

Table of Contents

List of Figures	xii
List of Tables	xviii
List of Abbreviations	xix
Abstract	xx
Chapter 1	1
Introduction	1
1.1 Hydrogen Energy	1
1.2 Hydrogen Production Processes.....	2
1.2.1 Renewable Production Methods.....	2
1.2.2 Steam Reforming Mechanisms.....	4
1.3 Catalysts for steam methane reforming.....	7
1.3.1 Literature review of steam methane reforming catalysts.....	8
1.4 Membrane Reformers.....	17
1.5 Motivation of study	25
1.6 Objectives.....	26
1.7 Structure of thesis.....	27
References.....	30
Chapter 2	41
Catalyst Preparation Methods, Characterization Techniques and Experimental Framework	41
2.1 Introduction to Catalysts	41
2.2 Catalyst Preparation Methods	41
2.2.1 Impregnation Method	42
2.2.2 Precipitation Method	43
2.2.3 Co-precipitation Method.....	43
2.2.4 Sol-Gel Method	44
2.2.5 Chemical Vapor Deposition (CVD).....	45
2.2.6 Atomic Layer Deposition (ALD).....	45

2.3. Characterization Techniques for Catalysts	46
2.3.1 X-ray Diffraction (XRD)	46
2.3.2 Scanning Electron Microscopy (SEM).....	48
2.3.3 Transmission Electron Microscopy (TEM)	48
2.3.4 X-ray Photoelectron Spectroscopy (XPS)	50
2.3.5 Brunauer-Emmett-Teller (BET) Surface Area Analysis	51
2.3.6 FTIR Spectroscopy	52
2.4. Experimental Framework.....	53
2.4.1 Catalyst Preparation.....	54
2.4.2 Catalyst evaluation	58
2.4.3 Gas Chromatography (GC).....	58
References.....	62
Chapter 3	67
Monometallic Catalyst: Performance and Shape Morphology Effect	67
3.1 Monometallic Catalysts for steam methane reforming	67
3.1.1 Nickel Catalysts on Alumina Support	67
3.1.2 Nickel Catalysts on Ceria Support.....	68
3.1.3 Key literature review on Ni based monometallic catalyst.....	69
3.2 Preparation of monometallic catalysts	72
3.3 Results and discussion.....	73
3.3.1 SEM	73
3.3.2 XRD.....	74
3.3.3 BET.....	76
3.3.4 Activity Results.....	79
3.4 Summary	85
3.5 Effect of Shape morphology on Ceria.....	85
3.5.1 Literature review on shape morphology of ceria.....	86
3.5.2 Catalyst characterization.....	89
3.5.3 Catalyst synthesis procedure	90
3.5.4 Catalyst performance in packed bed reactor.....	90
3.6 Results and discussion.....	91

3.6.1 BET and XRD	91
3.6.2 TEM/EDX Results.....	96
3.6.3 Experimental results	100
3.6.4 Comparison with commercial ceria.....	102
3.7 Conclusions.....	104
References.....	106
Chapter 4	113
Role of Bimetallic Catalysts in Steam Methane Reforming.....	113
4.1 Introduction.....	113
4.2 Experimental analysis	114
4.2.1 Materials	114
4.2.2 Catalyst Synthesis.....	114
4.2.3 Catalyst Characterization.....	115
4.3 Catalyst Testing.....	116
4.4 Results and Discussion.....	117
4.4.1 Characterization results	117
4.4.2 Catalyst Activity Testing.....	123
4.5 Cobalt based bimetallic catalysts:	131
4.5.1 Alumina Supports	131
4.5.2 Cerium Oxide	131
4.6 Conclusions	133
References.....	136
Chapter 5	143
Role of Trimetallic Catalysts in Steam Methane Reforming	143
5.1 Role of trimetallic catalyst Ni-Fe-La/Al ₂ O ₃	143
5.1.1 Introduction	143
5.2 Experimental	147
5.2.1 Catalyst preparation.....	147
5.2.2 Catalyst characterization.....	147
5.2.3 Catalyst Test.....	148
5.3 Results and discussion.....	149

5.3.1 Catalytic Activity	149
5.3.2 Long term stability test	157
5.3.3 Characterization results	158
5.4 Conclusions	169
5.5 Cobalt based trimetallic catalyst Ni-Co-La/Al ₂ O ₃	170
5.5.1 Introduction	170
5.5.2 Methodology.....	174
5.5.3 Catalyst characterization.....	174
5.5.4 Catalyst testing	176
5.6 Results and discussion.....	178
5.6.1 Characterization results	178
5.6.2 Catalytic activity of steam methane reforming.....	193
5.7 Comparison of trimetallic catalysts to be used for upscaling.....	198
5.8 Conclusions	199
References.....	201
Chapter 6	211
Large scale studies of steam methane reforming in packed bed reactor.....	211
6.1 Introduction	211
6.2 Experimental section	212
6.2.1 Catalyst Preparation.....	212
6.2.2 Catalyst testing in packed bed reactor	212
6.3 Results and Discussion.....	216
6.3.1 Effect of temperatures	216
6.3.2 Effect of various W/F in large reactor	218
6.4 Large scale studies to 3kW.....	220
6.5 Effect of pressure	223
6.6 Characterization results.....	224
6.7 Conclusions	229
References.....	230
Chapter 7	235
Conclusions and Recommendations.....	235

7.1 Conclusions of study	235
7.2 Recommendations and future perspectives	240
Appendix-A.....	243
Effect of Mixed Supports.....	243
A1. Introduction	245
A2. Methodology	246
A3. Catalyst Preparation	249
A4. Catalyst Characterization	250
A5. Catalyst Activity.....	250
A6. Results and discussion	252
A7. Comparative analysis of mixed support with only alumina.....	255
A8. Characterization results.....	259
A9. Conclusions.....	262
References.....	263

LIST OF FIGURES

Fig 1.1 Qualitative percentage distribution of different catalyst used for steam methane reforming in literature.....	8
Fig 1.2 Membrane reformer technology for hydrogen production via steam methane reforming.....	18
Fig 2.1 Flow chart for synthesis of catalysts.....	57
Fig 2.2 Schematic diagram of packed bed reactor of internal diameter 11.74mm.....	59
Fig 2.3 Scale up reactor of internal diameter 6.35cm.....	60
Fig 3.1 Wet impregnation method for monometallic catalysts.....	73
Fig 3.2 SEM images of monometallic ceria and alumina supported catalysts.....	74
Fig 3.3 XRD graph of monometallic catalysts.....	76
Fig 3.4 BET graphs of monometallic catalysts (a) alumina supported (b) ceria supported.....	77
Fig 3.5 Conversion vs time graph of monometallic alumina supported catalysts.....	80
Fig 3.6 Conversion vs time graph of monometallic ceria supported catalysts.....	81
Fig 3.7 CO selectivity vs time of monometallic alumina supported catalysts.....	82
Fig 3.8 CO selectivity vs time graph of monometallic ceria supported catalysts.....	83
Fig 3.9 CO ₂ selectivity vs time graph of (a) monometallic alumina supported (b) monometallic ceria supported.....	84
Fig 3.10 Brunauer–Emmett–Teller (BET) N ₂ adsorption desorption isotherm of Ni-doped ceria nanorod and nanocube calcined at 550°C.....	92
Fig 3.11 X-ray diffraction (XRD) analysis of Ni doped ceria (a) nanorod calcined at 550°C,	

(b) nanorod calcined at 970°C, (c) nanocube calcined at 550°C, and (d) nanocube calcined at 970°C.....95

Fig 3.12: Transmission electron microscopy (TEM) image of Ni-doped ceria support. (a) Nanorod calcined at 550°C, (b) nanocube calcined at 550°C, (c) nanorod calcined at 970°C, (d) nanocube calcined at 970°C, (e) spent nanorod catalyst calcined at 550°C and reduced at 850°C, and (f) spent nanocube calcined at 550°C reduced at 850°C.....98

Fig 3.13 EDX analysis of (a) Ni-doped nano cube calcined at 550°C and (b) Ni-doped nano rod calcined at 550°C as received and as implanted.....100

Fig 3.14 Conversion versus time graph of (a) nanorod calcined at 550°C and (b) nanocube calcined at 550°C.....101

Fig 3.15 CO selectivity vs time graph for (a) nanorod calcined at 550°C (b) nanocube calcined at 550°C, CO₂ selectivity (c) nanorod calcined at 550°C (d) nanocube calcined at 550°C.....102

Fig 3.16 Comparison of commercial ceria with shapes (a) conversion graph of samples calcined at 550°C (b) conversion graph of samples calcined at 970°C (c) CO selectivity graph of samples calcined at 550°C (d) CO selectivity graph of samples calcined at 970°C.....104

Fig 4.1. XRD graph of La and Fe doped bimetallic catalysts.....118

Fig 4.2. BET Analysis of Ni/CeO₂, Ni-La/CeO₂, Ni-Fe/CeO₂.....121

Fig 4.3. SEM images of a) Ni/Al₂O₃, b) Ni-La/Al₂O₃, c) Ni-Fe/Al₂O₃, d) Ni/CeO₂, e) Ni-La/CeO₂, and f) Ni-Fe/CeO₂123

Fig 4.4. a) EDS mapping of Ni-La/Al₂O₃, b) Ni-La/CeO₂.....123

Fig 4.5. Conversion vs temperature plots for a) Ni/Al₂O₃, Ni-La/Al₂O₃, Ni-Fe/Al₂O₃, b) Ni/CeO₂, Ni La/CeO₂, Ni Fe/CeO₂ (reaction conditions: P = 1 atm, H₂O/ CH₄ = 4.0, W/F= 26.8 Kg_{cat}.s/mol).....126

Fig 4.6. Conversion vs time graph for a) Ni-Fe/Al₂O₃, b) Ni-La/Al₂O₃ c) Ni-Fe/CeO₂ d) Ni-La/CeO₂ catalysts at different temperatures.....128

Fig 4.7. CO selectivity with temperature for a) alumina supported b) ceria supported catalysts.....128

Fig 4.8. CO₂ selectivity with temperature for a) alumina supported b) ceria supported catalysts.....129

Fig 4.9. Conversion vs time graph of (a) alumina supported catalysts (b) ceria supported catalysts.....131

Fig 4.10. Catalyst activity of Ni-Co/Al₂O₃ catalyst (a) Methane conversion vs time (b) CO selectivity vs time (c) CO₂ selectivity vs time graph.....132

Fig 5.1 (a) Conversion vs Temperature graph of different compositions (b) conversion vs time graph 75Ni-20Fe-5La (c) conversion vs time graph of 75Ni-15Fe-10La (d) conversion vs time graph of 75Ni-10Fe-10La.....151

Fig 5.2 Catalytic activity of 75Ni-15Fe-10La (a) Conversion vs time (b) H₂ yield vs time (c) CO selectivity vs time (d) CO₂ selectivity vs time.....152

Fig 5.3 Effect of W/F on 75Ni-15Fe-10La at 700 °C (a) Conversion vs time graph (b) H₂ Yield vs time (c) CO selectivity vs time (d) CO₂ selectivity vs time.....153

Fig 5.4 Conversion, H₂ production rate vs W/F value for 75Ni-15Fe-10La catalyst at 700 °C...154

Fig 5.5 (a) Conversion vs metal loading graph of 75Ni-15Fe-10La catalyst (b) Conversion vs time graph w.r.t metal loadings (c) CO₂ selectivity vs time graph (d) H₂ yield vs time graph.....155

Fig 5.6 Long term stability test of 75Ni-15Fe-10La catalyst for at least 130 hours.....156

Fig 5.7 SEM images of (a) Fresh 75Ni-10Fe-15La (b) Fresh 75Ni-15Fe-10La (c) spent 75Ni-10Fe-15La (d) 75Ni-15Fe-10La.....158

Fig 5.8. EDS analysis of catalysts (a) Fresh 75Ni-10Fe-15La (b) Spent 75Ni-10Fe-15La (c) Fresh 75Ni-15Fe-10La (d) Spent 75Ni-15Fe-10La.....	158
Fig 5.9 XRD graphs of fresh and spent trimetallic catalysts.....	162
Fig 5.10 XPS spectra Ni-Fe-La/Al ₂ O ₃ catalyst.....	164
Fig 5.11 FTIR spectra of fresh and spent 75Ni-15Fe-10La catalyst.....	165
Fig 5.12 TEM analysis of (a) Fresh 75Ni-15Fe-10La (b) SAED pattern of fresh catalyst (c) Average particle size of fresh catalyst (d) Spent 75Ni-15Fe-10La (e) SAED pattern of spent catalyst (f) Interplanar distant of spent catalyst.....	167
Fig 5.13 Schematic diagram of catalytic reformer.....	176
Fig 5.14 XRD graph of alumina and ceria supported catalysts.....	178
Fig 5.15 Adsorption-desorption isotherm of (a) ceria supported (b) alumina supported catalysts.....	180
Fig 5.16 SEM images of a) La/CeO ₂ , b) Co/CeO ₂ , c) Ni-Co/CeO ₂ , d) Co-La/CeO ₂ , e) La/Al ₂ O ₃ , f) Co/Al ₂ O ₃ , g) Ni-Co/Al ₂ O ₃ , h) Co-La/Al ₂ O ₃ (i) Ni-Co-La/Al ₂ O ₃ (j) Ni-Co-Fe/Al ₂ O ₃ (k) Spent Ni-Co-La/Al ₂ O ₃ (l) Spent Ni-Co-Fe/Al ₂ O ₃	183
Fig 5.17 EDS images (a) Spent Ni-Co-La/Al ₂ O ₃ and d) Spent Ni-Co-Fe/ Al ₂ O ₃	185
Fig 5.18 TEM images of a) Ni-Co/Al ₂ O ₃ , b) Ni-Co-Fe/Al ₂ O ₃ , c) Ni-Co-La/Al ₂ O ₃ d) Spent Ni-Co-La/Al ₂ O ₃ and e) Spent Ni-Co- Fe/Al ₂ O ₃	186
Fig 5.19 FTIR analysis of synthesized catalysts.....	189
Fig 5.20 (a) conversion vs temperature graph of all alumina supported catalysts (b) CO selectivity vs temperature graph (c) CO ₂ selectivity vs temperature graph (d) Conversion vs temperature graph of both trimetallic catalysts at 700°C.....	191

Fig 5.21 Conversion, H ₂ production rate vs W/F graph of Ni-Co-La/Al ₂ O ₃ catalyst.....	192
Fig 5.22 Life cycle study of Ni-Co-La/Al ₂ O ₃ catalyst.....	193
Fig 5.23 Conversion vs time graph of Ni-Co-La/Al ₂ O ₃ at different S/M ratios.....	194
Fig 5.24 Comparison of all trimetallic catalysts (a) Conversion graph (b) CO selectivity graph (c) CO ₂ selectivity.....	195
Fig 6.1 Experimental set up of scale up reactor of I.D 6.35cm.....	211
Fig 6.2 Conversion vs time graph of Ni-Co-La/Al ₂ O ₃ catalyst for all temperatures for 1 kW system.....	213
Fig 6.3 Ni-Co-La/Al ₂ O ₃ catalyst for all temperatures for 1 kW system (a) CO selectivity (b) CO ₂ selectivity vs time.....	214
Fig 6.4 Conversion vs time graph of Ni-Co-La/Al ₂ O ₃ catalyst for W/F values.....	215
Fig 6.5 Ni-Co-La/Al ₂ O ₃ catalyst for W/F for 1 kW system (a) CO selectivity (b) CO ₂ selectivity.....	216
Fig 6.6 Conversion vs time graph of Ni-Co-La/Al ₂ O ₃ catalyst for 3kW system at 700°C.....	218
Fig 6.7 Ni-Co-La/Al ₂ O ₃ catalyst for 3kW system for CO selectivity.....	219
Fig 6.8 Conversion vs time graph of Ni-Co-La/Al ₂ O ₃ catalyst for all pressures for 1 kW system at 700°C (a) Conversion (b) CO selectivity (c) CO ₂ selectivity.....	220
Fig 6.9 TEM image of Ni-Co-La/Al ₂ O ₃ catalyst powder pellets for 1 kW system (a-c) Fresh catalyst (d-f) Spent catalyst after small reactor of I.D 11.74mm (g-i) Spent catalyst after scale up reactor of I.D 6.35cm.....	222
Fig 6.10 Ni-Co-La/Al ₂ O ₃ catalyst powder pellets for 1 kW system (a) Fresh catalyst (b) Spent catalyst after scale up reactor.....	224

Fig A1. Conversion vs time graph (a) 75Al/25Ce (b) 50Al/50Ce (c) 80Al/20Ce.....	247
Fig A2. Conversion vs time graph of 80Al/20Ce ratio for all temperatures.....	249
Fig A3. (a) CO selectivity vs time graph of 80Al/20Ce catalyst (b) CO ₂ selectivity vs time graph.....	250
Fig A4. Conversion vs time graph of mixed support and without ceria support.....	251
Fig A5. (a) CO selectivity vs time graph (b) CO ₂ selectivity vs time graph.....	252
Fig A6. Effect of W/F for Ni-Co-La/Ce-Al ₂ O ₃ catalyst.....	253
Fig A7. SEM images of (a)75Al/25Ce (b) 80Al/20Ce (c) 50Al/50Ce.....	254
Fig A8. TEM images of mixed supports(a) 80Al/20Ce (b) 75Al/25Ce (c) 50Al/50Ce.....	256

LIST OF TABLES

Table 1.1 Key Literature on steam methane reforming catalysts.....	10
Table 1.2 Key literature on membrane reformer using methane.....	19
Table 2.1 Monometallic Catalysts synthesized on alumina and ceria supports.....	56
Table 2.2 Bimetallic Catalysts synthesized on alumina and ceria supports.....	56
Table 2.3 Trimetallic Catalysts synthesized on alumina support.....	56
Table 2.4 Calibration factors used in analysis of GC results for mixture of gases.....	61
Table 3.1 Literature survey on Nickel based monometallic catalyst.....	69
Table 3.2 Surface area, pore volume, pore diameter and crystallite size for monometallic alumina supported catalysts.....	79
Table 3.3 Catalyst shape morphology effect on steam reforming.....	87
Table 3.4 BET surface area, pore volume and pore diameter of different catalysts.....	94
Table 3.5 Crystallite sizes of various ceria shape morphologies.....	97
Table 4.1. Composition of prepared catalysts.....	115
Table 4.2. BET surface area analysis of synthesized catalysts.....	121
Table 4.3. Elemental composition of catalysts through EDS analysis.....	122
Table 5.1 Literature survey.....	144
Table 5.2 BET surface area, pore volume and pore diameter of catalysts.....	160
Table 5.3 Literature survey.....	171
Table 5.4 BET analysis of all the catalysts.....	180
Table 6.1 Specifications for small and scale up reactor.....	211
Table 6.2 BET surface area, pore volume, pore diameter and type of isotherm of catalysts.....	223
Table A1. Literature survey.....	241

List of abbreviations

SMR	Steam methane reforming
MR	Membrane reformer
GC	Gas chromatography
PEMFC	Proton exchange membrane fuel cell
XRD	X-ray diffraction
BET	Brunauer-Emmett-Teller
SEM	Scanning electron microscope
EDS	Energy dispersive X-ray spectroscopy
TEM	Transmission electron microscope
XPS	X-ray photoelectron spectroscopy
FTIR	Fourier transform infrared spectroscopy