference purposes, pure NiO and CuO were also analysed so as to determine the position of their peaks and identify their presence in a catalyst sample.

### 3.3.5 Thermo-gravimetric Analysis (TGA)

The calcination temperature was determined by the use of TGA instrument (Shimadzu TGA-50) which records the weight loss of a fresh uncalcined powder catalyst sample (23mg) with increasing temperature up to $800^0\text{C}$ at $10^0\text{C/min}$ while flowing an inert gas (ultrapure nitrogen) through the sample. This temperature is held for 30 minutes before the sample is cooled down to room temperature.

### 3.3.6 Temperature Programmed Reduction (TPR)

TPR enables us determine the reducibility of a catalyst material and an appropriate temperature suitable for activation. Consequently, the TPR technique was
used to analyse the nature of the species in the catalysts and the supports. A Quantachrome ChemBET 3000 unit equipped with a thermal conductivity detector (TCD) was employed. For a typical run, 50mg of the sample was degassed at 180°C for 2 hours in a pure nitrogen atmosphere. Afterwards, the sample was transferred to the analysis port and heated up to 1050°C at a heating rate of 15°C/min in the presence of a typical reducing gas mixture (5%H2/balance N2) with a flow rate of 75sccm. The H₂ uptake was measured as a function of TCD response and was plotted against temperature to give a TPR profile. T_max values were recorded and used to determine the reducibility of the sample, that is, 1/T_max.

3.3.7 Temperature Programmed Oxidation (TPO)

The TPO technique enables us determine the carbon propensity factor (CPF) of a catalyst. The CPF of a catalyst is a measure of the potential of carbon formation in a catalyst and is defined as the amount of carbon formed (mg) per gram catalyst per hour. The CPF was measured using the Shimadzu TGA-50 using equal amounts of used catalyst samples. In a typical run, 150mg of used catalyst was heated up from ambient temperature to 1050°C at a heating rate of 15°C/min using 5%O₂/balance N₂ as the reactive gas at a flow rate of 30ml/min. The O₂ burned off the carbon from the used catalyst which was recorded as a weight loss in the sample by the TGA unit. This weight loss was recorded as the amount of carbon and then used to determine the carbon propensity factor.
3.3.8 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

ICP-MS was used to determine the elemental composition of the catalysts in terms of the amount of Ni and Cu present. The ICP-MS allows the detection of metals by ionizing a sample with plasma at very high temperature (9727°C) and then using a mass spectrometer to separate and quantify the ions. Typically, a sample to be analysed is digested by mixing it with a mixture of acids and then the sample is pumped into a nebulizer which converts it into a fine aerosol with argon gas. As a droplet of the sample enters the plasma region, it evaporates and any dissolved solids present are broken down into atoms and at the prevailing temperatures in the plasma, the atoms are ionized. The ions are then sent to the mass spectrometer which separates them based on the mass to charge ratio and measures the concentration. The analysis was conducted at the Trace Analysis Facility (TAF), University of Regina.

3.4 CATALYST ACTIVITY EVALUATION – PBTR

The catalysts were evaluated for their activity by performing the water gas shift reaction in a conventional packed bed tubular reactor (PBTR) made of Inconel 625 with ½”I.D placed vertically in an electrical furnace. The rationale of using the packed bed reactor is to screen the portfolio of catalysts prepared, then optimize the preparation method and eventually use this optimum catalyst in the membrane reactor, to improve the recovery of pure hydrogen. The gases used for activity evaluation include 30%CO/balance N₂ and simulated reformate gas from biogas dry reforming comprising of 46% CO, 38% H₂, 9% CH₄, 7% CO₂ (Praxair). The flow rates of the gases were
regulated using a mass flow controller (Aalborg Instruments). A high performance liquid chromatography (Alltech) pump was used to supply water at the desired flow rate, while a sliding thermocouple was used to measure the reaction temperature inside the catalyst bed. The schematic diagram of the experimental setup is shown in Figure 3.1.
Figure 3.1 Schematic diagram of experimental setup for water gas shift reaction using PBTR
In a typical run, 0.25g of 0.8mm sized ($D_p$) catalyst particles was mixed with about 15g of $\alpha$-Al$_2$O$_3$ (Sasol GmbH, Germany) used as a diluent and of similar particle size to form a bed height ($L$) of about 9cm in the reactor. This helped to ensure that plug flow conditions were met because the values of $L/D_p$ and $D/D_p$ were 112.5 and 15.875 respectively which were greater than the minimum requirement of 50 and 10 respectively in the reactor (Froment and Bischoff, 1990). This also helped to minimize back mixing and channelling. Prior to the actual reaction, the catalyst was activated in situ by flowing 5%H$_2$/balance N$_2$ through the catalyst bed flowing at 161sccm for 2 hours. The purpose of activating the catalyst was to reduce the metal oxides, NiO and CuO to the active metal form, Ni and Cu respectively. The reduction temperature used was 650°C but for optimization purposes and based on the maximum temperature ($T_{\text{max}}$) obtained for Cu from TPR runs, the reduction temperature was later reduced to 500°C to prevent sintering of the catalyst. The water at a flow rate of 0.1ml/min and gas mixture flowing at 161 sccm was then fed into the reactor and maintained at the desired reaction temperature of 500°C for the duration of the reaction, typically 6 hours. The catalyst screening and parametric studies were done at atmospheric pressure. Subsequently, as part of the parametric studies in the PBTR, the reaction was carried out at high pressure ranging from 150 – 250 psi (10.2 – 17 atm). Other parameters varied in this study to understand their effects on the WGSR include reaction temperature, steam/CO ratio, catalyst calcination temperature and amount of surfactant used in catalyst preparation. The product stream exiting the reactor was then passed through a condenser to remove water and separate the gaseous product which was sent to the online gas chromatography
(Agilent 6890 N) for analysis equipped with Hayesep Q and Molecular Sieve A columns coupled with a thermal conductivity detector (TCD) and helium as the carrier gas.

3.5 MEMBRANE REACTOR STUDIES

The goal of these experiments was to show the effect of using a membrane reactor on the water gas shift reaction. The membrane reactor was first characterized to determine the rate of permeation of hydrogen and its dependence on temperature and partial pressure. Thereafter, the catalyst performance was evaluated in the membrane reactor. This section gives details of these experiments.

Figure 3.2 shows the cross sectional view of the membrane reactor. The membrane reactor (REB Research & Consulting, USA) consists of an Inconel reactor shell 0.5”I.D enclosing a single tubular Pd-Ag membrane 0.125”O.D and 6.5” effective length. There are two outlet tubes from the reactor; the raffinate/retentate stream and the pure H$_2$ stream. The catalyst is fed into the annular space between the reactor shell and membrane tube. A sliding three point thermocouple is also inserted into the reactor for temperature measurement. The reactor is placed vertically in an electrical furnace (REB Research & Consulting, USA). The experimental setup used is shown in Figure 3.3 and was similar to that of Figure 3.1.

The differences between both setups include; the presence of a back pressure regulator (TESCOM Corporation) and gauge, a membrane reactor as shown in Figure 3.2, a pressure gauge (Cole Parmer) upstream of the reactor through which the feed gas inlet pressure is measured and a cooler for the permeated pure H$_2$ stream.
Figure 3.2 Schematic diagram of membrane reactor
Figure 3.3 Schematic diagram of membrane reactor experimental setup

1. Reformate gas cylinder
2. 5%H2/N2 gas cylinder
3. UHP N2 gas cylinder
4. Two stage regulator
5. 3-way valve
6. Pressure gauge
7. HPLC pump
8. Membrane reactor
9. Electrical furnace
10. Pure H2 stream cooler
11. Pure H2
12. Retentate/raffinate
13. Condensate
14. Gas/liquid separator
15. Permanent gas
16. Downstream pressure gauge
17. Back pressure regulator
18. Gas to GC for analysis
3.5.1 Membrane Characterization

According to Sieverts’ law, the amount of hydrogen permeating through a membrane is linearly dependent on the difference of the square root of the H₂ partial pressure on both sides of the membrane (Morreale et al., 2003).

\[ N_{H_2} = Pe \left( P_{H_2 \text{ret}}^{0.5} - P_{H_2 \text{perm}}^{0.5} \right) \] ................................. (3.1)

The Sieverts’ law is represented as equation 3.1 where \( N_{H_2} \) is the H₂ molar flux (mol/m².s), \( Pe \) the permeance (mol/m².s.kPa\(^{0.5}\)), \( P_{H_2 \text{ret}} \) the partial pressure of hydrogen on the retentate side (kPa) and \( P_{H_2 \text{perm}} \) the partial pressure of hydrogen on permeate side. The hydrogen permeance represents the permeability per unit thickness of the membrane, this permeability depends on temperature according to Arrhenius law:

\[ Pe = P' \exp \frac{-E}{RT} \] ........................................... (3.2)

Combining equations 3.1 and 3.2 gives equation 3.3;

\[ N_{H_2} = \frac{P \exp \frac{-E}{RT}}{x} \left( P_{H_2 \text{ret}}^{0.5} - P_{H_2 \text{perm}}^{0.5} \right) \] ................................. (3.3)

Where \( Pe^* \) is permeability and \( P' \) is the pre-exponential factor both having units of mol.m/m².s.kPa\(^{0.5}\), \( x \) is membrane thickness, \( E \) is the activation energy (J/mol), \( R \) is the universal gas constant and \( T \) is the temperature (Kelvin).

Membrane characterization studies were therefore carried out to show the relationship between hydrogen flux and pressure as well as temperature and to determine the permeance of hydrogen through the membrane. The experiments were performed using 30%H₂/balance N₂ 40%H₂/balance N₂ and 50%H₂/balance N₂ gas mixtures within a
temperature range of 300 – 500°C and pressure range of 150 – 250psi (10.2 – 17 atm). Prior to the test, the reactor was filled with α-Al₂O₃ particles of 0.8mm to ensure even distribution of heat and mass transfer and to mimic an actual catalytic run. The temperature was raised to the desired value in the presence of UHP N₂ and then the gas switched to the desired H₂/N₂ mix. The pressure on the retentate side was then increased gradually from atmospheric pressure to the desired pressure by means of the upstream gas regulator on the cylinder and the back pressure regulator (TESCOM Corporation) downstream of the reactor, keeping the inlet gas flow (275sccm) hence residence time constant for all pressures. The permeate side of the reactor was operated at atmospheric pressure thereby creating a trans-membrane pressure differential acting as a driving force to allow for the permeation of hydrogen. The retentate and pure H₂ stream were sent to the online GC for analysis and the outlet flow rates of each stream was recorded so as to determine the hydrogen recovery (R_{H₂}) defined according to equation 3.4.

\[ R_{H₂} = \frac{(H₂)_{perm}}{(H₂)_{perm} + (H₂)_{ret}} \times 100\% \]  

Where \( (H₂)_{perm} \) is the amount of hydrogen that permeated through the membrane and \( (H₂)_{ret} \) is the amount of hydrogen left in the retentate section. Hydrogen recovery \( (R_{H₂}) \) is a measure of the amount of hydrogen that can be recovered on the permeate side as compared to the original amount fed to the reactor.
3.5.2 Catalyst Evaluation in Membrane Reactor

The catalyst with the best performance from the catalyst screening in the packed bed tubular reactor was selected for the WGSR in the membrane reactor in order to determine its suitability for membrane reactor conditions. Reformate gas from biogas dry reforming comprising of 46% CO, 38% H₂, 9% CH₄, 7% CO₂ (Praxair) was used. The flow rates of the gases were measured using a mass flow controller (Aalborg Instruments) downstream of the setup. The pressure of the gases was controlled using the upstream and downstream pressure regulators. The downstream back pressure regulator was used to build the pressure as well as regulate the flow to the desired rate. A HPLC (Alltech) pump supplied water at the desired flow rate, while a three-point thermocouple was used to measure the reaction temperature inside the catalyst bed. The thermocouple (REB Research & Consulting) was designed to measure temperatures at the bottom, middle and top of the reactor. This is important in placing the catalyst bed at the point of optimum heat transfer.

In a typical run, about 15g of α-Al₂O₃ is poured into the reactor to create an elevated bed for the actual catalyst mix to sit on, such that the catalyst bed is positioned at a point close to the middle of the reactor were optimum heat transfer occurs. 0.25g of 0.8mm sized (Dₚ) catalyst particles was then mixed with another 15g of α-Al₂O₃ (Sasol GmbH, Germany) used as a diluent thus forming a catalyst bed height (L) of about 9cm in the reactor. The catalyst weight, size, bed height, temperature and steam/CO ratio were maintained at similar values to the experiments performed in the packed bed reactor for the purpose of comparison. Plug flow conditions (zero radial velocity and temperature gradient profiles) were met by ensuring the values of L/Dₚ and D/Dₚ were
greater than the minimum requirement of 50 and 10 respectively in the reactor (Froment and Bischoff, 1990). Prior to the actual reaction, the catalyst was activated at atmospheric pressure and 500°C in situ by flowing 5%H₂/balance N₂ through the catalyst bed for 2 hours. Water at a flow rate of 0.26ml/min and gas mixture flowing at 275 sccm was fed into the reactor by means of a HPLC pump (Alltech) and maintained at the desired reaction temperature of 500°C for the duration of the reaction, typically 6 hours. The two product streams – raffinate and pure H₂ - exiting the reactor were passed through a condenser/gas-liquid separator and cooler respectively to condense the water in the raffinate stream thus leaving the gaseous phase and reduce the temperature of the pure H₂ stream which was sent to the GC.
3.6 PERFORMANCE EVALUATION CRITERIA

The water gas shift reaction is shown in the following equation:

\[ \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2 \] ............ (1.6)

The criteria used to evaluate the performance of the reaction are shown below.

\[ \text{CO Conversion (X}_{\text{CO}}) = \frac{\text{Moles of CO}_{\text{in}} - \text{Moles of CO}_{\text{out}}}{\text{Moles of CO}_{\text{in}}} \times 100 \] .................. (3.4)

\[ \text{H}_2 \text{ Yield (Y}_{\text{H}_2}) = \frac{\text{Moles of H}_2 \text{produced}}{\text{Theoretically expected H}_2} \times 100 \] .................. (3.5)

\[ \text{H}_2 \text{ Selectivity (S}_{\text{H}_2}) = \frac{\text{H}_2 \text{ yield}}{\text{Conversion (X}_{\text{CO}})} \times 100 \] .................. (3.6)

Turnover frequency based on CO molecules reacting is defined as follows;

\[ \text{TOF} = \frac{\text{Number of Molecules of reactant converted per second}}{\text{Number of atoms of active site}} \text{[s}^{-1}] \] ........ (3.7)
3.7 KINETIC EXPERIMENTS

The catalyst selected for the kinetic study exhibited good activity and stability for an extended time on stream of 12 hours. The kinetic studies were carried out using reformate gas at reaction temperatures of 400, 450 and 500°C. The catalyst weight time (W/F\textsubscript{A0}) was varied between 1.1, 1.6 and 2.7 g-cat.hr/mol by keeping the weight of the catalyst constant at 0.5g while changing the feed flow rate between 161, 275 and 389sccm. These conditions were selected such that equilibrium conversion was avoided (Amphlett et al., 1991) while keeping the catalyst bed height and feed composition constant. The kinetic reactions were carried out in the PBTR at atmospheric pressure and elevated pressure of 200 psi (13.6atm) as well as in the membrane reactor, making a total of 27 runs. Table 3.2 shows the experimental matrix for the kinetic studies.
Table 3.3 Design of kinetic experiments

<table>
<thead>
<tr>
<th>PBTR – Atmospheric pressure</th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>W/F_{A,0} (g_{catalyst}*hr/mol)</td>
<td>1.1</td>
<td>1.6</td>
<td>2.7</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>Run 1</td>
<td>Run 2</td>
<td>Run 3</td>
</tr>
<tr>
<td>400</td>
<td>Run 4</td>
<td>Run 5</td>
<td>Run 6</td>
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<tr>
<td>450</td>
<td>Run 7</td>
<td>Run 8</td>
<td>Run 9</td>
</tr>
<tr>
<td>500</td>
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<table>
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<tr>
<th>PBTR – High pressure (200psi)</th>
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</tr>
</thead>
<tbody>
<tr>
<td>W/F_{A,0} (g_{catalyst}*hr/mol)</td>
<td>1.1</td>
<td>1.6</td>
<td>2.7</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>Run 10</td>
<td>Run 11</td>
<td>Run 12</td>
</tr>
<tr>
<td>400</td>
<td>Run 13</td>
<td>Run 14</td>
<td>Run 15</td>
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<td>450</td>
<td>Run 16</td>
<td>Run 17</td>
<td>Run 18</td>
</tr>
<tr>
<td>500</td>
<td></td>
<td></td>
<td></td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Membrane reactor (200psi)</th>
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<th></th>
<th></th>
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</thead>
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<td>W/F_{A,0} (g_{catalyst}*hr/mol)</td>
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<td>1.6</td>
<td>2.7</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>Run 19</td>
<td>Run 20</td>
<td>Run 21</td>
</tr>
<tr>
<td>400</td>
<td>Run 22</td>
<td>Run 23</td>
<td>Run 24</td>
</tr>
<tr>
<td>450</td>
<td>Run 25</td>
<td>Run 26</td>
<td>Run 27</td>
</tr>
<tr>
<td>500</td>
<td></td>
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</tr>
</tbody>
</table>
CHAPTER 4
RESULTS AND DISCUSSION

4.1 CATALYST CHARACTERIZATION

4.1.1 Catalysts

The catalysts prepared for the studies were characterized to elucidate the relationship between the structural properties of the catalysts and the observed performance. This is important in order to design catalysts with improved performance. The portfolio of ternary oxide supports and their corresponding catalysts as shown in Table 3.1 were considered for this characterization study. They were designated as 3Ni-5Cu/CeZrM were M is La, Gd, Ca, Mg and Y. The results obtained are presented in the following sub-sections. Binary oxide catalyst with formulation of 3Ni5Cu/CeZr was also characterized and used as a benchmark for comparison.

4.1.2 N$_2$ Physisorption

The BET surface area, pore volume and pore size of the supports and the complete catalysts were measured using N$_2$ Physisorption. The isotherms obtained for the supports and catalysts are shown in Figure 4.1a and 4.1b, respectively revealing the variation of volume of N$_2$ adsorbed versus relative pressure (P/P$_0$) were P is equilibrium pressure and P$_0$ is the saturated vapor pressure of liquid N$_2$ which is 1 atm. As seen in the figures, the shapes of the isotherms correspond to the ‘Type IV’ category, which is typical of materials with a mesoporous structure and a strong affinity for adsorption. Each exhibits a hysteresis between the adsorption and desorption arms. The hysteresis loop for Ca and La are of type H2 indicating the interconnectivity of the pores while that of Mg, Y and Gd correspond to type H3 hysteresis which shows the absence of a limiting
adsorption at high relative pressure and is characteristic of materials with slit shaped pores or containing aggregates of plate-like particles with no well defined mesoporous structure (IUPAC Recommendations, 1994; Thommes, 2010). Table 4.1 shows the measurements of surface area, pore volume, average pore diameter and pore volume to surface area ratio for the catalysts and their supports. The effect of varying the amount of surfactant and calcination temperature on their textural properties is also shown. The average pore diameter was in the range of 44 - 122 Å which is within the mesoporous range (20-500 Å). High surface area catalysts with mesopores are highly desired in heterogeneous catalysis because the pores provide accessibility for diffusion of the reactant molecules to the active sites on which the reactions take place, while a high surface area provides a large number of active sites on the catalyst surface (Levenspiel, 2009).

The catalysts and supports prepared by surfactant assisted route exhibited high surface areas >112m²/g unlike the catalyst/support prepared by co-precipitation method. The high surface areas with the catalysts and supports prepared by surfactant route is attributed to the controlled precipitation of the support in the presence of the surfactant involving the exchange of the surface ternary hydroxyl protons [CeZrM(O⁻-H⁺)₄] with the surfactant, cetyltrimethylammonium cation [(C₁₆H₃₃)N⁺(CH₃)₃] to form a nuclei of high surface area (Sukonket et al., 2011). This also results in a reduced surface tension of water in the pores of the support and, coupled with the duration (days) of ageing, gives rise to porous materials capable of withstanding the conditions of drying and calcination without shrinking or collapsing of the pores.
Figure 4.1 (a) $N_2$ isotherms of CeZrM supports
Figure 4.1 (b) $N_2$ isotherms of $3\text{Ni5Cu/CeZrM}$ catalysts
Table 4.1 N\textsubscript{2} Physisorption Results

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET Surface Area (m\textsuperscript{2}/g)</th>
<th>Pore Volume (cm\textsuperscript{3}/g)</th>
<th>Pore Size (Å)</th>
<th>Pore V. / S. Area (10\textsuperscript{-9} m)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Catalyst: 3Ni5Cu/CeZrM, Surfactant/Metal = 1.25</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>143</td>
<td>0.32</td>
<td>68</td>
<td>2.24</td>
</tr>
<tr>
<td>Mg</td>
<td>119</td>
<td>0.38</td>
<td>99</td>
<td>3.19</td>
</tr>
<tr>
<td>Y</td>
<td>165</td>
<td>0.42</td>
<td>76.6</td>
<td>2.55</td>
</tr>
<tr>
<td>Ca (normal)</td>
<td>119</td>
<td>0.29</td>
<td>74.4</td>
<td>2.46</td>
</tr>
<tr>
<td>Ca (vacuum)</td>
<td>109</td>
<td>0.28</td>
<td>77.8</td>
<td>2.57</td>
</tr>
<tr>
<td>Gd</td>
<td>138</td>
<td>0.48</td>
<td>115</td>
<td>3.48</td>
</tr>
<tr>
<td>M=0(Binary)</td>
<td>182</td>
<td>0.30</td>
<td>50.6</td>
<td>1.62</td>
</tr>
<tr>
<td><strong>Support: CZM, Surfactant/Metal = 1.25</strong></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>La</td>
<td>133</td>
<td>0.32</td>
<td>75</td>
<td>2.41</td>
</tr>
<tr>
<td>Mg</td>
<td>152</td>
<td>0.50</td>
<td>104</td>
<td>3.29</td>
</tr>
<tr>
<td>Y</td>
<td>187</td>
<td>0.28</td>
<td>44.7</td>
<td>1.50</td>
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<tr>
<td>Ca</td>
<td>122</td>
<td>0.38</td>
<td>99</td>
<td>3.11</td>
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<tr>
<td>Gd</td>
<td>201</td>
<td>0.73</td>
<td>122</td>
<td>3.63</td>
</tr>
<tr>
<td><strong>Catalyst: 3Ni5Cu/CeZrCa, Various Surfactant to Metal Ratio (S/M)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S/M = 0</td>
<td>110</td>
<td>0.17</td>
<td>46</td>
<td>1.55</td>
</tr>
<tr>
<td>S/M = 0.2</td>
<td>143</td>
<td>0.24</td>
<td>49</td>
<td>1.68</td>
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<tr>
<td>S/M = 0.5</td>
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<td>0.27</td>
<td>64</td>
<td>2.21</td>
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<tr>
<td>S/M = 1.25</td>
<td>119</td>
<td>0.32</td>
<td>92</td>
<td>2.69</td>
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Support: CeZrCa, Various Surfactant to Metal Ratios (S/M)

<table>
<thead>
<tr>
<th>S/M=0</th>
<th>112</th>
<th>0.16</th>
<th>57</th>
<th>1.43</th>
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<tr>
<td>S/M=0.2</td>
<td>167</td>
<td>0.32</td>
<td>78</td>
<td>1.92</td>
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<tr>
<td>S/M=0.5</td>
<td>141</td>
<td>0.27</td>
<td>77</td>
<td>1.91</td>
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<tr>
<td>S/M=1.25</td>
<td>121</td>
<td>0.33</td>
<td>110</td>
<td>2.73</td>
</tr>
</tbody>
</table>

Catalyst: 3Ni5Cu/CeZrCa, Various calcination temperatures

<table>
<thead>
<tr>
<th>T=500°C</th>
<th>109</th>
<th>0.32</th>
<th>92</th>
<th>2.94</th>
</tr>
</thead>
<tbody>
<tr>
<td>T=575°C</td>
<td>109</td>
<td>0.33</td>
<td>91</td>
<td>3.03</td>
</tr>
<tr>
<td>T=650°C</td>
<td>109</td>
<td>0.28</td>
<td>78</td>
<td>2.57</td>
</tr>
</tbody>
</table>
It is observed that the surface area and pore volume decreased upon impregnation of the active metals on the support with the exception of La. This is because of the penetration of the dispersed nickel and copper oxides into the pores of the support thereby narrowing the pore diameter. The same theory holds for the reduced surface area observed for the ternary catalysts compared to the binary supported catalyst. Furthermore, two methods of impregnation were employed for the catalysts: under atmospheric and vacuum conditions. These were characterized to evaluate the effect of impregnation conditions on the performance and structural characteristics. The results reveal that the BET surface area and pore volume is lower in the vacuum prepared catalyst relative to that prepared under atmospheric pressure owing to the deep penetration of the active metal particles into the inner pores of the support under vacuum conditions. A similar trend was reported by Zhou et al. (2011) for a Co/SiO₂ catalyst. The pore volume to surface area ratio is a measure of the porosity of the materials; supports and corresponding catalysts possessing high PV/SA are expected to exhibit good activity. It is also observed that increasing the amount of surfactant increases the pore volume, average pore diameter and PV/SA as shown in Table 4.1 and Figure 4.2 (a) but has a negligible effect on the surface area. The effect of reducing the calcination temperature has negligible effect on the surface area of the catalysts; however, it can be observed that at higher calcination temperatures, the pore diameter and volume slightly decrease as shown in Figure 4.2 (b). This can be attributed to sintering of the catalyst at higher temperatures and should be avoided.
Figure 4.2(a) Variation of PV/SA with surfactant/metal ratio

Figure 4.2 (b) Variation of pore size with calcination temperatures
4.1.3 H$_2$-Chemisorption and ICP-MS

The metallic surface area and metal dispersion of the active components (Ni and Cu) were determined by means of the H$_2$ chemisorption technique. All catalysts were prepared by wet impregnation method and loaded with the same amount of nickel and copper, i.e. 3%Ni and 5%Cu. However the actual composition in terms of weight fraction, of Ni and Cu loaded on the catalyst was determined using Inductively Coupled Plasma-Mass Spectrometry technique (ICP-MS). From the ICP-MS findings, it is then possible to make appropriate corrections to the metallic surface area and metal dispersion measurements. Table 4.2 shows the metal dispersion and metallic surface area alongside the ICP-MS elemental composition results.

It can be seen that the catalyst with the highest metal dispersion is 3Ni5Cu/CeZrCa, which should translate into better catalytic activity. Higher Ni and Cu dispersions are required for proper distribution of active sites over the catalyst surface, rather than agglomerates which are more prone to coking and show less catalytic activity. Also, the catalyst calcined at 500°C has the highest metal dispersion of 4.1%, which means that the use of higher temperatures for thermal treatment tends to cause agglomeration of Ni and Cu particles thus reducing the dispersion of the active metals and reducing the catalytic activity. It is also observed that the metal dispersions for the catalysts prepared with surfactant are higher than that prepared without surfactant. An increase in metal loading (ICP-MS) beyond the theoretical amount results in low dispersion of metals on the support.
Table 4.2 H₂-Chemisorption and ICP-MS results

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metal Surface Area (m²/g sample)</th>
<th>Metal Dispersion (%)</th>
<th>Ni Mass fraction (ICP-MS) (%)</th>
<th>Cu Mass fraction (ICP-MS) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst: 3Ni₅Cu/CeZrM, Surfactant/Metal = 1.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>1.12</td>
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<td>2.9</td>
<td>5.0</td>
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<tr>
<td>Mg</td>
<td>0.83</td>
<td>1.5</td>
<td>3.3</td>
<td>5.3</td>
</tr>
<tr>
<td>Y</td>
<td>1.21</td>
<td>2.3</td>
<td>2.3</td>
<td>3.6</td>
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<tr>
<td>Ca</td>
<td>0.99</td>
<td>2.4</td>
<td>2.4</td>
<td>3.8</td>
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<tr>
<td>Gd</td>
<td>1.11</td>
<td>2.0</td>
<td>3.2</td>
<td>5.3</td>
</tr>
<tr>
<td>Catalyst: 3Ni₅Cu/CeZrCa, Various calcination temperature</td>
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<td></td>
</tr>
<tr>
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<td>4.1</td>
<td>2.5</td>
<td>4.8</td>
</tr>
<tr>
<td>T=575°C</td>
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<td>1.9</td>
<td>2.4</td>
<td>4.3</td>
</tr>
<tr>
<td>T=650°C</td>
<td>0.99</td>
<td>2.4</td>
<td>2.4</td>
<td>3.8</td>
</tr>
<tr>
<td>Catalyst: 3Ni₅Cu/CeZrCa, Various Surfactant to Metal Ratio (S/M)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>S/M = 0</td>
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<td>3.0</td>
<td>2.6</td>
<td>4.3</td>
</tr>
<tr>
<td>S/M = 0.2</td>
<td>2.90</td>
<td>5.6</td>
<td>1.9</td>
<td>3.2</td>
</tr>
<tr>
<td>S/M = 0.5</td>
<td>2.28</td>
<td>4.4</td>
<td>4.1</td>
<td>6.7</td>
</tr>
<tr>
<td>S/M = 1.25</td>
<td>1.63</td>
<td>4.1</td>
<td>2.5</td>
<td>4.8</td>
</tr>
</tbody>
</table>
4.1.4 Temperature Programmed Reduction (TPR)

The TPR patterns of the ternary oxide supports and their corresponding Ni-Cu impregnated catalysts are represented in Figure 4.3. The thermal conductivity detector (TCD) signal output on the graphs represents the H\textsubscript{2} consumption of the sample during the analysis and the occurrence of peaks indicates reduction of the oxides. The TPR profiles of the Gd, Y, La and Mg supports reveal two peaks representing the reduction of surface and bulk oxygen species in the Ceria lattice. As in the case of La, the surface oxygen is reduced at 646\textdegree C whilst the bulk oxygen is reduced at 837\textdegree C. This is because the high mobility of the surface oxygen ions allows for ease of removal during reduction while the bulk oxygen ions needs to be diffuse to the surface before it can be reduced, thus the higher temperature required for bulk reduction. ZrO\textsubscript{2} is not reduced within this temperature range due to its refractory nature. On the other hand, the Ca support presents a broad peak over the range of 300 – 900\textdegree C which is as a result of the formation of a solid solution. Furthermore, the profiles of the bimetallic catalysts show increased hydrogen consumption in the lower temperature region representing the reduction of Cu\textsuperscript{2+} species to Cu\textsuperscript{0} at about 300\textdegree C as indicated on the profiles while the reduction of Ni\textsuperscript{2+} to Ni\textsuperscript{0} occurs at temperatures close to 400\textdegree C.

The temperature at which reduction of CuO occurs is taken as T\textsubscript{max} to determine the reducibility (1/T\textsubscript{max}) of the catalysts whereby a lower value of T\textsubscript{max} implies a more reducible catalyst. From Figure 4.3, the catalyst with Ca as the promoter element exhibited the least T\textsubscript{max} of 262\textdegree C which translates to higher reducibility while Gd had the highest T\textsubscript{max} of 348\textdegree C. This shows the varying effects of different promoter elements on the reducibility of the catalysts.
The profiles that appear to have a single peak at a temperature lower than 500°C are as a result of the superimposition of the Cu and Ni peaks.
Figure 4.3 TPR profiles for CeZrM supports and 3Ni5Cu/CeZrM catalysts
4.1.5 Thermogravimetric Analysis (TGA)

Thermo gravimetric analysis was carried out on uncalcined catalyst samples with La and Ca promoter elements to determine the variation of the catalyst weight with increasing temperature thereby aiding in the selection of a more suitable calcination temperature for the catalysts. The resulting TGA curves are shown in Figure 4.4.

Two stages of weight loss can be observed in both curves; the first stage occurs between room temperature and 200°C while the second stage occurs between 280°C and 500°C. The first stage of weight loss can be attributed to removal of moisture from the catalyst pores and hydrated salts of Ni(NO$_3$)$_2$.6H$_2$O and Cu(NO$_3$)$_2$.xH$_2$O that were impregnated on the support, while the second stage is the removal of the nitrates (NO$_3$$^-$). A somewhat third stage is observed in the case of Ca catalyst at 720°C which is ascribable to possible sintering of the catalyst which occurs at very high temperatures causing a reduction of pore size and further deactivation of catalyst. Based on these results, a calcination temperature higher than 500°C would be unnecessary and could damage the catalyst. Therefore, a lower temperature of 500°C was chosen as the optimum calcination temperature for subsequent tests.
Figure 4.4 TGA pattern for 3Ni5Cu/CeZrM, M=La and Ca
4.1.6 Temperature Programmed Oxidation (TPO)

The used catalysts obtained after undergoing the WGS reaction were analysed for the amount of carbon deposited on the catalyst under certain operating conditions over a period of testing (time on stream - TOS) using the TPO technique. The TPO technique used was similar to the TGA method and was based on the weight difference in the catalyst before and after the analysis which is carried out in an oxygen atmosphere. Oxygen burns off any carbon present while the time on stream to which the catalyst was exposed during the reaction (5 – 6 hours) was also used to determine the carbon propensity factor. The results are shown in Table 4.3.

The CPF depends on several factors such as the feed formulation, catalyst composition, operating conditions and duration of reaction. The results show a generally low CPF value for all the catalysts less than 40 mg C/g catalyst.hr as compared to data reported in literature for similar support composition (Sengupta, 2011). This is because of the catalyst composition of ceria-zirconia mixed oxides, which are known to reduce coke formation, in addition to the promoter elements selected. The ternary oxide catalysts show a CPF lower than the binary oxide catalyst which reveals the effect of adding a promoter element to reduce the coking affinity of the catalyst; the only exception is La with a higher CPF value. Catalysts with Mg and Gd promoter elements exhibited more tolerance to coking. The effect of increasing the amount of surfactant used in catalyst preparation on the coking tolerance of the catalyst with Ca as the promoter element was also investigated. The results show that the CPF reduced with a higher amount of surfactant thus re-emphasizing the benefit of using the surfactant assisted route as a preparation method.
Table 4.3 Carbon Propensity factors for 3Ni5Cu/CeZrM catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Carbon Propensity Factor (mg C/g catalyst.hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3Ni5Cu/CeZrM)</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>23.8</td>
</tr>
<tr>
<td>Mg</td>
<td>9.6</td>
</tr>
<tr>
<td>Y</td>
<td>12.1</td>
</tr>
<tr>
<td>Ca (T_{calc} = 650\degree C)</td>
<td>12.7</td>
</tr>
<tr>
<td>Gd</td>
<td>6.4</td>
</tr>
<tr>
<td>Binary (M=0)</td>
<td>13.5</td>
</tr>
</tbody>
</table>

Effect of S/M ratio on CPF for 3Ni5Cu/CeZrCa

<table>
<thead>
<tr>
<th>S/M</th>
<th>CPF (mg C/g catalyst.hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20.8</td>
</tr>
<tr>
<td>0.2</td>
<td>18.1</td>
</tr>
<tr>
<td>0.5</td>
<td>17.7</td>
</tr>
<tr>
<td>1.25</td>
<td>15.3</td>
</tr>
</tbody>
</table>
4.1.7 X-Ray Diffraction (XRD)

XRD measurements were carried out to determine the crystallinity and composition of the catalysts and their support. The XRD pattern for the various catalysts and supports prepared by surfactant assisted route alongside pristine NiO and CuO are shown in Figures 4.5 (a) – (b). The pristine NiO and CuO were used to identify the presence or absence of crystalline phases of the active metals on the impregnated support. Figure 4.5 (c) shows the XRD spectra for the Ca catalyst prepared by co precipitation route without any surfactant.

Based on the figures, the XRD patterns are representative of a true mixed oxide phase having a cubic fluorite structure. There is no other phase present or phase segregation in the diffraction patterns. Also, the varying promoter elements have no effect on the nature of the spectra. It can be observed that in the case of all the catalysts prepared by surfactant route, the diffraction peaks of the supports are identical to those of the catalysts with no indication of any crystalline NiO and CuO phases present which establishes the presence of a highly dispersive monolayer of the active metals provided by the use of surfactant method in preparing the catalysts. In the case of the Ca catalyst produced by co precipitation with no surfactant, the peaks of Ni and Cu can be identified as shown in Figure 4.5(c) indicating the presence of bulk crystalline phases of NiO and CuO. The presence of bulk crystalline phases of the active metal is detrimental to the water gas shift reaction as it could catalyze coke forming reactions. This finding corresponds with the results of H₂ chemisorption in which catalyst produced with surfactant exhibit higher metal dispersion than that prepared without surfactant.
Figure 4.5 (a) XRD pattern for 3Ni5Cu/CeZrM, M= Gd and Mg
Figure 4.5 (b) XRD pattern for 3Ni5Cu/CeZrM, M=La and Y
Figure 4.5 (c) XRD pattern for 3Ni5Cu/CeZrM, M=Ca for S/M = 1.25 and 0
4.2 CATALYTIC ACTIVITY EVALUATION

4.2.1 CATALYST SCREENING

The activities of the developed ternary oxide catalysts 3Ni5Cu/CeZrM (M = Ca, Mg, La, Y, Gd) were tested for the water gas shift reaction under identical operating conditions using 30%CO/balance N₂ in a packed bed tubular reactor at atmospheric pressure and 500°C. A binary oxide catalyst 3Ni5Cu/CeZr previously developed in-house was also tested to serve as a benchmark for evaluating the effect of adding a promoter element to the support on the activity of the catalyst in the water gas shift reaction. At this stage, the catalyst supports were prepared with surfactant/metal ratio of 1.25 and the corresponding results are shown in Figures 4.6 (a) and (b). The impregnation of the active metals for the catalysts presented in Figure 4.6 (a) was performed at atmospheric pressure while those presented in Figure 4.6 (b) were impregnated under vacuum conditions in a rotary evaporator; in both cases the impregnated catalysts were calcined at 650°C. From the results, it is evident that the only ternary oxide catalyst with a higher activity in terms of CO conversion and H₂ yield than the binary catalyst is the one with Ca as the promoter. All the other ternary systems have lower conversions and H₂ yields than the binary catalyst. It is also observed that the catalysts prepared under vacuum conditions gave better results than those prepared under atmospheric conditions. The order of the activity exhibited by the ternary catalysts is as follows; Ca > Gd > Mg > La > Y, with Ca giving a CO conversion of 47% and 58% in Figure 4.6 (a) and (b) respectively while Y with the least activity gave a CO conversion of 17% and 21% for atmospheric and vacuum impregnated catalysts, respectively.
The activity of the Ca catalyst and the binary catalyst appeared stable but in the case of Mg, Y, La and Gd, the conversion tends to decrease steadily, this is more evident in the catalysts prepared under normal atmospheric conditions. The better performance of the catalysts prepared under vacuum conditions can be attributed to the strong interaction between the Ni and Cu particles with the support. This interaction occurs during impregnation under vacuum whereby the active metal particles penetrate deeply into the inner pores of the CeZrM support causing a uniform dispersion of the active metal and thereby preventing the agglomeration of the particles. Under vacuum conditions, a pressure gradient is formed between the support and the external surroundings which improve the rate of diffusion of the active metal particles into the pores of the support (Zhou et al., 2011). This is further evidenced in Table 4.1 where the physisorption results for 3Ni-5Cu/CeZrCa catalyst in which the BET surface area and pore volume is lower when prepared under vacuum compared to that prepared by normal conditions. Also, the chemisorption results for the binary catalyst, 3Ni5Cu/CeZr further supports this trend as the vacuum prepared sample yields a metal dispersion of 3.2% while the sample prepared under atmospheric pressure yields a lower metal dispersion of 2.2%. Thus, the vacuum impregnation method was employed for other catalyst samples used for subsequent studies. The H₂ selectivity of all the catalysts was greater than 90% showing the suitability of the catalyst for hydrogen production by the water gas shift reaction. An important observation was the non-existence of methane in the product stream and minimal coke deposition on the used catalyst as evidenced in the GC analysis and TPO measurements.
The ternary oxide catalyst with Ca was thus selected as the best catalyst and was used for further tests in the rest of the study in order to optimize its preparation method and operating conditions as well as to test its stability and activity in the presence of reformate gas and other reactor conditions.
Figure (4.6a) Performance evaluation of 3Ni5Cu/CeZrM catalysts (normal atmospheric impregnation) for water gas shift reaction using 30% CO/balance N₂ at 500°C in PBTR at atmospheric pressure.
Figure (4.6b) Performance evaluation of 3Ni5Cu/CeZrM catalysts (vacuum impregnation) for water gas shift reaction using 30% CO/balance N\textsubscript{2} at 161sccm and 500\degree C in PBTR at atmospheric pressure.
Figure (4.6c) Turnover frequency of 3Ni5Cu/CeZrM catalysts
4.2.2 PARAMETRIC STUDY

Several operating parameters were varied in order to optimize the catalyst preparation method of the best catalyst selected, 3Ni5Cu/CeZrCa, based on activity screening. The parameters varied include calcination temperature, surfactant/metal ratio, reaction temperature, feed composition, total pressure and time on stream. The results of the parametric studies are discussed in the sub-sections below.

4.2.2.1 Effect of Calcination Temperature

Initially, the catalysts screened for the WGSR were calcined at 650°C after impregnation of the active metals Ni and Cu. However, results from the TGA characterization as shown in Figure 4.4 reveal that such a high calcination temperature is unnecessary and could promote sintering of the catalyst and a subsequent reduction in the activity. Based on this finding, the calcination temperature of 3Ni5Cu/CeZrCa catalyst was varied between 425 – 650°C to evaluate the effect of thermal treatment on the activity of the resulting catalyst. The activation of the catalyst was performed at the corresponding calcination temperature and the reaction was carried out at 500°C with 30% CO/balance N₂ in the packed bed reactor at atmospheric pressure. The result shown in Figure 4.7 illustrates this effect. The catalyst calcined at 425°C and 500°C gave almost similar CO conversion of 61.9% and 62.6% with H₂ yield of 56.2% and 58.9%, respectively. In contrast, the catalysts calcined at 575°C and 650°C resulted in lower CO conversions and yields. The H₂ selectivity was not strongly influenced by the varying calcination temperature. It can be deduced from the result that the optimum temperature for calcination of the catalyst is 500°C whereas employing higher temperatures such as
575°C or 650°C is detrimental to the catalytic activity. This can be attributed to a loss in metallic surface area and porosity as the temperature increases; this is illustrated in the characterization results in Table 4.1 and 4.2. Higher calcination temperature also causes agglomeration of the active metal particles leading to non-uniform dispersion and reduced activity.
Figure (4.7) Effect of variation of calcination temperatures on activity of 3Ni5Cu/CeZrCa catalyst using 30% CO/balance N₂ at 500°C in PBTR at atmospheric pressure.
4.2.2.2 Effect of Surfactant/Metal Ratio

The amount of surfactant used in the preparation of the catalyst support was varied so as to determine the effect on the catalytic activity. The ratio of surfactant/metal employed were 0.2, 0.5 and 1.25 in addition to the co-precipitated catalyst prepared without surfactant (S/M = 0), and the results obtained thereof are presented in Figure 4.8. It is evident that the use of surfactant in the preparation of the support causes an increase in the CO conversion and H₂ yield. However, increasing the surfactant/metal ratio beyond S/M = 0.5 causes no further improvement in catalyst activity. If the use of surfactant can be limited to S/M ratio of 0.5, it would translate into a reduced cost in terms of amount of surfactant utilized and cost of disposal of waste that results during catalyst making. The improvement in catalyst activity observed with increasing surfactant amount can be ascribed to the improved textural characteristics of the resulting catalyst as evidenced in the TPO, XRD, chemisorption and Physisorption results discussed previously in section 4.1. The catalyst prepared with surfactant provides a homogenous dispersion of the active metals and prevents the formation of Ni and Cu crystallites which would otherwise promote coke formation if present. This is supported by the TPO measurement of the carbon propensity factor in Table 4.3 which steadily reduced with increasing surfactant/metal ratio. To further support this observation, the results show that the metal dispersion, and surface area, pore volume and pore diameter were improved upon addition of surfactant. This shows that the amount of surfactant utilized in the catalyst preparation plays an important role in the catalyst structure and resultant activity. From this analysis, it is clear that the optimum surfactant/metal ratio is 0.5 and going forward, this ratio was applied to catalysts used for subsequent studies.
Figure (4.8) Effect of surfactant/metal ratio on activity of $3\text{Ni5Cu/CeZrCa}$ catalyst using 30% CO/balance N$_2$ at 500$^\circ$C in PBTR at atmospheric pressure.
4.2.2.3 Effect of Reaction Temperature

The water gas shift reaction is a reversible and slightly exothermic reaction; this implies that, a lower temperature would be thermodynamically beneficial for the forward reaction but kinetically unfavourable for the reaction. In order to study the influence of reaction temperature on the dynamics of the WGSR on the developed Ca catalyst, various temperatures ranging between 450°C and 550°C were employed for performance evaluation, and the results are presented in Figure 4.9. From the graphs, at 450°C, the CO conversion obtained was 38% with a H₂ yield of 37% whereas at 500°C and 550°C, CO conversion of 65% and 62% and H₂ yield of 60% and 57% were obtained, respectively. This result indicates that the catalytic activity for the WGSR increases with increasing temperature from 450°C up to 500°C because of the kinetic limitation experienced at a lower temperature of 450°C which limits the rate of the forward water gas shift reaction whereas with any further increase in temperature beyond 500°C, the reaction becomes controlled by thermodynamics thus reducing the observed activity. This indicates an optimum reaction temperature of 500°C. On the other hand, the H₂ selectivity at a lower temperature of 450°C appears to be slightly favoured than at high temperatures whereas there is no significant difference between the H₂ selectivity at 500°C and 550°C. This is because the rate of increase of CO conversion is faster than the rate of increase of H₂ yield between 450°C and 500°C leading to formation of more CO₂ than H₂ as shown in Figure 4.9b. A similar trend was reported by Osa et al. (2012).
Figure (4.9a) Effect of reaction temperature on activity of 3Ni5Cu/CeZrCa catalyst using 30% CO/balance N₂ in PBTR at atmospheric pressure.
Figure (4.9b) Effect of reaction temperature on product distribution of 3Ni5Cu/CeZrCa catalyst using 30% CO/balance N\textsubscript{2} in PBTR at atmospheric pressure.
4.2.2.4 Effect of Feed Composition

A very important part of this study is to apply the developed catalyst to reformate gas feed containing a higher amount of CO (46.2%) in addition to 8.5% CH₄, 7.2% CO₂ and 38.1% H₂ to determine the efficiency of the catalyst on WGSR under real industrial conditions of reformate gas obtained from biogas dry reforming process. The results are presented in Figures 4.10 and 4.11. A constant feed gas flow rate of 161 ml/min (sccm) and H₂O of 0.1 ml/min (sccm) giving a steam/CO ratio of 1.7 for reformate gas and 2.7 for 30%CO mixture was utilized for both catalysts. Figure 4.10a and 4.10b compares the performance of the binary and ternary oxide catalysts using reformate gas; it is clear that the Ca catalyst yields a higher and more stable CO conversion of 22% compared to the binary catalyst which exhibits a declining conversion. Although the fresh binary catalyst 3Ni5Cu/CeZr started with a conversion of 17%, the performance began to deteriorate with prolonged time on stream due to coke deposition. This is quite different from the results obtained using pure CO because of the higher carbon content in the reformate gas.

The better performance of the ternary oxide catalyst indicating higher activity and stability within 5 hours time on stream can be attributed to the presence of a promoter element (Ca). In addition, the GC analysis (Appendix A) of the product stream reveals negligible conversion of the CH₄ present in the feed and no additional methane formation. This shows the superior performance of the catalyst since it does not promote undesired methanation side reaction. A non-catalytic run was also performed to show the influence of using a catalyst for the WGSR at a temperature of 500°C.
Under similar gas and liquid flow rate, the ternary catalyst exhibited higher CO conversion with a lower CO content as a result of the reduced steam/CO ratio for the reformate gas compared to the 30% CO mix as shown in Figure 4.11a. This implies that higher steam ratios are desired for better conversions, as discussed in section 4.2.2.5.
Figure (4.10a) Comparison of 3Ni5Cu/CeZrCa and 3Ni5Cu/CeZr catalysts using reformate gas at 500°C in PBTR at atmospheric pressure.

Figure (4.10b) Product distribution comparison of 3Ni5Cu/CeZrCa and 3Ni5Cu/CeZr catalysts using reformate gas at 500°C in PBTR at atmospheric pressure.
Figure (4.11) Comparison of reformate and 30% CO/balance N₂ feed using 3Ni5Cu/CeZrCa catalyst at 500°C in PBTR at atmospheric pressure.
4.2.2.5 Effect of Steam/CO Ratio

The stoichiometry of the WGSR requires an equimolar ratio of steam to carbon monoxide in order to proceed. However, ratios higher than 1 are usually employed to prevent the occurrence of side reactions such as methanation and CO disproportionation thereby pushing the reaction in the forward direction. Methanation reaction is undesired because it utilizes some of the H\(_2\) produced to form methane thereby causing a reduction in H\(_2\) yield; meanwhile the exothermic nature of the methanation reaction could cause thermal shock. Furthermore, the CO disproportionation reaction leads to carbon deposition on the catalyst thereby causing catalyst deactivation.

In order to evaluate the effect of increasing the ratio of steam/CO on the catalytic activity of 3Ni5Cu/CeZrCa, a set of runs varying the amount of steam/CO between 1.7, 2.7 and 3.7 were performed. CO conversion and H\(_2\) yield results were obtained based on different reformate flow rates with a constant H\(_2\)O flow rate of 0.1 ml/min. The results are presented in Figure 4.12a. An average conversion of 33% and H\(_2\) yield of 32% was obtained at steam/CO ratio of 1.7, which increased to 48% conversion and 58% H\(_2\) yield upon increasing the amount of steam to a ratio of 2.7. Further increase in the ratio of steam/CO to 3.7 had no significant change on the CO conversion, thus an optimum steam/CO ratio of 2.7 can be employed whilst saving cost of steam utilization. Methane formation was found to be negligible for all steam/CO ratios employed.

The observed increase in CO conversion between 1.7 and 2.7 ratios is due to the oxidation of coke deposited on the catalyst surface thereby minimizing catalyst deactivation and the prevention of other side reactions from occurring. Although no further increase was observed in the CO conversion at steam/CO of 3.7, a clear
increment is exhibited in the H₂ yield as a result of using excess steam. This indicates that under the given conditions, the water gas shift reaction becomes stabilized whilst the excess steam oxidizes any carbon present to form more H₂ and CO₂ thereby increasing the H₂ yield drastically. This observation was further confirmed by the H₂/CO₂ ratio in the product distribution which was greater than 1. The use of excess steam tends to increase the catalyst surface coverage with oxygen thereby partly oxidizing the surface atoms of the active metals, Ni and Cu, and reducing the accessibility to active Ni and Cu atoms. This results in an insignificant change in CO conversion.
Figure (4.12) Effect of steam/CO ratio using reformate gas as feed with 3Ni5Cu/CeZrCa catalyst at 500°C in PBTR at atmospheric pressure.
4.2.2.6 Effect of Pressure in PBTR

The water gas shift reaction can be applied to several processes ranging from biomass/coal gasification to reforming reactions in order to either improve the yield of H₂ or to shift the CO/H₂ ratio in syngas for use in gas-to-liquid applications. In a typical gasification process, high pressure conditions can be expected. Majority of studies have focused on performing the WGSR at atmospheric pressures with minimal work done at high pressures. In this section, the effect of operating at high pressure in a conventional packed bed reactor was investigated and the results are presented in Figure 4.13. It is known that the WGSR is an equimolar reaction and would not be affected by a change in pressure. Interestingly, the results of this study show a different trend. The conversion is observed to increase threefold from 9% to 28% when the pressure is increased from atmospheric to 200 psi (13.6atm). However, a further increase in pressure beyond 200 psi (13.6atm) yields no additional increase in conversion; instead, a slight decrease is observed. Similar trends in which the relationship between WGSR activity and increasing pressure either follows a downward convex curve or stabilises according to a Langmuir isotherm curve have been reported by Padovani and Lotteri (1937), Atwood et al. (1950) and Chinchen et al. (1984). The observed increase of activity with pressure is as a result of the longer contact time created and increased reactant concentration allowing more reactant molecules to convert to products. The observed decrease in activity with further increase in pressure reported by Padovani and Lotteri (1937) was attributed to the formation of methane at pressures greater than 20 bar (20 atm), they had observed an increase in activity up to a maximum of 10 – 20 bar (atm).
Atwood et al. (1950) reported a two fold increase in activity up to 10 atm and only a slight increase in activity with further increase in pressure. Other authors such as Rhodes and Hutchings (2003) and Bohlbro (1962) reported a linear relationship over the range of pressures used. In this study, a slight decline was observed upon increasing the pressure beyond 200 psi (13.6 atm). There was also no observation of methane formation and the amount of decline was far smaller than Padovani’s work (1937); it is therefore safe to infer that the pattern observed in this study followed the Langmuir isotherm curve. An optimum pressure of 200 psi (13.6 atm) was thus selected for further kinetic studies as discussed in subsequent sections.
Figure (4.13) Effect of pressure on WGSR using reformate gas at 275sccm gas with steam/CO ratio of 2.7 and 3Ni5Cu/CeZrCa catalyst at 500°C in PBTR
4.2.2.7 Statistical Analysis of Operating Parameters affecting Catalyst Activity

Statistical analysis was performed on the various parameters studied in this section using the Analysis of Variance (ANOVA) technique to investigate their effect on activity, in terms of conversion. Minitab statistical software was employed for this purpose. In this study, the general linear model was utilized to fit the experimental data available. The results of the analysis are shown in Figures 4.14 and 4.15 with the detailed test results in Appendix B. The main effects plot in Figure 4.14 reveal that the major factors contributing to the reactant conversion are feed gas composition, steam ratio, promoter element (M) and reaction temperature and pressure based on their distance from the mean line. The interaction plots (Figure 4.15) show the interacting effects of two or more parameters on the conversion selected from the 4 major effects. The interaction of high temperature (500°C), moderate steam/CO ratio (2.7) and gas composition using Ca catalyst results in a higher effect on the overall conversion of reactants. The quantitative contribution of each parameter is represented in the pareto plot of Figure 4.16 which reveals that the gas composition and steam ratio are the major contributors to the observed conversion which is similar to the results of the main effect plot. A normal probability plot of the two level factorial used to obtain the pareto plot is also shown in Figure 4.17 and is based on the design of experiment (DOE) statistical analysis method.
Figure 4.14 Main Effects ANOVA plot for parameters affecting catalyst activity

Figure 4.15 Interaction Effects plot for parameters affecting catalyst activity
Figure 4.16 Pareto plot for parameters affecting catalyst activity

Figure 4.17 Normal Probability Plot of effect of operating parameters on conversion
4.2.2.8 Extended TOS stability test

The stability of the 3Ni5Cu/CeZrCa catalyst for the WGSR using reformate feed was tested in a PBTR for an extended time on stream of 12 hours and the results are presented in Figure 4.18. It is evident that the catalyst delivered steady catalytic activity with an average CO conversion of 21% and H₂ yield of 30% under the prevailing conditions. This shows there was no deactivation due to coking and no formation or utilization of methane present in the reformate gas.
Figure 4.18 Extended TOS stability test using reformate gas with steam/CO ratio of 1.7 and 3Ni5Cu/CeZrCa catalyst at 500°C in PBTR at atmospheric pressure.
4.3 STRUCTURE ACTIVITY RELATIONSHIP (SAR)

The inherent structural and textural characteristics of the 3Ni5Cu/CeZrCa catalyst such as the pore size, surface area, reducibility, basicity, metal dispersion and carbon propensity factor contribute to the activity of the catalyst and can be tailored to fine-tune the water gas shift reaction. It is therefore imperative to establish any possible relationships between these surface/bulk characteristics and the resulting activity through structure-activity relationships (SAR). SARs aid in determining the contribution of a given characteristic to the unique performance of a catalyst in a given reaction based on its structure and provide a better understanding of the thermodynamic, catalytic and mass transfer phenomena in the water gas shift reaction. In this study, the structural properties were determined using bulk/surface characterization techniques such as N\textsubscript{2} physisorption, H\textsubscript{2} chemisorption, TPR and TPO while the activity was determined from the average CO conversion over the operating time on stream of 5 hours and plotted against the corresponding characterization data as shown in Figures 4.19 (a) and (b). The structural traits studied were the pore volume/surface area ratio obtained by Physisorption, metal dispersion obtained by chemisorption, carbon propensity factor from TPO, reducibility from TPR and the basicity. The reducibility was obtained from the correlation, $1/T_{\text{max}}$ where $T_{\text{max}}$ represents the reduction of CuO to Cu as reported by (Khan and Smirniotis, 2008; Sengupta et al., 2012).

Figure 4.19 (a)-I represents the correlation between activity and pore volume/surface area, it is evident that the Ca, Mg and Gd catalysts which gave high conversion possess high pore volume/surface area. This implies that the pore volume/surface area which is a measure of the catalyst porosity plays a critical role in the
catalyst performance. Figure 4.19 (a)-II illustrates the relationship between metal dispersion and conversion with the Ca catalyst having the highest metal dispersion which translates into the high activity exhibited because a high metal dispersion improves the density of the active sites on the catalyst surface. The metal dispersion of the other catalysts does not show any particular trend or influence on their activity. In Figure 4.19 (a)-III, the effect of the carbon propensity factor on catalytic activity is evaluated; the results show that the catalysts (Ca, Mg, Gd) which exhibited better conversion have lower CPF values. In Figure 4.19 (a)-IV, the reducibility of the catalysts is correlated with its activity, it is clear that the Ca catalyst exhibits the highest reducibility which translates into the highest activity observed. This is because of the ease with which activation of the catalyst can be performed at lower temperatures.

In Figure 4.19 (b)-I, the activity of the catalysts is correlated with the Hammett basicity function (H-) obtained from literature (Suguman et al., 1995; Idem et al., 2012). The Hammett basicity function is a measure of the number of basic sites whose basic strength is represented by the H-value. From the correlation, a more basic catalyst yields higher activity for the WGSR with Ca exhibiting the highest basicity of 25 and a corresponding conversion of 47% whereas Y displayed the lowest conversion of 18.8% with a lower basicity of 6. The order of the basicity directly relates with the order of the activity observed. This can be explained in terms of the formate-associative mechanism typical of the WGSR in which carbon monoxide is adsorbed on the catalyst surface as carbonyl specie and interacts with the hydroxyl groups from the H2O on Ni-Cu/CeZrM interface to produce formate intermediates which is decomposed into the products, CO2 and H2 (Lee et al., 2013). The number of basic sites possessed by the catalyst thus
controls the rate of the reaction and the observed activity hence the observed high activity of Ca catalyst having a high number of basic sites. Figure 4.19 (b)-II relates the basicity with the reducibility indicating that a highly basic catalyst reduces the activation temperature required therefore making the catalyst easily reducible. From the SARs, it can be inferred that a combination of metal dispersion, porosity, reducibility, basicity and carbon propensity factor contribute to some degree in the overall activity of the catalyst and the absence of any desired trait could lead to poor catalyst performance.
Figure (4.19a) Structure activity relationship for 3Ni5Cu/CeZrM catalyst in WGSR; (I) Activity versus Pore volume/surface area (II) Metal dispersion (III) Carbon Propensity Factor (IV) Reducibility
Figure (4.19b) Structure activity relationship for 3Ni5Cu/CeZrM catalyst in WGSR; (I) Activity versus Hammett Basicity (II) Basicity versus Reducibility
4.3.1 Statistical Analysis for Structure Activity Relationship

Several statistical analyses were performed on the experimental data obtained from the characterization techniques and activity evaluation. The analysis carried out include (i) Analysis of Variance (ANOVA) to determine the main effects and interaction effects of the explanatory variables (catalyst structure) on the response variable (catalyst activity) (ii) Pareto Quality analysis tool to determine the quantitative contribution of each variable to the overall performance of the system. These analyses were performed using Minitab statistical software.

The SAR data was analysed using the Fully Nested ANOVA technique based on its suitability for the experimental data available and the results are given in the Appendix B. The main effects plot of the structural characteristics on the catalyst activity represented in Figure 4.20 (I) reveals that each of the measured catalyst characteristic contributes to the observed activity. However it does not give a distinct difference on the contribution of each property as all the characteristics have equal distance from the mean line. However, Figure 4.20 (II) shows that basicity, reducibility and dispersion have greater effects than pore volume/surface area. Another approach was thus employed using a two level factorial analysis to obtain a pareto chart (Figure 4.21) which shows that the reducibility and basicity are the key contributing factors to the observed catalytic activity. This trend was further confirmed by obtaining a radar chart, Figure 4.22. The interaction plot in Figure 4.20 (III) shows the interacting effects of the choice of promoter element and the measured structural characteristics on the conversion observed. The plot indicates that the Ca catalyst with the highest mean conversion possesses a high basicity, reducibility and dispersion and intermediate pore
volume/surface area. Reducibility is also observed to increase with basicity. The other relationships do not have a strong relationship but each contribute to some degree in the overall effect of the catalyst as observed in the pareto plot.

Regression analysis was also performed to derive a correlation between the conversion and structural characteristics of the catalyst. The resulting equation is shown below:

\[
\text{Conversion} = -42.9887 + 117.18 \text{ reducibility} - 28.5524 \text{ PV/SA} - 86.7063 \text{ dispersion} - 2.9163 \text{ basicity} \tag{4.1}
\]

From the expression, the largest positive coefficient belongs to reducibility which implies that reducibility plays a major effect in the subsequent outcome of the catalyst activity. This result corresponds to that of the pareto plot. Figure 4.23 shows the parity plot of the predicted conversion obtained from equation 4.1 against the experimental conversion. A good fit with coefficient of variance \(r^2\) of 1 was obtained.
Figure 4.20 Analysis of Variance plots for structure activity relationship; (I)- (II) Main Effects Plot (III) Interaction Plot *PV represents PV/SA
Figure 4.21 Pareto Plot showing the contribution of each structural characteristic to the catalytic activity *PV represents PV/SA

Figure 4.22 Radar Plot showing the contribution of each structural characteristic to the catalytic activity
Figure 4.23 Parity plot of experimental versus predicted conversion
4.4 MEMBRANE CHARACTERIZATION RESULTS

The membrane reactor used in this study was characterized using different H\textsubscript{2} mixtures first to verify the perm-selectivity of the membrane to pure H\textsubscript{2} under varying operating conditions of temperature and pressure and then to determine the relationship between the rate of permeation of H\textsubscript{2} and the difference in partial pressure and temperature. The results of the characterization tests are presented in Figure 4.24 (a) and (b) in terms of H\textsubscript{2} recovery and flux. In all cases, pure H\textsubscript{2} (from GC analysis) was obtained on the permeate side indicating the 100\% H\textsubscript{2} selectivity of the membrane. As mentioned earlier in equation 3.4, H\textsubscript{2} recovery is defined as the molar ratio of H\textsubscript{2} that permeated through the membrane to the total amount of H\textsubscript{2} supplied to the membrane. On the other hand, the H\textsubscript{2} flux is a measure of the number of moles of H\textsubscript{2} permeating per unit surface area per unit time. Both parameters relay information on the ease of permeation of H\textsubscript{2} through the membrane.

In Figure 4.24 (a)-I, the variation of the amount of H\textsubscript{2} recovered is correlated with the temperature and total pressure employed using 30\% H\textsubscript{2}/balance N\textsubscript{2} while Figure 4.24 (a)-II relates the influence of gas composition and total pressure to the H\textsubscript{2} recovery. It is important to note that the pressure on the permeate side is at atmospheric conditions in all runs with no sweep gas employed, thus creating a trans-membrane pressure differential allowing the permeation of hydrogen. The results show a linear increase in the H\textsubscript{2} recovery with increasing temperature and pressure. In Figure 4.24 (a)-II, the increasing gas composition from 30\% to 50\% H\textsubscript{2} translates to an increase in partial pressure thereby increasing the recovery even at a constant temperature of 300°C. This observation is in consonance with Sievert’s law in equation 3.1 which relates the flux of
H₂ through a Pd membrane to the difference in partial pressure with an exponent of 0.5, while the temperature dependence of the H₂ recovery is described by Arrhenius law relating the H₂ permeability to the temperature as shown in equation 3.2.

\[ N_{H_2} = P_e (p_{H_2 \text{ret}}^{0.5} - p_{H_2 \text{perm}}^{0.5}) \]  \hspace{1cm} (3.1)

\[ P_e = p' \exp \frac{-E}{RT} \]  \hspace{1cm} (3.2)

Combining equations 3.1 and 3.2 gives equation 3.3;

\[ N_{H_2} = \frac{p' \exp \frac{-E}{RT}}{x} (p_{H_2 \text{ret}}^{0.5} - p_{H_2 \text{perm}}^{0.5}) \]  \hspace{1cm} (3.3)

\[ R_{H_2} = \frac{(H_2)_{\text{perm}}}{(H_2)_{\text{perm}} + (H_2)_{\text{ret}}} \times 100\% \]  \hspace{1cm} (3.4)

The Sievert’s law is in agreement with the dissociative adsorption, diffusion, recombination and desorption mechanism of hydrogen on the surface of a Pd membrane. Based on Sievert’s law, a plot of hydrogen flux against partial pressure difference was obtained as illustrated in Figures 4.24 (b)-I and II. The hydrogen flux was computed using the molar flow rate of hydrogen on the permeate side and known dimensions of the membrane which gives a surface area of 1.65 x 10⁻³ m². The equations describing the linear relationship between flux and partial pressure difference is indicated in the plots whereby the slope represents the permeance of hydrogen.

From Figures 4.24 (b)-I and II, it is evident that the permeance increases from 5 x 10⁻⁴ to 3.3 x 10⁻³ mol/m²s.kPa⁰.⁵ when the H₂ composition of the gas increases at constant temperature while an increase from 5 x 10⁻⁴ to 1.7 x 10⁻³ mol/m²s.kPa⁰.⁵ was observed with increasing temperature from 300 – 500°C at a constant gas composition.
and increasing total pressure. Knowing the membrane thickness of 76 µm, the flux data was regressed with the temperature data yielding an activation energy of 22.7 kJ/mol, and a pre-exponential factor of $4.56 \times 10^{-6} \text{mol.m/m}^2\cdot\text{s.kPa}^{0.5}$. The activation energy obtained in this work is slightly higher than those reported in literature. Itoh et al. (1992) obtained activation energy of 18.45kJ/mol with a Pd membrane of 200 µm thickness and pre-exponential factor of $1.02 \times 10^{-5} \text{mol.m/m}^2\cdot\text{s.kPa}^{0.5}$ at a temperature of 200°C and $\Delta P$ of 1 bar (101.3 kPa). Augustine et al. (2011) reported activation energy of 16.6kJ/mol for a Pd-Ag/Inconel membrane of 7 µm thickness at temperature of 300 – 500°C and $\Delta P$ of 14 bar (1,418.2kPa). The higher activation energy obtained in the current study can be attributed to negligible mass transfer resistance across the membrane which results in higher flux, unlike the lower activation energy reported in literature which indicates that the bulk diffusion and/or surface process is the rate limiting step (Hwang et al., 2012).
Figure 4.24 (a) Membrane Characterization Results in terms of H₂ Recovery
Figure 4.24 (b) Membrane Characterization results showing Sievert’s law
4.5 WGSR IN MEMBRANE REACTOR

The water gas shift reaction was performed in the membrane reactor varying the pressure between 150 – 250 psi (10.2 – 17 atm) at 500°C using reformate gas with a flow rate of 275 sccm and steam/CO ratio of 2.7. It is observed that unlike the case of operating at atmospheric pressure, operations using the membrane reactor require about 2 hours to stabilize. The results are shown in Figures 4.25 (a) and (b) in terms of CO conversion, H₂ yield, H₂ selectivity and H₂ recovery. The result indicates an improvement in CO conversion from 70% to 80% when the pressure is increased from 150psi to 200psi (10.2 – 13.6 atm). Increasing the pressure further to 250psi (17 atm) yields no significant effect on the CO conversion. When compared to similar conditions of feed composition and temperature at atmospheric pressure, the use of a membrane reactor is advantageous due to the continuous removal of H₂ through the permeate side, thus promoting the forward reaction.

At atmospheric pressure, the membrane reactor operates as a conventional packed bed tubular reactor due to the absence of a pressure differential driving force. Operating at high pressures in the packed bed tubular reactor as presented in section 4.2.2.6 also yields lower conversions than the case of the membrane reactor; this is because of the absence of a membrane which allows for withdrawal of one of the products. On the other hand, the H₂ yield is independent of the pressure increase while H₂ selectivity tends to decrease with increasing pressure. This implies that more CO is converted to CO₂ than H₂. In all cases, there is negligible conversion of CH₄ present in the reformate gas; appendix A shows the GC chart for the product stream from the reactor. Although, the composition of CH₄ shows 15%, this does not imply formation of
CH₄ but results from the H₂ permeating through the membrane thus increasing the fraction of the CH₄ in the raffinate stream per unit volume. It is also clear from Figure 4.25 (b) that the H₂ recovery increases linearly from 6% to 16% with increasing pressure from 150 psi to 250 psi (10.2 – 17 atm) despite the independence of CO conversion and H₂ yield on pressure above 200 psi (13.6 atm). This is in accordance with the Sievert’s law such that the increasing partial pressure improves the driving force across the membrane, hence the continuous increase in H₂ recovery. However, it is pertinent to note that the H₂ recovery obtained during the WGSR is lower than that obtained from the permeation tests were H₂/N₂ mixtures were used. This is because the rate of H₂ permeation is influenced by external gas phase mass transfer limitations such as the presence of other species, in this case, CO, CO₂ and CH₄, which tend to compete with hydrogen molecules for adsorption on the membrane surface, thereby reducing the amount of hydrogen permeating through the membrane as reported by Abdollahi (2011) and Liguori et al. (2012). An optimum operating pressure is therefore chosen based on a balance of CO conversion, H₂ yield, selectivity and recovery; in this case, 200 psi (13.6 atm) was selected for subsequent parametric and kinetic studies.
Figure (4.25a) WGSR performance in membrane reactor in terms of CO conversion and H₂ yield using reformate gas at 275sccm gas with steam/CO ratio of 2.7 and 3Ni5Cu/CeZrCa catalyst at 500°C in PBTR
Figure (4.25b) WGSR performance in membrane reactor in terms of H\textsubscript{2} selectivity and recovery using reformate gas at 275sccm gas with steam/CO ratio of 2.7 and 3Ni5Cu/CeZrCa catalyst at 500\textdegree}C in PBTR.
4.6 PARAMETRIC STUDY IN MEMBRANE REACTOR

In this section, several parameters were varied to determine the effect on the performance of the WGSR in a membrane reactor. The parameters varied include (i) catalyst weight, (ii) feed flow rate, and (iii) steam/CO ratio. The results obtained thereof are presented in Figures 4.26 and 4.27.

4.6.1 Effect of Catalyst Weight and Feed Flowrate in Membrane Reactor

The effect of varying the weight of catalyst was investigated using 0.25 g, 0.5 g and 1.0 g of 3Ni5Cu/CeZrCa catalyst under similar conditions of 500°C, 200 psi and steam/CO ratio of 2.7. The flow rate of reformate gas feed was also varied between 161 and 275 sccm keeping the steam/CO ratio constant to evaluate the influence of feed flow rate on the WGSR. Figure 4.26 (a) and (b) illustrates the results in terms of CO conversion, H₂ yield, selectivity and recovery. It is observed that increasing the weight of catalyst from 0.25 g to 0.5 g causes an increase in CO conversion from 79% to 90% when the reformate flow rate is 275 sccm and only a slight increase from 90% to 93% for reformate flow rate of 161 sccm. Increasing the catalyst weight beyond 1.0 g has a negligible effect on the resulting CO conversion for both flow rates. At both flow rates, the equilibrium conversion of 90.7% (indicated by the dashed line) under the prevailing conditions is surpassed with 0.5g – 1g of catalyst, which is one of the advantages of using a membrane reactor. CO conversion of 84% was obtained at 161 sccm which is slightly higher than the 81% conversion obtained at 275 sccm using a catalyst weight of 0.25 g. This is as a result of a higher residence time attained at lower flow rate allowing more CO molecules to be converted to products. A similar trend is also observed for the H₂ yield, selectivity and recovery with a more significant improvement in performance at
a lower flow rate. For instance, at 0.25 g, the average H₂ yield, selectivity and recovery obtained at 161 sccm was 71%, 84% and 23%, respectively whereas lower values of 59%, 73% and 12% were obtained at 275 sccm feed flow rate. On the other hand, it is observed that H₂ yield and selectivity reduced slightly when the catalyst weight was increased from 0.25 g to 0.5 g and no significant change was observed between 0.5 g and 1.0 g while the hydrogen recovery is found to be independent of the catalyst weight change. This implies that, although increasing the amount of catalyst may be beneficial for improving the CO conversion, this variation does not necessarily improve the amount of hydrogen obtained. Using 1.0 g of catalyst, however, tends to quickly stabilise the H₂ yield and selectivity for the duration of the run. Again, in this case negligible CH₄ conversion was observed.
Figure (4.26a) Effect of catalyst weight and flow rate on WGSR performance in membrane reactor in terms of CO conversion and H₂ yield using reformate gas steam/CO ratio of 2.7 and 3Ni5Cu/CeZrCa catalyst at 500°C at 200psi. 

\[ K_p = \frac{x^2_{eq}}{(1-x_{eq})(2.7-x_{eq})} \]
Figure (4.26b) Effect of catalyst weight and flow rate on WGSR performance in membrane reactor in terms of H₂ selectivity and H₂ recovery using reformate gas steam/CO ratio of 2.7 and 3Ni5Cu/CeZrCa catalyst at 500°C at 200psi
4.6.2 Effect of Steam/CO Ratio in Membrane Reactor

The effect of steam/CO ratio in the range of 1.7, 2.7 and 3.7 was studied for the WGSR in the membrane reactor using reformate gas at a high pressure of 200 psi (13.6 atm) and 500°C and the results are presented in Figure 4.27. The plots reveal a drastic increase in CO conversion from 34% to 90% and H₂ yield from 22% to 52% upon increasing the steam/CO ratio from 1.7 to 2.7. A further increase in the steam/CO ratio to 3.7 yielded no additional improvement in conversion but a gain in H₂ yield from 52% to 100%. This trend is similar to the results obtained from varying the steam/CO ratio in the PBTR at atmospheric pressure as discussed in section 4.2.2.6. In this case, the gain in hydrogen yield can be attributed to the steam reforming of methane present in the reformate feed according to equation 4.2.

\[
\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2 \quad \text{.................................. (4.2)}
\]

This is apparent in the product distribution of the product stream in which the amount of methane in the product stream is significantly lower than that in the feed composition. It is evident that a higher amount of steam would be required in the PBTR to attain a similar performance to that achieved in the membrane reactor.

The overall performance of the membrane reactor with various steam/CO ratios is therefore better than that of the PBTR using the 3Ni5Cu/CeZrCa catalyst. This indicates that the efficiency of the WGSR can be improved by the incorporation of a membrane reactor along with a highly active and stable catalyst, such as the one developed in this study while utilizing a low steam/CO ratio of 2.7, thereby saving the
amount of steam which would otherwise be required in a conventional reactor to attain the same performance.
Figure (4.27) Effect of steam/CO on WGSR performance in membrane reactor using reformate gas and 3Ni5Cu/CeZrCa catalyst at 500°C at 200psi
4.7 RESULTS OF KINETIC EXPERIMENTS

The reaction kinetics for the WGSR using reformate gas over 3Ni5Cu/CeZrCa was studied in three different systems; (i) Membrane Reactor at 200 psi (13.6 atm), (ii) High Pressure Packed Bed Reactor at 200 psi (13.6 atm), and (iii) Packed Bed Reactor at atmospheric pressure. The catalyst particle size used for all the reactors was 0.8mm. Two parameters were varied, namely, (i) feed flow rate and (ii) reaction temperature. This was achieved by changing the flow rate between 161 – 389 sccm using a constant catalyst weight of 0.5 g and water flow rate between 0.16 – 0.37 ml/min to maintain a H₂O/CO ratio of 2.7 at reaction temperatures of 400, 450 and 500°C (673, 723, 773K). This resulted in a variation of W/Fₐ₀ (catalyst weight time) between 1.1 and 2.67 g-cat.hr/mol representing the residence time for the reaction. All the operating conditions used were to ensure that mass transfer and heat transfer limitations that could affect the kinetic data were eliminated. The following section describes the criteria used to investigate the absence of heat and mass transfer limitations.

4.7.1 INVESTIGATION OF HEAT AND MASS TRANSFER LIMITATIONS

In the kinetic study of any reaction, data collection can only be considered intrinsic in the absence of heat and mass transfer resistance. In this section, the interparticle and intraparticle mass and heat transfer resistances and the effects on the rate of the reaction will be investigated at 773K; the highest temperature used for the kinetic studies.

4.7.1.1 Heat Transport Effects

According to the Prater analysis, the internal pore heat transfer resistance is given by:

\[ \Delta T_{\text{max}} = \frac{D_{\text{eff}} (C_{\text{As}} - C_{\text{Ac}}) \Delta H_{\text{rxn}}}{\lambda_{\text{eff}}} \]  (4.3)
Were; \( \Delta T_{\text{max}} \) = upper limit to the temperature difference between the pellet centre and surface (K)

\[
D_{\text{eff}} = \frac{D_{AB} \varepsilon_p}{\tau} \quad \text{effective diffusivity, m}^2/\text{s}
\]

\( D_{AB} \) = bulk diffusivity of component A (CO) in B (oxygen), m\(^2\)/s

\( \varepsilon = \) void fraction, dimensionless

\( \tau = \) tortuosity factor, dimensionless

\( C_{AS} = \) Concentration at pellet surface, mol/dm\(^3\)

\( C_{AC} = \) Concentration at pellet centre, mol/dm\(^3\)

\( \Delta H_R = \) Heat of reaction, KJ/mol

\( \lambda_{\text{eff}} = \) Effective thermal Conductivity, KJ/m.s.K

The value of \( D_{AB} \) was found to be \( 1.16 \times 10^{-4} \) m\(^2\)/s at a temperature of 773K using the Brokaw equation. The effective diffusivity \( D_{\text{eff}} \) obtained was \( 1.01 \times 10^{-5} \) m\(^2\)/s. The void fraction, \( \varepsilon \) estimated as the ratio of volume occupied by voids to the total bed volume was 0.5 calculated using the equation

\[
\varepsilon_p = 0.38 + 0.073 \left[ 1 + \frac{(d/dp - 2)^2}{(d/dp)^2} \right]
\]

(Beankoplis, 2003) were \( d \) and \( d_p \) are the internal reactor diameter and particle diameter respectively. The tortuosity factor was taken as 8 (Kumar and Idem, 2007). The effective thermal conductivity \( \lambda_{\text{eff}} \) was obtained from

\[
\lambda_{\text{eff}}/\lambda = 5.5 + 0.05N_{\text{Re}}
\]

(Walas, 1990). A value of \( 5.47 \times 10^{-5} \) kW/m/K for \( \lambda \) which is the thermal conductivity was gotten from the Wassiljewa correlation (Perry and Green 1997). The effective thermal conductivity \( \lambda_{\text{eff}} \) calculated was \( 8.096 \times 10^{-4} \) kW/m/K. Substituting these values in equation 4.3 resulted in a value of 0.1K for \( \Delta T_{\text{max}} \) which shows the uniform temperature in a catalyst pellet.
To determine the heat transfer limitation across the gas film, the following correlation adopted from Kumar and Idem (2007) was employed;

$$\Delta T_{\text{film,max}} = \frac{L_c (-r_{A,\text{obs}}) \Delta H_{\text{rxn}}}{h}$$ ................................. (4.4)

Where,

$\Delta T_{\text{film,max}}$ is the upper limit of temperature difference between the gas bulk and the pellet surface,

$L_c$ is the characteristic length,

$r_{A,\text{obs}}$ is the observed rate of reaction,

$h$ is the heat transfer coefficient (estimated from the correlation $J_H = J_D = \left( \frac{h}{\varepsilon_p \rho u} \right) N_{\text{Pr}}^{2/3}$, where $J_H$ is the heat transfer J factor, $N_{\text{Pr}} = \frac{C_p \mu}{\lambda}$, $\lambda$ is the molecular thermal conductivity, $C_p$ is the heat capacity). $J_D$ factors is given by the following correlations: $J_D = \left( \frac{0.4548}{\varepsilon_p} \right) N_{\text{Re}}^{-0.4069}$ (Geankoplis, 2003); $N_{\text{Re}} = \frac{d \rho \mu u}{\mu (1-\varepsilon_p)}$. $k_c$ is the mass transfer coefficient obtained to be 0.183m/s. The heat transfer coefficient, $h$ obtained was 0.106 kJ/m$^2$.s.K and a value of 5.3K resulted for $\Delta T_{\text{film,max}}$.

Furthermore, a more rigorous criterion developed by Mears (1971) for determining heat transport limitation during reaction was employed to further confirm the negligible resistance offered by heat transfer on the rate of the reaction.

$$\frac{r_{A,\text{obs}}^f \beta R_c E \Delta H_{\text{rxn}}}{hT^2R} < 0.15$$ ................................. (4.5)
Upon substituting the required terms on the left hand side of the equation, a value of 0.8 x 10^{-4} was obtained which is far less than 0.15. Therefore, based on this result, the interparticle heat transfer resistance is considered to be absent. A detailed computation is given in Appendix D.

4.7.1.2 Mass Transport Effects

The Weisz Prater criterion was used to determine the internal pore mass transfer resistance as follows;

\[ C_{wp, ipd} = \frac{-r'_{A, obs} \rho_c R_c^2}{D_{eff} C_{As}} \]  \hspace{1cm} (4.6)

Where, \( C_{wp, ipd} \) is the Weisz–Prater criterion for internal pore diffusion, \( \rho_c \) the pellet density, \( R_c \) catalyst radius. The \( C_{wp, ipd} \) value estimated was 0.982 which is slightly less than 1 indicating the potential for mass transfer limitation within the catalyst pores. However to further prove that the mass transfer limitation has no significant effect on the rate of reaction, the following ratio was employed:

\[ \frac{\text{Observed rate}}{\text{rate if film resistance controls}} = \frac{-r'_{A, obs}}{c_A b_k c} \frac{d_p}{6} \]  \hspace{1cm} (4.7)

This ratio obtained was 4.7 x 10^{-2} indicating that the observed rate is far less than the rate if external resistance was controlling. Thus the resistance to external mass transfer does not affect the reaction rate. A more rigorous criterion developed by Mears was also applied to determine the onset of film mass transfer limitation.

\[ \frac{r'_{A, obs} \rho_b R_c c_n}{k_c c_A} < 0.15; \] \hspace{1cm} (4.8)
The value obtained from the LHS was 0.08 which is far less than 0.15 implying that there was no mass limitation in the film.

### 4.7.2 KINETIC RATE MODEL

#### 4.7.2.1 Power Law Model

The power law model is a simple empirical rate expression that does not consider any particular reaction mechanism and has been widely applied in kinetic studies. The overall reaction used for the development of the kinetic model for water gas shift reaction is given as;

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2; \quad \text{------------------------------------------ (1.6)}
\]

\[
\Delta H^\circ_{\text{rxn}} = -41 \ \text{kJ/mol}^2.
\]

An empirical, reversible power law rate model can be written as:

\[
\frac{\text{d}A}{\text{d}t} = A \varepsilon t \cdot N_A^m N_B^n N_C^o N_D^p (1-\beta) \quad \text{------------------------------------------ (4.9)}
\]

\[
\beta = \frac{1}{K_{eq}} \times \frac{N_{\text{CO}_2} N_{\text{H}_2}}{N_{\text{CO}} N_{\text{H}_2\text{O}}} \quad \text{------------------------------------------ (4.10)}
\]

\[
\ln K_{eq} = \left( \frac{4577.8}{T} \right) - 4.33 \quad \text{------------------------------------------ (4.11)}
\]

Here, \( A = \text{CO}; \ B = \text{H}_2\text{O}; \ C = \text{H}_2; \ D = \text{CO}_2; \)

\( r_A \) = rate of reaction with respect to CO, mol/g-cat.hr

\( A \) = pre exponential factor
E = activation energy, kJ/mol
T = reaction temperature, K
R = molar gas constant, 8.314 J/mol/K
N_i = molar flow rate of A, B, C, D, mol/hr
m = order of reaction with respect to A
n = order of reaction with respect to B
o = order of reaction with respect to C
p = order of reaction with respect to D
β = degree of reversibility of reaction
K_{eq} = reaction equilibrium constant

However in this study, the ratio of H2 to CO2 was not varied and the ratio of H2O/CO was constant at 2.7. Consequently, it was necessary to drop the ‘b, c, d’ terms because the species for which they are exponents are not linearly independent thereby leaving the power law expression as follows:

\[ r_A' = k \cdot N_A^m \] (4.12)

Were k = Ae^{(-E/RT)} is the reaction rate constant.

4.7.2.2 Experimental Rates of Reaction

The results of each set of operating conditions are presented in Figure 4.28. From the results, it can be seen that in all three systems, increasing the W/F_{A0} generally results in an increase of CO conversion. However, the increase in conversion tends to slow
down beyond 1.6 g-cat.hr/mol, because of thermodynamic limits imposed on the reaction under the prevailing conditions.

It is also evident that increasing the temperature at a particular W/F\textsubscript{A0} results in an increase in CO conversion; however, the degree of increase in CO conversion between 450 – 500°C is higher than that between 400-450°C. At 450°C, the increase in conversion with respect to catalyst weight time is slower than at other temperatures. This observation is further revealed in the reaction rates represented in Table 4.4. More importantly, the results in Figure 4.28 show that the CO conversions obtained from the membrane reactor are higher than those of the packed bed reactor operating at high pressure and atmospheric pressure.
Figure 4.28 Conversion versus W/F_{A0} for all three systems using reformate gas and 0.5g of 3Ni5Cu/CeZrCa catalyst
To find out the rate of the water gas shift reaction experimentally by integral (plug flow) reactor, the differential method of analysis was used. Details of this method of analysis can be found in Levenspiel (1999), in chapters 3 and 18. For integral (plug flow) reactor, differential analysis gave us the following equation:

\[-r_A' = \frac{dx_{CO}}{d(W/F_{A,0})}; \text{---------------------------------------- (4.13)}\]

From equation 4.13, we can see that the slope of \(X_{CO}\) vs. \(W/F_{A,0}\) will give us the experimental reaction rate (mol/g\(_\text{cat}\)·hr) at a \(W/F_{A,0}\). The \(X_{CO}\) vs. \(W/F_{A,0}\) graphs were drawn for all the temperatures and reactor systems resulting in Figure 4.28. Now, the experimental rates of the reaction were obtained from Figure 4.20 as the derivatives of the CO conversion vs. \(W/F_{A,0}\) curves after fitting with MATLAB. Here, \(N_A, N_B, N_C,\) and \(N_D\) were calculated using the following equations:

\[N_A = N_{A,0} - X_AN_{A,0}; \text{---------------------------------------- (4.14)}\]
\[N_B = N_{B,0} - (X_AN_{A,0}); \text{---------------------------------------- (4.15)}\]
\[N_C = N_{C,0} + (X_AN_{A,0}); \text{---------------------------------------- (4.16)}\]
\[N_D = N_{D,0} + (X_AN_{A,0}); \text{---------------------------------------- (4.17)}\]

Where, \(N_{A,0} = \) initial molar flow rate of CO (A), mol/hr; \(N_{B,0} = \) initial molar flow rate of \(H_2O(B), \) kmol/s; \(X_A = \) CO conversion, from experimental data. The partial pressures \(P_A\) in Table 4.4 were calculated using the mole fractions of each component and the total pressure as follows:

\[p_i = y_i \times P_T \text{---------------------------------------- (4.18)}\]
Where $y_i$ = mole fraction of component $i$ and $P_T$ is the total pressure.

The partial pressure of CO was computed in order to evaluate the relationship between reaction rate and partial pressure at atmospheric pressure and high operating pressure of 200psi (13.6atm). The results of this correlation are given in Figure 4.29.
Table 4.4: Experimental kinetic data

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**Membrane Reactor**

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4.7.2.3 Effect of Pressure on Reaction Rate

The kinetic studies were carried out at different total pressures; atmospheric pressure and high pressure of 200 psi (1379kPa) in a packed bed tubular reactor and a membrane reactor. The rates determined from the conversion versus W/F<sub>A0</sub> graphs are represented as a function of CO partial pressures at a constant temperature of 500°C and are given in Figure 4.29.

It is clear that the increasing partial pressure of CO in any particular reaction system causes a corresponding increase in the reaction rate, although at high total pressure as in the membrane reactor and PBTR-HP, the increase in rate slows down between 170 – 180 kPa (1.7 – 1.8atm), whereas at low atmospheric pressure, the rate of reaction continues to increase linearly with partial pressure. This observation corresponds to studies by Atwood et al. (1950) and Chinchen et al. (1984).
Figure 4.29 Rate-Pressure relationships of all three systems
4.7.2.4 Estimation of Parameters of Rate Model

The power law model parameters were estimated using a multi-nonlinear regression software (NLREG), which is based on the minimization of the sum of residual squares of the reaction rates according to Gauss-Newton and Levenberg-Marquardt algorithm. The values obtained for the parameters are presented in Table 4.5. To validate the models, the percentage average absolute deviation (AAD%) between the predicted rate from the power law model and experimentally obtained rate was determined.

The AAD is calculated as follows:

$$\text{AAD\%} = \left( \frac{|\text{Experimental rate} - \text{Predicted rate}|}{\text{Experimental rate}} \right) \times 100\%; \quad \text{-----------------} \quad (4.19)$$

A parity plot as shown in Figure 4.30 is also used to depict how well the power law model fits the data.

From the parity plot, the rates determined using the power law model matches the experimentally determined rate. Thus, the final power law rate expressions for the three systems are given as follows:

For the membrane reactor; $r_A' = 3.66 \times 10^6 e^{-\left(\frac{99950}{RT}\right)} N_A^{0.23}$

For the high pressure packed bed tubular reactor; $r_A' = 1.17 \times 10^{19} e^{-\left(\frac{190300}{RT}\right)} N_A^{1.78}$
Table 4.5: Estimation of the values of the parameters of the models

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Figure 4.30 Parity plot for the reaction rates of all three systems
For the atmospheric pressure packed bed tubular reactor;

\[ r_A' = 1.79 \times 10^{13} e^{(-\frac{136900}{RT})}N_A^{1.27} \]

The results show an increase with activation energy from 137.2kJ/mol to 190.3kJ/mol when the operating pressure is increased from atmospheric to high pressure of 200 psi (13.6 atm) and a corresponding increase in the pre-exponential factor. This is probably because with higher partial pressures of CO in the feed mixture, more energy is required to initiate the WGSR. Moreover, at similar high pressure of 200 psi (13.6 atm), the activation energy required for the membrane reactor is 99.95kJ/mol which is lower than the packed bed reactor; this re-emphasizes the benefits of using a membrane reactor. The rate constants based on the evaluated parameters are also given in Table 4.5 and in a similar fashion; the rate constant increases with pressure but is lowest in the membrane reactor. This shows the resistance posed by the system and reveals that such resistance is lowest in the membrane reactor. The order of the reaction with respect to CO varies amongst the different systems with the membrane system giving the lowest order of 0.23 and the high pressure PBTR system having the highest order of 1.78 showing a stronger dependence of the reaction rate on the concentration of CO. The reaction order for the atmospheric PBTR is 1.27 which is similar to other studies in literature which show a first order dependence of WGSR reaction rate on CO. The activation energies obtained is observed to be in agreement with some studies in literature. Mars (1961) reported activation energy of 134kJ/mol operating at atmospheric pressure, Chinchen et al. (1984) reported 129.4kJ/mol, Bustamante et al. (2005) obtained 288.3kJ/mol and Hla et al. (2009) reported 111kJ/mol.
Other studies have reported lower activation energies; for instance, Lei et al. (2005) reported 60 kJ/mol and Koryabkina et al. (2003) obtained 79 kJ/mol. The low activation energies obtained from such studies could either be as a result of the low concentrations or pure CO employed as the reactant without considering the presence of other components in the feed material such as CH₄, CO₂ and H₂ which give a typical composition of a real reformate gas. According to Chinchen et al. (1984), another reason for the low activation energies reported in the literature for the WGSR is due to the inadequacy of pore diffusion. Few studies, however, have considered the effect of these components, particularly for reformate from coal gasification (Abdollahi et al., 2011; Hla et al., 2011). To the best of our knowledge, detailed kinetic studies on WGSR have not been performed on reformate gas from biogas dry reforming in different systems including a membrane reactor and on the 3Ni5Cu/CeZrCa catalyst, thus making this work the first of its kind.
CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

A group of ceria based ternary oxide catalysts having a formulation of 3Ni-5Cu/CeZrM (M=La,Y, Gd, Ca, Mg) were developed and screened for the high temperature water gas shift reaction using H₂O/CO ratio of 2.7 at 500°C. Amongst the tested catalysts, 3Ni5Cu/CeZrCa showed the best performance giving a CO conversion of 58% and H₂ yield and selectivity of 60% and 90% respectively; thus was selected for further parametric studies. Amongst the parameters studied were: impregnation method (vacuum and atmospheric), calcination temperature (425 – 650°C) and surfactant/metal ratio (0 – 1.25) to optimise the catalyst preparation method; also, reaction temperature (450 – 550°C), steam/CO ratio (1.7 – 3.7), feed composition (pure CO/N₂ and reformate) and pressure (atmospheric – 250psi) were varied to evaluate optimum operating conditions.

The catalysts impregnated under vacuum conditions yielded better results than those impregnated under normal atmospheric condition. In addition, catalysts calcined at 500°C showed better performance than catalysts calcined at other temperatures. An optimum surfactant/metal ratio of 0.5 was determined which gave similar performance to catalysts prepared with a ratio of 1.25, thus minimizing the quantity and cost of surfactant used in catalyst preparation. An optimum reaction temperature of 500°C was obtained revealing the kinetic and thermodynamic limitations of operating at a lower temperature of 450°C and a higher range of 550°C. Increasing the steam/CO ratio from
1.7 to 2.7 resulted in a drastic increase in CO conversion from 33% to 48% but further increase of the steam/CO ratio had negligible change in the CO conversion. For reformate gas having a composition of 46.2% CO, 8.5% CH₄, 7.2% CO₂ and 38.1% H₂ which is typical for reformate from biogas dry reforming the results showed the superior performance of the ternary oxide catalyst over its binary oxide counterpart, as no deactivation was observed in the ternary catalyst. For comparative studies to the membrane reactor, the total pressure in a packed bed tubular reactor was varied, it was found that increasing the reaction pressure resulted in a fourfold increase in the CO conversion from 7% to 28% up to a pressure of 200 psi (13.6 atm); beyond which additional pressure increase yielded no substantial change in conversion. Extended TOS stability test carried out on the 3Ni5Cu/CeZrCa catalyst for duration of 12 hours revealed a highly stable catalyst with no evidence of deactivation. Analysis of Variance (ANOVA) and two level factorial design of experiment (DOE) analysis of the parametric study revealed that the reaction temperature, gas composition and steam ratio were the major operating conditions affecting the CO conversion.

In order to evaluate the performance of the catalysts based on their physicochemical structure, several characterization techniques were employed ranging from X-Ray Diffraction (XRD), N₂ Physisorption, H₂ Chemisorption, Temperature Programmed Reduction (TPR) and Oxidation (TPO), ICP-MS. The results of these characterizations were then related to the activity observed in the catalysts through Structure Activity Relationships (SAR). The results revealed that a homogeneously dispersed catalyst having high pore volume/surface area, metal dispersion, reducibility and basicity in addition to low carbon propensity factor gives high performance as in the
case of the Ca catalyst. From the statistical analysis performed, the pareto chart resulting from the two level factorial design of experiment analysis reveals that the reducibility, basicity and dispersion are the major contributing factors in the catalyst activity.

In order to evaluate the potential to minimize the number of process units utilized in an industrial hydrogen production process, a membrane reactor was incorporated into the current study. Membrane characterization was performed to evaluate the selectivity of the membrane to H₂ and then derive a correlation between the amount of H₂ permeated and temperature as well as partial pressure. The results showed an increase in H₂ recovery and flux with increasing partial pressure from 100psi to 300 psi (6.8 – 20.4 atm) and temperature ranging from 300°C to 500°C. The studies also resulted in H₂ permeation activation energy of 4.4kJ/mol. Furthermore, the membrane reactor was then applied to the water gas shift reaction using the 3Ni5Cu/CeZrCa catalyst on reformate gas at 500°C varying the pressure between 150 – 250 psi (10.2 – 17 atm). An increase in CO conversion was observed with increasing pressure from 150 psi (10.2 atm) to 200 psi (13.6 atm), however upon increasing the pressure beyond 200 psi (13.6 atm), there was no significant increase in performance. An optimum pressure of 200 psi (13.6 atm) was therefore selected for use in parametric and kinetic studies. Meanwhile, upon comparing the performance of the membrane reactor to the packed bed tubular reactor operating at high pressure and atmospheric conditions, a superior performance was revealed in the membrane reactor.

Parametric studies were also performed on the membrane reactor varying the catalyst weight between 0.25 – 1.0 g, flow rate between 161 – 275 sccm and steam/CO ratio of 1.7 – 3.7. It was observed that increasing the catalyst weight resulted in an
increase in CO conversion up to 0.5 g, beyond which no significant change was observed, while reducing the flow rate resulted in an increase in the amount of hydrogen recovered while slightly improving the CO conversion. Varying the steam/CO ratio gave similar results to the packed bed tubular reactor.

Finally, the kinetics of the water gas shift reaction using reformate gas was studied in a packed bed reactor at atmospheric and high pressure as well as in a membrane reactor. Activation energies of 137.2kJ/mol, 190.3kJ/mol and 99.8kJ/mol were obtained from the power law model with acceptable AAD% and parity plot. To the best of our knowledge, the current study is the first of its kind on water gas shift reaction for reformate gas from biogas dry reforming on 3Ni5Cu/CeZrCa catalyst.

5.2 RECOMMENDATIONS

The following recommendations for future research can be made based on the scope of the current work;

- The reaction mechanism should be determined using a mechanistic approach either based on Langmuir Hinshelwood-Hougen Watson or Eley-Rideal formulations.
- The ratio of H₂/CO₂ and H₂O/CO should be varied in the kinetic experiments to determine the rate dependence on concentration of CO₂, H₂ and H₂O.
- Reactor modelling and simulation studies using software like COMSOL, should be performed for suitable reactor design.
• The catalyst developed in this work should be tested in the feed flexible hydrogen production pilot plant for further demonstration of its performance.

• The pure hydrogen produced from the membrane reactor should be tested on a fuel cell to determine the energy efficiency of the process.
REFERENCES


50. Hua, N., Haitao, W., Yukou, D., Ming, S., Ping, Y. (2005) Ultrafine Ru and C-Fe₂O₃ Particles Supported on MgAl₂O₄ spinel For Water-Gas Shift Reaction. Catal. comm. (6) 491–496.


APPENDICES

APPENDIX A: Representative GC Datasheets for experiment

Membrane Characterization result showing pure hydrogen permeate.
Result of WGSR on 30%CO/balance N₂ gas using 3Ni5Cu/CeZrCa catalyst at 500°C reaction temperature.
Reformate gas composition before start of reaction in membrane reactor at 200psi.
Results of product composition after performing WGSR in PBTR at atmospheric pressure.
Results of product composition after performing WGSR in PBTR at high pressure.
Results of product composition after performing WGSR in membrane reactor at atmospheric pressure.

| Results of product composition after performing WGSR in membrane reactor at atmospheric pressure. | }
APPENDIX B: Results for SAR statistical analysis using Minitab

General Linear Model: Conversion versus S/M, Tcalc, ...

<table>
<thead>
<tr>
<th>Factor</th>
<th>Type</th>
<th>Levels</th>
<th>Values</th>
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</thead>
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<td>0.00, 0.50, 1.25</td>
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<tr>
<td>Tcalc</td>
<td>fixed</td>
<td>3</td>
<td>500, 575, 650</td>
</tr>
<tr>
<td>Trxn</td>
<td>fixed</td>
<td>3</td>
<td>450, 500, 550</td>
</tr>
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<td>S/CO</td>
<td>fixed</td>
<td>3</td>
<td>1.7, 2.7, 3.7</td>
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<tr>
<td>Prxn</td>
<td>fixed</td>
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<tr>
<td>M</td>
<td>fixed</td>
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<td>Ca, Gd, Mg</td>
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<tr>
<td>Gas comp</td>
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<td>pure CO, reformate</td>
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Analysis of Variance for Conversion, using Adjusted SS for Tests

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<th>Adj MS</th>
<th>F</th>
<th>P</th>
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<td>57.20</td>
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<td>729.00</td>
<td>364.50</td>
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S = 0.366515 R-Sq = 99.99% R-Sq(adj) = 99.96%

Nested ANOVA: conversion, reducibility, PV, Dispersion, basicity

Nested ANOVA: conversion versus Promoter

Analysis of Variance for conversion

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<tr>
<th>Source</th>
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<td>594.7341</td>
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Variance Components

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<th>% of Total</th>
<th>StDev</th>
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</thead>
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<td>12.194</td>
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Expected Mean Squares

1  Promoter  1.00(1)

Nested ANOVA: reducibility versus Promoter

Analysis of Variance for reducibility

<table>
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<tr>
<th>Source</th>
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<th>MS</th>
<th>F</th>
<th>P</th>
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<tr>
<td>Total</td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Variance Components

Source | Var Comp. | % of Total | StDev
---|---|---|---
Promoter | 0.142 | 100.00 | 0.377
Total | 0.142 | | 0.377

Expected Mean Squares

1 Promoter 1.00(1)

**Nested ANOVA: PV versus Promoter**

Analysis of Variance for PV

Source | DF | SS | MS | F | P
---|---|---|---|---|---
Promoter | 4 | 1.1049 | 0.2762 | | |
Total | 4 | 1.1049 | | | |

Variance Components

Source | Var Comp. | % of Total | StDev
---|---|---|---
Promoter | 0.276 | 100.00 | 0.526
Total | 0.276 | | 0.526

Expected Mean Squares

1 Promoter 1.00(1)

**Nested ANOVA: Dispersion versus Promoter**

Analysis of Variance for Dispersion

Source | DF | SS | MS | F | P
---|---|---|---|---|---
Promoter | 4 | 0.5080 | 0.1270 | | |
Total | 4 | 0.5080 | | | |

Variance Components

Source | Var Comp. | % of Total | StDev
---|---|---|---
Promoter | 0.127 | 100.00 | 0.356
Total | 0.127 | | 0.356

Expected Mean Squares

1 Promoter 1.00(1)

**Nested ANOVA: basicity versus Promoter**

Analysis of Variance for basicity

Source | DF | SS | MS | F | P
---|---|---|---|---|---
Promoter | | | | | |
Promoter  4  576.8000  144.2000
Total    4  576.8000

Variance Components

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<th>% of Total</th>
<th>StDev</th>
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<tr>
<td>Total</td>
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<td>100.00</td>
<td>12.008</td>
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</table>

Expected Mean Squares

1  Promoter  1.00(1)
APPENDIX C: Non linear regression results for reaction kinetics using NLREG

— Final Results —

NLREG version 6.3
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atmospheric kinetics

Number of observations = 15
Maximum allowed number of iterations = 1000
Convergence tolerance factor = 1.000000E-003
Stopped due to: Relative function convergence.
Number of iterations performed = 190
Final sum of squared deviations = 7.7865663E-004
Final sum of deviations = -1.9561522E-002
Standard error of estimate = 0.0080531
Average deviation = 0.0060391
Maximum deviation for any observation = 0.01272
Proportion of variance explained (R^2) = 0.9380 (93.80%)
Adjusted coefficient of multiple determination (R_adj^2) = 0.9277 (92.77%)
Durbin-Watson test for autocorrelation = 1.558

Warning: Covariance matrix could not be computed because
the finite-difference Hessian was indefinite.

Analysis completed 25-Nov-2013 12:58. Runtime = 0.09 seconds.

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<td>723</td>
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<td></td>
</tr>
<tr>
<td>rate</td>
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<td>0.094367</td>
<td>0.02241494</td>
<td>0.02994949</td>
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<tr>
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<td>8.2963E-005</td>
<td>4.830542E-005</td>
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</table>

<table>
<thead>
<tr>
<th>Parameter</th>
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<th>Standard error</th>
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<th>Prob(t)</th>
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<tbody>
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<td>k0</td>
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<td>0.00000</td>
<td>1.0E+030</td>
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</tr>
<tr>
<td>E</td>
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<td>1.0E+030</td>
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<td>a</td>
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<td>1.0E+030</td>
<td>0.00000</td>
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— Final Results —

NLREG version 6.3
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HP kinetics

Number of observations = 15
Maximum allowed number of iterations = 1000
Convergence tolerance factor = 1.000000E-006
Stopped due to: Relative function convergence.
Number of iterations performed = 244
Final sum of squared deviations = 1.6809092E-003
Final sum of deviations = 1.0488370E-002
Standard error of estimate = 0.0110354
Average deviation = 0.00831815
Maximum deviation for any observation = 0.0272256
Proportion of variance explained (R^2) = 0.8392 (83.92%)
Adjusted coefficient of multiple determination (Ra^2) = 0.8124 (81.24%)
Durbin-Watson test for autocorrelation = 1.333

Note: Parameter t-statistics and confidence intervals were not computed because constrain statements were used.
Analysis completed 25-Nov-2013 13:09. Runtime = 0.05 seconds.

— Descriptive Statistics for Variables —

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— Calculated Parameter Values —

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— Analysis of Variance —
— Final Results —

NLREG version 6.3
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MR kinetics

Number of observations = 15
Maximum allowed number of iterations = 1000
Convergence tolerance factor = 1.000000E-003
Stopped due to: Relative function convergence.
Number of iterations performed = 105
Final sum of squared deviations = 3.5855255E-003
Final sum of deviations = 3.1238036E-002
Standard error of estimate = 0.0172857
Average deviation = 0.0119202
Maximum deviation for any observation = 0.0386642
Proportion of variance explained \( R^2 \) = 0.8126 [81.26%]
Adjusted coefficient of multiple determination \( R_{\text{adj}}^2 \) = 0.7814 [78.14%]
Durbin-Watson test for autocorrelation = 0.963
Warning: Covariance matrix could not be computed because
the finite-difference Hessian was indefinite.
Analysis completed 25-Nov-2013 13:04. Runtime = 0.04 seconds.

— Descriptive Statistics for Variables —

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<th>Standard dev.</th>
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<tbody>
<tr>
<td>T</td>
<td>673</td>
<td>773</td>
<td>723</td>
<td>42.25771</td>
</tr>
<tr>
<td>rate</td>
<td>0.002979637</td>
<td>0.1012132</td>
<td>0.0390408</td>
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— Calculated Parameter Values —

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<td></td>
</tr>
</tbody>
</table>
APPENDIX D: Heat & Mass transfer Resistance determination

Heat Transport Effects

Prater analysis:

\[ \Delta T_{\text{max,particle}} = \frac{D_{\text{eff}}(C_{A_i} - C_{A_e})(\Delta H_f)}{\lambda_{\text{eff}}} . \]

\[ D_{\text{eff}} = \text{effective diffusivity}, \, m^2/s = D_{AB} \frac{\varepsilon}{\tau} \]

\[ D_{AB} = \frac{0.001558T^{3/2}M_{AB}^{1/2}}{P\sigma_{AB}^2\Omega_D} \quad \text{.........(D1)} \]

Where; \( T \) is the temperature of study = 773K

\( M_{AB} \) = the average molecular weight of the gas mixture

\( M_{AB} = \sum x_i M_i \) \quad (D2) (Geankoplis, 2003)

\( M_A \) = molecular weight of component A, CO = 28g/mol

\( M_B \) = molecular weight of component B, water = 18g/mol

\( X_i \) = mol fraction

\( P \) = total pressure

\( \sigma_{AB} \) = characteristic length or average collision diameter, \( \text{A}^o \)

\( \sigma_{AB} = (\sigma_A + \sigma_B)/2 \) \quad (D3)

\( \Omega_D \) = Diffusion collision integral, dimensionless

\( \Omega_D = (44.54T^{-e^{-0.309}} + 1.9111T^{-1.579})^{0.10} \) \quad (D4)

\( T^* \) is given by \( kT/\varepsilon_{AB} \) \quad (D5)

\( \varepsilon_{AB} = (\varepsilon_A \varepsilon_B)^{1/2} \) \quad (D6)

\( \varepsilon_i/k = 0.75 \, T_c \) \quad (D7)
$\varepsilon_i$ is the characteristic Lennard Jones energy,

$k = \text{Boltzmann constant}, \ T_c = \text{the critical temperature}$

$$\sigma_i = 0.841V_c^{1/3}, \quad (D8)$$

$V_c$ is the specific volume at critical temperature

Let $A$ be CO and $B$ is Water

From Chemsep version 6.90 pure component database (2012);

$T_c (\text{CO}) = 133K \quad T_c (\text{Water}) = 647K$

$V_c (\text{CO}) = 93.1 \text{cm}^3/\text{mol} \quad V_c (\text{Water}) = 55.9 \text{ cm}^3/\text{mol}$

$M_A (\text{CO}) = 28 \text{ kg/kmol} \quad M_A (\text{Water}) = 18 \text{kg/kmol}$

From equation (D7);

$$\varepsilon_A/k = 99.7K$$

$$\varepsilon_B/k = 485.3K$$

Replace in equation (D6)

$$\varepsilon_{AB} = 3.036 \times 10^{-21}$$

Substitute in equation (D5)

$$T^* = 3.5$$

Substitute in equation (D4)

$$\Omega_D = (44.54 \ (3.5)^{-4.909} + 1.911 \ (3.5)^{-1.575})^{0.10} = 0.9$$

From equation (D3);

$$\sigma_B = 0.841(55.9 \times 10^{-3})^{1/3} = 3.22 \AA^o$$

$$\sigma_A = 0.841(93.1 \times 10^{-3})^{1/3} = 3.81 \AA^o$$
Substitute in equation (D3);

\[ \sigma_{AB} = 3.517A^0 \]

From equation (D2);

2.7 mol of H\textsubscript{2}O is fed with 1 mol of CO, therefore mol fraction x\textsubscript{CO}=0.27, x\textsubscript{H\textsubscript{2}O}=0.73

\[ M_{AB} = 20.7 \text{ g/mol} \]

Substitute in equation (D1);

\[ D_{AB} = \frac{0.001858(773)^{3/2}(20.7)^{7/2}}{(1.01 \times 10^5) \times (3.517)^2 \times 0.9} = 1.61 \times 10^{-4} \text{ m}^2/\text{s} \]

According to Geankoplis, void fraction \( \varepsilon = 0.38 + 0.073 \left[ 1 + \frac{(d - 2d_p)^2}{(d_p^2)} \right] \) (D9)

From this work, \( d/d_p \) of 15.9 was used according to Froment, Bischoff and Rase criteria for \( d/d_p \geq 10 \), thus from equation (11) this yields a void fraction \( \varepsilon = 0.5 \). Tortuosity factor, \( \tau \) is taken as 8 (Fogler, 1999).

Thus \( D_{eff} = \frac{0.5(1.61 \times 10^{-4})}{8} = 1.01 \times 10^{-5} \text{ m}^2/\text{s} \)

To compute effective thermal conductivity, \( \lambda_{eff} \), the correlation according to Walas, 1990 is as follows:

\[ \frac{\lambda_{eff}}{\lambda} = 5.5 + 0.05N_{Re} \] (D10)

\[ N_{Re} = \frac{\rho_f v d_p}{\mu (1-\varepsilon)} \] (D11)

Were \( \rho_f \) is density of fluid mixture, kg/m\textsuperscript{3}

\( v \) is average fluid velocity for the mixture, m/s

\( d_p \) is the particle size = 0.8 mm

\( \mu \) is the fluid viscosity for the mixture, Pa.s
From Felder and Rousseau (1986), density of a mixture is given by

\[ \frac{1}{\rho_{\text{mix}}} = \sum_{i=1}^{n} \frac{w_i}{\rho_i} \]  \hspace{1cm} (D12) were w_i = mass fraction of component i

From Buddenberg & Wilke (F.J. Krieger, 1951), viscosity of mixture is given by

\[ \mu_{\text{mix}} = \sum_{i=1}^{n} \frac{\mu_i}{1 + \frac{113.6M_iT}{x_i[M_i]} \sum_{j=1,j\neq i}^{n} x_j} \]  \hspace{1cm} (D13) D_{ij} = diffusion coefficient

\( x_j \) is mole fraction of water, \( x_i \) is mole fraction of CO

If \( i = \text{CO} \) and \( j = \text{water} \),

From Chemsep database for pure compounds,

\[ \rho_{\text{CO}} = 1.165 \text{kg/m}^3 \]
\[ \rho_{\text{H2O}} = 0.804 \text{kg/m}^3 \]

Inserting the above values in equation (D12) therefore yields:

\[ \rho_{\text{mix}} = 0.91 \text{kg/m}^3 \]

Also, from Chemsep database for pure compounds, vapour viscosity was obtained as follows;

\[ \mu_{\text{CO}}(273K) = 23.5 \times 10^{-5} \text{Pa.s} \]
\[ \mu_{\text{H2O}} = 2.8 \times 10^{-5} \text{Pa.s} \]
\[ \mu_{\text{mix}} = 1.08 \times 10^{-7} \text{Pa.s} \]

To calculate for fluid velocity for gas mixture, the following correlation was used (Cussler, 1985);

\[ V_{\text{avg}} = y_1v_1 + y_2v_2 \]  \hspace{1cm} (D14) were \( y_i \) is mole fraction, \( v_i \) is velocity of individual component

From the experimental data, velocity, \( v \), can be obtained from the volumetric flow rates (\( V^*_{i} \)) and area of the reactor (A) using the following equation:
\[ v = \frac{V^*}{A} \]  \hspace{1cm} (D15)

\[ V^*(CO) = 6.48 \times 10^{-6} \text{m}^3/\text{s} \]

\[ V^*(H_2O) = 6.17 \times 10^{-9} \text{m}^3/\text{s} \]

Reactor diameter, \( d = 12.7 \times 10^{-3} \text{m} \)

Cross sectional area, \( A = \pi d^2/4 = 1.267 \times 10^{-4} \text{m}^2 \)

Therefore from equation (D15), \( v(H_2O) = 4.87 \times 10^{-5} \text{m/s} \)

\( v (CO) = 5.11 \times 10^{-2} \text{m/s} \)

Thus from equation (D14), \( v_{\text{avg}} = 0.0138 \text{m/s} \)

\( N_{Re} \) from equation (D11) can then be computed as follows:

\[ N_{Re} = 186 \]

To compute for \( \lambda \) - thermal conductivity for gas mixtures at low pressure using Wassiljewa correlation (Perry, 1997):

\[
k_m = \sum_{i=1}^{n} \frac{y_i k_i}{\sum_{j=1}^{n} y_j A_{ij}}
\]  \hspace{1cm} (D16)

where \( k_m \) = mixture thermal conductivity, W/m K

\( n \) = number of components

\( y_{i,j} \) = mole fraction of component \( i \) or \( j \) in the vapor mixture

\( k_i \) = thermal conductivity of pure component \( i \) at the temperature of interest

The binary interaction parameter \( A_{ij} \) is obtained by the method of Lindsay and Bromley:

\[
A_{ij} = \frac{1}{4} \left\{ 1 + \left[ \frac{\mu_i}{\mu_j} \left( \frac{M_j}{M_i} \right)^{3/4} \left( \frac{T + S_i}{T + S_j} \right) \right]^{1/2} \left( \frac{T + S_i}{T + S_j} \right) \right\}^{3/2}
\]  \hspace{1cm} (D17)

\[ S_p = C(S_i S_j)^{1/2} \]

\[ S_{ij} = 1.5 T_{hi} \]  \hspace{1cm} (D18)
μ_{i,j} = vapor viscosity of pure component i or j at the temperature 
T of interest and low pressure, Pa·s

M_{i,j} = molecular weight of pure component i or j

T = temperature, K

C = 1.0

T_{bi,j} = normal boiling temperature of pure component i or j, K

The normal boiling point and thermal conductivity for each of the components were obtained from Chemsep v6.9 as follows;

k (CO) = 0.05W/m.K

k (H_2O) = 0.06W/m.K

T_b (CO) = 82K

T_b (H_2O) = 373K

Thus S_{CO} = 123

S_{H_2O} = 560

S_{ji} = 262.3

Substituting in equation (D17),

A_{12} = 0.534

A_{11} = A_{22} = 1

A_{21} = (0.534)^{-1} = 1.87

Insert in equation (D16) gives

k_m = \lambda=5.47 \times 10^{-5} KJ/m.s.K

Computing \lambda_{eff} with equation (D10)

\lambda_{eff} = 8.096 \times 10^{-4} KJ/m.s.K

To compute C_{AS} from experimental data, Run 15
\[ C_{AS} = \frac{N_{CO}}{V_{CO}} = \frac{1.08 \times 10^{-7}}{6.48 \times 10^{-6}} = 0.0167 \text{kmol/m}^3 \]

\( C_{AC} \) is assumed to be zero as suggested by Levenspiel, 1999

\[ \Delta H_{\text{rxn}} = -41 \text{kJ/mol} \]

Eventually \( \Delta T_{\max} = 0.1 \text{K} \)

To determine the **heat transfer limitation across the gas film**, the following correlation is used;

\[ \Delta T_{\text{max,film}} = \frac{L(-r_{A,\text{obs}})(\Delta H_{\text{rxn}})}{h} \]

\[ J_H = J_D = \left( \frac{h}{c_p v_p} \right) N_{Pr}^{2/3} \]

\[ J_D = (0.4548/c) N_{Re}^{-0.4069} \]

\[ J_D = \left( \frac{k_c}{v} \right) N_{Sc}^{2/3} \]

\[ N_{Pr} = C_p \mu / \lambda \]

\[ N_{Sc} = (\mu / \rho D_{AB}) \]

To compute for characteristic length, \( L = \) Hydraulic diameter = \( D \), were \( D = \) diameter of the reactor. Thus, \( L = 12.7 \text{mm} \) (diameter of reactor).

Also, to obtain \( r_{A,\text{obs}} \), I took run 15 as my base case at temperature of 773K and molar ratio of \( \text{H}_2\text{O}/\text{CO} = 2.7 \). Thus \( r_{A,\text{obs}} = 1.4 \times 10^{-2} \text{kmol/kgcat.s} \). Writing the rate in terms of \( \text{kmol/m}^3 \text{s} \) and taking a basis of 1s for the volume flow rate, \( r_{A,\text{obs}} = 1.08 \text{kmol/m}^3 \text{s} \)

\[ \Delta H_{\text{rxn}} = -41 \text{kJ/mol} \]

Computing for Schmidt number,

\[ N_{Sc} = 7.37 \times 10^{-4} \]
According to Massoud Kaviani (1995), to compute for $c_p$ for a mixture of gases, $c_{pij} = y_i c_{pi} + y_j c_{pj}$

$y_i =$ mole fraction, $c_{pi}$ is specific heat capacity for each component.

From Chemsep, $c_p$(CO) at 773K = 1.13KJ/kg.K

$c_p$(H$_2$O) = 2.13KJ/kg.K

Therefore $c_p$ for the mixture = 1.86KJ/kg.K

Computing for Prandtl number,

$N_{pr} = 3.67 \times 10^{-3}$

To compute for $J_D$ factor, $N_{Re} = 186$;

$J_D = 0.108$

From $k_c = 0.183m/s$

$h = 0.106KJ/m^2s.K$

$\Delta T_{max,film} = 5.3K$

Mears correlation is used as follows;

$$\frac{r_{obs} \rho \rho E(\Delta H)}{hT^2R} < 0.15$$

From www.engin.umich.edu $\rho_b = \frac{\text{weight of catalyst (g)}}{\text{reactor volume (cm$^3$)}}$

From experimental data, $\rho_b = 1359kg/m^3$

$\rho_c = 2719kg/m^3$

$E = 137.2KJ/mol$

Substituting gives $0.8 \times 10^{-4} < 0.15$

Thus the heat transport limitation is negligible.