

**HYDROGEN PRODUCTION VIA STEAM REFORMING OF METHANE
OVER Ni-SUPPORTED NaY ZEOLITE CATALYST**

Ms. Orawan Chankam

A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
Case Western Reserve University and Institut Français du Pétrole
2007

501987

Thesis Title: Hydrogen Production via Steam Reforming of Methane over Ni-Supported NaY Zeolite Catalysts.
By: Ms. Orawan Chankam
Program: Petrochemical Technology
Thesis Advisors: Asst. Prof. Apanee Luengnaruemitchai
Asst. Prof. Sirirat Jitkarnka

Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.

Nantaya Yanumet
..... College Director
(Assoc. Prof. Nantaya Yanumet)

Thesis Committee:

Apanee Luengnaruemitchai
.....
(Asst. Prof. Apanee Luengnaruemitchai)

Sirirat Jitkarnka
.....
(Asst. Prof. Sirirat Jitkarnka)

Pramoch Rangsunvigit
.....
(Assoc. Prof. Pramoch Rangsunvigit)

Thirasak Rirksomboon
.....
(Assoc. Prof. Thirasak Rirksomboon)

ABSTRACT

4871018063: Petrochemical Technology Program

Orawan Chankam: Hydrogen Production via Steam Reforming of Methane using Ni-Supported NaY Zeolite Catalysts.

Thesis Advisors: Asst.Prof. Apanee Luengnaruemitchai and Asst.Prof. Sirirat Jitkarnka 89 pp.

Keywords: Hydrogen/ Methane Reforming/ NaY/ Nickel/ Steam/ Zeolite

The development of steam reforming catalysts recently involves solving the risk of catalytic deactivation caused by carbon deposition and the sintering of metal crystallites. In this research, supported Ni catalysts were developed over NaY zeolite. The catalysts were prepared by two different methods; ion-exchange and incipient wetness impregnation. The catalytic reaction was performed at 700°C under atmospheric pressure with various steam/carbon ratios of 1, 1.5, and 2. The effect of metal loading was investigated in terms of carbon formation, activity and selectivity. XRD, TPR, TPO and SAA were applied for the catalyst characterization, which revealed that 11% Ni/NaY prepared by impregnation exhibited higher activity than the ion-exchanged catalyst with an initial methane conversion of 89.84% and hydrogen selectivity of 88.80%; however, the stability of the ion-exchanged catalyst was slightly higher than that of the impregnated catalyst. In addition, the product distribution of the catalyst was investigated in a bench-scale fuel processor utilizing natural gas as the H₂ carrier. The steam reformer generates a stable hydrogen content of approximately 83.59% with the undesired gas products concentration in the gas stream below 5% (dry basis).

บทคัดย่อ

อรวรรณ จันทร์คำ: การผลิตก๊าซไฮโดรเจนด้วยปฏิกิริยารีฟอร์มมิ่งก๊าซมีเทนด้วยไอน้ำโดยใช้ตัวเร่งปฏิกิริยานิกเกิลบนตัวรองรับซีโอไลต์ชนิดโซเดียมวาย (Hydrogen Production via Steam Reforming of Methane over Ni-Supported NaY Zeolite Catalysts) อาจารย์ที่ปรึกษา : ผู้ช่วยศาสตราจารย์ อาภาณี เหลืองนฤมิตรชัย และ ผู้ช่วยศาสตราจารย์ ศิริรัตน์ จิตการคำ 89 หน้า

ปัจจุบันการพัฒนาประสิทธิภาพของตัวเร่งปฏิกิริยารีฟอร์มมิ่งด้วยไอน้ำมุ่งเน้นการหาแนวทางเพื่อแก้ไขข้อจำกัดในด้านการเสื่อมสภาพของตัวเร่งปฏิกิริยาอันเนื่องมาจากสาเหตุต่างๆ ได้แก่ การเกิดสารคาร์บอน (Coke Formation) ปกคลุมพื้นผิวของตัวเร่งปฏิกิริยา และปริมาณความร้อนสูงที่ใช้ในปฏิกิริยาส่งผลให้เกิดการสูญเสียพื้นผิวที่ว่องไวของตัวเร่งปฏิกิริยา (Thermal Sintering) สำหรับงานวิจัยนี้ แสดงให้เห็นถึงผลการพัฒนาตัวเร่งปฏิกิริยานิกเกิลบนตัวรองรับซีโอไลต์ชนิดโซเดียมวาย (Ni/NaY Zeolite) ซึ่งเตรียมขึ้นโดยวิธีการแลกเปลี่ยนไอออน (ion-exchange method) และวิธีการเตรียมแบบฝังเปือก (impregnation method) โดยทดสอบกระบวนการรีฟอร์มมิ่งมีเทนด้วยไอน้ำกับตัวเร่งปฏิกิริยาดังกล่าวกระทำที่อุณหภูมิ 700 องศาเซลเซียส ภายใต้สภาวะความดันบรรยากาศ และมีการแปรเปลี่ยนสัดส่วนระหว่างไอน้ำและคาร์บอนเป็น 1:1 1.5:1 และ 2:1 ในขั้นต้นได้ทำการศึกษาผลของปริมาณโลหะบนตัวรองรับที่มีต่อการเกิดสารคาร์บอน ความว่องไวและความเลือกจำเพาะของตัวเร่งปฏิกิริยา สำหรับการวิเคราะห์คุณลักษณะของตัวเร่งปฏิกิริยาอาศัยเครื่องมือต่างๆ เช่น XRD, TPR, TPO และ SAA ผลการทดลองแสดงให้เห็นว่าปริมาณโลหะนิกเกิลบนตัวรองรับ 11 เปอร์เซ็นต์โดยน้ำหนักที่เตรียมโดยวิธีการฝังเปือก มีประสิทธิภาพมากที่สุดในการเร่งปฏิกิริยา โดยมีค่าการเปลี่ยนแปลงก๊าซมีเทนเริ่มต้นเท่ากับ 89.84 เปอร์เซ็นต์และความเลือกจำเพาะในการเกิดก๊าซไฮโดรเจน 88.80 เปอร์เซ็นต์ แต่สำหรับตัวเร่งปฏิกิริยาที่เตรียมขึ้นจากวิธีการแลกเปลี่ยนไอออนนั้นกลับให้ผลดีกว่าในด้านความมีเสถียรภาพ นอกจากนี้ยังได้ทำการทดสอบตัวเร่งปฏิกิริยาดังกล่าวกับชุดต้นแบบการผลิตไฮโดรเจน (Fuel Processor) โดยใช้ก๊าซธรรมชาติเป็นสารตั้งต้น ซึ่งหน่วยรีฟอร์มเมอร์ (steam reformer) สามารถผลิตก๊าซไฮโดรเจนได้ในปริมาณความเข้มข้น 83.59 เปอร์เซ็นต์ โดยมีปริมาณความเข้มข้นของก๊าซอื่นๆปะปนมากับรีฟอร์มเมต (reformat) ต่ำกว่า 5 เปอร์เซ็นต์ (คิดเทียบจากก๊าซแห้ง)

ACKNOWLEDGEMENTS

Working on this thesis brings me about the great opportunities in any aspect including a lot of knowledge has been fulfilled.

At first, I would like to express my deep and sincere gratitude to my advisors: Assist. Prof. Apanee Luengnaruemitchai and Assist.Prof. Sirirat Jitkarnka for understanding, encouraging and any guidance. The wide vision and logical way of thinking have been of great value for me.

I would like to express sincerely appreciation to Assoc.Prof. Pramoch Rangsunvigit and Assoc.Prof. Thirasak Rirksoomboon for being my thesis committee.

I warmly thank all faculties and staff at the PPC for knowledge, their valuable advice and friendly help. Further, I wish to thank my senior and all of my friends for their kindness of any help and all suggestions.

At last, but not least, I am proud to grant this accomplishment to my parents who are my inspiration to succeed this work. They always encourage and stand by me in anytime with the sympathy.

I am grateful for the scholarship and funding of the thesis work provided by the Petroleum and Petrochemical College and the National Excellence Center for Petroleum, Petrochemicals, and Advanced Materials, Thailand.

I am also grateful for the support from Department of Alternative energy Development and Efficiency (DADE) providing fund of bench-scale fuel processor.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	ix
List of Figures	x
 CHAPTER	
I INTRODUCTION	1
 II LITERATURE REVIEW	
2.1 Hydrogen Energy	3
2.2 Hydrogen Production	4
2.3 Steam Reforming Methane	6
2.4 Steam Reforming Catalyst	7
2.5 Carbon Formation	9
2.6 Development of Reforming Catalyst	10
2.6.1 Ceramic-based Support	11
2.6.2 Zeolite Supports	12
2.7 Preparation Method	13
2.7.1 Metal Loading	15
2.8 Reaction Condition	15
2.8.1 Temperature Effect	15
2.8.2 Feed Composition Effect	16
2.8.3 Gas Hourly Space Velocity (GHSV) Effect	16

CHAPTER	PAGE
III EXPERIMENTAL	18
3.1 Materials	18
3.1.1 Chemical for Catalyst Preparation	18
3.1.2 Gases	18
3.2 Catalyst Preparation Procedure	20
3.2.1 Incipient Wetness Impregnation Method	20
3.2.2 Ion-exchange Method	20
3.3 Reactor Set-up and Catalytic Testing	21
3.3.1 Lab-scale Steam Reforming Unit	21
3.3.2 Bench-scale Fuel Processor	24
3.4 Experimental Condition	28
3.4.1 Effect of Ni Loading and Preparation Techniques	28
3.4.2 Effect of Feed Ratio	28
3.4.3 Effect of Feed Component	28
3.4.4 Bench-Scale Testing	28
3.5 Catalyst Characterization	29
3.5.1 Atomic Absorption Spectroscopy (AAS)	29
3.5.2 BET Surface Area Measurement (SAA)	29
3.5.3 X-Ray Diffraction Spectrophotometry (XRD)	30
3.5.4 Temperature Programmed Reduction (TPR)	30
3.5.5 Temperature Programmed Oxidation (TPO)	31
3.5.6 Thermogravimetric Analysis (TGA)	31
3.5.7 Transmission Electron Microscopy (TEM)	31
IV RESULTS AND DISCUSSION	32
4.1 Catalyst Characterization	32
4.1.1 Surface Area Measurement	32
4.1.2 X-ray Diffraction (XRD)	33
4.1.3 Temperature Programmed Reduction (TPR)	37

	PAGE
4.1.4 Temperature Programmed Oxidation (TPO)	41
4.1.5 Thermogravimetric Analysis (TGA)	45
4.1.6 Transmission Electron Microscope (TEM)	47
4.2 Evaluation of Catalytic Testing	51
4.2.1 Effect of Ni Loading over NaY Support	51
4.2.2 Steam to Carbon Ratio	56
4.2.3 Catalytic Activity of the Ion-exchanged Catalysts	60
4.2.4 Effect of Feed Component	65
4.2.5 Bench-scale Fuel Processor Testing	67
CHAPTER	
V	
CONCLUSIONS AND RECOMMENDATIONS	70
5.1 Conclusions	70
5.2 Recommendations	71
REFERENCES	72
APPENDICES	76
Appendix A Calculations	76
Appendix B Table	79
CURRICULUM VITAE	89

LIST OF TABLES

TABLE	PAGE
3.1 Natural gas composition.	19
4.1 BET characterization results of the fresh and spent catalysts.	30
4.2 The oxidizing temperature of the impregnated catalysts (IM) and the ion-exchanged catalyst (IE) with various loading.	43
4.3 Methane conversions with different Ni-loaded ion-exchanged catalysts.	60
4.4 Condition for bench-scale fuel processor testing.	68

LIST OF FIGURES

FIGURE		PAGE
2.1	IEO 2005 and IEO 2006 world oil price projections, 1980-2030.	3
2.2	World capacity of hydrogen production source.	4
2.3	Hydrogen as dominant feed chemical for polymer electrolyte membrane chemical fuel cells.	6
2.4	Faujasite, Y-type zeolite structure and 12 T-ring.	12
3.1	Schematic of catalyst bed in the reactor.	22
3.2	Schematic of lab-scale experimental apparatus.	23
3.3	Bench-scale fuel processor	24
3.4	(a) Steam reforming unit, (b) Steam generator combined of syringe pump and evaporator, and (c) Steam generate through HT and LT water-gas shift unit.	25
3.5	Scheme of bench-scale fuel processor	27
4.1	XRD patterns of NaY zeolite and calcined impregnated catalysts with different Ni loadings; (a) NaY zeolite, (b) IM-05, (c) IM-07, (d) IM-11, and (e) IM-15; where (★) denotes reflection of NiO phase.	34
4.2	XRD patterns of NaY zeolite and supported NaY catalysts, prepared through ion-exchange technique, with various Ni loadings; (a) NaY zeolite, (b) IE-5.4, (c) IE-6.4, and (d) IE-7.3.	34
4.3	XRD patterns of NaY zeolite and reduced catalysts with various Ni content; (a) NaY zeolite, (b) IM-05, (c) IM-07, (d) IM-11, and (e) IM-15; where (⊕) denotes reflection of Ni metal.	36
4.4	XRD patterns of NaY zeolite and reduced NaY catalysts with different Ni loadings; (a) NaY zeolite, (b) IE-5.4, (c) IE-6.4, and (d) IE-7.3; where (⊕) denotes reflection of Ni metal.	36

	PAGE
4.5 Comparison of XRD patterns of reduced and spent catalysts (a) reduced IM-11, (b) spent IM-11, (c) reduced IE-7.3, and (d) spent IE-7.3; where (⊕) denotes reflection of Ni metal.	37
4.6 TPR profiles of the impregnated catalysts with various Ni content; (a) IM-05, (b) IM-07, (c) IM-11, and IM-15.	38
4.7 TPR profiles of the ion-exchanged catalysts with various Ni content; (Solid) IE-5.4, (Dash-dot) IE-6.4, and (Dotted) IE-7.3.	40
4.8 TPO profiles of the impregnated catalysts; (—) IM-05, (—) IM-07, (—) IM-11, and (—) IM-15	42
4.9 TPO profiles of the impregnated catalysts; (—) IE-5.4, (—) IE-6.4, and (—) IE-7.3.	42
4.10 TPO profiles of different feed component; (— · · —) natural gas feed and (—) methane feed.	44
4.11 Amount of coke deposition on various Ni content catalysts.	45
4.12 Amount of coke deposition on catalysts with various S/C ratios.	46
4.13 TEM images of fresh and spent catalysts; (a) fresh IM-11 and (b) spent IE-7.3 for 4 h at 700°C.	47
4.14 The particles size distribution (%) determined by TEM of the fresh IM-11 (dark bar) and the spent IM-11 (light bar).	48
4.15 TEM images of the spent IM-11 catalysts exposed in various S/C ratio; (a) S/C = 1.5 and (b) S/C = 2 investigated for 4 h at 700°C.	48
4.16 The particles size distribution (%) determined by TEM of spent IM-11 with various S/C ratio; S/C = 1 (dark), S/C = 1.5 (gray), and S/C=2 (light bar).	49
4.17 TEM images of fresh and spent catalysts; (a) Spent IM-07, (b) Spent IE-7.3 taken after reactivity measurements for 4 h at 700°C, an average Ni particle size.	49
4.18 TEM images of used catalysts for 10 h at 700°C; (a) Spent IM-11 (b) carbon nanotube.	50

	PAGE
4.19 Methane conversion of the impregnated catalysts as a function of time-on-stream with various Ni loadings; (-○-) 5, (-▽-) 7, (-□-) 11, and (-◇-) 15wt% at 700°C, 1 atm, and H ₂ O/CH ₄ ratio of 1.	51
4.20 H ₂ yield of the impregnated catalysts as a function of time-on-stream with various Ni loadings; (-○-) 5, (-▽-) 7, (-□-) 11, and (-◇-) 15wt% at 700°C, 1 atm, and H ₂ O/CH ₄ ratio of 1.	53
4.21 H ₂ selectivity of the impregnated catalysts as a function of time-on-stream with various Ni loadings; (-○-) 5, (-▽-) 7, (-□-) 11, and (-◇-) 15wt% at 700°C, 1 atm, and H ₂ O/CH ₄ ratio of 1.	53
4.22 CO selectivity of the impregnated catalysts as a function of time-on-stream with various Ni loadings; (-○-) 5, (-▽-) 7, (-□-) 11, and (-◇-) 15wt% at 700°C, 1 atm, and H ₂ O/CH ₄ ratio of 1.	54
4.23 CO ₂ selectivity of the impregnated catalysts as a function of time-on-stream with various Ni loadings; (-○-) 5, (-▽-) 7, (-□-) 11, and (-◇-) 15wt% at 700°C, 1 atm, and H ₂ O/CH ₄ ratio of 1.	54
4.24 Methane conversion of the IM-11 as a function of time-on-stream with various feed ratio; (-○-) S/C= 1, (-▽-) S/C=1.5, and (-□-) S/C=2 at 700°C and 1 atm.	57
4.25 H ₂ yield of the IM-11 as a function of time-on-stream with various feed ratio; (-○-) S/C= 1, (-▽-) S/C=1.5, and (-□-) S/C=2 at 700°C and 1 atm.	57
4.26 Product selectivity of the IM-11 as a function of time-on-stream with various feed ratio at 700°C and 1 atm.	58
4.27 H ₂ selectivity of the IM-11 as a function of time-on-stream with various feed ratio; (-○-) S/C= 1, (-▽-) S/C=1.5, and (-□-) S/C=2 at 700°C and 1 atm.	59
4.28 CO selectivity of the IM-11 as a function of time-on-stream with various feed ratio; (-○-) S/C= 1, (-▽-) S/C=1.5, and (-□-) S/C=2 at 700°C and 1 atm.	59

	PAGE
4.29 Methane conversion of the ion-exchanged catalysts as a function of time-on-stream with various Ni loadings; (-○-) 5.4, (-▽-) 6.4, and (-□-) 7.3 wt% at 700°C, 1 atm, and H ₂ O/CH ₄ ratio of 1.	61
4.30 H ₂ yield of the ion-exchanged catalysts as a function of time-on-stream with various Ni loadings over NaY zeolite; (-○-) 5.4, (-▽-) 6.4, and (-□-) 7.3 wt% at 700°C, 1 atm, and H ₂ O/CH ₄ ratio of 1.	62
4.31 H ₂ selectivity of the ion-exchanged catalysts as a function of time-on-stream with various Ni loadings; (-○-) 5.4, (-▽-) 6.4, and (-□-) 7.3wt% at 700°C, 1 atm, and H ₂ O/CH ₄ ratio of 1.	62
4.32 CO selectivity of the ion-exchanged catalysts as a function of time-on-stream with various Ni loadings; (-○-) 5.4, (-▽-) 6.4, and (-□-) 7.3wt% at 700°C, 1 atm, and H ₂ O/CH ₄ ratio of 1.	63
4.33 CO ₂ selectivity of the ion-exchanged catalysts as a function of time-on-stream with various Ni loadings; (-○-) 5.4, (-▽-) 6.4, and (-□-) 7.3wt% at 700°C, 1 atm, and H ₂ O/CH ₄ ratio of 1.	63
4.34 The concentration of light hydrocarbons; (dark bar) the initial natural gas component and (light bar) the reformed gas component after reactivity measurements for 4 h.	65
4.35 The comparison of concentration of the gas products detected at 4 h; (dark bar) the reformat in the reaction utilized methane as reactant (light bar) the reformat in the reaction utilized natural gas as reactant.	66
4.36 The profile of reformed gas concentration after SRM unit of fuel processor.	67
4.37 The profile of reformed gas concentration detected individual reaction zones of the integrated fuel processor.	68