

ETHANOL DRY REFORMING OVER  
LANTHANIDE-PROMOTED Ni/Al<sub>2</sub>O<sub>3</sub>  
CATALYSTS FOR SYNGAS PRODUCTION

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## **SUPERVISOR'S DECLARATION**

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Master of Engineering in Gas.

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I hereby declare that the work in this thesis is based on my original work except for quotations and citation which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

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## TABLE OF CONTENTS

	<b>Page</b>
<b>DECLARATION</b>	
<b>TITLE PAGE</b>	i
<b>ACKNOWLEDGEMENTS</b>	ii
<b>ABSTRAK</b>	iii
<b>ABSTRACT</b>	iv
<b>TABLE OF CONTENTS</b>	v
<b>LIST OF TABLES</b>	x
<b>LIST OF FIGURES</b>	xi
<b>LIST OF SYMBOLS</b>	xvi
<b>LIST OF ABBREVIATIONS</b>	xviii
<b>CHAPTER 1 INTRODUCTION</b>	
1.1 Introduction	1
1.2 Problem Statement	3
1.3 Objectives	3
1.4 Scope of the Study	4
1.5 Overview of Thesis	4
<b>CHAPTER 2 LITERATURE REVIEW</b>	
2.1 Fossil Fuels	6
2.1.1 Overview	6
2.1.2 Limitation of Fossil Fuels	7
2.2 Overview of Syngas	9
2.2.1 Introduction	9

2.2.2	Syngas Production Technologies	9
2.3	Ethanol	14
2.3.1	Overview	14
2.3.2	Partial Oxidation of Ethanol (POE)	16
2.3.3	Ethanol Steam Reforming (ESR)	17
2.3.4	Oxidative Steam Reforming of Ethanol (OSRE)	18
2.4	Ethanol Dry Reforming (EDR)	18
2.4.1	Reactions of Ethanol Dry Reforming	22
2.4.2	Thermodynamics Analysis	23
2.5	Ethanol Dry Reforming Catalysts	25
2.5.1	Introduction	25
2.5.2	Noble Metals	26
2.5.3	Non-Noble Metals	26
2.5.4	Catalyst Supports	27
2.5.5	Catalyst Promoters	27
2.6	Catalyst Deactivation	28
2.6.1	Poisoning	29
2.6.2	Fouling	30
2.6.2	Sintering	30
2.7	Concluding Remarks	31
<b>CHAPTER 3 METHODOLOGY</b>		
3.1	Introduction	32
3.2	Materials and Equipment	32
3.3	Catalyst Preparation	34
3.4	Catalyst Characterization Techniques	35

3.4.1	Textural Analysis	35
3.4.2	X-ray Diffraction (XRD) Measurement	38
3.4.3	Temperature-programmed Calcination (TPC)	40
3.4.4	Temperature-programmed Reduction (H <sub>2</sub> -TPR)	40
3.4.5	Temperature-programmed Oxidation (TPO)	40
3.4.6	Temperature-programmed Desorption (NH <sub>3</sub> -TPD)	41
3.4.7	X-ray Photoelectron Spectroscopy (XPS)	41
3.4.8	Raman Spectroscopy	42
3.4.9	Scanning Electron Microscopy (SEM)	42
3.4.10	Transmission Electron Microscopy (TEM)	43
3.5	Experimental Set Up	43
3.6	Gas Chromatography (GC)	45

## **CHAPTER 4 PRELIMINARY WORK**

4.1	Introduction	46
4.2	Blank Test	46
4.3	Transport Resistance Considerations	47
4.3.1	External Mass Transfer	49
4.3.2	Internal Mass Transfer	50
4.3.3	External Heat Transfer	51
4.3.4	Internal Heat Transfer	52
4.3.5	Wall and Radial Heat Dispersion Effects	52
4.4	Ethanol Dry Reforming Reaction Metrics	53
4.5	Syringe Pump and Mass Flow Controller (MFC) Calibration	55



## **CHAPTER 5 CATALYST CHARACTERIZATION**

5.1	Introduction	56
5.2	N <sub>2</sub> -Physisorption Measurements	56
5.3	X-ray Diffraction Measurement	58
5.4	Temperature-programmed Calcination (TPC)	60
5.5	Temperature-programmed Reduction (TPR)	62
5.6	NH <sub>3</sub> Temperature-programmed Desorption (TPD)	63
5.7	X-ray Photoelectron Spectroscopy (XPS)	65
5.8	Raman Spectroscopy Measurements	66
5.9	SEM Measurement	67
5.10	Concluding Remarks	69

## **CHAPTER 6 ETHANOL DRY REFORMING REACTION STUDY**

6.1	Introduction	70
6.2	Transient Profiles	70
6.3	Effect of Operation Conditions	72
6.3.1	Effect of Reaction Temperature	72
6.3.2	Effect of CO <sub>2</sub> Partial Pressure	76
6.3.3	Effect of C <sub>2</sub> H <sub>5</sub> OH Partial Pressure	80
6.4	Effect of La-promoter Loading	83
6.5	Longevity Test	84
6.6	Post-Reaction Characterizations	88
6.6.1	Raman Spectroscopy Measurement	88
6.6.2	SEM and TEM Measurements	90
6.6.3	Temperature-programmed Oxidation (TPO)	94
6.7	Concluding Remarks	96

## **CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS**

7.1 Conclusions 97

7.2 Recommendations 99

**REFERENCES** 100

## **APPENDICES**

A Catalyst Preparation Calculations 113

B Transport Resistance Calculations 116

C Ethanol Dry Reforming Reaction Calculations 127

D Calibration Curve 130

## LIST OF TABLES

Table 2.1	Summarizes of previous research on dry reforming reaction	13
Table 2.2	Advantages and disadvantages of syngas reforming technologies	14
Table 2.3	List of top ten countries by their annual palm oil production in 1000 MT	16
Table 2.4	The summarized results of previous studies for ethanol dry reforming	20
Table 2.5	The summary of thermodynamic features in EDR reaction	24
Table 2.6	Mechanisms of catalyst deactivation	28
Table 2.7	Examples of poisons encountered in industrial processes	29
Table 3.1	List of used chemicals and gas	33
Table 3.2	List of equipment used for the preparation of catalyst and catalytic study	34
Table 3.3	Standard gas data	45
Table 4.1	Properties used in the calculation of transport resistances	48
Table 5.1	Textural properties of fresh $\gamma$ -Al <sub>2</sub> O <sub>3</sub> support, unpromoted and promoted catalysts	57
Table 5.2	The acidic properties of promoted and unpromoted 10%Ni/Al <sub>2</sub> O <sub>3</sub> catalysts from NH <sub>3</sub> -TPD measurements	64
Table 6.1	Summary of $I_D/I_G$ ratio for spent promoted and unpromoted catalysts	90
Table 6.2	The weight loss of the promoted and unpromoted Ni-based catalysts during TPO measurements	96

## LIST OF FIGURES

Figure 2.1	The share of global energy consumption in 2013	6
Figure 2.2	The sources of CO <sub>2</sub> emissions in the world	7
Figure 2.3	Discovery versus production of conventional oil	8
Figure 2.4	Structure of ethanol molecule	15
Figure 2.5	Biomass production in Malaysia	15
Figure 2.6	The change in Gibbs free energy for the all reactions in EDR at various temperatures.	23
Figure 2.7	Energy pathway of catalytic reaction	25
Figure 3.1	Flowchart of catalyst preparation	35
Figure 3.2	N <sub>2</sub> adsorption and desorption isotherm profiles	37
Figure 3.3	The Bragg Law for XRD analysis	39
Figure 3.4	Ejection of photoelectrons	41
Figure 3.5	Schematic diagram for ethanol dry reforming reaction	44
Figure 3.6	Fixed-bed reactor for EDR reaction	44
Figure 5.1	X-ray diffractograms of (a) $\gamma$ -Al <sub>2</sub> O <sub>3</sub> support, (b) 10%Ni/Al <sub>2</sub> O <sub>3</sub> , (c) 3%Ce-10%Ni/Al <sub>2</sub> O <sub>3</sub> and (d) 3%La-10%Ni/Al <sub>2</sub> O <sub>3</sub> catalysts	59
Figure 5.2	XRD patterns of (a) 10%Ni/Al <sub>2</sub> O <sub>3</sub> , (b) 2%La-10%Ni/Al <sub>2</sub> O <sub>3</sub> , (c) 3%La-10%Ni/Al <sub>2</sub> O <sub>3</sub> and (d) 5%La-10%Ni/Al <sub>2</sub> O <sub>3</sub> catalysts	60
Figure 5.3	Derivative weight profiles for temperature-programmed calcination of promoted and unpromoted Ni-based catalysts	61
Figure 5.4	H <sub>2</sub> -TPR profiles of promoted and unpromoted catalysts at a ramping rate of 15 K min <sup>-1</sup>	63
Figure 5.5	NH <sub>3</sub> -TPD profiles for promoted and unpromoted 10%Ni/Al <sub>2</sub> O <sub>3</sub> catalysts	64

## LIST OF FIGURES

Figure 5.6	XPS spectra of unpromoted and promoted Ni-based catalysts	65
Figure 5.7	The Raman spectra of fresh promoted and unpromoted Ni-based catalysts	66
Figure 5.8	SEM image of 10%Ni/Al <sub>2</sub> O <sub>3</sub> catalyst	67
Figure 5.9	SEM image of 3%Ce-10%Ni/Al <sub>2</sub> O <sub>3</sub> catalyst	68
Figure 5.10	SEM image of 3%La-10%Ni/Al <sub>2</sub> O <sub>3</sub> catalyst	68
Figure 6.1	CO <sub>2</sub> and C <sub>2</sub> H <sub>5</sub> OH conversion profiles for EDR reaction without catalyst at 973 K, $P_{CO_2} = 20$ kPa and $P_{C_2H_5OH} = 20$ kPa	71
Figure 6.2	CO <sub>2</sub> and C <sub>2</sub> H <sub>5</sub> OH conversion profiles for EDR reaction of 10%Ni/Al <sub>2</sub> O <sub>3</sub> catalyst at 973 K, $P_{CO_2} = 20$ kPa and $P_{C_2H_5OH} = 20$ kPa	71
Figure 6.3	Effect of temperature on C <sub>2</sub> H <sub>5</sub> OH conversion of 10%Ni/Al <sub>2</sub> O <sub>3</sub> catalyst at $P_{CO_2} = P_{C_2H_5OH} = 20$ kPa	72
Figure 6.4	Effect of temperature on C <sub>2</sub> H <sub>5</sub> OH conversion of unpromoted and promoted Ni-based catalysts at $P_{CO_2} = P_{C_2H_5OH} = 20$ kPa	73
Figure 6.5	Effect of temperature on CO <sub>2</sub> conversion of unpromoted and promoted Ni-based catalyst at $P_{CO_2} = P_{C_2H_5OH} = 20$ kPa	74
Figure 6.6	Effect of temperature on yield of H <sub>2</sub> over Ni-based catalysts at $P_{CO_2} = P_{C_2H_5OH} = 20$ kPa	75
Figure 6.7	Effect of temperature on CH <sub>4</sub> /CO ratio of 10%Ni/Al <sub>2</sub> O <sub>3</sub> , 3%Ce-10%Ni/Al <sub>2</sub> O <sub>3</sub> and 3%La-10%Ni/Al <sub>2</sub> O <sub>3</sub> catalysts at $P_{CO_2} = P_{C_2H_5OH} = 20$ kPa	75
Figure 6.8	Effect of temperature on H <sub>2</sub> /CO ratio of 10%Ni/Al <sub>2</sub> O <sub>3</sub> , 3%Ce-10%Ni/Al <sub>2</sub> O <sub>3</sub> and 3%La-10%Ni/Al <sub>2</sub> O <sub>3</sub> catalysts at $P_{CO_2} = P_{C_2H_5OH} = 20$ kPa	76

## LIST OF FIGURES

Figure 6.9	Influence of $P_{CO_2}$ on C <sub>2</sub> H <sub>5</sub> OH conversion of promoted and unpromoted catalysts at $P_{C_2H_5OH} = 20$ kPa and T = 973 K	77
Figure 6.10	Effect of $P_{CO_2}$ on CO <sub>2</sub> conversion of promoted and unpromoted catalysts at $P_{C_2H_5OH} = 20$ kPa and T = 973 K	77
Figure 6.11	Effect of $P_{CO_2}$ on H <sub>2</sub> yield of Ni-based catalysts at $P_{C_2H_5OH} = 20$ kPa and T = 973 K	78
Figure 6.12	Effect of $P_{CO_2}$ on H <sub>2</sub> /CO ratio of promoted and unpromoted catalysts at $P_{C_2H_5OH} = 20$ kPa and 973 K	79
Figure 6.13	Effect of $P_{CO_2}$ on CH <sub>4</sub> /CO ratio of promoted and unpromoted catalysts at $P_{C_2H_5OH} = 20$ kPa and 973 K	79
Figure 6.14	Influence of $P_{C_2H_5OH}$ on C <sub>2</sub> H <sub>5</sub> OH conversion of 10%Ni/Al <sub>2</sub> O <sub>3</sub> , 3%Ce-10%Ni/Al <sub>2</sub> O <sub>3</sub> and 3%La-10%Ni/Al <sub>2</sub> O <sub>3</sub> catalysts at $P_{CO_2} = 20$ kPa and 973 K	80
Figure 6.15	Influence of $P_{C_2H_5OH}$ on CO <sub>2</sub> conversion of 10%Ni/Al <sub>2</sub> O <sub>3</sub> , 3%Ce-10%Ni/Al <sub>2</sub> O <sub>3</sub> and 3%La-10%Ni/Al <sub>2</sub> O <sub>3</sub> catalysts at $P_{CO_2} = 20$ kPa and 973 K	81
Figure 6.16	Effect of $P_{C_2H_5OH}$ on H <sub>2</sub> yield during EDR at $P_{CO_2} = 20$ kPa and T = 973 K	82
Figure 6.17	Effect of $P_{C_2H_5OH}$ on H <sub>2</sub> /CO ratio during EDR at $P_{CO_2} = 20$ kPa and T = 973 K	82
Figure 6.18	Effect of La loadings on C <sub>2</sub> H <sub>5</sub> OH conversion and CH <sub>4</sub> yield at $P_{C_2H_5OH} = 20$ kPa and T = 973 K	84

## LIST OF FIGURES

Figure 6.19	Time-on-stream profile for ethanol conversion at $P_{CO_2} = P_{C_2H_5OH} = 20$ kPa and $T = 973$ K	85
Figure 6.20	Time-on-stream profile for $CO_2$ conversion at $P_{CO_2} = P_{C_2H_5OH} = 20$ kPa and $T = 973$ K	85
Figure 6.21	Time-on-stream profile for $H_2$ yield at $P_{CO_2} = P_{C_2H_5OH} = 20$ kPa and $T = 973$ K	86
Figure 6.22	Time-on-stream profile for $CH_4/CO$ ratio at $P_{CO_2} = P_{C_2H_5OH} = 20$ kPa and $T = 973$ K	87
Figure 6.23	Time-on-stream profile for $H_2/CO$ ratio at $P_{CO_2} = P_{C_2H_5OH} = 20$ kPa and $T = 973$ K	87
Figure 6.24	The Raman spectra of spent Ni-based catalysts after EDR at $P_{CO_2} = 40$ kPa, $P_{C_2H_5OH} = 20$ kPa and $973$ K	89
Figure 6.25	The SEM microphotograph of spent 10%Ni/ $Al_2O_3$ catalyst at $P_{CO_2} = P_{C_2H_5OH} = 20$ kPa and $973$ K	91
Figure 6.26	The SEM microphotograph of spent 3%Ce-10%Ni/ $Al_2O_3$ catalyst at $P_{CO_2} = P_{C_2H_5OH} = 20$ kPa and $973$ K	91
Figure 6.27	The SEM microphotograph of spent 3%La-10%Ni/ $Al_2O_3$ catalyst at $P_{CO_2} = P_{C_2H_5OH} = 20$ kPa and $973$ K	92
Figure 6.28	TEM images of spent 10%Ni/ $Al_2O_3$ at $P_{CO_2} = 30$ kPa, $P_{C_2H_5OH} = 20$ kPa and $973$ K	93
Figure 6.29	TEM images of spent 3%Ce-10%Ni/ $Al_2O_3$ at $P_{CO_2} = 30$ kPa, $P_{C_2H_5OH} = 20$ kPa and $973$ K	93
Figure 6.30	TEM images of spent 3%La-10%Ni/ $Al_2O_3$ at $P_{CO_2} = 30$ kPa, $P_{C_2H_5OH} = 20$ kPa and $973$ K	94

## LIST OF FIGURES

Figure 6.31	TPO profiles of the spent promoted and unpromoted Ni-based catalysts	95
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## LIST OF SYMBOLS

$A$	Pre-exponential factor
$B$	The line broadening at half the maximum intensity (FWHM)
$c$	A constant characteristic of adsorbate
$C_{Ab}$	Bulk gas-phase concentration of component A
$C_D$	Percentage of amorphous carbon
$C_P$	Specific heat capacity
$D_{eff}$	Effective diffusivity
$E_A$	Activation energy
$E_l$	The excitation of laser energy
$F$	Flow rate
$h$	Heat transfer coefficient
$j_D$	Colburn's mass transfer factor
$k_c$	Mass transfer coefficient
$L_a$	Crystallite size
$n_m$	Number of molecules adsorbed
$N$	Avogadro's number
$n$	Reaction order
$M_{ad}$	Molecular weight of adsorbate
$P$	Gas pressure
$Pr$	Prandtl number
$P_s$	Saturation pressure of adsorbed gas
$R$	Universal gas constant
$r$	Production rate
$r_{exp}$	Rate of reaction

$R_p$	Catalyst particle radius
$r_p$	Actual radius
$S_A$	Total surface area of sample
$Sc$	Schmidt number
$T_b$	Boiling point
$t_{ads}$	Thickness of the adsorbed layer
$U$	Superficial gas velocity
$V_a$	Volume of gas adsorbed
$W_{cat}$	Weight of the catalyst
$\lambda$	Wavelength
$\theta$	Bragg angle
$\rho_b$	Bulk density of catalyst bed
$\omega_p$	Catalyst pellet porosity
$\sigma_c$	Construction factor
$\tilde{\tau}$	Tortuosity
$\lambda_p$	Thermal conductivity
$\varepsilon$	Void fraction
$\beta$	Heating rate
$\Delta H$	Heat of reaction
$\Delta G$	Gibbs free energy

## LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
DC	Direct current
DOE	Department of Energy
EDR	Ethanol dry reforming
EPA	Environmental Protection Agency
ESR	Ethanol steam reforming
FID	Flame ionization detector
FTS	Fischer-Tropsch synthesis
GHSV	Gas hourly space velocity
I.D.	Inner diameter
LPG	Liquefied Petroleum Gas
O.D.	Outer diameter
OSR	Oxidative steam reforming
POE	Partial oxidation of ethanol
SEM	Scanning electron microscopy
SOFCs	Solid Oxide Fuel Cells
TCD	Thermal conductivity detector
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
TPC	Temperature-programmed calcination
TPD	Temperature-programmed desorption
TPO	Temperature-programmed oxidation
TPR	Temperature-programmed reduction
WGS	Water-gas shift

## LIST OF ABBREVIATIONS

XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

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## ABSTRAK

Pembaharuan semula kering etanol telah dianggap sebagai satu pendekatan yang menarik dan menjanjikan peluang cerah kerana ia menggunakan gas rumah hijau, CO<sub>2</sub> dan bio-komponen yang boleh diperbaharui iaitu etanol untuk menghasilkan produk bernilai. Pemangkin berasaskan Ni adalah pemangkin yang selalu digunakan dalam pembaharuan semula kerana mempunyai kebolehan yang tinggi untuk membelah ikatan C-C dan C-O. Walaubagaimanapun, pemangkin ini mengalami masalah pensinteran dan karbon terapan yang terbentuk hasil daripada tindak balas pempolimeran etilena, Boudouard dan penguraian metana. Oleh itu, tesis ini mengkaji kesan penggalak (CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub>) dan kadar kuantiti penggalak terhadap sifat-sifat fizikokimia bagi pemangkin 10%Ni/Al<sub>2</sub>O<sub>3</sub> menggunakan penjerapan fizik N<sub>2</sub> (kaedah BET), pengkalsinan suhu berprogram (TPC), penurunan suhu berprogram (TPR), pengoksidaan suhu berprogram (TPO), penyahjerapan suhu berprogram (TPD), analisis pembelauan sinar-X (XRD), mikroskop elektron pengimbasan (SEM), mikroskop elektron transmisi (TEM), spektroskopi electron sinar-X (XPS) dan spektroskopi Raman. Pengaruh keadaan operasi yang berbeza termasuk tindak balas tekanan separa dan suhu terhadap prestasi pembentukan semula kering etanol juga dikaji dalam projek ini. Pemangkin 10%Ni/Al<sub>2</sub>O<sub>3</sub> dengan penggalak dan tanpa penggalak telah disediakan dengan kaedah pengisitepuan dan dikaji dalam reaktor kuarza turus tetal pada nisbah berbeza CO<sub>2</sub>:C<sub>2</sub>H<sub>5</sub>OH 2.5:1 hingga 1:2.5 dan suhu 923-973 K pada tekanan atmosfera. Pemangkin dengan penggalak dan tanpa penggalak memiliki luas permukaan yang tinggi iaitu kira-kira 71-108 m<sup>2</sup> g<sup>-1</sup> dan semua penggalak telah tersebar rata di atas permukaan sokongan. Kedua-dua fasa, NiO dan NiAl<sub>2</sub>O<sub>4</sub> telah dikesan pada permukaan pemangkin dengan penggalak dan tanpa penggalak manakala fasa CeO<sub>2</sub> dan La<sub>2</sub>O<sub>3</sub> telah dilihat bagi pemangkin dengan penggalak Ce dan La. Penurunan spesies NiO kepada logam Ni<sup>0</sup> berlaku pada dua suhu penurunan yang berbeza bergantung kepada tahap interaksi diantara logam dan sokongan. Selain itu, kadar kepekatan tapak asid telah bekurangan dengan ketara sebanyak 30.45% dan 40.68% bagi penambahan unsur penggalak Ce dan La. Untuk penilaian pemangkin, kedua-dua penukaran C<sub>2</sub>H<sub>5</sub>OH dan CO<sub>2</sub> telah dipertingkatkan dengan ketara apabila suhu tindak balas ditingkatkan dari 923 hingga 973 K kerana sifat endoterma bagi tindak balas pembaharuan semula kering etanol. Peningkatan tekana separa bagi CO<sub>2</sub> dari 20 hingga 50 kPa memperbaiki kadar penukaran bahan tindak balas untuk kesemua pemangkin manakala tekanan separa yang optimum bagi C<sub>2</sub>H<sub>5</sub>OH dilihat pada 30-40 kPa bergantung kepada jenis pemangkin. Menariknya, nisbah H<sub>2</sub>/CO sentiasa mencapai jumlah 1.1 hingga 1.9 tidak mengira keadaan operasi sesuai untuk process Fischer-Tropsch. Tanpa mengira operasi parameter, pemangkin dengan unsur penggalak La muncul sebagai pemangkin terbaik dari segi penghasilan H<sub>2</sub> dan kandungan 3%La adalah kandungan penggalak yang optimum bagi pemangkin yang berunsurkan pengalok La kerana mempunyai kandungan oxygen yang tinggi dalam La<sub>2</sub>O<sub>3</sub>. Pemangkin 3%La-10%Ni/Al<sub>2</sub>O<sub>3</sub> mencapai kestabilan dalam 24 jam pada komposisi stoikiometri dan pada suhu tindak balas 973 K dari segi kadar penukaran bahan tindak balas dan nisbah H<sub>2</sub>/CO. Sifat heterogen karbon terbukti dengan kehadiran kedua-dua karbon amorfus dan grafit di permukaan pemangkin yang telah digunakan. Walau bagaimanapun, peratusan karbon telah berkurang dengan tambahan penggalak dalam turutan; La-penggalak < Ce-penggalak < pemangkin tanpa penggalak 10%Ni/Al<sub>2</sub>O<sub>3</sub>. Di akhir kajian ini, kesemua objektif yang ditetapkan telah tercapai secara keseluruhannya.

## ABSTRACT

Ethanol dry reforming has been regarded as an alluring and promising approach since it consumes greenhouse gas, CO<sub>2</sub> and renewable bio-component of ethanol to generate value-added products. Ni-based catalysts are the conventional reforming catalysts due to their high capacity of C-C and C-O bond cleavage. However, these catalysts suffer from sintering and deposited carbon formed from ethylene polymerization, Boudouard and methane decomposition reactions. Therefore, the aim of this thesis was to investigate the effect of promoters (CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub>) and promoter loading on the physicochemical properties of 10%Ni/Al<sub>2</sub>O<sub>3</sub> catalyst using N<sub>2</sub> physisorption (BET method), temperature-programmed calcination (TPC), temperature-programmed reduction (TPR), temperature-programmed oxidation (TPO), temperature-programmed desorption (TPD), X-ray diffraction (XRD) analysis, X-ray photoelectron spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy. The influence of different operation conditions including reactant partial pressure and temperature on catalytic performance of ethanol dry reforming was also studied in this project. Promoted and unpromoted 10%Ni/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by co-impregnation method and evaluated in a quartz fixed-bed reactor at different CO<sub>2</sub>:C<sub>2</sub>H<sub>5</sub>OH ratios of 2.5:1 to 1:2.5 and temperature of 923-973 K under atmospheric pressure. Promoted and unpromoted catalysts possessed relatively high BET surface area of about 71-108 m<sup>2</sup> g<sup>-1</sup> and both promoters were well dispersed on catalyst surface. Both NiO and NiAl<sub>2</sub>O<sub>4</sub> phases were detected on the surface of promoted and unpromoted catalysts whilst CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> phases were observed for Ce- and La-promoted catalysts, respectively. The reduction of NiO species to metallic Ni<sup>0</sup> phase occurred at two different reduction temperatures depending on the degree of metal-support interaction. Moreover, the acid site concentration was significantly reduced about 30.45% and 40.68% with the addition of Ce and La promoters, respectively. For catalytic evaluation, both C<sub>2</sub>H<sub>5</sub>OH and CO<sub>2</sub> conversions enhanced considerably with growing reaction temperature from 923 to 973 K due to the endothermic nature of ethanol dry reforming reaction. The increase in CO<sub>2</sub> partial pressure from 20 to 50 kPa improved reactant conversions for all catalysts whilst the optimal C<sub>2</sub>H<sub>5</sub>OH partial pressure was observed at 30-40 kPa depending on catalyst types. Interestingly, H<sub>2</sub>/CO ratio was always achieved within 1.1 to 1.9 regardless of operation conditions suitable for downstream Fischer-Tropsch synthesis. Irrespective of operating parameters, La-promoted catalyst appeared to be the best catalyst in terms of H<sub>2</sub> yield and 3%La loading was the optimal promoter loading for La-doped catalysts because of the high mobile oxygen storage capacity of La<sub>2</sub>O<sub>3</sub>. 3%La-10%Ni/Al<sub>2</sub>O<sub>3</sub> catalyst also seemed to be stable for 24 h on-stream at stoichiometric feed composition and reaction temperature of 973 K in terms of reactant conversion and H<sub>2</sub>/CO ratio. The heterogeneous nature of deposited carbons was evident with the presence of both amorphous and graphitic carbons on spent catalyst surface. However, the percentage of deposited carbon was reduced with promoter addition in the order; La-promoted < Ce-promoted < unpromoted 10%Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. At the end of this research, all the objectives that were set out have been achieved completely.

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