EFFECTS OF PREPARATION, Ni/Co RATIO, AND SULFURE POISONING OF Ni-Co BIMETALLIC CATALYST FOR DRY REFORMING REACTION

A Thesis Submitted to the College of Graduate Studies and Research in Partial Fulfillment of the Requirements for the Degree of Master of Science in the Department of Chemical and Biological Engineering

University of Saskatchewan

Saskatoon

By

Mohsen Shakouri

© Copyright Mohsen Shakouri, November 2011. All rights reserved.
PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a Postgraduate degree from the University of Saskatchewan, I agree that the Libraries of this University may make it freely available for inspection. I further agree that permission for copying of this thesis/dissertation in any manner, in whole or in part, for scholarly purposes may be granted by Professor Hui Wang who supervised my thesis work. It is understood that any copying or publication or use of this thesis or parts for financial gain shall not be allowed without my written permission. It is also understood that due recognition shall be given to me and to the University of Saskatchewan in any scholarly use which may be made of any material in my thesis.

DISCLAIMER

The University of Saskatchewan was exclusively created to meet the thesis and exhibition requirements for the degree of Master of Science at the University of Saskatchewan. Reference in this thesis to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not constitute or imply its endorsement, recommendation, or favouring by the University of Saskatchewan. The views and opinions of the author expressed herein do not state or reflect those of the University of Saskatchewan, and shall not be used for advertising or product endorsement purposes.

Requests for permission to copy or to make other uses of materials in this thesis in whole or part should be addressed to.
Prof. D.-Y. Peng,

Department of Chemical and Biological Engineering
University of Saskatchewan
College of Engineering
1C119, 57 Campus Drive
Saskatoon, SK S7N 5A9
Canada

OR

Dean

College of Graduate Studies and Research
University of Saskatchewan
107 Administration Place
Saskatoon, Saskatchewan S7N 5A2
Canada
**ABSTRACT**

Ni-Co/AlMgO₃ bimetallic, Ni/AlMgO₃ and Co/AlMgO₃ monometallic catalysts were prepared with various Ni/Co ratios by using the precipitation and impregnation methods for dry reforming reaction. The effects of Ni/Co ratio and preparation methods on the catalyst were analyzed by using different characterization techniques such as BET, ICP, EXAFS, and XANES. It was observed that due to the lack of metal-metal interactions between impregnated catalysts the Ni/Co ratio was better controlled as compared to the precipitated catalysts. On the other hand, with the same Ni/Co ratio the impregnated catalyst was reduced more than the precipitated catalyst. The performance of each catalyst for CO₂ reforming of CH₄ reaction at 710 °C was studied in a quartz tube reactor. Among the prepared catalysts, the precipitated Ni-Co bimetallic catalyst with Ni/Co ratio of 1 showed the best performance. The Co monometallic catalysts did not show desired activity for CO₂ reforming of CH₄. Therefore, to observe the stability of the selected catalyst with Ni/Co ratio of 1 a life-time test was carried out for 65 days at two different temperatures of 710 °C and 760 °C. The precipitated catalyst with Ni/Co ratio of 1 showed higher activity and better stability at 760 °C as compared to 710 °C. Finally, the prepared catalysts were poisoned by adding 30 ppm of H₂S for CO₂ reforming of CH₄ reaction. The Ni monometallic catalysts, whether prepared by impregnation or precipitation method, showed better resistance to H₂S in all cases. Moreover, the Ni monometallic catalysts had higher ability for regeneration as compared to the other prepared catalysts. It was observed that the prepared catalysts with impregnation were more active and had a higher capability for regeneration after H₂S poisoning as compared to precipitated catalysts.
ACKNOWLEDGMENT

I would like to acknowledge the people who contributed to a successful completion of this work. My appreciations go to my parent and sisters for their moral and financial support. I am very grateful to my supervisor, Professor Hui Wang, for all his unflinching support, encouragement and guidance. His deep understanding of situation is greatly valued and highly appreciated. My gratitude also goes to Dr. Ajay K. Dalai, Richard W. Evitts, and Dr. D.-Y. Peng for their valuable course of materials. To Dr. Mehdi Nemati, and Dr. Dae Kun Hwang, and Dr. Jafar Soltan my committee members, I say big thank you for your time. I also would like to thank Dr. Stephen R. Foley for his time as the external examiner. The financial support the Natural Sciences and Engineering Research Council of Canada (NSERC) for this research project in form of Discovery Grant to my supervisor is highly appreciated. I also wish to acknowledge Jianguo Zhang and Chunyu Xi for their assistance and support in my experimental work. I also would like to thank S. Sameen A. Ziadi and Armin Moniri for their helps in the writing of my thesis. Lastly, lots of thanks to all the department technicians, office support staff, other graduate students and especially my very supportive friends for their support.
DEDICATION

I would like to dedicate this thesis to my beloved mother (R.I.P.)

Also, the honor of this thesis is going to my lovely father who has been a great source of motivation and inspiration.
TABLE OF CONTENTS

PERMISSION TO USE ............................................................................................................. I

ABSTRACT ............................................................................................................................. III

ACKNOWLEDGMENT .............................................................................................................. IV

DEDICATION .......................................................................................................................... V

TABLE OF CONTENTS .......................................................................................................... VI

LIST OF TABLES .................................................................................................................... X

LIST OF FIGURES .................................................................................................................. XII

NOMENCLATURE .................................................................................................................. XV

ABBREVIATIONS .................................................................................................................. XVII

CHAPTER 1: INTRODUCTION ............................................................................................... 1

1.1 OVERVIEW ....................................................................................................................... 1

1.2 MOTIVATION ..................................................................................................................... 2

1.3 THESIS ARRANGEMENT ................................................................................................. 4

CHAPTER 2: LITERATURE REVIEW ....................................................................................... 6

2.1 GREENHOUSE GASES AND SYNTHESIS GAS ................................................................. 6

2.2 SYNTHESIS GAS PRODUCTION ..................................................................................... 12

2.2.1 STEAM REFORMING .................................................................................................. 12

2.2.2 PARTIAL OXIDATION OF METHANE .......................................................................... 12

2.2.3 AUTO – THERMAL REFORMING ............................................................................... 13
3.1 EXPERIMENTAL PROCEDURE ............................................................................. 34

3.1.1 CATALYST PREPARATION PROCEDURE ......................................................... 34

3.1.2 CATALYST TEST PROCEDURE ....................................................................... 37

3.2 CATALYST CHARACTERIZATION ANALYSES ..................................................... 37

3.2.1 BET SURFACE AREA ....................................................................................... 37

3.2.2 ICP ANALYSIS .............................................................................................. 38

3.2.3 XAS ANALYSIS ............................................................................................. 38

3.3 EXPERIMENTAL SET-UP OF CATALYST TESTING .......................................... 39

3.3.1 CATALYST ACTIVITY TEST ........................................................................... 39

3.3.2 CATALYST LIFE-TIME TEST ......................................................................... 40

3.3.3 H₂S POISONING TEST .................................................................................. 40

3.4 DATA ANALYSIS PROCEDURE ........................................................................ 41

CHAPTER 4: RESULTS AND DISCUSSION ................................................................ 43

4.1 REPRODUCIBILITY OF THE RESULTS ............................................................ 43

4.2 CATALYST CHARACTERIZATION .................................................................... 47

4.2.1 BET SURFACE AREA ..................................................................................... 47

4.2.2 ICP ANALYSIS ............................................................................................. 48

4.2.3 XAS ANALYSIS ............................................................................................. 51

4.3 CATALYST ACTIVITY TEST ............................................................................. 56

4.3.1 EFFECT OF Ni/Co RATIO ON CDRM REACTION (PRECIPITATED CATALYSTS) 56

VIII
4.3.2 Effect of Ni/Co ratio on CDRM reaction (impregnated catalysts) 60

4.3.3 Effects of preparation methods for the Ni-Co/AlMgO\textsubscript{x} catalysts for CDRM reaction 64

4.3.3.1 Effect of preparation method for monometallic catalysts .... 64

4.3.3.2 Effect of preparation method for Ni-Co bimetallic catalysts 66

4.3.3.3 Overall comparison .............................................. 68

4.4 Life-time activity and stability test of Ni-Co bimetallic catalyst (CopCat-Ni2Co4 with Ni/Co ratio of 0.6) .............................................. 72

4.5 Catalyst poisoning with 30 ppm of H\textsubscript{2}S .............................................. 76

CHAPTER 5: CONCLUSION AND RECOMMENDATION .............................................. 83

5.1 Conclusion .................................................................................. 83

5.2 Recommendation ....................................................................... 85

REFERENCES ...................................................................................... 87

APPENDIX A: CALIBRATION OF MASS FLOW (MFC) CONTROLLER ......................... 95

APPENDIX B: CALIBRATION OF GAS CHROMATOGRAPHY ........................................ 98

APPENDIX C: TEMPERATURE CALIBRATION IN THE MIDDLE OF THE REACTOR ........ 104

APPENDIX D: CARBON BALANCE ........................................................................ 105

APPENDIX E: CATALYST CHARACTERIZATION ANALYSIS ........................................ 107

APPENDIX F: OVEN TEMPERATURE PROFILE OF GC ........................................... 111
LIST OF TABLES

Table 2.1 Processes produce synthesis gas ................................................................. 9
Table 2.2 Synthesis gas applications ........................................................................ 10
Table 2.3 Natural gas compositions in Canada .......................................................... 11
Table 2.4 Proposed mechanism for carbon dioxide reforming of methane .............. 22
Table 2.5 Physical data of common metals used as catalyst ..................................... 25
Table 2.6 Comparison chart of catalyst preparation method ..................................... 32

Table 3.1 Chemicals and amounts used for preparation of catalysts by precipitated..... 36
Table 3.2 Chemicals and amounts used for preparation of catalysts by impregnation .. 36

Table 4.1 Results of repeated BET analysis .............................................................. 44
Table 4.2 Reproducibility results of ICP analysis ......................................................... 44
Table 4.3 Repeated catalyst activity test results ......................................................... 45
Table 4.4 BET surface area of the prepared Ni-Co/AlMgO₅ bimetallic catalyst ....... 47
Table 4.5 Metal composition of Ni-Co/AlMgO₅ bimetallic and Ni or Co metallic catalysts by ICP analysis ............................................................... 48
Table 4.6 Solubility products of metal hydroxides at 25 °C ........................................ 49
Table 4.7 Co K-edge XANS and EXAFS results for Ni/Co ratio 0.6 ......................... 52
Table 4.8 XANES results of the prepared catalysts ................................................... 53
Table 4.9 EXAFS results of the prepared catalysts .................................................... 54
Table 4.10 Reduced metal content (wt %) of precipitated catalysts ....................... 55
Table 4.11 Reduced metal content (wt %) of impregnated catalysts ....................... 55
Table 4.12 Activity and stability of Ni-Co precipitated catalysts ................................ 58
Table 4.13 Activity and stability of Ni-Co impregnated catalysts ............................... 62
Table 4.14 Formation rate of products and reactant conversions of the life-time ........ 75
Table 4.15 Reactant conversions for the poisoning test, precipitated catalysts .......... 79
Table 4.16 Reactant conversions for the poisoning test, impregnated catalysts .......... 80

Table A.1 Heat capacity values of H\textsubscript{2}, N\textsubscript{2}, CO\textsubscript{2}, and CH\textsubscript{4} at 21 °C. ................................. 95

Table B.1 GC calibration data for H\textsubscript{2}.................................................................. 99
Table B.2 GC calibration data for N\textsubscript{2}................................................................ 100
Table B.3 GC calibration data for CO ........................................................................ 101
Table B.4 GC calibration data for CH\textsubscript{4}.............................................................. 102
Table B.5 GC calibration data for CO\textsubscript{2}.............................................................. 103

Table D. 1 Carbon balance for CopCat-Ni3Co2 within 14h........................................ 106

Table F.1 GC oven temperature values ...................................................................... 111
LIST OF FIGURES

Fig. 2.1 Canada’s total gas emissions breakdown by gas ........................................7
Fig. 2.2 Steps in catalyst design ................................................................................20
Fig. 2.3 Proposed surface mechanism for CDRM reaction on metallic catalyst ........23
Fig. 2.4 Brief chart of precipitation procedure .........................................................29
Fig. 2.5 Schematic of the experimental set-up for catalyst preparation .......................30
Fig. 2.6 Summary chart of impregnation procedure ..................................................31

Fig. 4.1 Methane conversion for the repeated catalyst activity test .........................46
Fig. 4.2 H₂/CO ratio of the repeated catalyst activity test .........................................46
Fig. 4.3 Effect of preparation method on the intent Ni/Co ratios ...............................50
Fig. 4.4 Effect of preparation method on the obtained Mg/Al ratios ...........................51
Fig. 4.5 Activity and stability of precipitated catalysts in term of CH₄ conversion ......57
Fig. 4.6 Activity and stability of precipitated catalysts in term of CO₂ conversion ......58
Fig. 4.7 H₂/CO ratios of precipitated catalysts .........................................................59
Fig. 4.8 Activity and stability of impregnated catalysts in term of CH₄ conversion ......61
Fig. 4.9 Activity and stability of impregnated catalysts in term of CO₂ conversion ......62
Fig. 4.10 H₂/CO ratios of Impregnated catalysts .......................................................63
Fig. 4.11 Activity and stability of monometallic catalysts .........................................65
Fig. 4.12 H₂/CO ratios of the monometallic catalysts .................................................66
Fig. 4.13 Activity and stability of bimetallic catalysts ................................................67
Fig. 4.14 H₂/CO ratios of Ni/Co bimetallic catalysts ..................................................67
Fig. 4.15 Activity and stability of Ni-Co catalysts .....................................................69
Fig. 4.16 H₂/CO ratios of Ni-Co catalysts ................................................................. 70
Fig. 4.17 CH₄ rates of CDRM reaction based on the total reduced metal weight ........ 71
Fig. 4.18 CO₂ rates of CDRM reaction based on the total reduced metal weight ........ 72
Fig. 4.19 Activity and stability of CopCat-Ni2Co4 (Life-Time) .................................. 74
Fig. 4.20 Production rates of the life-time CDRM test ............................................. 74
Fig. 4.21 H₂/CO ratio during the life-time test period at 710 °C and 760 °C ............. 76
Fig. 4.22 Activity of Ni-Co precipitated catalysts in term of CO₂ conversions during H₂S poisoning test ................................................................................................. 78
Fig. 4.23 Activity of Ni-Co precipitated catalysts in term of CH₄ conversions during H₂S poisoning test ................................................................. 79
Fig. 4.24 Activity of Ni-Co impregnated catalysts in term of CO₂ conversions during H₂S poisoning test ....................................................................................... 81
Fig. 4.25 Activity of Ni-Co impregnated catalysts in term of CH₄ conversions during H₂S poisoning test ....................................................................................... 81

Fig.A.1 Calibration curve for N₂ mass flow controller ........................................ 96
Fig.A.2 Calibration curve for CH₄ mass flow controller ........................................ 96
Fig.A.3 Calibration curve for CO₂ mass flow controller ....................................... 97
Fig.A.4 Calibration curve for H₂ mass flow controller ......................................... 97

Fig.B.1 GC calibration curve for H₂ ........................................................................... 99
Fig.B.2 GC calibration curve for N₂ .......................................................................... 100
Fig.B.3 GC calibration curve for CO ......................................................................... 101
Fig.B.4 GC calibration curve for CH₄ ........................................................................ 102
Fig.B.5 GC calibration curve for CO\textsubscript{2} ................................................................. 103

Fig.D. 1 Carbon flow in inlet and outlet streams of the reactor................................. 105

Fig.C.1 Heater temperature calibration in the middle of the reactor ......................... 104

Fig.E.1 Three main regions in an XAS spectrum ......................................................... 109

Fig.F.1 Oven temperature profile of GC................................................................. 111
**NOMENCLATURE**

\( A \)  
\text{molar mass of adsorbed species}

b.b.c.  
\text{body centered cubic}

\( c \)  
\text{BET constant}

\( F_{\text{in}, \ i} \)  
\text{flow rate of component “i” before a reaction (mL/min)}

\( F_{\text{out}, \ i} \)  
\text{flow rate of component “i” after a reaction (mL/min)}

f.c.c.  
\text{faced centered cubic}

HFCs  
\text{hydro-fluorocarbons}

h.c.p.  
\text{hexagonal close packing}

Me  
\text{metal}

\( N \)  
\text{Avogadro’s number = 6.022×10^{23}}

\( P \)  
\text{equilibrium pressure of the adsorbed gas,}

\( P_0 \)  
\text{saturation pressure of the adsorbed gas}

PFCs  
\text{per-fluorocarbons}

\( \text{pH} \)  
\text{a measure of the acidity or basicity}
$Q$  the adsorbed gas quantity

$Q_m$  quantity of the monolayer adsorbed gas

$s$  molecular cross-sectional area

$V$  molar volume of adsorbed gas

wt %  weight percent
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANL</td>
<td>Argonne National Laboratory</td>
</tr>
<tr>
<td>APS</td>
<td>Advanced Photon Source</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing Material</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmett, and Teller</td>
</tr>
<tr>
<td>CDRM</td>
<td>carbon dioxide reforming of methane</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>GHG</td>
<td>greenhouse gas</td>
</tr>
<tr>
<td>GHSV</td>
<td>gas hourly space velocity</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively Coupled Plasma</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
</tr>
<tr>
<td>LUM</td>
<td>Lagrange Undetermined Multiplier</td>
</tr>
<tr>
<td>MTE</td>
<td>multi-reaction thermodynamic equilibrium</td>
</tr>
<tr>
<td>MFC</td>
<td>mass flow controller</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>NEXAFS</td>
<td>Near-edge X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>RDS</td>
<td>Rate Determining Step</td>
</tr>
<tr>
<td>RLS</td>
<td>Rate Limiting Step</td>
</tr>
<tr>
<td>RWGSR</td>
<td>reverse water gas shift reaction</td>
</tr>
<tr>
<td>SNG</td>
<td>synthetic natural gas</td>
</tr>
<tr>
<td>TCD</td>
<td>thermal conductivity detector</td>
</tr>
<tr>
<td>TOS</td>
<td>Time On Stream</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray Absorption Near-Edge Structure</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray Absorption Spectroscopy</td>
</tr>
</tbody>
</table>
CHAPTER 1: INTRODUCTION

1.1 OVERVIEW

CO₂ reforming of CH₄, or dry reforming, has attracted attentions among the other CH₄ reforming reactions, because it uses CO₂ and CH₄ which are greenhouse gases, and produces synthesis gas which is desired for industry.

Natural gas mainly contains CH₄ is in direct competition with oil and coal as a fuel in many applications. Besides, some low grades of natural gas contain significant amount of CO₂ as compared to its CH₄ content. In addition, land fill gas and coal gas contain significant amount of CH₄ and CO₂. Also, CO₂ is generated as a waste by-product in processes like fossil fuel combustion, synthesis fuels manufacturing, and chemical production. Therefore significant amount of CO₂ and CH₄ are easily available. Also, CO₂ and CH₄ are known as the main parts of greenhouse gas which is environmentally undesirable due to its direct effect on global temperature.

The conversion of gases to transportable fuels such as gasoline, diesel, and methanol has attracted much attention from both industrial and environmental aspects. Therefore, different methane reforming applications, like dry reforming, are studied to produce synthesis gas (mixture of H₂ + CO). As an example, syngas is used in Fischer–Tropsch synthesis that produces liquid hydrocarbons from synthesis gas.
Due to the importance of synthesis gas as feedstock for industry and an increase in \( \text{H}_2 \) demand, dry reforming is applied in landfill gas utilization and coal gas polygeneration. On the other hand, dry reforming reaction reduces the amount of \( \text{CH}_4 \) and \( \text{CO}_2 \) noticeably, therefore; many catalysts are being developed for dry reforming reaction. The major problem associated to this reaction is the lack of a stable catalyst to eliminate a significant amount of carbon formation during a long period of time on the stream.

1.2 Motivation

Our research group in University of Saskatchewan has developed a Ni-Co/AlMgO\(_x\) bimetallic catalyst with Ni/Co ratio of one prepared by precipitation method which is highly active and stable for dry reforming reaction (Zhang et al., 2007). To find a good catalyst which has the lowest carbon formation for CDRM reaction Zhang made four different bimetallic catalysts. The catalysts were Ni-Me/AlMgO\(_x\) (Me = Co, Fe, Cu, or Mn) which prepared by precipitation method. Among them Ni-Co/AlMgO\(_x\) catalyst was tested for CDRM reaction for 2000h (GHSV of 110,000 mL/g.h; 750 °C; 1 atm; catalyst load of 0.05 g). The Ni-Co bimetallic catalyst showed 2000 h stability with relatively high conversion (\( \text{CH}_4 \) conversion: 90%, \( \text{CO}_2 \) conversion: 91%) and the carbon formation was as low as 0.44 g\(_{\text{carbon}}\)/g\(_c\) (Zhang et al., 2007). Zhang also studied the mechanism and kinetic study of the reaction with Ni-Co catalyst. It is remarkable that the Ni-Co/AlMgO\(_x\) bimetallic catalyst for dry reforming reaction was awarded a patent in July 2011 as a catalyst for production of synthesis gas (US Patent 7,985,710). Also, Carbon Science Inc. (Santa Barbara, USA) announced a worldwide

---

\(^1\) The main part of greenhouse gases
exclusive licence agreement with University of Saskatchewan for the Ni-Co bimetallic catalyst, in December 2010.

Further observations on the Ni-Co/AlMgOₓ were done by Xi in our group. Xi studied effects of preparation conditions (especially pH value of precipitation) on the Ni-Co catalyst properties and performances (Xi and Wang, 2009).

Further investigations are going to be described for the Ni-Co catalyst for CDRM reaction during the thesis. The main observations are based on the following considerations:

1- A catalyst can be prepared by using different preparation methods such as precipitation method or impregnation method and each preparation method can affect the catalyst performance for a reaction.

2- Running CDRM reaction over related catalyst, metallic part is known as the active site. Ni-Co bimetallic catalyst contains both Ni and Co as the metals therefore various Ni/Co ratios may affect the catalyst performance for CDRM reaction.

3- H₂S is known as a poison for catalysts and may affect the catalyst performance. Since natural gas may contain few amounts of H₂S, therefore effect of H₂S on the Ni-Co/AlMgOₓ catalyst performance for CDRM reaction should be investigated.

To commercialize Ni-Co bimetallic catalyst, the effects of preparation methods, various Ni/Co ratios and effect of H₂S as a poison on the Ni-Co/AlMgOₓ catalyst performance for CDRM reaction need to be evaluated. To investigate the effects of
Ni/Co ratio on the Ni-Co bimetallic catalysts, the catalysts were prepared with Ni/Co ratio of 0.5, 1, and 2. Also, Ni and Co monometallic catalysts supported on AlMgOx were prepared. Furthermore, to observe the effects of preparation method on the catalyst performance all the catalysts were prepared with both impregnation and precipitation. The catalyst activity and stability for carbon dioxide reforming of methane were tested in a quartz fixed bed reactor. As Carbon Science Inc. requirement, the optimum catalyst was selected and used for CDRM reaction for almost 1600 h. Lastly, all the prepared catalysts were poisoned using H₂S in order to investigate the effects of H₂S on the catalysts.

1.3 THESIS ARRANGEMENT

The arrangement of the thesis is as follows:

**Chapter 1: Introduction** focuses on the general background and development of methane dry reforming technology.

**Chapter 2: Literature review** consists of relevant information for various methane reforming reactions. It also introduces the previous studies done for CDRM reaction using different catalysts. Then, the catalyst design and selection procedure is explained. The catalyst preparation methods are described as well.

**Chapter 3: Experimental set-up and procedure** focuses on the procedure of the catalysts preparation, catalyst characterization techniques and the activity tests. The data analysis method and equations are explained.
Chapter 4: Results and discussion contains the results of the research and related discussion. Briefly, the results of BET, ICP and XAS as catalyst characterization analyses are shown and discussed. Also, the effects of various Ni/Co ratios and preparation methods on catalyst performance for CDRM reaction are discussed. Furthermore, the stability of Ni-Co/AlMgO$_x$ with Ni/Co ratio of 1 for CDRM reaction is described. The effects of H$_2$S poisoning on the catalyst performance for CDRM are explained as well.

Chapter 5: Conclusion and recommendation are made for future work.
Chapter 2: Literature Review

2.1 Greenhouse Gases and Synthesis Gas

The greenhouse gases (abbreviated as GHG) adsorb and emit infrared radiation in the earth’s atmosphere. The major greenhouse gases in the atmosphere are water vapor, carbon dioxide, nitrous oxide, and methane. Since the industrial revolution, the concentration of carbon dioxide, methane, and nitrous oxide have being increased because of fossil fuel combustion, human activities, and land-use changes.

The assessment report compiled by the Intergovernmental Panel on Climate Change (IPCC, 2007) has observed that the changes in atmospheric concentrations of greenhouse gases, aerosols, land cover, and solar radiation are altering the energy balance of the climate system. The report has concluded that the increase in anthropogenic greenhouse gas (GHG) concentration is very likely to have caused most of the increase in global average temperature since the mid-20th century. The Canada’s total emissions breakdown by gas, reported by the Environment Canada, is shown in Figure 2.1.
Figure 2.1 shows that the CO$_2$ was the major greenhouse gas mainly caused by combustion of fossil fuels. Methane was laid on the second place with 13%, which mainly came from the activities in the Agriculture and Waste sectors, and emissions from oil and natural gas. The third place was given to nitrous oxide with 7%. Also, Per-fluorocarbons (PFCs), sulphur hexafluoride (SF$_6$) and hydro-fluorocarbons (HFCs) were close to 1% of total emissions.

Syngas$^1$ is a gas mixture containing various amounts of carbon monoxide and hydrogen. Because highly usage of H$_2$ and CO mixture as an intermediate feed in production of synthetic natural gas (SNG), the name of synthesis gas is given to the mixture of H$_2$ and CO. The examples of syngas production methods are steam reforming of natural gas or liquid hydrocarbons to produce hydrogen, the gasification of

---

$^1$ Short from of synthesis gas
coal. Syngas is also used as a feed in Fischer Tropsch synthesis process to produce methanol and is used for ammonia production as well.

The production of hydrogen is of great importance due to its use in the chemical and fuel industries (Barreto et al., 2003; Goff et al., 1987). Currently, the dominant method of hydrogen production is the catalytic reforming of CH\textsubscript{4} with steam\footnote{CH\textsubscript{4} + H\textsubscript{2}O $\rightleftharpoons$ CO + 3H\textsubscript{2}}. Industrially, the reaction is carried out at high temperatures (1073 – 1103 K) and high pressures (20 – 40 bar) to obtain high yields of the products (Goff et al., 1987). The hydrogen is used in many applications. As a pure product, it can be used in refinery processes, ammonia synthesis, hydrogenation, and fuel cells.

As a mixture with CO, hydrogen also has extensive usages, such as methanol synthesis, hydroformylation, and long-chain hydrocarbon synthesis via Fisher-Tropsch reaction. Hydrogen can be used more efficiently in fuel cells than the other fuels which need combustion to convert their potential to mechanical energy. In addition, the breakdown of hydrogen does not generate pollutants, unlike the fossil fuels. It is noteworthy that hydrogen is the only fuel whose production and use can contribute directly in eliminating many of environmental, economic, and health problems.

The synthesis gas produced from various reactions with different H\textsubscript{2}/CO ratio. Based on H\textsubscript{2}/CO ratio, the produced syngas can be consumed by various processes. Some of the reactions that can produce synthesis gas from methane are partial oxidation of methane, steam reforming, dry reforming, and auto-thermal reforming. Based on the
H₂/CO ratio of the synthesis gas which is produced by different processes, it can be used in different reactions. Table 2.1 shows reaction which can produce synthesis gas.

**Table 2.1 Processes produce synthesis gas**

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction Equation</th>
<th>H₂/CO ratio</th>
<th>ΔH°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Partial oxidation</td>
<td>CH₄ + 0.5O₂ ⇌ CO + 2H₂</td>
<td>2</td>
<td>-36</td>
</tr>
<tr>
<td>Steam reforming</td>
<td>CH₄ + H₂O ⇌ CO + 3H₂</td>
<td>&gt;3</td>
<td>+206</td>
</tr>
<tr>
<td></td>
<td>CO + H₂O ⇌ CO₂ + H₂</td>
<td></td>
<td>-41</td>
</tr>
<tr>
<td>Dry reforming</td>
<td>CH₄ + CO₂ ⇌ 2CO + 2H₂</td>
<td>1</td>
<td>+247</td>
</tr>
<tr>
<td>Auto-thermal</td>
<td>CH₄ + 2O₂ ⇌ CO₂ + 2H₂O</td>
<td></td>
<td>-802</td>
</tr>
<tr>
<td>reforming</td>
<td>(Methane in excess)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₄ + CO₂ ⇌ 2CO + 2H₂</td>
<td></td>
<td>+247</td>
</tr>
<tr>
<td></td>
<td>or</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₄ + H₂O ⇌ CO + 3H₂</td>
<td></td>
<td>+206</td>
</tr>
</tbody>
</table>

Table 2.2 shows some applications of synthesis gas in various processes. Table 2.3 shows the composition of natural gas as reported by Uniongas Company in Canada, Ontario.
Table 2.2 Synthesis gas applications

<table>
<thead>
<tr>
<th>Reaction</th>
<th>H₂/CO ratio</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry reforming</td>
<td>1</td>
<td>e.g. Oxo alcohols, formaldehyde production</td>
</tr>
<tr>
<td>Partial oxidation</td>
<td>2</td>
<td>e.g. Methanol synthesis, Fischer-Tropsch synthesis</td>
</tr>
<tr>
<td>Steam reforming</td>
<td>&gt;3</td>
<td>e.g. H₂ Production, ammonia synthesis</td>
</tr>
</tbody>
</table>

Table 2.3 shows that the main part of the natural gas is composed of methane. Therefore the feed needed for syngas reaction can be found easily. On the other hand, due to high cost of natural gas transporting on site natural gas conversion to other more valuable and easily transportable products is desirable.
<table>
<thead>
<tr>
<th>Component</th>
<th>Typical Analysis (mole %)</th>
<th>Range (mole %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>95.2</td>
<td>87.0 - 96.0</td>
</tr>
<tr>
<td>Ethane</td>
<td>2.5</td>
<td>1.5 - 5.1</td>
</tr>
<tr>
<td>Propane</td>
<td>0.2</td>
<td>0.1 - 1.5</td>
</tr>
<tr>
<td>iso - Butane</td>
<td>0.03</td>
<td>0.01 - 0.3</td>
</tr>
<tr>
<td>normal - Butane</td>
<td>0.03</td>
<td>0.01 - 0.3</td>
</tr>
<tr>
<td>iso - Pentane</td>
<td>0.01</td>
<td>trace - 0.14</td>
</tr>
<tr>
<td>normal - Pentane</td>
<td>0.01</td>
<td>trace - 0.04</td>
</tr>
<tr>
<td>Hexanes plus</td>
<td>0.01</td>
<td>trace - 0.06</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.3</td>
<td>0.7 - 5.6</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>0.7</td>
<td>0.1 - 1.0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.02</td>
<td>0.01 - 0.1</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>trace</td>
<td>trace - 0.02</td>
</tr>
</tbody>
</table>

*Typical sulphur content is 5.5 mg/m³ which, based on 25 °C and 1 atm, means 4 ppm. Water vapour content is typically between 16-32 mg/m³.*
2.2 SYNTHESIS GAS PRODUCTION

2.2.1 STEAM REFORMING

Steam reforming is known as the main and well-developed process for producing synthesis gas and/or hydrogen. The steam reforming reaction is as follows:

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2; \quad \Delta H^{\circ}_{298 \text{K}} = +206 \text{ kJ/mole} \]

This endothermic reaction can be mixed with methane dry reforming to adjust the \( \text{H}_2/\text{CO} \) ratio as a feedstock for other processes. All group VIII metals show good activity for steam reforming. Among them, Ni for its cheap availability is the most commonly used catalyst while Ru and Rh show the highest activity for the process. Also, MgO and \( \alpha\)-Al\(_2\)O\(_3\) were used as the common support for these metals because of their good stability under high reaction temperature. (Bitter et al., 1997)

2.2.2 PARTIAL OXIDATION OF METHANE

The syngas is also obtained by the partial oxidation of \( \text{CH}_4 \) as follows:

\[ \text{CH}_4 + 0.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2; \quad \Delta H^{\circ}_{298 \text{K}} = +247 \text{ kJ/mole} \]

While steam reforming needs a huge amount of energy, partial oxidation seems to be a good alternative process to produce synthesis gas. From economical point of view, the main problem related to this process is the cost of pure oxygen supply. The partial oxidation process can be operated both catalytically and non-catalytically. According to non-catalytic process methane and oxygen typically react at high temperature (1350-1800 K); therefore, most of the researchers were attracted to use catalyst for the process.
Typical reaction condition for catalytic partial oxidation is atmospheric pressure and temperature in range of 673 K to 1273 K (Bjørn Christian Enger et al., 2008).

2.2.3 Auto-thermal Reforming

The combination of non-catalytic partial oxidation and reforming of methane developed by Haldor Topsøe in the late 1950s was named auto-thermal reforming. The process was developed by having both partial oxidation and reforming of methane in a single reactor. Due to the occurrence of undesired in combustion zone, the reaction may lead to carbon deposition on downstream tubes. The carbon deposition may cause various operational problems like catalyst deactivation, pressure drop, damaging the equipment, and poor heat transfer (Pena et al., 1996).

2.2.4 CO₂ Reforming of CH₄

In recent years, the reforming of CH₄ with CO₂ has attracted great attention as an alternative method for hydrogen production since this reaction utilizes an environmentally problematic greenhouse gases. The CDRM reaction is as follows:

\[
\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2 \text{CO} + 2 \text{H}_2; \quad \Delta H_{298 K}^{\circ} = +247.4 \text{ kJ/mol}
\]

However, the CH₄ reforming reactions are energy extensive, because they are endothermic in nature and must be carried out at high temperatures to obtain high conversions (high yield of H₂). Therefore different applications are studied to reduce the amount of greenhouse gases and produce syngas. One of the best processes which attract
great attention in the last decade is catalytic CO$_2$ reforming of methane (Ramachandran et al., 1998).

As before mentioned, a beneficial procedure for producing syngas (CO and H$_2$) is dry reforming of methane which is an endothermic reaction producing a mixture of low molar ratio of CO and H$_2$.

CH$_4$ + CO$_2$ ⇌ 2CO + 2H$_2$ ; $\Delta H^{0}_{298 K} = +247.4$ kJ/mole (2.1)

CO$_2$ + H$_2$ ⇌ CO + H$_2$O (Reverse Water Gas Shift) ; $\Delta H^{0}_{298 K} = +41.4$ kJ/mole (2.2)

2.3 Carbon Dioxide Reforming of Methane (CDRM)

A number of studies have been performed on dry reforming of methane. Some of them have compared the conversion of the reactants and the yield of product in various ranges of conditions of temperature and pressure. For dry reforming of methane different types of reactors are used such as packed bed, fluidized bed, and membrane reactors. Also, Different catalyst materials and supports are used for this reaction and many efforts have been focused to develop the catalyst activity, selectivity, and resistance to deactivation (Cornaglia et al., 2004). According to the reaction, the production of water through the reverse water gas shift reaction and some other side reactions in dry reforming of methane will limit the maximum yield of products, i.e. hydrogen and CO.

It is also reported that the major problems for catalyst deactivation in dry reforming reaction are carbon formation and sulphur poisoning. These problems are
The CALCOR and SPARG processes are currently known as the two commercial processes using CDRM reaction. The following sections briefly describe these processes (Teuner et al., 2001 and Udengaard et al., 1992).

2.3.1 CALCOR PROCESS

Since carbon monoxide is required as raw material for different applications, therefore various processes were developed for CO production. The limitation in transporting CO due to its toxicity and economical aspects, the on-site production of CO is desired. The standard CALCOR process is designed to produce CO under low pressure and high temperature using catalytic reforming of methane or liquefied petroleum gas (LPG). Figure 2.2 shows a schematic of the process as developed by Teuner et al. (2001).

In order to protect the catalyst, the feed has to be desulfurized before mixing with CO₂. Then mixture of CH₄ and CO₂ is passed through the reformer which is charged with reforming catalyst. The product consists of syngas, H₂O, CO₂, and traces of CH₄. The syngas is then cooled down to ambient temperature to recover CO₂. Finally, in the CO purification unit, H₂, CH₄ and traces of CO₂ are removed from carbon monoxide. The recovered CO₂ is recycled to the feed line for further use and the tail gas from the purification step is burned as fuel.
2.3.2 SPARG PROCESS

To produce synthesis gas with the $\text{H}_2/\text{CO}$ ratio lower than steam reforming product, the sulfur passivated reforming process was designed (Udengaard et al., 1992). The process was commercially developed in Sterling Chemical Inc. (Texas City, USA) in 1987. In order to achieve lower $\text{H}_2/\text{CO}$ ratio, a part of steam in the reforming process is replaced by CO$_2$. Therefore, $\text{H}_2/\text{CO}$ ratio lower as compared to steam reforming is obtained to be used in the synthesis of acetic acid, dimethyl ether, and oxo-alcohols. In SPARG process, due to adding CO$_2$ to the process, the possibility of increasing carbon formation and catalyst deactivation is minimized by introducing partially sulfur-poisoned reforming catalyst which is mainly nickel based.

2.3.3 CATALYSTS FOR DRY REFORMING REACTION

Different catalyst materials and supports are used for dry reforming of methane. Many efforts have been focused to develop the catalyst activity, selectivity, and resistance to catalyst deactivation (Cornaglia et al., 2004). It is generally known that the transition metals are used for catalytic carbon dioxide reforming of methane. Researchers have used the catalysts such as Ni (Bradford et al., 1996), Pt (Bradford et al., 1998), Pd (ErdoÈhelyi et al., 1994), Rh (Zhang et al., 1996), and Ir (ErdoÈhelyi et al., 1997).

A catalyst is usually composed of an active element, a promoter, and a support. In our research group, Zhang et al. (2007) found that the Ni-Co/AlMgO$_x$ bimetallic catalyst which was produced by precipitation method from Ni, Co, Al, and Mg exhibited an excellent performance on carbon dioxide reforming of methane. The developed
catalyst not only has a higher activity, but also because of its resistance to carbon deposition has a better stability as compared to the other Ni-Me bimetallic catalysts (Me = Fe, Cu, and Mn). Also, the Ni-Co catalyst has the higher surface area and the lower pore diameter in contrast the other Ni-Me bimetallic catalysts. Zhang was able to obtain higher conversion of the reactants by using this catalyst (Zhang et al., 2007).

Section 2.4 will describe the method which will lead to the selection of this catalyst.

2.3.4 HYDROGEN AND SYNGAS PRODUCTION THROUGH CDRM REACTION

Yaw and Amin (2005) found that equilibrium compositions of the reaction improved from 600 K to 1000 K, but the effect of temperature above the 1000 K was insignificant. They also found that a lower CO₂/CH₄ ratio of unity was favourable in order to produce syngas besides reducing the water formation as a product of side reaction (RWGSR). Although they reported that the higher CO₂/CH₄ feed ratio above unity, the higher H₂ and CO yields, but higher occurrence of side reaction (RWGSR). For these approaches, they used multi-reaction thermodynamic equilibrium (MTE) method, and minimization of Gibbs free energy using Lagrange Undetermined Multiplier (LUM) method. Figure 2 and Figure 3 of Yaw and Amin (2005) paper showed the results for MTE and LUM, respectively.

Tsai and Wang (2008) worked on thermodynamic equilibrium prediction for natural gas dry reforming in a thermal plasma reformer. By using the HSC Chemistry 5.1® software, they tested temperature in the range of 500-1150 °C and CH₄/CO₂ flow ratios of 1/1, 1/1.25, 1/1.5, 1/1.75, and 1/2. They found that the optimum operating
conditions for temperature and CO$_2$/CH$_4$ flow ratio were 850 °C and was 1.25, respectively.

Aparicio (et al., 2002) calculated the theoretical conversion of the reaction by using equivalent volume proportion of CH$_4$ and CO$_2$ from Gibbs free energy values of the reactants and products at different temperatures as shown in Figure 5 of Aparicio’s (et al., 2002) report.

Múnera et al. (2003) and Cornaglia’s (et al., 2004) studied the CDRM reaction in a plug flow reactor and a dense Pd/Ag membrane reactor. The catalyst used was Pt/La$_2$O$_3$ and Rh/La$_2$O$_3$. They found that Rh/La$_2$O$_3$ was more stable than Pt/La$_2$O$_3$, and the highest conversion was achieved by the membrane reactor. As shown in Figure 3 of Cornaglia’s (et al., 2004) paper, they obtained the highest conversion of 34% by using Rh/La$_2$O$_3$ (containing 0.6% of Rh) in a membrane reactor.

Zhang et al. (2011) studied “in-situ synthesis of nickel modified molybdenum carbide catalyst” for CDRM reaction. They have observed up to 83% of CH$_4$ 93% of CO$_2$ conversions for the Ni-Mo$_2$C catalysts that were in-situ synthesized in CH$_4$/CO$_2$ and CH$_4$/H$_2$ from NiMoO$_x$. Also, they have obtained the H$_2$/Co ratio of 0.54 in a period of 35 h (at 800 °C).

Guo et al. (2004) examined Ni/Al$_2$O$_3$ and Ni/MgAl$_2$O$_4$ for CDRM reaction. Their conditions were GHSV of 500 ml$^{-1}$g$^{-1}$h$^{-1}$, CH$_4$/CO$_2$ ratio of 1 and T of 1023 °C. They observed methane conversion of 31.8 % and 85.3 % using Ni/Al$_2$O$_3$ and Ni/MgAl$_2$O$_4$ catalyst, respectively. Also, they reported that continuous catalyst deactivation was found for both Ni/Al$_2$O$_3$ and Ni/MgAl$_2$O$_4$ catalyst.
Bouarab et al. (2004) reported that supported Co catalysts (Co/SiO$_2$, Co/5%MgO-SiO$_2$, Co/35%MgO-SiO$_2$) gave better results in comparison with Ni in terms of carbon formation. However, they could not reach to a methane conversion over 42.7% using Co/35%MgO-SiO$_2$ catalyst.

2.3.5 Deactivation of Reforming Catalyst

The deactivation of CDRM reaction catalysts is mainly due to losing the metal active sites from the available surface area of the catalysts. The problem may be caused by coke formation or sintering of the metal active sites. Because of the mechanism of CDRM reaction, the main reason for catalyst deactivation is carbon formation. Therefore various efforts have been done to develop a catalyst with noticeable stability while reducing carbon formation. Our research group has developed Ni-Co/AlMgO$_x$ bimetallic catalyst for CDRM reaction (Zhang et al., 2007). Zhang reported that the Ni-Co bimetallic catalyst with Ni/Co ratio of 1 did not show any carbon formation after 250 h TOS. For industrial use, the natural gas is mainly used as the feedstock for CDRM reaction. The natural gas generally contains sulphur compounds, which may deactivate the catalyst through sintering. Therefore, it is desired to study the effects of sulphur compounds on the catalyst which may be used for CDRM reaction.

2.4 Catalyst Design

This section includes the methods of the Ni-Co/AlMgO$_x$ catalyst selection and preparation. The selection is briefly described through the procedure presented by
Dowden *et al.* (1968) According the procedures of Dowden *et al.* (1968) the following steps are used as shown in Figure 2.2.

![Diagram showing steps in catalyst design](image)

**Fig.2.2** Steps in catalyst design (Dowden *et al.* 1968)

2.4.1 **TARGET REACTION**

CO₂ reforming of methane is used as the target reaction to produce synthesis gas:

\[
\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2; \quad \Delta H^\circ_{298 K} = +247 \text{ kJ/mole (2.3)}
\]

The reaction is highly endothermic, and at temperature lower than 916 K the Gibbs free energy change is positive (\(\Delta G^0_{T<916K}>0\)). Therefore, temperature higher than 916 K should be selected for the reaction to take place. Also, it should be considered that at
higher temperature the possibility of reaction sites will be increased. According to literature (Bradford and Vannice, 1999), commonly used temperature for this reaction is 1023 K.

2.4.2 STOICHIOMETRIC ANALYSIS

Probable reactions are listed below (Richardson 1989):

1- primary reactant reactions
2- reactant self-interactions
3- reactant cross-interactions
4- reactant-product reactions
5- product-product reactions

2.4.3 THERMODYNAMIC ANALYSIS

Regarding thermodynamic analysis the equilibrium figures; such as composition vs. temperature, equilibrium constant vs. temperature, composition vs. pressure, conversion vs. temperature, \( \text{H}_2 \) selectivity vs. temperature, effects of inert gas, are considered which facilitating the prediction of reaction performance.

2.4.4 PROPOSED MECHANISM

For CDRM reaction, methane dissociation is believed to be one of the initial steps (Hickman and Schmidt, 1993). Also, it is reported that at equilibrium the methane adsorption on the surface of the catalyst leads to the methane cracking which is the rate determining step (Schuurman et al., 1998; Tsipouriari and Verykios, 1999; 2001). Bitter
et al. (1997, 1998) observed that CO$_2$ can dissociate into Oxygen and CO that are adsorbed on the support site. Solymosi (1991) reported the CO-S releases to gas phase CO immediately.

The reaction steps are briefly mentioned in Table 2.4 (Zhang, 2008).

**Table 2.4** Proposed mechanism for carbon dioxide reforming of methane

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Description</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$ + M$^*$ ⇌ CH$_4$-M</td>
<td>CH$_4$ adsorption, equilibrium step</td>
<td>(2.4)</td>
</tr>
<tr>
<td>CH$_4$-M → C-M + 2H$_2$</td>
<td>CH$_4$ cracking, Rate Determining Step (RDS)</td>
<td>(2.5)</td>
</tr>
<tr>
<td>CO$_2$ + 2S$^*$ ⇌ CO-S + O-S</td>
<td>CO$_2$ dissociative chemisorption</td>
<td>(2.6)</td>
</tr>
<tr>
<td>C-M + O-S → CO + M + S</td>
<td>Oxidation step, Rate Limiting Step (RLS)</td>
<td>(2.7)</td>
</tr>
<tr>
<td>CO$_2$ + C-M → 2CO + M</td>
<td></td>
<td>(2.8)</td>
</tr>
</tbody>
</table>

* M and S orderly stand for Metal active site species and Support active site species.

The rate limiting step (RLS) in each reaction is the step which controls the rate of the reaction. Kroll *et al.* (1996) suggested for CDRM reaction, that the reaction between M-C species and activated S-CO$_2$ can be assumed as the rate limiting step. It is believed that carbon deposition is the dominant catalyst deactivation reason for the catalysts which are used for CDRM reaction. Carbon deposition occurs when the rate of carbon species removal is lower than that of carbon species accumulation. Therefore, oxidation step (Eq. 2.7) is RLS and CH$_4$ dissociation is RDS. In addition, CO$_2$ may react directly with C-M species to form CO (Erdohelyi *et al.*, 1994; Schuurman *et al.*, 1998).
Based on the above-mentioned description, a surface reaction mechanism is proposed for catalytic CO\textsubscript{2} reforming of methane. Figure 2.3 shows the schematic of proposed mechanism (Zhang, 2008).

![Proposed Surface Mechanism for CDRM Reaction on Metallic Catalyst (Zhang, 2008)](image)

**Fig. 2.3** Proposed surface mechanism for CDRM reaction on metallic catalyst (Zhang, 2008).

### 2.4.5 DESIRED CATALYST PROPERTIES

In general, if a catalyst has a higher activity, a better selectivity, and more stability then it will be closed to an ideal catalyst. A catalyst can enhance the rate of a reaction by accelerating the rate of RLS. On the other hand, a good selective catalyst produces the desired products more as compared to the potential products that can produce from the possible side reaction(s). Furthermore, if a catalyst has more life-time and lower rate of deactivation, then it will be a more stable catalyst.

In accordance to the proposed mechanism, it is desired that the catalyst enhance the ease of RLS occurrence. In our reaction system the side reaction is Reverse Water Shift Gas Reaction (RWSGR):

\[
\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}; \quad \Delta H^\circ_{298\text{ K}} = 247 \text{ kJ/mole (2.9)}
\]
Therefore, a good catalyst should affect RWSGR and carbon formation reactions. The major problems of catalyst deactivation in CO$_2$ reforming of CH$_4$ are carbon deposition on surface, sintering, and metal oxidation. The desired properties of the catalyst, according to aforesaid mechanism and analysis, should have the following description:

D1- To increase dissociation of methane to CH$_x$ species and to move out H atom from intermediate species to form hydrogen, the catalyst should have dehydrogenation sites on the surface.

D2- To remove C species obtained from the decomposition of methane on the surface, the catalyst should have surface sites which can adsorb CO$_2$ in order to enhance contribution of CO$_2$ on surface reaction.

D3- To have higher reaction rate, the catalyst should have the adjusted D1 and D2 sites for assisting the reaction between C and the activated CO$_2$.

D4 Because of the high temperature of reaction (1023 K), the catalyst should have thermal stability in order to preserve its physical properties.

2.4.6 CATALYST SELECTION

The major objectives for designing the catalyst are in general:

1- Recognition of the required properties of catalyst for CO$_2$ reforming of CH$_4$,
2- Composition of desired catalyst,
3- Selecting the catalyst materials,
4- Low cost and availability.
A catalyst is usually composed of active element, promoter, and support. In Table 2.5, the most commonly used metals used in catalysts are shown (Anderson, 1975).

**Table 2.5 Physical data of common metals used as catalyst**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Atomic weight</th>
<th>Crystal structure</th>
<th>Lattice parameter (nm)</th>
<th>Neighbour atomic distance (nm)</th>
<th>Melting point (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>26.98</td>
<td>f.c.c.</td>
<td>0.404</td>
<td>0.286</td>
<td>1033</td>
</tr>
<tr>
<td>Ba</td>
<td>137.34</td>
<td>b.c.c.</td>
<td>0.501</td>
<td>0.434</td>
<td>998</td>
</tr>
<tr>
<td>Cr</td>
<td>52.00</td>
<td>b.c.c.</td>
<td>0.289</td>
<td>0.249</td>
<td>2163</td>
</tr>
<tr>
<td>Co</td>
<td>48.93</td>
<td>f.c.c.</td>
<td>0.355</td>
<td>0.251</td>
<td>1768</td>
</tr>
<tr>
<td>Cu</td>
<td>63.54</td>
<td>f.c.c.</td>
<td>0.361</td>
<td>0.255</td>
<td>1356</td>
</tr>
<tr>
<td>Ir</td>
<td>192.20</td>
<td>f.c.c.</td>
<td>0.383</td>
<td>0.271</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>55.85</td>
<td>b.c.c.</td>
<td>0.286</td>
<td>0.248</td>
<td>1808</td>
</tr>
<tr>
<td>La</td>
<td>138.91</td>
<td>h.c.p.</td>
<td>0.372; 0.606</td>
<td>0.371</td>
<td>1193</td>
</tr>
<tr>
<td>Mg</td>
<td>24.31</td>
<td>h.c.p.</td>
<td>0.321; 0.521</td>
<td>0.320</td>
<td>924</td>
</tr>
<tr>
<td>Mn</td>
<td>54.94</td>
<td>Complex</td>
<td>-</td>
<td>-</td>
<td>1517</td>
</tr>
<tr>
<td>Mo</td>
<td>95.94</td>
<td>b.c.c.</td>
<td>0.314</td>
<td>0.272</td>
<td>2883</td>
</tr>
<tr>
<td>Ni</td>
<td>58.71</td>
<td>f.c.c.</td>
<td>0.352</td>
<td>0.249</td>
<td>1726</td>
</tr>
<tr>
<td>Pd</td>
<td>106.40</td>
<td>f.c.c.</td>
<td>0.388</td>
<td>0.275</td>
<td>1825</td>
</tr>
<tr>
<td>Pt</td>
<td>195.09</td>
<td>f.c.c.</td>
<td>0.392</td>
<td>0.277</td>
<td>2042</td>
</tr>
<tr>
<td>K</td>
<td>39.10</td>
<td>b.c.c.</td>
<td>0.531</td>
<td>0.462</td>
<td>337</td>
</tr>
<tr>
<td>Re</td>
<td>186.20</td>
<td>h.c.p.</td>
<td>0.276; 0.445</td>
<td>0.274</td>
<td>3453</td>
</tr>
<tr>
<td>Rh</td>
<td>102.91</td>
<td>f.c.c.</td>
<td>0.380</td>
<td>0.268</td>
<td>2239</td>
</tr>
</tbody>
</table>
Table 2.5 Continued

<table>
<thead>
<tr>
<th>Metal</th>
<th>Atomic weight</th>
<th>Crystal structure</th>
<th>Lattice parameter (nm)</th>
<th>Neighbour atomic distance (nm)</th>
<th>Melting point (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>101.07</td>
<td>h.c.p.</td>
<td>0.270; 0.427</td>
<td>0.267</td>
<td>2523</td>
</tr>
<tr>
<td>Ag</td>
<td>197.87</td>
<td>f.c.c.</td>
<td>0.408</td>
<td>0.288</td>
<td>1234</td>
</tr>
<tr>
<td>Na</td>
<td>22.99</td>
<td>b.c.c.</td>
<td>0.428</td>
<td>0.371</td>
<td>371</td>
</tr>
<tr>
<td>Ti</td>
<td>47.96</td>
<td>h.c.p.</td>
<td>0.295; 0.468</td>
<td>0.293</td>
<td>1948</td>
</tr>
<tr>
<td>W</td>
<td>183.85</td>
<td>b.c.c.</td>
<td>0.316</td>
<td>0.274</td>
<td>3683</td>
</tr>
<tr>
<td>V</td>
<td>50.94</td>
<td>b.c.c.</td>
<td>0.302</td>
<td>0.263</td>
<td>2163</td>
</tr>
<tr>
<td>Zn</td>
<td>65.37</td>
<td>h.c.p.</td>
<td>0.266; 0.494</td>
<td>0.266</td>
<td>692</td>
</tr>
<tr>
<td>Zr</td>
<td>91.22</td>
<td>h.c.p.</td>
<td>0.322; 0.512</td>
<td>0.319</td>
<td>2125</td>
</tr>
</tbody>
</table>

It is well known that the transition metals are mainly used for dry reforming reaction. Trimm (1980) has reported the order of activity of metal catalysts that are used for hydrogenation or dehydrogenation as follows:

Ru, Pd, Ir, Pt, Rh > Ni, Co, Fe > W, Cr-Cu

From another point of view, the stability of number of metals increases in the following order (Satterfield, 1991):

Cu < Au < Pd < Ni < Co < Pt < Rh < Ir

The industry prefers non-precious metal-based catalyst for their lower cost and ease of availability. Ni is chosen because of its high activity and ease of use. The
deactivation of Ni is the main area of concern. An optimum selection of promoter and support may resolve the deactivation related issue of Ni. Takanabe et al. (2005) found that a homogeneous alloy of Ni and Co and a small Ni substitution of Co increase the activity, stability, and resistance to metal oxidation.

From thermodynamic point of view in order to achieve more conversion of reactants, the reaction should take place at high temperatures. Therefore, the support should be composed of high melting point materials to enhance the resistance to sintering by producing a stable surface (D4). The stability against sintering will decrease in the following order (Satterfield, 1991):

\[ \text{MgO} > \text{Al}_2\text{O}_3 > \text{SiO}_2 > \text{TiO}_2 \]

Therefore MgO is selected because of its high melting point (3346 K) and stability against sintering. Also, since MgO has more basic sites, it can enrich the activation and participation of acidic CO\textsubscript{2} in the reaction (D2). The major problem of MgO is its low surface area. To increase the total surface area, Al\textsubscript{2}O\textsubscript{3} was selected because of having large surface area to be combined with MgO. Therefore, AlMgO\textsubscript{x} has a high thermal stability due to MgO, and high surface area due to Al\textsubscript{2}O\textsubscript{3}. Also, by choosing the optimum catalyst preparation method, we can achieve the purpose of D3 (Zhang, et al., 2007). Therefore, it was decided to prepare Ni-Co/AlMgO\textsubscript{x} bimetallic catalyst for CO\textsubscript{2} reforming of CH\textsubscript{4}.  

27
2.5 CATALYST PREPARATION METHODS AND PROCEDURES

Usually, the industrial catalysts are produced by using either impregnation or precipitation method. Each method has its own advantages and disadvantages comparing with the other method. The following sections describe both precipitation and impregnation methods.

2.5.1 PRECIPITATION METHOD

This method is commonly comprised of a solution of aqueous metal salt which is combined with a reagent to cause precipitation (co-precipitation) of an insoluble metal species. After that the filtration and washing, drying, calcination, and forming of the catalyst are carried out to finally produce the catalyst. The following steps are used for the participation procedure:

1) **Solution Preparation:** Metal solution is prepared by dissolving the metal (Ni, Co, Al, and Mg) nitrates in di-ionized water. The solution made is based on the composition of the desired catalyst.

2) **Precipitation:** The precipitation of metal in solution is carried out by adjusting the pH of the solution. This is done by adding ammonium hydroxide (NH$_4$OH) as a reagent.

3) **Filtering and washing:** To remove undesired ions and water, the solution is washed and filtered at room temperature. The washing step is stopped when the pH value of the water after washing reaches to 7. The phenomena can be observed from the color of the after-wash water which needs to be clear. Through this step, a precipitated cake is produced.
4) **Drying:** To remove the water content in the precipitated cake, the cake is dried in an oven at 120 °C for overnight (i.e. 16 h minimum). The presence of water in the catalyst may lead to severe effects on the catalyst.

5) **Calcination:** This is one of the most important pre-treatment steps for making the catalyst. The dried catalyst is generally calcined in an oven at temperatures slightly higher than the reaction temperature. The catalyst is calcined at 850 °C in air for 6 h.

6) **Forming operation:** after calcination, the catalyst is grinded and sieved to particle sizes between No.45 and No.60 U.S.A standard testing sieves (A.S.T.M. E-11 specification) which correspond to catalyst size between 250 and 355 micrometer. The selection of the catalyst size is based on a smaller pressure drop in the packed bed reactor.

Figure 2.4 briefly shows the precipitation procedure. Also, Figure 2.5 Shows a schematic of the experimental set-up which used for catalyst production.

![Flowchart](image)

**Fig. 2.4** Brief chart of precipitation procedure
Catalysts which are prepared with the precipitation method have some advantages as compared to the impregnated method. The major advantages can be generalized as:

1) On molecular level the catalyst components form a uniform mixture.

2) Catalyst has uniform distribution of active species.

However, precipitation method may be costly than the impregnation method because a significant amount of active components remain inside the catalyst bulk in comparison with the impregnated method. Also, it is hard to produce a catalyst with very small particle size and surface area greater than 200 m$^2$/g (Wijngaarden et al., 1998).

![Diagram of experimental setup for catalyst preparation](image)
2.5.2 Impregnation Method

In this method, a support is made first which is based upon the participated procedure. Then the support is dipped into excess amount of solution of metal salts, or the metal solution is sprayed on the support. The metal uptake by the support is the sum of the solution occluded inside the pores of the support and the material adsorbed on the pore surface. The catalyst is finally produced after drying and calcination. Figure 2.6 shows the procedure of impregnation method.

**Fig. 2.6** Summary chart of impregnation procedure

The major advantages of impregnation method are:

1) Ability to use commercially available catalyst

2) Lower cost than precipitation method, especially in case of valuable metals,

3) Separation between the metal active phase and the support phase is clear

Based on the above description a comparison is made in Table 2.6 between the impregnation method and the precipitated method.
Table 2.6 Comparison chart of catalyst preparation method

<table>
<thead>
<tr>
<th>Description</th>
<th>Impregnation method</th>
<th>Precipitation method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular scale mixing of catalyst components</td>
<td>Difficult</td>
<td>Easy</td>
</tr>
<tr>
<td>Uniform distribution of multi-active components</td>
<td>Difficult</td>
<td>Easy</td>
</tr>
<tr>
<td>Surface area up to 200 m²/g</td>
<td>Easy</td>
<td>Easy</td>
</tr>
<tr>
<td>Surface area more than 200 m²/g</td>
<td>Easy</td>
<td>Difficult</td>
</tr>
<tr>
<td>High metal loading</td>
<td>Difficult</td>
<td>Easy</td>
</tr>
<tr>
<td>High metal dispersion</td>
<td>Easy</td>
<td>Easy</td>
</tr>
<tr>
<td>Instrument availability</td>
<td>Easy</td>
<td>Easy</td>
</tr>
<tr>
<td>Relative cost</td>
<td>Easy</td>
<td>Difficult</td>
</tr>
</tbody>
</table>

2.6 KNOWLEDGE GAP

The Ni-Co bimetallic catalyst prepared by precipitation method in our research group is known as a novel and new-developed catalyst for CDRM reaction. Based on the previous work and literature review the following knowledge gaps are concluded toward commercialization:

1- Effect of preparation methods of Ni-Co/AlMgOₓ bimetallic, Ni/AlMgOₓ monometallic and Co/AlMgOₓ monometallic catalyst performance on CDRM reaction need to be evaluated.
2- Effect of various Ni/Co ratios on performance of Ni-Co/AlMgO\textsubscript{x} bimetallic catalyst running CDRM reaction has not been studied.

3- Performance of the Ni-Co/AlMgO\textsubscript{x} bimetallic, Ni/AlMgO\textsubscript{x} monometallic and Co/AlMgO\textsubscript{x} monometallic catalyst while poisoned by H\textsubscript{2}S during CDRM reaction has not been investigated yet.

2.7 RESEARCH OBJECTIVES AND THESIS SCOPE

The following questions will be answered as the specific objectives:

- What are the effects of different Ni/Co ratios on the activity and stability of the Ni-Co bimetallic catalyst for CDRM reaction?
- What are the effects of the Ni monometallic and Co monometallic catalysts for CDRM reaction?
- What are the effects of preparation method on the Ni-Co/AlMgO\textsubscript{x} bimetallic, Ni monometallic and Co monometallic catalysts for CDRM reaction?
- How the Ni-Co/AlMgO\textsubscript{x} bimetallic, Ni monometallic and Co monometallic catalysts prepared by precipitation and impregnation with various Ni/Co ratios will act for CDRM reaction if the catalysts are poisoned by H\textsubscript{2}S? Which catalyst(s) have the best performance after the H\textsubscript{2}S poisoning?
CHAPTER 3: EXPERIMENTAL SET-UP AND PROCEDURE

This chapter describes the reactor set-up and the experimental procedure used for the catalyst activity for CDRM reaction.

3.1 EXPERIMENTAL PROCEDURE

3.1.1 CATALYST PREPARATION PROCEDURE

According to Zhang’s observations Ni-Co bimetallic, Ni monometallic, and Co monometallic catalysts can be prepared by both precipitation and impregnation methods (Zhang, 2008). Different catalysts were prepared in order to observe the effects of preparation methods and various Ni/Co ratios. In the following sections, the term “catalyst” is used for Ni-Co/AlMgOₓ bimetallic catalyst. (Zhang et al., 2007)

In preparing precipitated catalysts, all of the Ni-Co/AlMgOₓ catalysts (5-7 metal wt %) were prepared by using nickel nitrate (hexahydrate; Alfa Aesar), cobalt nitrate (hexahydrate; Alfa Aesar), aluminum nitrate (nanohydrate; Alfa Aesar), and magnesium nitrate (hxahydrate; Alfa Aesar). The ammonium hydroxide (EMD Chemicals) was used as a reagent. After preparation, the obtained product was washed and filtered with 2 L of de-ionized water, and then dried and calcined in air at 120 °C (overnight) and 850 °C (for 6h), respectively. Finally, the product was grinded and sieved to get the desired catalyst.
In order to prepare impregnated catalysts, the Al-Mg support was prepared first. The support was prepared by using the precipitation technique, and then the metal solution was added to it. The important part in this preparation was the volume of the metal solution that is added to the support. Several ways are available to find the amount of metal solution that is required to be added to the support. One of the methods adopted after support preparation and calcination was that, the required volume of the metal solution measured by adding water to the known amount of support. The procedure was the addition of water on the support until the first drop of water appeared on the surface of the support which indicated that the catalyst support was saturated and was not able to absorb water anymore. At this point the support and the water were mixed together like a paste. This condition was indicative of the amount of metal solution that was required by the support. As an example, for each gram of prepared support 1.2 mL of de-ionized water was added.

Based on the desired Ni/Co ratio, the metal solution was prepared and sprayed onto the surface of the prepared support. The catalysts were then dried and calcined to obtain the desired catalyst.

Ni-Co/AlMgOₓ bimetallic catalysts were prepared by both precipitation and impregnation methods using different Ni/Co ratios of 0.5, 1, and 2. Also, Ni/AlMgOₓ and Co/AlMgOₓ monometallic catalysts were prepared using both impregnation and precipitation methods. In Tables 3.1 and 3.2, the names and compositions of the prepared catalysts are summarized.
### Table 3.1 Chemicals and amounts used for preparation of catalysts by precipitated

<table>
<thead>
<tr>
<th>Name</th>
<th>Intent</th>
<th>Ni/Co</th>
<th>Ni(NO(_3))(_2) (g)</th>
<th>Co(NO(_3))(_2) (g)</th>
<th>Al(NO(_3))(_3) (g)</th>
<th>Mg(NO(_3))(_2) (g)</th>
<th>Water (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CopCat-Co6</td>
<td>Only Co</td>
<td>-</td>
<td>6.0000</td>
<td>50.0005</td>
<td>124.0004</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>CopCat-Ni1Co4</td>
<td>0.5</td>
<td>2.0001</td>
<td>4.0003</td>
<td>50.0004</td>
<td>124.0004</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>CopCat-Ni2Co4</td>
<td>1</td>
<td>3.0008</td>
<td>3.0008</td>
<td>25.0000</td>
<td>124.0006</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td>CopCat-Ni3Co2</td>
<td>2</td>
<td>3.9198</td>
<td>1.9600</td>
<td>48.9923</td>
<td>121.5005</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>CopCat-Ni4</td>
<td>Only Ni</td>
<td>6.0000</td>
<td>-</td>
<td>50.0004</td>
<td>124.0005</td>
<td>500</td>
<td></td>
</tr>
</tbody>
</table>

### Table 3.2 Chemicals and amounts used for preparation of catalysts by impregnation

<table>
<thead>
<tr>
<th>Name</th>
<th>Intent</th>
<th>Ni/Co</th>
<th>Ni(NO(_3))(_2) (g)</th>
<th>Co(NO(_3))(_2) (g)</th>
<th>AlMgO(_x) (g)</th>
<th>Water (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ImpCat-Co5</td>
<td>Only Co</td>
<td>-</td>
<td>0.7974</td>
<td>2.5300</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>ImpCat-Ni2Co3</td>
<td>0.5</td>
<td>0.2649</td>
<td>0.5267</td>
<td>2.5030</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>ImpCat-Ni3Co3</td>
<td>1</td>
<td>0.3960</td>
<td>0.3947</td>
<td>2.5030</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>ImpCat-Ni3Co2</td>
<td>2</td>
<td>0.5278</td>
<td>0.2633</td>
<td>2.5020</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>ImpCat-Ni5</td>
<td>Only Ni</td>
<td>0.7913</td>
<td>-</td>
<td>2.5020</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>
3.1.2 CATALYST TEST PROCEDURE

After preparing all the Ni-Co/AlMgOₓ bimetallic and monometallic catalysts by using precipitation and impregnation methods the following analytical and experimental procedures were used for each catalyst:

1) BET surface area of all the samples was analyzed by using the prepared catalysts in powder form. The BET was re-analyzed for couple of catalysts to make sure the reproducibility of the results.

2) ICP analysis was done to observe the amount of Ni, Co, Al, and Mg in the catalyst. Also, the analysis was repeated for couple of catalysts for reproducibility.

3) XAS analysis of the catalysts was done by professor Hui Wang at ANL after catalyst reduction (H₂ (3.5%) + He at 750 °C in a cell reactor).

4) The activity test was done on each catalyst by carrying out the reaction of carbon dioxide reforming of methane. A quartz tube was used as the reactor.

5) After the activity test, the sulfur poisoning was carried by using 30 ppm of H₂S as a catalyst poison.

6) The results from above were analyzed and are reported in the subsequent sections.

3.2 CATALYST CHARACTERIZATION ANALYSES

3.2.1 BET SURFACE AREA

BET surface area is known as an important property for many kinds of materials and especially solid catalysts. B.E.T. (or BET) stands for Brunauer, Emmett, and Teller,
the scientists who proposed the theory for measuring the surface area (Brunauer et al., 1938). The concept of the theory is based on the Langmuir theory. Different methods are used to calculate and measure the BET surface area, but most of them are based on isothermal adsorption of nitrogen. The BET is measured by the use of nitrogen adsorption/desorption isotherms at liquid nitrogen temperature and relative pressures. For the experiments, the BET surface area machine from Micromeritics (ASAP 2020, Surface Area and Porosity Analyzer) in Department of Chemical and Biological Engineering, University of Saskatchewan was used.

3.2.2 ICP ANALYSIS

Inductively Coupled Plasma or ICP is an analytical technique used for elemental determination. By using ICP, the compositions of prepared catalyst are analyzed. The ICP analysis was done with analysing the catalysts in the Department of Geology, University of Saskatchewan using ICP-MS machine from Perkin Elmer (Nexion 300D).

3.2.3 XAS ANALYSIS

To observe the electronic arrangement and/or local geometry of the catalyst, X-ray Absorption Spectroscopy (XAS) is a well-developed technique. The experiment usually is performed in a synchrotron by using X-ray beam-lines.

To further understand of particle size growth of the catalysts during the reduction condition, XAFS and EXANS analysis were analyzed by professor Hui Wang by using the Advanced Photon Source (APS) synchrotron at Argonne National Laboratory (ANL).
3.3 **EXPERIMENTAL SET-UP OF CATALYST TESTING**

Three sets of experiments were carried out for CDRM reaction. The catalyst activity test was used to determine the most active catalyst among the prepared catalysts. The life-time test was conducted to determine the stability of the optimum catalyst. Finally the catalyst poisoning test was carried out to determine the regeneration trend of the prepared catalysts.

### 3.3.1 **CATALYST ACTIVITY TEST**

The catalysts were evaluated in a fixed bed quartz reactor with 6 mm ID and 30 cm in length. The test was carried out until the catalyst activity became stable for methane conversion. In order to compare the effects of both Ni/Co ratio and preparation method, a 0.02 g of each catalyst was mixed with 0.48 g of quartz sand. The average particle size of the catalysts was 300 nm. The catalysts were loaded in the middle of the reactor. Before the testing, the catalysts were reduced in presence of H$_2$:N$_2$ with ratio of 1:4 at 800 °C for 4 h. For reduction H$_2$ (99.9% purity, Praxair Canada Inc.), and N$_2$ (99.9% purity, Praxair Canada Inc.) were used. The testing was carried out at 710 °C and GHSV (Gas Hour Space Velocity) of 558,000 (mL/g$_c$.h). The reactant gas consisting of an equimolar mixture of N$_2$ (99.9% purity, Praxair Canada Inc.), CH$_4$ (99.2% purity, Praxair Canada Inc.) and CO$_2$ (99.9% purity, Praxair Canada Inc.) was injected to the reactor. The product gas was analysed by an on-line Agilent 6890N GC, equipped with TCD and a GS-GASPRO capillary column (J&W Scientific) of 60 m in length and 0.32 mm of inner diameter using GC ChemStation software (Rev.b.04.02(96)). Helium (Ultra high purity 5.0, PRAXAIR Canada Inc.) was used as
the carrier gas. Finally, the obtained data was analyzed, based on the procedure and equations which are explained in section 3.4.

3.3.2 CATALYST LIFE-TIME TEST

The Ni-Co/AlMgO₅ bimetallic catalyst as prepared by precipitation method was evaluated for life-time test for 65 days in the same set-up as explained in section 3.3.1. The reaction conditions were different from the catalyst activity test. The catalyst load was 0.05 g which was mixed with 0.45 g of sand. The average particle size was 300 nm. The catalyst was loaded in the middle of the reactor and reduced at 800 °C for 4 h in presence of H₂:N₂ mixture with the ratio of 1:4. The testing was carried out at 710 °C and GHSV (Gas Hour Space Velocity) of 110,000 (mL/gₐ. h) with equimolar flow rates of CH₄, CO₂ and N₂.

3.3.3 H₂S POISONING TEST

Running the tests three sections are distinguished called “before poisoning” (P-1), “during poisoning” (P-2), and “after poisoning” (P-3). The reaction conditions for the P-1 and P-3 sections were the same as explained in section 3.3.1. For the P-2, the flow rates of the gases were adjusted in order to keep the equimolar mixture of CH₄, CO₂, and N₂. Depending on instrument limitations, catalyst loadings, and poison availability a certain value of poisonous gas is chosen. The catalysts were poisoned by 30 ppm of H₂S and the temperature of the reaction was kept constant at 710 °C (the beginning of P-2). Then to make sure that all the catalysts are poisoned, the H₂S poisoning was stopped as soon as GC could not recognize the H₂ peak (the end of P-2).
Disappearance of hydrogen peak indicates that the catalyst is totally poisoned with H$_2$S. Then the flow rates of CH$_4$, CO$_2$, and N$_2$ gases were adjusted to the condition prior to the poisoning (beginning of P-3). It is notable that in this section time zero points to the time at which H$_2$S was injected to the reactor (beginning of P-2).

### 3.4 DATA ANALYSIS PROCEDURE

The conversion of reactants and yield of the products are calculated based on the following explained procedure. Consider $X_i$ (volume/volume) obtained as the GC result:

\[
X_i = \frac{F_{out,i}}{\sum_i F_{out,i}}
\]

(3.1)

where, $F_{out,i}$ is flow rate of component “i” after the reaction (mL/min) and “i” could be CO$_2$, CH$_4$, N$_2$, H$_2$, or CO.

The flow rate of each component exiting from the reactor is calculated based on N$_2$ which is constant during the reaction. N$_2$ does not react with the other existing components in the CDRM reaction.

For example the flow rate of product containing methane can be calculated by the following procedure:

\[
X_{N_2} = \frac{F_{out,N_2}}{\sum_i F_{out,i}}
\]

(3.2)

\[
X_{CH_4} = \frac{F_{out,CH_4}}{\sum_i F_{out,i}}
\]

(3.3)

Dividing Eq. 3.3 by Eq. 3.2:
\[
\frac{F_{\text{out}, \text{CH}_4}}{F_{\text{out}, \text{N}_2}} = \frac{x_{\text{CH}_4}}{x_{\text{N}_2}} \rightarrow F_{\text{out}, \text{CH}_4} = F_{\text{out}, \text{N}_2} \times \frac{x_{\text{CH}_4}}{x_{\text{N}_2}} \tag{3.4}
\]

So, like the above procedure, Eq. 3.4 is generalized for the other component.

\[
F_{\text{out}, i} = F_{\text{out}, \text{N}_2} \times \frac{x_{\text{N}_2}}{x_1}, \text{ i: CO}_2, \text{ CH}_4, \text{ N}_2, \text{ H}_2, \text{ CO} \tag{3.5}
\]

where, \( F_{\text{out}, i} \) means the flow rate of component “i” which is exiting from reactor.

Since \( \text{N}_2 \) does not react during CDRM reaction, therefore \( F_{\text{out}, \text{N}_2} \) is equal to \( F_{\text{in}, \text{N}_2} \). The values of \( x_i \) are obtained from GC, therefore \( F_{\text{out}, i} \) can be calculated from Eq. 3.5.

The reactant conversion can be obtained from Eq. 3.6 and 3.7.

\[
\text{Methane (CH}_4 \text{) conversion, } \% = \frac{(F_{\text{in, CH}_4} - F_{\text{out, CH}_4})}{F_{\text{in, CH}_4}} \times 100 \tag{3.6}
\]

\[
\text{Carbon Deoxide (CO}_2 \text{) conversion, } \% = \frac{(F_{\text{in, CO}_2} - F_{\text{out, CO}_2})}{F_{\text{in, CO}_2}} \times 100 \tag{3.7}
\]

where, \( F_{\text{out}, i} \) means flow rate of component “i” after the reaction (mL/min), and \( F_{\text{in}, i} \) is flow rate of component “i” before the reaction (mL/min).

To calculate consumption rate of reactants and formation rate of products, the following equations were used:

\[
-r_{\text{reactant}} = \frac{(F_{\text{in, reactant}} - F_{\text{out, reactant}})}{m_{\text{catalyst}}} \text{, (mol/g_c.h)} \tag{3.8}
\]

\[
r_{\text{product}} = \frac{F_{\text{out, product}}}{m_{\text{catalyst}}} \text{, (mol/g_c.h)} \tag{3.9}
\]

where flow rates are used based on mol/h.
CHAPTER 4: RESULTS AND DISCUSSION

In this chapter the reproducibility of the results are firstly covered. Then a detailed discussion is carried out on the results obtained from ICP, XAS and BET surface area of the prepared catalysts. Also, the effects of Ni/Co ratios and the preparation methods on the activity and selectivity of Ni or Co monometallic and Ni-Co bimetallic catalysts running CDRM reaction are discussed. Following the catalyst tests, the stability of highly performed catalysts was evaluated for 60 days TOS. Finally, the performance of the poisoned catalysts was investigated with CDRM reaction.

4.1 REPRODUCIBILITY OF THE RESULTS

In order to observe whether the results of the study are reproducible, some of the catalysts were characterized at the second time. The percent difference of two experimental values \(x_1\) and \(x_2\) is calculated by dividing the absolute difference of them by their average value. Equation 4.1 shows the formula which was used.

\[
\text{Diff.} = \left| \frac{x_1 - x_2}{\frac{x_1 + x_2}{2}} \right| \times 100, \% \quad (4.1)
\]

For BET surface area analysis, the precipitated CopCat-Ni1Co4 catalyst with (Ni/Co ratio of 0.37) and the impregnated ImpCat-Ni3Co3 catalyst (Ni/Co ratio of 0.97) were selected. The results are shown in Table 4.1.
Table 4.1 Results of repeated BET analysis

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Try</th>
<th>CopCat-NiCo4</th>
<th>Diff., %</th>
<th>ImpCat-Ni3Co3</th>
<th>Diff., %</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET (m²/g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( x_1 )</td>
<td>94</td>
<td></td>
<td>5.5</td>
<td>103</td>
<td>1.0</td>
</tr>
<tr>
<td>( x_2 )</td>
<td>89</td>
<td></td>
<td></td>
<td>102</td>
<td></td>
</tr>
<tr>
<td>Pore volume (ml/g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( x_1 )</td>
<td>0.189</td>
<td></td>
<td>4.9</td>
<td>0.297</td>
<td>1.0</td>
</tr>
<tr>
<td>( x_2 )</td>
<td>0.180</td>
<td></td>
<td></td>
<td>0.300</td>
<td></td>
</tr>
<tr>
<td>Pore size (Å)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( x_1 )</td>
<td>80.4</td>
<td></td>
<td>0.3</td>
<td>115.4</td>
<td>1.8</td>
</tr>
<tr>
<td>( x_2 )</td>
<td>76.9</td>
<td></td>
<td></td>
<td>117.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1 indicates that the errors of the BET results, pore volume and pore size were significantly negligible.

The ICP analysis was repeated for the impregnated ImpCat-Ni2Co3 catalyst (Ni/Co ratio of 0.52) as presented in Table 4.2.

Table 4.2 Reproducibility results of ICP analysis

<table>
<thead>
<tr>
<th>ICP analysis</th>
<th>Mg (ppm)</th>
<th>Al (ppm)</th>
<th>Co (ppm)</th>
<th>Ni (ppm)</th>
<th>Mg/Al</th>
<th>Ni/Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x_1 )</td>
<td>298262</td>
<td>130774</td>
<td>36707</td>
<td>19050</td>
<td>2.28</td>
<td>0.52</td>
</tr>
<tr>
<td>( x_2 )</td>
<td>333000</td>
<td>165000</td>
<td>37600</td>
<td>19400</td>
<td>2.02</td>
<td>0.51</td>
</tr>
<tr>
<td>Diff., %</td>
<td>11.0</td>
<td>23.1</td>
<td>2.4</td>
<td>1.8</td>
<td>12.0</td>
<td>1.9</td>
</tr>
</tbody>
</table>

The measured metal content values of the same ImpCat-Ni2Co3 catalyst by ICP analysis are fairly close indicating acceptable measurement error especially in terms of Ni and Co content.
The catalyst activity test for the CopCat-Ni3Co2 (Ni/Co ratio of 1.51) catalyst prepared by precipitation method was repeated on CDRM reaction. The reaction was carried out with the same conditions which described in section 3.3.1. The first 5 h results of both tests are summarized in Table 4.3. Also, Figure 4.1 and 4.2 show reactant conversion and H₂/CO ratio for the first and second runs.

**Table 4.3** Repeated catalyst activity test results

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>CH₄ Conversion, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x_1$</td>
</tr>
<tr>
<td>1</td>
<td>52.2</td>
</tr>
<tr>
<td>2</td>
<td>48.7</td>
</tr>
<tr>
<td>3</td>
<td>46.5</td>
</tr>
<tr>
<td>4</td>
<td>43.8</td>
</tr>
<tr>
<td>5</td>
<td>41.4</td>
</tr>
</tbody>
</table>

The methane conversions are significantly close to each other for the selected catalyst (CopCat-Ni3Co2 with Ni/Co ratio of 1.51) in both runs as illustrated in Table 4.3 and Figure 4.1. Also, the calculated H₂/CO ratios are following the same trend in term of reproducibility for both runs. It can be concluded that the CopCat-Ni3Co2 (Ni/Co ratio of 1.51) catalyst showed almost the same performance (2-8% difference) during CDRM reaction implying acceptable results accuracy.
Fig. 4.1 Methane conversion for the repeated catalyst activity test; reaction conditions: 710 °C, 1 atm, 558000 mL/gₜ.ₜ (GHSV), CH₄/CO₂/N₂=1/1/1, catalyst loading of 0.02 g

Fig. 4.2 H₂/CO ratio of the repeated catalyst activity test; reaction conditions: 710 °C, 1 atm, 558000 mL/gₜ.ₜ (GHSV), CH₄/CO₂/N₂=1/1/1, catalyst loading of 0.02 g
4.2 CATALYST CHARACTERIZATION

4.2.1 BET SURFACE AREA

Table 4.4 shows BET analysis results of prepared catalyst.

Table 4.4 BET surface area of the prepared Ni-Co/AlMgOₓ bimetallic catalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET (m²/g)</th>
<th>Pore volume (mL/g)</th>
<th>Pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CopCat-Co6</td>
<td>106</td>
<td>0.277</td>
<td>105</td>
</tr>
<tr>
<td>CopCat-Ni1Co4</td>
<td>94</td>
<td>0.189</td>
<td>80</td>
</tr>
<tr>
<td>CopCat-Ni2Co4</td>
<td>111</td>
<td>0.287</td>
<td>104</td>
</tr>
<tr>
<td>CopCat-Ni3Co2</td>
<td>110</td>
<td>0.246</td>
<td>89</td>
</tr>
<tr>
<td>CopCat-Ni4</td>
<td>113</td>
<td>0.227</td>
<td>81</td>
</tr>
<tr>
<td>Support (AlMgOₓ)</td>
<td>85</td>
<td>0.226</td>
<td>106</td>
</tr>
<tr>
<td>ImpCat-Co5</td>
<td>102</td>
<td>0.296</td>
<td>116</td>
</tr>
<tr>
<td>ImpCat-Ni2Co3</td>
<td>124</td>
<td>0.359</td>
<td>116</td>
</tr>
<tr>
<td>ImpCat-Ni3Co3</td>
<td>103</td>
<td>0.297</td>
<td>115</td>
</tr>
<tr>
<td>ImpCat-Ni3Co2</td>
<td>112</td>
<td>0.328</td>
<td>118</td>
</tr>
<tr>
<td>ImpCat-Ni5</td>
<td>114</td>
<td>0.340</td>
<td>119</td>
</tr>
</tbody>
</table>

Table 4.4 indicates that the difference between BET surface areas of all the prepared catalysts is negligible. BET surface area of almost all the prepared catalysts was greater than 100 (m²/g) which is good enough for CDRM reaction. The other basic information from Table 4.4 is that the impregnated catalysts have larger pore volume and pore size as compared to precipitated catalysts. Moreover, the difference in pore
sizes of all the impregnated catalysts is negligible. Also, the precipitated catalyst with Ni/Co ratio of 1 (CopCat-Ni2Co4) had the largest pore volume and pore size among the other precipitated catalysts.

4.2.2 ICP ANALYSIS

According to Table 4.5 the Ni/Co ratios of the precipitated catalysts are lower than the intent Ni/Co ratio, while that of impregnated samples are fairly close the intent one.

Table 4.5 Metal composition of Ni-Co/AlMgO_x bimetallic and Ni or Co metallic catalysts by ICP analysis (Intent Mg/Al ratio for all the catalysts is 2)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Intent Ni/Co</th>
<th>Ni</th>
<th>Co</th>
<th>Mg</th>
<th>Al</th>
<th>Ni/Co</th>
<th>Mg/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>CopCat-Co6</td>
<td>0</td>
<td>6</td>
<td>69</td>
<td>26</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CopCat-Ni1Co4</td>
<td>0.5</td>
<td>1</td>
<td>4</td>
<td>67</td>
<td>28</td>
<td>0.4</td>
<td>2.4</td>
</tr>
<tr>
<td>CopCat-Ni2Co4</td>
<td>1.0</td>
<td>2</td>
<td>4</td>
<td>68</td>
<td>26</td>
<td>0.6</td>
<td>2.6</td>
</tr>
<tr>
<td>CopCat-Ni3Co2</td>
<td>2.0</td>
<td>3</td>
<td>2</td>
<td>60</td>
<td>35</td>
<td>1.5</td>
<td>1.7</td>
</tr>
<tr>
<td>CopCat-Ni4</td>
<td>4</td>
<td>0</td>
<td></td>
<td>69</td>
<td>27</td>
<td></td>
<td>2.6</td>
</tr>
<tr>
<td>Support (AlMgO_x)</td>
<td></td>
<td></td>
<td></td>
<td>69</td>
<td>31</td>
<td></td>
<td>2.2</td>
</tr>
<tr>
<td>ImpCat-Co5</td>
<td>0</td>
<td>5</td>
<td></td>
<td>65</td>
<td>30</td>
<td></td>
<td>2.1</td>
</tr>
<tr>
<td>ImpCat-Ni2Co3</td>
<td>0.5</td>
<td>2</td>
<td>3</td>
<td>68</td>
<td>27</td>
<td>0.5</td>
<td>2.5</td>
</tr>
<tr>
<td>ImpCat-Ni3Co3</td>
<td>1.0</td>
<td>3</td>
<td>3</td>
<td>67</td>
<td>27</td>
<td>1.0</td>
<td>2.5</td>
</tr>
<tr>
<td>ImpCat-Ni3Co2</td>
<td>2.0</td>
<td>3</td>
<td>2</td>
<td>66</td>
<td>29</td>
<td>1.9</td>
<td>2.3</td>
</tr>
<tr>
<td>ImpCat-Ni5</td>
<td>5</td>
<td>0</td>
<td></td>
<td>65</td>
<td>30</td>
<td></td>
<td>2.2</td>
</tr>
</tbody>
</table>

* All the numbers are rounded based on the ICP results
The metal nitrates solutions affect the pH controlling step of precipitation method. Because of pH variation the obtained Ni/Co ratios might be different from the intent Ni/Co ratios. On the other hand, controlling the amount of metal contents is much easier in impregnation method than the precipitation method resulting in the similarity of intent and obtained Ni/Co ratio which is attributed to the nature of impregnation method.

Regarding the obtained Mg/Al ratio of MgAlO\textsubscript{x} support prepared by precipitation method, the same behaviour is observed as for the Ni/Co ratio.

Using precipitation procedure for catalyst preparation, the metal nitrates will dissolve in water in the form of metal ions which will precipitate as metal hydroxides. The amount of precipitated metal hydroxide is dependent of the related solubility product (K\textsubscript{sp}). The higher obtained ratio of Mg/Al than the intent one may be due to the higher K\textsubscript{sp} value of Mg(OH)\textsubscript{2} than Al(OH)\textsubscript{3}. The same phenomenon clarifies the variant values for metal ratios (Ni/Co ratio). K\textsubscript{sp} values are shown in Table 4.6.

**Table 4.6** Solubility products of metal hydroxides at 25 °C

\[
\begin{array}{ccccc}
\text{Metal hydroxide} & \text{Mg(OH)\textsubscript{2}} & \text{Al(OH)\textsubscript{3}} & \text{Ni(OH)\textsubscript{2}} & \text{Co(OH)\textsubscript{2}} \\
K\textsubscript{sp} & 5.61\times10^{-12} & 3\times10^{-34} & 5.48\times10^{-16} & 5.92\times10^{-15} \\
\end{array}
\]

Unlike precipitation method, the Ni and Co nitrates do not contribute to the pH controlling step of preparation; therefore, by using impregnation method, the possibility of Ni and Co hydroxides precipitations is reduced resulting in a negligible difference.
between Ni/Co intent ratio and the actually obtained. The results are shown in Table 4.5 and Figure 4.5.

![Graph showing the effect of preparation method on Ni/Co ratios.](image)

**Fig. 4.3** Effect of preparation method on the intent Ni/Co ratios of the bimetallic catalysts after preparation

The effect of catalyst preparation methods on the intent Mg/Al ratio of the catalyst support is shown in Figure 4.4. It can be seen that the Mg/Al ratios are closed to each other for all the catalyst as for all the support prepared by precipitation procedure. The difference between Mg/Al ratio and related intent value might be because of the difference between solubility product of Mg and Al hydroxides as shown in Table 4.6.
Effect of preparation method on the obtained Mg/Al ratios of the catalysts after preparation

4.2.3 XAS ANALYSIS

All the prepared catalysts (Table 3.1 and Table 3.2) was reduced in a cell reactor in the presence of H₂ (3.5%) and He mixture at 750 °C or 850 °C for 4 h. The catalysts were cooled down to the room temperature in presence of He. With He protection in the cell reactor, the XAS was scanned. Then EXANS data were analyzed with WinXas3.2 software to get the numerical results.

During catalyst reduction, some amounts of metal were reduced in metal forms. Zhang et al. (2007) observed that in order to have an active Ni-Co/AlMgOₓ bimetallic catalyst, metal particle size of the reduced catalyst should be smaller than 100 Å. In the precipitation method the metal particles grow inside the pores of the support that allows limited growth of particles. On the other hand, in impregnation method the metal
particles grow on the surface of the support which does not limit the metal particle size. Therefore the final metal particle size after reduction is bigger in impregnated catalyst as compared to the precipitated catalyst. In impregnation method the metals acquire the position on the prepared surface; therefore during the reduction process the metals easily migrate and grow to bigger particles. While in precipitation it is harder for metals to migrate and grow as they are located inside the support structure.

The Ni K-edge and Co K-edge of the precipitated CopCat-Ni2Co4 catalyst (with Ni/Co ratio of 0.6) was analyzed at 750 °C and 850 °C. Reconsider it that the amount of reduced Co at 850 °C was greater than 750 °C. However, the particle size at 850 °C was larger than 100 Å, which is not desired for CDRM reaction according Zhang (2008).

<table>
<thead>
<tr>
<th>Precipitated catalysts</th>
<th>Treatment</th>
<th>Co-O*</th>
<th>Co</th>
<th>Co size Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>CopCat-Ni2Co4</td>
<td>750 °C , H₂</td>
<td>0.80</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>850 °C , H₂</td>
<td>0.33</td>
<td>0.67</td>
<td>&gt;100</td>
</tr>
</tbody>
</table>

*CoO is used to represent Co²⁺. It is not the exact structures in catalysts.

Table 4.8 shows XANES result of the catalysts at 750 °C reduction temperature. Table 4.8 indicates that no matter how the catalysts were prepared, the Ni reduced more than Co in all bimetallic catalysts. Also, cobalt mostly is an unreduced (Co-O-Co) form, especially in the precipitated catalysts. In precipitated catalysts, the metallic Co did not show any reducibility while with increasing Ni content; Co was able to be reduced. In the other words, increasing Ni content helps Co reduction.
Table 4.8 XANES results of the prepared catalysts, 750 °C reduction temperature, H₂ (3.5%) and He mixture

<table>
<thead>
<tr>
<th>Precipitated catalyst</th>
<th>Ni</th>
<th>NiO*</th>
<th>Co</th>
<th>CoO*</th>
<th>Impregnated catalyst</th>
<th>Ni</th>
<th>NiO*</th>
<th>Co</th>
<th>CoO*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co6</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>1</td>
<td>Co5</td>
<td>-</td>
<td>-</td>
<td>0.43</td>
<td>0.57</td>
</tr>
<tr>
<td>Ni₁Co₄</td>
<td>0.52</td>
<td>0.48</td>
<td>0.20</td>
<td>0.80</td>
<td>Ni₂Co₃</td>
<td>0.82</td>
<td>0.18</td>
<td>0.37</td>
<td>0.63</td>
</tr>
<tr>
<td>Ni₂Co₄</td>
<td>0.52</td>
<td>0.48</td>
<td>0.20</td>
<td>0.80</td>
<td>Ni₃Co₃</td>
<td>0.83</td>
<td>0.17</td>
<td>0.37</td>
<td>0.63</td>
</tr>
<tr>
<td>Ni₃Co₂</td>
<td>0.55</td>
<td>0.48</td>
<td>0.25</td>
<td>0.75</td>
<td>Ni₃Co₂</td>
<td>0.79</td>
<td>0.21</td>
<td>0.51</td>
<td>0.49</td>
</tr>
<tr>
<td>Ni₄</td>
<td>0.87</td>
<td>0.13</td>
<td>-</td>
<td>-</td>
<td>Ni₅</td>
<td>0.84</td>
<td>0.16</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* NiO and CoO are used to represent Ni²⁺ and Co²⁺. They are not the exact structures in catalysts.

Table 4.8 shows that impregnated catalysts are reduced more in form of metals, especially in case of Co which was almost two times as compared to the precipitated catalysts. Furthermore, the Co monometallic catalyst prepared by precipitation method did not show any reduction ability of metal, whereas, the Co from impregnation method showed 43% reduction.

The EXAFS analysis was carried out to obtain the information about the particle size. Table 4.9 shows EXAFS result of the catalysts at 750 °C reduction temperature. Table 4.9 represents that the precipitated catalysts grow smaller particle sizes than the impregnated catalysts as explained earlier. Also, the Co monometallic impregnated catalyst has the reduced particle size greater than 100 Å which is not favoured for CDRM reaction.
Table 4.9 EXAFS results of the prepared catalysts, 750 °C reduction temperature, H₂ (3.5%) and He mixture

<table>
<thead>
<tr>
<th>Precipitated catalyst</th>
<th>Ni-Ni Bond, Å</th>
<th>Particle Size, Å</th>
<th>Co-Co Bond, Å</th>
<th>Particle Size, Å</th>
<th>Impregnated catalyst</th>
<th>Ni-Ni Bond, Å</th>
<th>Particle Size, Å</th>
<th>Co-Co Bond, Å</th>
<th>Particle Size, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Co5</td>
<td>2.50</td>
<td>&gt;100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni1Co4</td>
<td>2.50</td>
<td>40</td>
<td>2.51</td>
<td>-</td>
<td>Ni2Co3</td>
<td>2.48</td>
<td>80</td>
<td>2.50</td>
<td>80</td>
</tr>
<tr>
<td>Ni2Co4</td>
<td>2.49</td>
<td>40</td>
<td>2.51</td>
<td>-</td>
<td>Ni3Co3</td>
<td>2.48</td>
<td>75</td>
<td>2.49</td>
<td>80</td>
</tr>
<tr>
<td>Ni3Co2</td>
<td>2.50</td>
<td>50</td>
<td>2.51</td>
<td>-</td>
<td>Ni3Co2</td>
<td>2.48</td>
<td>90</td>
<td>2.49</td>
<td>80</td>
</tr>
<tr>
<td>Ni4</td>
<td>2.48</td>
<td>70</td>
<td>-</td>
<td>-</td>
<td>Ni5</td>
<td>2.48</td>
<td>90</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* NiO and CoO are used to represent Ni²⁺ and Co²⁺. They are not the exact structures in catalysts.

Table 4.9 indicates that the reduced metal particle size was lower than 100 Å for the bimetallic catalysts that were prepared at 750 °C. However, the particle size was more than 100 Å for precipitated CopCat-Ni2Co4 catalyst at 850 °C (Table 4.7). EXAFS results showed that the reduced Co size in the ImpCat-Co5 catalyst was more than 100 Å. This means that the Co monometallic impregnated catalyst may not have desired activity in comparison with other catalysts.

Table 4.10 and 4.11 show a summary of XAS and ICP analysis done on the prepared catalysts.
Table 4.10 Reduced metal content (wt %) of precipitated catalysts from XANES and ICP results

<table>
<thead>
<tr>
<th>Participated catalysts</th>
<th>Nickel content (wt %)</th>
<th>Cobalt content (wt %)</th>
<th>Fraction of reduced Nickel</th>
<th>Fraction of reduced Cobalt</th>
<th>Reduced Ni content (wt %)</th>
<th>Reduced Co content (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co6</td>
<td>0</td>
<td>5.9</td>
<td>0</td>
<td>0</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Ni1Co4</td>
<td>1.52</td>
<td>4.18</td>
<td>0.52</td>
<td>0.2</td>
<td>0.79</td>
<td>0.84</td>
</tr>
<tr>
<td>Ni2Co4</td>
<td>2.67</td>
<td>4.53</td>
<td>0.52</td>
<td>0.2</td>
<td>1.39</td>
<td>0.91</td>
</tr>
<tr>
<td>Ni3Co2</td>
<td>2.83</td>
<td>1.87</td>
<td>0.55</td>
<td>0.25</td>
<td>1.56</td>
<td>0.47</td>
</tr>
<tr>
<td>Ni4</td>
<td>4.9</td>
<td>0</td>
<td>0.87</td>
<td>0</td>
<td>4.26</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 4.11 Reduced metal content (wt %) of impregnated catalysts from XANES and ICP results

<table>
<thead>
<tr>
<th>Impregnated catalysts</th>
<th>Nickel content (wt %)</th>
<th>Cobalt content (wt %)</th>
<th>Fraction of reduced Nickel</th>
<th>Fraction of reduced Cobalt</th>
<th>Reduced Ni content (wt %)</th>
<th>Reduced Co content (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co5</td>
<td>0</td>
<td>6.6</td>
<td>0</td>
<td>0.43</td>
<td>0.00</td>
<td>2.84</td>
</tr>
<tr>
<td>Ni2Co3</td>
<td>1.93</td>
<td>3.67</td>
<td>0.82</td>
<td>0.37</td>
<td>1.58</td>
<td>1.36</td>
</tr>
<tr>
<td>Ni3Co3</td>
<td>2.94</td>
<td>3.06</td>
<td>0.83</td>
<td>0.37</td>
<td>2.44</td>
<td>1.13</td>
</tr>
<tr>
<td>Ni3Co2</td>
<td>4</td>
<td>2.1</td>
<td>0.79</td>
<td>0.51</td>
<td>3.16</td>
<td>1.07</td>
</tr>
<tr>
<td>Ni5</td>
<td>5.9</td>
<td>0</td>
<td>0.84</td>
<td>0</td>
<td>4.96</td>
<td>0.00</td>
</tr>
</tbody>
</table>
4.3 **Catalyst Activity Test**

To observe the effects of preparation method and Ni/Co ratio, the prepared catalysts were tested for CDRM reaction. The experimental conditions were as explained in section 3.3.1. The results were compiled according to the procedure and equations as described in section 3.4. To compare the effects of catalysts on CDRM reaction, the data for the first 11 h of each reaction is shown in this section.

4.3.1 **Effect of Ni/Co Ratio on CDRM Reaction (Precipitated Catalysts)**

Figures 4.5 and 4.6 show the conversion of CH$_4$ and CO$_2$, respectively. The CO$_2$ conversion has the same trend as shown for CH$_4$ conversion. Also, as expected, conversion of former is slightly higher than the latter because of the occurrence of RWGS which is supplied from reactants and H$_2$ produced in CDRM reaction. Figures 4.5 and 4.6 depict that the cobalt catalyst did not show an acceptable activity which was close to 9% of conversion after 11 h. Also, the CopCat-Ni$_2$Co$_4$ (Ni/Co ratio of 0.6) showed higher conversion than the other bimetallic and Ni monometallic catalysts, while the difference was insignificant. In case of CO$_2$ conversion, the conversions for the catalysts containing Ni were close to each other for the first 11 h. This could be due to the proposed mechanism at which CO$_2$ is activated by support.
Table 4.12 presents the conversions of CH$_4$ and CO$_2$ in the beginning and at the end of 11 h period. The effect of RWGSR on consumption rate of carbon dioxide is more tangible than methane as the CO$_2$ conversion is higher than CH$_4$. The larger difference between CH$_4$ and CO$_2$ conversions show a larger impact of RWGSR that may result in more CO production reducing the H$_2$/CO ratio. Therefore, the closer the H$_2$/CO ratio to unity the lower the contribution of side reaction (RWGSR).
Fig. 4.6 Activity and stability of Ni-Co precipitated catalysts in term of CO\textsubscript{2} conversion; reaction conditions: 710 °C, 1atm, 558000 mL/g\textsubscript{c}.h (GHSV), and CH\textsubscript{4}/CO\textsubscript{2}/N\textsubscript{2}=1/1/1, catalyst load of 0.02 g

Table 4.12 Activity and stability of Ni-Co precipitated catalysts in terms of CH\textsubscript{4} and CO\textsubscript{2} conversions at the beginning and after 11 h

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CH\textsubscript{4} conversion (%)</th>
<th>CO\textsubscript{2} conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Beginning</td>
<td>End</td>
</tr>
<tr>
<td>CopCat-Co6</td>
<td>54</td>
<td>8.6</td>
</tr>
<tr>
<td>CopCat-Ni2Co5</td>
<td>82.8</td>
<td>73.7</td>
</tr>
<tr>
<td>CopCat-Ni3Co5</td>
<td>82.7</td>
<td>76.1</td>
</tr>
<tr>
<td>CopCat-Ni3Co2</td>
<td>54.9</td>
<td>32.2</td>
</tr>
<tr>
<td>CopCat-Ni5</td>
<td>82.6</td>
<td>72.4</td>
</tr>
</tbody>
</table>

Apart from catalytic activity, selectivity is defined as one of the most important criterion of selecting a suitable catalyst. In our case selectivity may change H\textsubscript{2}/CO ratio
significantly. Figure 4.7 shows the product H₂/CO ratios versus time for the tested catalysts. Due to instrument limitation\(^1\), the H₂/CO was not calculated for CopCat-Co6 as illustrated in Figure 4.7.

![Graph](image)

**Fig. 4.7** H₂/CO ratios of precipitated catalysts; reaction conditions: 710 °C, 1 atm, 558000 mL/gₚ·h (GHSV), and CH₄/CO₂/N₂=1/1/1, catalyst load of 0.02 g

Figure 4.7 shows that bimetallic catalysts have higher H₂/CO ratio than the monometallic catalyst indicating higher selectivity of precipitated bimetallic catalysts compared to precipitated monometallic catalyst. Also, the CopCat-Ni2Co4 (Ni/Co ratio of 0.6) has the highest H₂/CO ratio during the testing period suggesting a lower side reaction (RWGS) and higher selectivity among other catalysts.

Based on the results obtained from catalyst activity tests, the CopCat-Ni2Co4 (Ni/Co ratio of 0.6) gained more selectivity as compared to the other precipitated

---

\(^1\) TCD was not able to detect hydrogen peak when the conversion of reactants was lower than 20%
catalysts. It can be confirmed by comparing the reactant conversion and H\textsubscript{2}/CO ratio as shown in Figure 4.5, 4.6, and 4.7.

To summarize, the CopCat-Ni2Co4 (Ni/Co ratio of 0.6) bimetallic catalyst prepared by precipitation method has almost the same activity in comparison with the other catalysts, but it had the highest selectivity among the other precipitated catalysts during CDRM reaction. Also, it is observed that a higher percentage of reduced metals does not lead to higher activity and selectivity. This can be confirmed by comparing the activity and selectivity of Ni monometallic catalyst (87\% reduced Ni) and CopCat-Ni2Co4 bimetallic catalyst (52\% reduced Ni).

4.3.2 Effect of Ni/Co Ratio on CDRM Reaction (Impregnated Catalysts)

Generally, it is expected that the catalysts with higher nickel content show better activity. Also, like the precipitated catalysts, a higher CO\textsubscript{2} conversion is expected due to the RWGSR. Additionally, the catalysts with higher reduced metal content may show better activity for CDRM reaction.

Figure 4.8 illustrates the CH\textsubscript{4} conversion, and Figure 4.9 shows the CO\textsubscript{2} conversion versus time on stream while using impregnated catalysts. Also, Table 4.13 shows the reactants conversion at the beginning and at the end of 11 h of reaction. It can be seen that ImpCat-Co5 catalyst is not active for CDRM reaction. The reason could be interpreted by XAS results since the only catalyst having the reduced Co particle with size more than 100 Å is ImpCat-Co6 catalyst. On the other hand Bouarab et al. (2004) reported that supported Co catalysts gave better results in comparison with Ni in terms
of carbon formation implying that presence of Co in the Ni-Co bimetallic catalyst ameliorates the carbon formation resistance of bimetallic catalysts.

In addition, it can be observed that increasing the Ni content of the bimetallic catalysts increased the reactant conversion. Regarding, XAS results more reduction took place by increasing Ni content; therefore, more activity is gained. Also, ImpCat-Ni5 has almost the same activity in term of methane conversion in comparison with the bimetallic catalysts. On the other hand, increasing the amount of Ni from Ni/Co ratio of 1.9 (ImpCat-Ni3Co2) to only Ni (ImpCat-Ni5) does not make significant change in the amount of methane conversion. It can be concluded that excess amount of Ni content more than Ni/Co=1.9 may not improve the catalyst activity.

![Chart](chart.png)

**Fig. 4.8** Activity and stability of Ni-Co impregnated catalysts in term of CH\(_4\) conversion; reaction conditions: 710 °C, 1atm, 558000 mL/g\(_c\).h (GHSV), and CH\(_4\)/CO\(_2\)/N\(_2\)=1/1/1, catalyst load of 0.02 g
**Fig. 4.9** Activity and stability of Ni-Co impregnated catalysts in term of CO$_2$ conversion; reaction conditions: 710 °C, 1atm, 558000 mL/g$\cdot$h (GHSV), and CH$_4$/CO$_2$/N$_2$=1/1/1, catalyst load of 0.02 g.

**Table 4.13** Activity and stability of Ni-Co impregnated catalysts in terms of CH$_4$ and CO$_2$ conversions at the beginning and after 11 h.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CH$_4$ conversion (%)</th>
<th>CO$_2$ conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Beginning</td>
<td>End</td>
</tr>
<tr>
<td>ImpCat-Co5</td>
<td>28.5</td>
<td>7.3</td>
</tr>
<tr>
<td>ImpCat-Ni2Co3</td>
<td>75.6</td>
<td>68.7</td>
</tr>
<tr>
<td>ImpCat-Ni3Co3</td>
<td>84.1</td>
<td>71.6</td>
</tr>
<tr>
<td>ImpCat-Ni3Co2</td>
<td>83.4</td>
<td>76.8</td>
</tr>
<tr>
<td>ImpCat-Ni5</td>
<td>85.8</td>
<td>77</td>
</tr>
</tbody>
</table>
Table 4.13 provides basic information about the impacts of the side reaction (RWGSR) which can be observed due to differences between CH$_4$ and CO$_2$ conversions.

To observe the effect of side reaction (RWGSR) on the CDRM reaction over different impregnated catalysts, the H$_2$/CO ratios are depicted versus time as presented in Figure 4.10. Generally, the closeness value of H$_2$/CO to unity indicates that RWGSR has negligible contribution. Higher H$_2$/CO ratio associated with Ni monometallic catalyst indicating the catalyst is more selective for CDRM than RWGSR among the other impregnated bimetallic catalysts as illustrated in Figure 4.10. As it can be seen, increase in Ni content raises H$_2$/CO ratio and consequently the selectivity of the catalysts towards CDRM reaction.

![Graph showing H$_2$/CO ratios for different catalysts.](image)

**Fig. 4.10** H$_2$/CO ratios of Impregnated catalysts; reaction conditions: 710 °C, 1atm, 558000 mL/g$_c$.h (GHSV), and CH$_4$/CO$_2$/N$_2$=1/1/1, catalyst load of 0.02 g
A general trend can be concluded in this section to see how Ni content can affect the performance of the impregnated catalysts. The Catalysts with Ni/Co ratio equal or greater than 1 obtained conversions of about 84% for CH$_4$ and 89% for CO$_2$ after 30 min of reaction time. More specifically, the only Ni monometallic catalyst had the highest conversion and selectivity towards CDRM reaction resulting in the highest H$_2$/CO ratio as for the product stream.

4.3.3 Effects of preparation methods for the Ni-Co/AlMgO$_x$ catalysts for CDRM reaction

This section describes the effects of preparation methods on the catalysts activity for CDRM reaction. First of all the effects of preparation methods on the performance of monometallic catalysts are described. Then, the bimetallic catalyst with almost the same Ni/Co ratio$^1$ is investigated. Finally, the catalysts that showed better performance for CDRM reaction among each group will be selected.

4.3.3.1 Effect of preparation method for monometallic catalysts

Figure 4.11 and 4.12 show reactant conversions and H$_2$/CO ratios using monometallic catalysts on CDRM reaction. As discussed in sections 4.3.1 and 4.3.2, the conversion of the Co monometallic catalysts was relatively low$^2$ within the first 11 h of the reaction. On one hand, Ni monometallic catalysts gained quite high activity$^3$ for CDRM reaction. On the other hand, ImpCat-Ni5 sample has higher activity than the

---

$^1$ CopCat-Ni2Co4 (Ni/Co = 0.5), and ImpCat-Ni2Co3 (Ni/Co = 0.6)

$^2$ Less than 10% conversion for both reactants

$^3$ More than 80% of conversion for both reactants
precipitated catalyst because of either highly reduced Ni metal on the surface or large values of Ni loading.

**Fig. 4.11** Activity and stability of monometallic catalysts in term of reactant conversion; reaction conditions: 710 °C, 1 atm, 558000 mL/g·h (GHSV), and CH₄/O₂/N₂=1/1/1, catalyst load of 0.02 g
**Fig. 4.12** $\text{H}_2/\text{CO}$ ratios of the monometallic catalysts; reaction conditions: $710 \, ^\circ\text{C}$, 1 atm, 558000 mL/g·h (GHSV), and $\text{CH}_4/\text{CO}_2/\text{N}_2 = 1/1/1$, catalyst load of 0.02 g

4.3.3.2 EFFECT OF PREPARATION METHOD FOR Ni-Co BIMETALLIC CATALYSTS

Although the available Ni content of precipitated catalyst was significantly lower than impregnated one, precipitated catalyst had more activity than impregnated one as shown in Figure 4.13.

Figure 4.14 shows that the precipitated catalyst has higher H2/CO ratio during the 15 h of reaction time. The results are in agreement with Zhang’s (Zhang et al., 2007) study.
Fig. 4.13 Activity and stability of bimetallic catalysts in term of reactant conversions; reaction conditions: 710 °C, 1atm, 558000 mL/g\cdot h (GHSV), and CH\textsubscript{4}/CO\textsubscript{2}/N\textsubscript{2}=1/1/1, catalyst load of 0.02 g

Fig. 4.14 H\textsubscript{2}/CO ratios of Ni/Co bimetallic catalysts; reaction conditions: 710 °C, 1atm, 558000 mL/g\cdot h (GHSV), and CH\textsubscript{4}/CO\textsubscript{2}/N\textsubscript{2}=1/1/1, catalyst load of 0.02 g
4.3.3.3 Overall Comparison

According to sections 4.3.1 and 4.3.2, the CopCat-Ni2Co4 bimetallic (Ni/Co ratio of 0.6) and the CopCat-Ni4 monometallic catalysts were chosen among the precipitated samples. Similarly, the ImpCat-Ni3Co2 bimetallic (Ni/Co ratio of 1.9) and the ImpCat-Ni5 monometallic catalysts were selected from the impregnated samples. Figure 4.15 shows reactant conversions of the CDRM reaction over the selected catalysts.

As Figure 4.15 shows, the initial conversions for the impregnated samples are slightly higher than the precipitated samples. However, after the first 8 h of the reaction CH₄ conversion of the Impregnated catalysts dropped slightly while the conversion of CopCat-Ni2Co4 catalyst remained almost constant.
Fig. 4.15 Activity and stability of Ni-Co catalysts in term of reactant conversions; reaction conditions: 710 °C, 1 atm, 558000 mL/g·h (GHSV), and CH$_4$/CO$_2$/N$_2$=1/1/1, catalyst load of 0.02 g
A further comparison is made among different $\text{H}_2/\text{CO}$ ratios as shown in Figure 4.16. It can be observed that the $\text{H}_2/\text{CO}$ ratio has the highest value for the impregnated monometallic Ni catalyst (ImpCat-Ni5). It should be noted that except the precipitated monometallic Ni catalyst the values of $\text{H}_2/\text{CO}$ for all the others stay fairly stable.

One of the most influential factors determining the performance of a catalyst is the related amount of reduced metals content which is shown in Tables 4.10 and 4.11. Based on the total amount of reduced metals content associated with each catalyst the consumption rate of reactants are shown in Figures 4.17 and 4.18.

**Fig. 4.16** $\text{H}_2/\text{CO}$ ratios of Ni-Co catalysts; reaction conditions: 710 °C, 1 atm, 558000 mL/g·h (GHSV), and $\text{CH}_4/\text{CO}_2/\text{N}_2=1/1/1$, catalyst loading of 0.02 g
Regarding amount of reduced metal content Figure 4.18 clearly shows that the performance of the CopCat-Ni2Co4 catalyst (Ni/Co ratio of 0.6) is approximately two times than that of the only Ni impregnated catalyst. Zhang et al. (2007) and Bouarab et al. (2004) observed that the presence of Co in Ni-Co catalyst is necessary to improve the carbon formation resistance of the catalyst. In other words the presence of Co improves the selectivity of catalyst while the only Co monometallic catalyst is not active for CDRM reaction, as shown in Figure 4.11. Furthermore, the presence of Co in the precipitated Ni-Co bimetallic catalysts reduces the number of Ni active sites making RWGSR less favorable compared to the ImpCat-Ni5 catalyst. Thus, presence of Co is a must to get desired performance for CDRM reaction.
Based on the above discussion, Ni-Co/AlMgOₓ catalyst with Ni/Co ratio of 0.6 (CopCat-Ni2Co4) is selected as the optimum catalyst for CDRM reaction.

4.4 LIFE-TIME ACTIVITY AND STABILITY TEST OF Ni-Co BIMETALLIC CATALYST (CopCat-Ni2Co4 with Ni/Co ratio of 0.6)

To meet the requirement of Carbon Science Inc., the stability and activity of the Ni-Co/AlMgOₓ catalyst with Ni/Co ratio of 0.6 (CopCat-Ni2Co4) as the optimum catalyst for CDRM reaction was tested for almost 1600 h with the procedure described in section 3.3.2.
Based on the previous studies done in our research group desired stability and conversion were expected especially at 760 °C by using the Ni/Co ratio of 0.6 precipitated catalyst (CopCat-Ni2Co4) for CDRM reaction. The reactant conversion and production rate are shown in Figures 4.19 and 4.20. Also, Table 4.14 summarizes the reactant conversion and formation rate of products for the life-time test.

The test was performed within 65 days at two different temperatures i.e. 710 °C and 760 °C. The catalyst showed better performance in terms of activity and stability at 760 °C\(^1\) as compared to 710 °C as shown in Figure 4.19. The CH\(_4\) conversion at 710 °C dropped from 90% to 72% within 42 days. More interestingly, there was a significant increase in reactant conversions as soon as the temperature increased to 760 °C after the 42\(^{nd}\) day of reaction. The reactant conversion remained stable after 23 days on. It is noteworthy that there was not only an immediate recovery in conversion but also an improvement in stability. Figure 4.22 reveals formation rate of products.

\(^1\) Almost 93% CH\(_4\) conversion and 95% CO\(_2\) conversion
Fig. 4.19 Activity and stability of CopCat-Ni2Co4 with Ni/Co ratio of 0.6 catalyst in term of reactant conversions of CDRM reaction; reaction conditions: 710 °C for the first 42 days and 760 °C for the rest, 1 atm, 110,000 mL/g.c.h (GHSV), and CH₄/CO₂/N₂=1/1/1, catalyst load of 0.05 g.

Fig. 4.20 Production rates of the life-time CDRM test, reaction conditions: 710 °C for the first 42 days and 760 °C for the rest, 1 atm, 110,000 mL/g.c.h (GHSV), and CH₄/CO₂/N₂=1/1/1, catalyst load of 0.05 g.
Table 4.14 Formation rate of products and reactant conversions of the life-time test using CopCat-Ni2Co4 with Ni/Co ratio of 0.6, at 710 °C and 760 °C

<table>
<thead>
<tr>
<th>Time (day)</th>
<th>Temperature (°C)</th>
<th>CH₄ conversion (%)</th>
<th>CO₂ conversion (%)</th>
<th>Rate of H₂ (mol/gₐ.h)</th>
<th>Rate of CO (mol/gₐ.h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1ˢᵗ</td>
<td>710</td>
<td>90</td>
<td>94</td>
<td>1.70</td>
<td>1.74</td>
</tr>
<tr>
<td>20ᵗʰ</td>
<td>710</td>
<td>78</td>
<td>85.5</td>
<td>1.32</td>
<td>1.54</td>
</tr>
<tr>
<td>42ᵗʰ</td>
<td>710</td>
<td>72.5</td>
<td>81.5</td>
<td>1.20</td>
<td>1.42</td>
</tr>
<tr>
<td>43ᵗʰ</td>
<td>760</td>
<td>93</td>
<td>95</td>
<td>1.72</td>
<td>1.78</td>
</tr>
<tr>
<td>65ᵗʰ</td>
<td>760</td>
<td>93.5</td>
<td>95.5</td>
<td>1.78</td>
<td>1.79</td>
</tr>
</tbody>
</table>

Regarding Figure 4.21 there is a decreasing trend for H₂/CO ratio while it fluctuates versus time at 710 °C. On the other hand, at 760 °C although the H₂/CO ratio is fluctuating, it remained steady around 1.. This behaviour was described by Wei et al. (2000) as a periodic cycle of carbon deposition and elimination on the catalyst. Richardson (1998) called this phenomenon as an effective periodic carbon deposition and elimination stabilizing catalytic performance.
To conclude, the precipitated Ni-Co/AlMgO\textsubscript{x} catalyst with Ni/Co ratio of 0.6 has a high stability for CDRM reaction. This behavior improved when the reaction temperature was increased from 710 °C to 760 °C during the life-time test for 65 days.

### 4.5 Catalyst Poisoning with 30 PPM of H\textsubscript{2}S

As mentioned, both natural gas and landfill gas as the main sources of CH\textsubscript{4} may contain sulfur containing compounds\(^1\) as the poison. In order to investigate the effects of sulphur compounds on the activity of catalyst, all the prepared catalysts were poisoned with 30 ppm of H\textsubscript{2}S. The procedure for poisoning the catalysts was introduced in section 3.3.3. Among the catalysts prepared by both precipitation and impregnation methods, the monometallic Co catalysts were not active compared to other catalysts; therefore the

\(^1\) Mainly H\textsubscript{2}S
poisoning test was not conducted for them. This part of research is mainly focused on the activity and regeneration capability of the catalysts poisoned by H₂S.

In addition, after the poisoning, activities of the catalyst prepared by precipitation and impregnation techniques were compared based on the reduced metal contents.

Running the tests three sections are distinguished called “before poisoning” (P-1), “during poisoning” (P-2), and “after poisoning” (P-3). The reaction conditions for the P-1 and P-3 sections were the same as explained in section 3.3.1. For the P-2, the flow rates of the gases were adjusted in order to keep the equimolar mixture of CH₄, CO₂, and N₂. Because of instrument limitations, catalyst loadings, and poison availability a certain value of poisonous gas is chosen. The catalysts were poisoned by 30 ppm of H₂S and the temperature of the reaction was kept constant at 710 °C (the beginning of P-2). To make sure that all the catalysts are poisoned, the H₂S poisoning was stopped as soon as GC could not recognize the H₂ peak (the end of P-2) indicating the catalyst is totally poisoned with H₂S. Then the flow rates of CH₄, CO₂, and N₂ gases were adjusted to the condition prior to the poisoning (beginning of P-3). In this section, t=0 is the time at which H₂S was injected to the reactor (beginning of P-2).

Figure 4.22 shows results of the CO₂ conversion for the precipitated catalysts during and after H₂S poisoning (P-2 and P-3). As soon as poisoning starts a rapid drop in conversion of all catalysts is observed. In spite of very low conversions¹, all the precipitated bimetallic catalysts are still active. However, in case of Ni monometallic

¹ CO₂ conversion in the range of 10-15%
catalyst, the conversion starts to increase versus time while poisoning. The results indicate that catalyst with higher Ni content than Co has more ability of regeneration after being poisoned implying that the presence of Ni is essential for regeneration after poisoning. As presented in Table 4.8, Ni monometallic catalyst has a higher percentage of metal reduction among the others resulting in faster regeneration than the bimetallic catalysts.

Table 4.15 indicates the reactants conversion before, after, and at the end of the poisoning test. The CH$_4$ conversion trends of the catalysts were the same as CO$_2$ as shown in Figure 4.23.

![Graph showing CO$_2$ conversion over time for different catalysts](image)

**Fig. 4.22** Activity of Ni-Co precipitated catalysts in term of CO$_2$ conversions during H$_2$S poisoning test; CDRM reaction conditions: 710 °C, 1 atm, 558,000 mL/g$_c$.h (GHSV), and CH$_4$/CO$_2$/N$_2$=1/1/1, catalyst load of 0.02 g, 30 ppm H$_2$S
### Table 4.15 Reactant conversions for the poisoning test, precipitated catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CH₄ conversion (%)</th>
<th>CO₂ conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>before H₂S</td>
<td>after H₂S</td>
</tr>
<tr>
<td>CopCat-Co6</td>
<td>54</td>
<td>-</td>
</tr>
<tr>
<td>CopCat-Ni1Co4</td>
<td>82.8</td>
<td>8.8</td>
</tr>
<tr>
<td>CopCat-Ni2Co4</td>
<td>82.7</td>
<td>10.1</td>
</tr>
<tr>
<td>CopCat-Ni3Co2</td>
<td>54.9</td>
<td>2.9</td>
</tr>
<tr>
<td>CopCat-Ni4</td>
<td>82.6</td>
<td>8.8</td>
</tr>
</tbody>
</table>

**Fig. 4.23** Activity of Ni-Co precipitated catalysts in term of CH₄ conversions during H₂S poisoning test; CDRM reaction conditions: 710 °C, 1 atm, 558,000 mL/g₉·h (GHSV), and CH₄/CO₂/N₂=1/1/1, catalyst load of 0.02 g, 30 ppm H₂S
Figure 4.24 and 4.25 illustrate the results of catalyst poisoning test using 30 ppm of H$_2$S for the catalysts prepared by impregnation method. It can be observed that catalysts with higher Ni content can be quickly regenerated after being exposed to hydrogen sulfide. Also, the results indicate that the bimetallic catalyst prepared by impregnation method regenerate themselves faster than the precipitated ones implying that the impregnated catalysts with higher metal content on the surface have higher degree of reduction as shown in Tables 4.5 and 4.8. Table 4.16 presents the results of the poisoning test for impregnated catalyst. Despite the quick regeneration step, the longest deactivation time recorded for Ni monometallic catalyst showing more resistibility of Nickel toward H$_2$S poison.

**Table 4.16** Reactant conversions for the poisoning test, impregnated catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CH$_4$ conversion (%)</th>
<th>CO$_2$ conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>before H$_2$S</td>
<td>after H$_2$S</td>
</tr>
<tr>
<td>ImpCat-Co5</td>
<td>28.5</td>
<td>-</td>
</tr>
<tr>
<td>ImpCat-Ni2Co3</td>
<td>75.6</td>
<td>7.9</td>
</tr>
<tr>
<td>ImpCat-Ni3Co3</td>
<td>84.1</td>
<td>8.6</td>
</tr>
<tr>
<td>ImpCat-Ni3Co2</td>
<td>83.4</td>
<td>8.4</td>
</tr>
<tr>
<td>ImpCat-Ni5</td>
<td>84</td>
<td>7.7</td>
</tr>
</tbody>
</table>
**Fig. 4.24** Activity of Ni-Co impregnated catalysts in term of \( \text{CO}_2 \) conversions during \( \text{H}_2\text{S} \) poisoning test; CDRM reaction conditions: 710 °C, 1 atm, 558,000 mL/g\text{c}\cdoth (GHSV), and \( \text{CH}_4/\text{CO}_2/\text{N}_2=1/1/1 \), catalyst load of 0.02 g, 30 ppm \( \text{H}_2\text{S} \)

**Fig. 4.25** Activity of Ni-Co impregnated catalysts in term of \( \text{CH}_4 \) conversions during \( \text{H}_2\text{S} \) poisoning test; CDRM reaction conditions: 710 °C, 1 atm, 558,000 mL/g\text{c}\cdoth (GHSV), and \( \text{CH}_4/\text{CO}_2/\text{N}_2=1/1/1 \), catalyst load of 0.02 g, 30 ppm \( \text{H}_2\text{S} \)
To summarize, higher Ni content, increases the regeneration capability of the catalysts, no matter which method selected for preparation. On the other hand, the regeneration ability for the bimetallic impregnated catalysts was higher than precipitated catalysts. Also, the same regeneration behavior associated with both impregnated and precipitated Ni monometallic catalysts is observed as a result of having significantly close values of reduced Ni content as shown in Table 4.10 and 4.11. One may link the regeneration difficulties to pore blockage of the precipitated catalyst. The majority of sulfur compounds may block the active sites forming a stable structure on the catalyst surface (Metal-S). Consequently, the blocked sites will not be able to adsorb the CHX species anymore\(^1\). This justification can be proposed as a possible pathway for deactivation mechanism within poisoning period. It can be concluded that the regeneration time becomes shorter as the Ni/Co ratio increases although the regeneration is not complete.

\(^1\) Based on the proposed mechanism for CDRM reaction in section 2.4.4.
CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

- All the prepared catalysts with various Ni/Co ratios by impregnation and precipitation methods, had BET surface area greater than 100 m$^2$/g.

- It was observed that due to the lack of metal-metal interactions in impregnated catalysts the obtained Ni/Co and Mg/Al ratios were closer to the intent ones as compared to the precipitated catalysts.

- In the impregnated catalysts the amounts of reduced metals were almost two times of the precipitated catalysts. Furthermore, only the Co monometallic catalyst prepared by precipitation method did not show any Co reduction.

- No matter how the catalysts were prepared, the percentage of reduced Ni was very close in Ni monometallic catalysts.

- The amount of reduced metals at 850 °C was more than those at 750 °C, but the reduced metal particle size was lower than 100 Å for the bimetallic catalysts that were prepared at 750 °C. Whereas, the particle size was more than 100 Å for bimetallic catalysts that were prepared at 850 °C.

- The CO$_2$ conversion had the same trend as CH$_4$ conversion in all the prepared catalysts for CDRM reaction at 710 °C.
• The Co monometallic catalysts prepared by impregnation and precipitation did not show a good activity for CDRM reaction as compared to the other prepared bimetallic and metallic catalysts.

• The CopCat-Ni2Co4 catalyst (Ni/Co ratio of 0.6) leads the CDRM reaction to produce H₂/CO ratio (0.95-1.05) is achieved by dry reforming theoretically indicating that the catalyst is not suffering from a significant side reaction (RWGS) effect resulting in a desirable selectivity.

• The only Ni monometallic catalyst prepared by impregnation had the highest conversion and also the lowest side reaction for CDRM reaction at 710 °C.

• The precipitated bimetallic catalyst with Ni/Co ratio of 0.6 (CopCat-Ni2Co4) was more stable as compared to the impregnated Ni monometallic (CopCat-Ni4) catalyst.

• The precipitated Ni-Co/AlMgOx catalyst with Ni/Co ratio of 0.6 has a high stability for CDRM reaction. This behavior improved when the reaction temperature was increased from 710 °C to 760 °C during the life-time test for 65 days.

• The catalysts containing more Ni showed better H₂S resistance and regeneration after poisoning whether they were prepared by precipitation or impregnation method.

• The bimetallic impregnated catalysts regenerated themselves better as compared to the precipitated ones, which could be due to their higher metal content on the surface and reduction than the precipitated catalysts.
The same regeneration behavior associated with both impregnated and precipitated Ni monometallic catalysts is observed as a result of having significantly close values of reduced Ni content.

5.2 Recommendation

As general recommendations:

1- The H$_2$S poisoning test should be repeated with various concentrations of H$_2$S in order to obtain an optimum concentration of H$_2$S that may have a reduced effect on the catalyst performance.

2- Studying the stability of the catalyst for a periodic H$_2$S poisoning could be investigated.

3- To understand how H$_2$S poisons the catalyst, detailed characterization analyses are needed.

Some specific recommendations for the precipitated Ni-Co catalyst of ratio 1 to be used as a working catalyst in industry:

1- Finding the maximum H$_2$S concentration that may not affect the catalyst performance for long term use.

2- In reality natural gas mainly contains methane and relatively low concentrations of other gases compounds including sulfur containing compounds (H$_2$S, mercaptans, thiophen, ...). The effects of such impurities should be investigated on the catalyst performance.
3- To pelletize the catalyst, a suitable binder needs to be selected so that industrial shapes could leave desired impacts on the catalyst performance. In this way, catalyst shows a better performance in terms of mechanical properties such as high abrasion and attribution resistances. The pelletized catalyst on the bottom of a fixed bed in operation could be able to tolerate either the force from the above catalyst or the applied force by pressure drop as a result of oncoming gas flow.
REFERENCES


16. Environment Canada,


APPENDIX A: CALIBRATION OF MASS FLOW (MFC) CONTROLLER

To calibrate the MFC, N\textsubscript{2} was used. Then for gases other than N\textsubscript{2}, the flow rate of N\textsubscript{2} was converted to the corresponding gas flow rate using heat capacity of gases at constant pressure as shown in Table A.1. Equation A-1 was used to convert the flow rates.

\[ F_j = F_{N_2} \times \frac{C_{N_2}}{C_j} \]  \hspace{1cm} (A-1)

where, j stands for CH\textsubscript{4}, CO\textsubscript{2}, or H\textsubscript{2}.

| Table A.1 Heat capacity values of H\textsubscript{2}, N\textsubscript{2}, CO\textsubscript{2}, and CH\textsubscript{4} at 21 °C. |
|---|---|
| Gas   | Heat capacity (Cp) |
| N\textsubscript{2} | 0.2885 |
| H\textsubscript{2} | 0.2847 |
| CO\textsubscript{2} | 0.3749 |
| CH\textsubscript{4} | 0.3547 |

In the following calibration curves for mass flow controller, each point stands as the average of 10 measured flow rates with the same set-point.
A: N$_2$ mass flow controller (set-point vs measurement at STP)

![N$_2$ MFC Calibration Curve - No 1](image)

\[ y = 0.9834x - 12.958 \]
\[ R^2 = 1 \]

**Fig. A.1** Calibration curve for N$_2$ mass flow controller

B: CH$_4$ mass flow controller (set-point vs measurement at STP)

![CH$_4$ MFC Calibration Curve - No 2](image)

\[ y = 0.9374x - 4.5227 \]
\[ R^2 = 1 \]

**Fig. A.2** Calibration curve for CH$_4$ mass flow controller
C: CO₂ mass flow controller (set-point vs measurement at STP)

![CO₂ MFC Calibration Curve - No 3](image)

\[ y = 0.9878x - 4.1734 \]
\[ R^2 = 1 \]

**Fig. A.3** Calibration curve for CO₂ mass flow controller

D: H₂ mass flow controller (set-point vs measurement at STP)

![H₂ MFC Calibration Curve - No 4](image)

\[ y = 0.713x + 0.0645 \]
\[ R^2 = 1 \]

**Fig. A.4** Calibration curve for H₂ mass flow controller
**APPENDIX B: CALIBRATION OF GAS CHROMATOGRAPHY**

To calibrate the Gas Chromatography (GC), at least three times injection for each concentration was done. Then the average area was calculated to use in the calibration curve. Also the Standard Deviation of the obtained data is calculated based on the following equation:

\[
STD = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (x_i - \bar{x})^2}
\]  

(B-1)

where,

\( STD \): standard deviation of the obtained areas for each concentration,

\( N \): number of injections at each concentration,

\( x_i \): GC measured area for each injection with same concentration,

\( \bar{x} \): average of the GC measured areas for each injection with same concentration.
A: GC calibration curve for H₂ (area vs concentration (%v/v))

Table B.1 GC calibration data for H₂

<table>
<thead>
<tr>
<th>Ret. Time</th>
<th>Level</th>
<th>Concentration (%v/v)</th>
<th>Area</th>
<th>STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.37</td>
<td>1</td>
<td>6.60</td>
<td>16.35</td>
<td>0.19</td>
</tr>
<tr>
<td>1.37</td>
<td>2</td>
<td>10.00</td>
<td>20.75</td>
<td>0.03</td>
</tr>
<tr>
<td>1.37</td>
<td>3</td>
<td>18.00</td>
<td>37.98</td>
<td>0.06</td>
</tr>
<tr>
<td>1.36</td>
<td>4</td>
<td>26.00</td>
<td>55.23</td>
<td>0.09</td>
</tr>
<tr>
<td>1.36</td>
<td>5</td>
<td>32.00</td>
<td>69.21</td>
<td>0.34</td>
</tr>
<tr>
<td>1.36</td>
<td>6</td>
<td>40.00</td>
<td>87.40</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Fig. B.1 GC calibration curve for H₂

\[ y = 215.61x + 0.1706 \]

\[ R^2 = 0.998 \]
B: GC calibration curve for N₂ (area vs concentration (%v/v))

Table B.2 GC calibration data for N₂

<table>
<thead>
<tr>
<th>Ret. Time</th>
<th>Level</th>
<th>Concentration (%v/v)</th>
<th>Area</th>
<th>STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.546</td>
<td>1</td>
<td>10.2</td>
<td>4172.48</td>
<td>34.82</td>
</tr>
<tr>
<td>3.532</td>
<td>2</td>
<td>19.94</td>
<td>6076.19</td>
<td>14.48</td>
</tr>
<tr>
<td>3.516</td>
<td>3</td>
<td>29.73</td>
<td>8258.92</td>
<td>2.75</td>
</tr>
<tr>
<td>3.50</td>
<td>4</td>
<td>39.97</td>
<td>10628.14</td>
<td>15.40</td>
</tr>
</tbody>
</table>

\[ y = 21754x + 1854.2 \]
\[ R^2 = 0.9986 \]

Fig. B.2 GC calibration curve for N₂
C: GC calibration curve for CO (area vs concentration (%v/v))

**Table B.3** GC calibration data for CO

<table>
<thead>
<tr>
<th>Ret. Time</th>
<th>Level</th>
<th>Concentration (%v/v)</th>
<th>Area</th>
<th>STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.45</td>
<td>1</td>
<td>6.60</td>
<td>1427.55</td>
<td>6.51</td>
</tr>
<tr>
<td>4.45</td>
<td>2</td>
<td>10.00</td>
<td>2196.99</td>
<td>3.49</td>
</tr>
<tr>
<td>4.43</td>
<td>3</td>
<td>18.00</td>
<td>3956.71</td>
<td>1.03</td>
</tr>
<tr>
<td>4.41</td>
<td>4</td>
<td>26.00</td>
<td>5693.98</td>
<td>1.28</td>
</tr>
<tr>
<td>4.40</td>
<td>5</td>
<td>32.00</td>
<td>7045.00</td>
<td>15.60</td>
</tr>
<tr>
<td>4.39</td>
<td>6</td>
<td>40.00</td>
<td>8718.22</td>
<td>16.44</td>
</tr>
</tbody>
</table>

**Fig. B.3** GC calibration curve for CO

\[ y = 21870x + 6.4373 \]

\[ R^2 = 0.9999 \]
D: GC calibration curve for CH$_4$ (area vs concentration (%v/v))

Table B.4 GC calibration data for CH$_4$

<table>
<thead>
<tr>
<th>Ret. Time</th>
<th>Level</th>
<th>concentration (%v/v)</th>
<th>Area</th>
<th>STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.62</td>
<td>1</td>
<td>2.50</td>
<td>470.56</td>
<td>0.64</td>
</tr>
<tr>
<td>7.62</td>
<td>2</td>
<td>10.00</td>
<td>1583.54</td>
<td>0.44</td>
</tr>
<tr>
<td>7.59</td>
<td>3</td>
<td>19.90</td>
<td>3036.29</td>
<td>1.52</td>
</tr>
<tr>
<td>7.56</td>
<td>4</td>
<td>34.42</td>
<td>5528.09</td>
<td>4.97</td>
</tr>
</tbody>
</table>

Fig. B.4 GC calibration curve for CH$_4$

\[ y = 15826x + 10.907 \]

\[ R^2 = 0.9983 \]
E: GC calibration curve for CO₂ (area vs concentration (%v/v))

**Table B.5** GC calibration data for CO₂

<table>
<thead>
<tr>
<th>Ret. Time</th>
<th>Level</th>
<th>concentration (%v/v)</th>
<th>Area</th>
<th>STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.17</td>
<td>1</td>
<td>3.00</td>
<td>693.29</td>
<td>0.25</td>
</tr>
<tr>
<td>11.14</td>
<td>2</td>
<td>10.00</td>
<td>2071.19</td>
<td>0.45</td>
</tr>
<tr>
<td>11.11</td>
<td>3</td>
<td>19.80</td>
<td>4224.00</td>
<td>3.59</td>
</tr>
<tr>
<td>11.08</td>
<td>4</td>
<td>26.00</td>
<td>5897.01</td>
<td>6.28</td>
</tr>
<tr>
<td>11.05</td>
<td>5</td>
<td>35.25</td>
<td>8349.34</td>
<td>5.66</td>
</tr>
</tbody>
</table>

**Fig. B.5** GC calibration curve for CO₂

\[
y = 23771x - 224.38
\]

\[
R^2 = 0.9958
\]
APPENDIX C: TEMPERATURE CALIBRATION IN THE MIDDLE OF THE REACTOR

Fig. C.1 Heater temperature calibration in the middle of the reactor during CDRM reaction

\[ y = 1.006x - 43.15 \]

\[ R^2 = 1 \]
APPENDIX D: CARBON BALANCE

mole of C in = mole of CH\(_4\) in + mole of CO\(_2\) in \hspace{1cm} \text{(D-1)}

mole of C Out = mole of CH\(_4\) out + mole of CO\(_2\) out + 2*mole of CO out \hspace{1cm} \text{(D-2)}

Regarding equations D-1 and D-2, carbon flow (mol/h) in both inlet and outlet stream of the reactor using CopCat-Ni3Co2 catalyst on CDRM reaction is presented in Figure D.1.

**Fig.D. 1** Carbon flow in inlet and outlet streams of the reactor using CopCat-Ni3Co2 catalyst for CDRM reaction
The overall amount of carbon within TOS (14h is calculated) is integrated from the area below each line which shown in Figure D.1 as shown in Table D.1.

**Table D. 1 Carbon balance for CopCat-Ni3Co2 within 14h**

<table>
<thead>
<tr>
<th>Overall (h)</th>
<th>Carbon-Inlet (mol)</th>
<th>Carbon-Outlet (mol)</th>
<th>C balance mol</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>4.45</td>
<td>4.17</td>
<td>0.28</td>
<td>6.2</td>
</tr>
</tbody>
</table>


APPENDIX E: CATALYST CHARACTERIZATION ANALYSIS

E-1 BET surface area

BET surface area is known as an important property for many kinds of materials and especially solid catalysts. B.E.T. (or BET) stands for Brunauer, Emmett, and Teller, the scientists who proposed the theory for measuring the surface area (Brunauer et al., 1938). The concept of the theory is based on the Langmuir theory. Different methods are used to calculate and measure the BET surface area, but most of them are based on isothermal adsorption of nitrogen. The BET is measured by the use of nitrogen adsorption/desorption isotherms at liquid nitrogen temperature and relative pressures. The BET equation is:

\[
\frac{1}{Q[(\frac{P_0}{P})-1]} = \frac{c^{-1}}{Q_m c} \left(\frac{P}{P_0}\right) + \frac{1}{Q_m c} \quad (E-1)
\]

where,

\(Q\): the adsorbed gas quantity,

\(P_0\): saturation pressure of the adsorbed gas,

\(P\): equilibrium pressure of the adsorbed gas,

\(Q_m\): quantity of the monolayer adsorbed gas,
$c$: BET constant.

The BET plot is gained by plotting $\frac{1}{Q\left(\frac{P}{P_0}\right)-1}$ on the y-axis versus $\left(\frac{P}{P_0}\right)$ on the x-axis. $c$ and $Q_m$ can be calculated by using the slope and y-intercept of the BET plot. Then, $S_{BET,Total}$ and $S_{BET}$ will be calculated by the following equations:

$$S_{BET,Total} = \frac{Q_mNs}{V} \quad (E-2)$$

$$S_{BET} = \frac{S_{BET,Total}}{a} \quad (E-3)$$

where,

$N$: Avogadro’s number = $6.022 \times 10^{23}$,

$s$: molecular cross-sectional area,

$V$: molar volume of adsorbed gas,

$A$: molar mass of adsorbed species.

There are two parts, degassing and analysis. Degassing is to remove the dissolved gases from liquids, especially water. After degassing the sample is analysed for BET surface area. BET analysis also gives information about pores size and pore volume of the samples.

E-2: XAS analysis

In XAS method the core electron is excited by tuning the photon energy. Then after the excitation, a spectrum is generated through the XAS data. The spectrum
contains three main regions which are shown in Figure E.1. The regions orderly are Pre-edge, XANES, and EXAFS (Miller et al., 2006).

The name of “edge” is subjected to the excited core electron. The principle quantum numbers $n=1, 2, 3$ respectively relate to the K-, L-, and M-edge. To be more illustrative the excitation of 1s electron happens at K-edge, while 2s and 2p occur at L-edge.

Three main regions in an XAS spectrum schematically as shown in Figure E.1 are as follows:

1) **Pre-edge**: The name is given to the region in the energies lower than rising edge.
2) XANES: The main region above the Pre-edge is called XANES (X-ray Absorption Near-Edge Structure) or NEXAFS (Near-edge X-ray Absorption Fine Structure).

3) EXAFS: The region at energies above pre-edge is called EXAFS (Extended X-ray Absorption Fine Structure). EXAFS corresponds to scattering of the released photoelectron of neighbouring atoms.
**APPENDIX F: OVEN TEMPERATURE PROFILE OF GC**

**Table F.1** GC oven temperature values

<table>
<thead>
<tr>
<th>Oven ramp</th>
<th>Ramp rate (°C/min)</th>
<th>Next T (°C)</th>
<th>Hold time (min)</th>
<th>Run time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>-</td>
<td>40</td>
<td>3.00</td>
<td>3.00</td>
</tr>
<tr>
<td>Ramp 1</td>
<td>10.00</td>
<td>60</td>
<td>1.00</td>
<td>6.00</td>
</tr>
<tr>
<td>Ramp 2</td>
<td>35.00</td>
<td>125</td>
<td>5.20</td>
<td>13.06</td>
</tr>
<tr>
<td>Post run</td>
<td></td>
<td>40</td>
<td>0.00</td>
<td>13.06</td>
</tr>
</tbody>
</table>

**Fig. F.1** Oven temperature profile of GC