METHANE DRY REFORMING OVER COPPER AND IRON SUBSTITUTED STRONTIUM COBALT OXIDE PEROVSKITE CATALYST

CHANG YING SHI

BACHELOR OF CHEMICAL ENGINEERING UNIVERSITI MALAYSIA PAHANG

METHANE DRY REFORMING OVER COPPER AND IRON SUBSTITUTED STRONTIUM COBALT OXIDE PEROVSKITE CATALYST

CHANG YING SHI

Thesis submitted in partial fulfilment of the requirements

for the award of the degree of

Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering UNIVERSITI MALAYSIA PAHANG

SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

Signature :

Name of main supervisor : CHENG CHIN KUI

Position : ASSOCIATE PROFESSOR

Date : 10 DECEMBER 2016

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature :

Name : CHANG YING SHI

ID Number : KA13049

Date : JANUARY 2016

Dedication

"Research is what I'm doing when I don't know what I'm doing."

Wernher von Braun

ACKNOWLEDGEMENT

First and foremost, I would like thank my supervisor Associate Professor Dr. Cheng Chin Kui for his support and dedication in leading me throughout this work. I have received a lot of valuable lessons and knowledge from him. All of this has been made possible thanks to his belief in me.

This work is made possible through financial support in the form of Sciencefund from the Ministry of Science, Technology and Innovation Malaysia (RDU130501).

Many thanks also for the generous help from the staffs of the Faculty of Chemical and Natural Resources Engineering, in particular the technical staffs for their time and supervision.

Finally, my family who has always helped and supported me along the way also deserves the acknowledgement. I would like to thank them for their patience and love.

TABLE OF CONTENTS

SU	JPER'	VISOR'S DECLARATION	II			
S	TUDE	NT'S DECLARATION	III			
De	DedicationIV					
A	CKNC	OWLEDGEMENT	V			
A]	BSTR	ACT	VI			
A]	BSTR	AK	.VII			
TA	ABLE	OF CONTENTS	VIII			
LI	ST O	F FIGURES	X			
	LIST OF TABLESXIII					
LI	ST Ol	F ABBREVIATIONS	XIII			
1	IN	FRODUCTION	1			
	1.1	Background				
	1.2	Problem Statement and Motivation	2			
	1.3	Objective				
	1.4	Scopes				
	1.5	Outline of Thesis				
2		TERATURE REVIEW				
	2.1	General Overview				
	2.2	Statistics				
	2.3	Syngas				
	2.4	Steam Reforming reaction process				
	2.5	Dry Reforming reaction process				
	2.6	Partial Oxidation reaction process				
	2.7	Reforming Technologies				
	2.7.1	Auto-thermal Reforming (ATR)				
		Plasma Reforming				
	2.8	Reforming Catalysts				
	2.9	Catalyst Preparation				
	2.10	J control of the cont				
	2.11	· · · · · · · · · · · · · · · · · · ·				
3		ETHODOLOGY				
	3.1	Materials				
		Catalyst Preparation				
	3.3	Catalyst Characterization				
	3.4	Characterization Techniques				
	3.4.1	N ₂ physisorption				
	3.4.2	X-ray Diffraction (XRD)				
	3.4.3	Scanning Electron Microscopy (SEM)				
		Energy-dispersive X-ray Spectroscopy (EDX)				
		Fourier Transform Infrared (FT-IR)				
,	3.5	Catalyst reaction				
4		SULTS AND DISCUSSION				
	4.1	Catalyst Preparation	41			

	4.2	Fresh Catalysts Characterization	42
	4.2.1	Physical Properties of Fe- and Cu-Modified SrCoO _{3-δ} Catalysts	42
	4.2.2	X-ray Diffraction (XRD)	44
	4.2.3	Scanning Electron Microscopy (SEM)	47
		Dry Reforming Reaction Studies	
	4.3.1	Catalytic Evaluation	50
		Longevity Study	
	4.4	Used Catalysts Characterization	54
	4.4.1	N ₂ Physisorption	54
		X-ray Diffraction (XRD)	
	4.4.3	Fourier Transform InfraRed (FTIR)	55
	4.4.4	Scanning Electron Microscopy (SEM)-Energy Dispersive X-ray	
		spectrometry (EDX) Profiling	56
5	CO	NCLUSIONS AND RECOMMENDATIONS	58
	5.1	Conclusions	58
	5.2	Recommendations	59
R	EFER!	ENCES	60
A	PPEN	DICES	68

LIST OF FIGURES

Figure 2.1: Greenhouse gas emissions by gas in the United State (U.S.) from 1990 to 2013, (in
million metric tons of CO ₂ equivalent). Source: U.S. EPA, 20156
Figure 2.2: Greenhouse gas emissions and sinks by economic sector in the United State (U.S.)
from 1990 to 2013, (in million metric tons of CO ₂ equivalent). Source: U.S. EPA, 20157
Figure 2.3: Carbon deposition as a function of temperature and CO ₂ /CH ₄ ratio23
Figure 3.1: Basic components of volumetric physical adsorption analyzer
Figure 3.2: Braggs analysis for X-ray diffraction by crystal planes32
Figure 3.3: Basic components of X-ray diffractometers35
Figure 3.4: Schematic diagram of an electron optical column in SEM
Figure 3.5: Schematic diagram of EDX
Figure 3.6: A simple FT-IR spectrometer layout
Figure 3.7: Experimental setup
Figure 4.1: Formation of sol-gel via heating and stirring process in order to synthesize
$SrCo_{0.8}Fe_{0.2}O_{3-\delta}$, $SrCo_{0.8}Cu_{0.2}O_{3-\delta}$ and $SrCoO_{3-\delta}$ perovskite-type oxides respectively
Figure 4.2: Formation of flakes after drying process
Figure 4.3: The powder form of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$, $SrCo_{0.8}Cu_{0.2}O_{3-\delta}$ and $SrCoO_{3-\delta}$ perovskite-type
oxides were obtained after calcination
Figure 4.4: N ₂ physisorption isotherm for fresh parent and M-modified perovskite catalysts43
Figure 4.5: XRD patterns of parent and M-modified perovskite catalysts, fresh and spent: (a)
Fresh $SrCoO_{3-\delta}$; (b) Spent $SrCoO_{3-\delta}$; (c) Fresh $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$; (d) Spent $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$; (e)
Fresh $SrCo_{0.8}Cu_{0.2}O_{3-\delta}$ and (f) Spent $SrCo_{0.8}Cu_{0.2}O_{3-\delta}$ 46
Figure 4.6: SEM microstructural analysis of $SrCo_{0.8}M_{0.2}O_{3-\delta}$ catalysts (a) before reaction and (b)
after dry reforming reaction
Figure 4.7: Transient conversion profiles at the stoichiometric ratio and reaction temperature of
1023 K 50

Figure 4.8: Conversion (%) of CH_4 and CO_2 and Product Yield (%) over $SrCo\ O_{3-\delta}$ and
$SrCo_{0.8}M_{0.2}O_{3-\delta}$ where M = Fe or Cu. The feed was was $25\%CH_4 + 25\%CO_2$, N_2 -balance, 1023
K52
Figure 4.9: Longevity. The feed was was 25%CH ₄ + 25%CO ₂ , N ₂ -balance, 1023 K54
Figure 4.10: FTIR analysis at 400-4000 cm ⁻¹ before and post-DRM reaction respectively, at 1023
K with (\circ) 1435 cm ⁻¹ ; (\bullet) 856 cm ⁻¹ ; (Δ) 700 cm ⁻¹ ; (∇) 660 cm ⁻¹ and (*) 560 cm ⁻¹ 56
Figure 4.11: EDX profiling of the used catalysts representing (a) SrCoO _{3-δ} , (b) SrCo _{0.8} Fe _{0.2} O _{3-δ}
and (c) SrCo _{0.8} Cu _{0.2} O _{3-δ}

LIST OF TABLES

Table 2.1: Summary of previous research on Ni based perovskites an results	
Table 2.2: Summary of previous research on Co based perovskites an results	
Table 3.1: List of chemicals and its source and purity	25
Table 3.2: List of gases and its source and purity	25
Table 4.1: Chemical analysis, crystalline phases and textural properties of Sr	$Co_{0.8}M_{0.2}O_{3-\delta}$ (M is
either Cu or Fe)	49
Table 4.2: Crystalline phases and textural properties of spent catalysts	49

LIST OF ABBREVIATIONS

a : effective cross-sectional area of one adsorbate molecule

C : dimensionless constant related to the enthalpy adsorption of adsorbate gas

d : spacing between layers of atoms

D : crystalline size

 I_{α} (hkl): intensity of the diffraction line (hkl) from a phase α

K : dimensionless shape factor

 $K_{\alpha}(hkl)$: constant for a given phase structure α , diffraction line (hkl)

k_{Sch} : Scherrer constant

m : mass of test powder

n : order of reflection (integer)

N : Avogadro constant

P : partial vapour pressure of adsorbate gas in equilibrium

 P_0 : saturated pressure of adsorbate gas

P/P_o : relative pressure

R : gas constant

STP : standard temperature and pressure

T : temperature

 V_a : volume of gas adsorbed at STP

 V_M : volume of gas adsorbed corresponding to monolayer coverage

 X_{α} : weight fraction of phase α

Greek

 λ : wavelength

 β : line broadening at half the maximum intensity (FWHM)

 θ : Bragg angle

 ρ_{α} : mass fraction of phase α

 $(\mu/\rho)_m$: mass absorption coefficient of the mixture

LIST OF ABBREVIATIONS

BET Brunauer-Emmett-Teller

EDX Energy Dispersive X-ray Spectroscopy

FESEM Field Emission Scanning Electron Microscopy

SEM Scanning Electron Microscope

XRD X-ray Diffraction