METHANE DEHYDROGENATION AND COUPLING TO ETHYLENE USING Ni/HZSM-5 CATALYSTS

Suchada Kongbin

A Thesis Submitted in Partial Fulfillment 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
2014

Thesis Title:	Methane Dehydrogenation and Coupling to Ethylene Using Ni/HZSM-5 Catalysts
By:	Suchada Kongbin
Program:	Petrochemical Technology
Thesis Advisor:	Assoc. Prof. Thirasak Rirksomboon

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

..... College Dean

(Asst. Prof. Pomthong Malakul)

Thesis Committee:

.....

(Assoc. Prof. Thirasak Rirksomboon)

.....

(Asst. Prof. Boonyarach Kitiyanan)

.....

(Dr. Tanate Danuthai)

ABSTRACT

5571031063: Petrochemical Technology Program
Suchada Kongbin: Methane Dehydrogenation and Coupling to Ethylene Using Ni/HZSM-5 Catalysts.
Thesis Advisor: Assoc. Prof. Thirasak Rirksomboon 58 pp.
Keywords: Direct methane conversion/ Methane/ Ethylene/ HZSM-5/ Non-oxidative coupling

Direct methane conversion to ethylene which is an important substance for petrochemical industry has been extensively studied under oxidative condition. To avoid the formation of CO and CO_2 in oxidative reaction, direct methane conversion to ethylene via dehydrogenation and coupling reaction under non-oxidative condition using Ni/HZSM-5 catalysts was attempted in this research. The Ni/HZSM-5 catalysts were prepared by polyol mediate process using a commercially available and modified HZSM-5 catalysts (SiO_2/Al_2O_3=50). The catalytic activity testing was carried out under non-oxidative conditions at atmospheric pressure, GHSV of 1500 ml/g/h, using a continuous flow fixed-bed reactor. At the given condition, the effects of Ni loading, reaction temperature, hydrofluorination, and methane concentration were studied. From the results, the presence of Ni plays an important role in both dehydrogenation and coupling reactions. While increasing Ni loading, ethylene selectivity and yield decreased. Besides, the effect of reaction temperature and the effect of methane concentration significantly improve favourable thermodynamics of reaction and decrease coke formation respectively. In additional, the effect of hydrofluorination develops the catalyst stability. Therefore, it can be concluded that the best condition to produce ethylene under non-oxidative condition is using 1%Ni/HZSM-5 carried out at 800 °C and using 20% methane balanced in N_2 as a feed.

บทคัดย่อ

สุชาดา กงบิน : การสังเคราะห์เอทิลีนด้วยปฏิกิริยาดีไฮโดรจีเนชันและคู่ควบของมีเทนโดยใช้ตัวเร่งปฏิกิริยา Ni/HZSM-5 (Methane Dehydrogenation and Coupling to Ethylene Using Ni/HZSM-5 Catalysts) อ. ที่ปรึกษา : รศ. ดร. ธีรศักดิ์ ฤกษ์สมบูรณ์ 58 หน้า

การใช้มีเทนเพื่อการสังเคราะห์เอทิลีนซึ่งเป็นสารตั้งต้นสำคัญในอุตสาหกรรมปิโตรเคมีในสภาวะที่มีออกซิเจนก็ได้มีการศึกษาอย่างแพร่หลาย แต่เพื่อหลีกเลี่ยงการเกิดคาร์บอนมอนออกไซด์และคาร์บอนไดออกไซด์จากปฏิกิริยาออกซิเดชัน ในงานวิจัยนี้จึงศึกษาการสังเคราะห์เอทิลีนจากมีเทนโดยตรงในสภาวะไร้ออกซิเจนด้วยปฏิกิริยาดีไฮโดรจีเนชันและคู่ควบของมีเทน โดยมี Ni/HZSM-5 เป็นตัวเร่งปฏิกิริยา ที่เตรียมโดยวิธีโพลีออลโดยใช้ตัวรองรับ HZSM-5 (SiO_2/Al_2O_3=50) จากนั้นอัตราการเกิดปฏิกิริยาผ่านตัวเร่งได้ถูก ทดสอบภายใต้สภาวะไร้ออกซิเจนที่ความดันบรรยากาศ ที่อัตราการไหลมีเทน GHSV 1500 ml/g/h ผ่านปฏิกรณ์แบบเบดนิ่งเป็นเวลา 180 นาที ภายใต้การศึกษาผลกระทบจากตัวแปรต่าง ๆ ได้แก่ ปริมาณนิกเกิล, อุณหภูมิในการทำปฏิกิริยา, การปรับปรุง HZSM-5 ด้วย ไฮโดรฟลูออริเนชัน และความเข้มข้นของมีเทนขาเข้า จากผลการทดลองพบว่า การเพิ่มปริมาณนิกเกิลส่งผลอัตรา การเลือกเกิดของเอทิลีนลดลง และแสดงผลอย่างมีนัยสำคัญในการเปลี่ยนมีเทนเป็นเอทิลีนด้วยปฏิกิริยาดีไฮโดรจีเนชันและคู่ควบของมีเทน โดยการเพิ่มปริมาณนิกเกิลจะลดอัตราการเลือกเกิดและและผลผลิตของเอทิลีน นอกจากนี้ยังพบว่าผลของอุณหภูมิในการทำปฏิกิริยาและความเข้มข้นของมีเทนขาเข้าช่วยเพิ่มปริมาณการเกิดเอทิลีนได้อย่างมีนัยสำคัญ โดยมีผลในการช่วยลดความเสถียรทางเทอร์โมไดนามิคของปฏิกิริยาและลดปริมาณ Coke ที่เกิดขึ้นได้ ตามลำดับ อีกทั้งการปรับปรุง HZSM-5 ด้วยกรดไฮโดร ฟลูออริกยังส่งผลต่อการเพิ่มความทนทานของตัวเร่งปฏิกิริยาได้อีกด้วย ดังนั้นสภาวะที่ เหมาะสมในการสังเคราะห์เอทิลีน คือ ใช้ 1%Ni/HZSM-5 เป็นตัวเร่งปฏิกิริยา ณ อุณหภูมิ 800 องศาเซลเซียส และใช้ 20% มีเทนเจือจางในไนโตรเจนเป็นสารป้อน

ACKNOWLEDGEMENTS

This thesis work could be completely successful with the assistance of many following persons and organizations.

Firstly, I would like to give special thanks to my advisor Assoc. Prof. Thirasak Rirksomboon who provides the valuable knowledge and offers me many ideas to solve many problems. I would also like to extend my sincere appreciation for all kind suggestions throughout this research.

I also sincere thank Asst. Prof. Boonyarach Kitiyanan and Dr. Tanate Danuthai for being my thesis committee and comments. I also give appreciative thank to The Petroleum and Petrochemical College for research instruments support and all knowledge from the lecturers and staff from all of courses.

To my advisor group members and my friends, I would like to thank all of you for your helps, your support and your suggestions that help this project could be successful conveniently.

The author gratefully acknowledge for the scholarship and funding of the thesis work provided by The Petroleum and Petrochemical College, and by Center of Excellence on Petrochemical and materials Technology, Thailand.

Finally, I would like to thank my family for the support and spirit. I always appreciate your love and your kindness that give me the opportunity for success in Master Degree at The Petroleum and Petrochemical College Chulalongkorn University.

TABLE OF CONTENTS

		PAGE
Title Page		i
Abstract (in English)		iii
Abstract (in Thai)		iv
Acknowledgement		v
Table of Contents		vi
List of Tables		viii
List of Figures		x
CHAPTER		
I	**INTRODUCTION**	1
II	**THEORETICAL BACKGROUND AND LITERATURE REVIEW**	3
	2.1 Background	3
	2.2 Methane	3
	2.3 Ethylene	5
	2.4 Non-Oxidative Methane Conversion	7
	2.5 Catalyst for Non-Oxidative Methane Conversion	12
	2.6 Zeolite	16
	2.7 Nanoparticle Preparation	19
	2.7.1 Polyol Mediated Synthesis	20
III	**EXPERIMENTAL**	22
	3.1 Materials	22
	3.2 Equipment	22
	3.3 Methodology	23
	3.3.1 Preparation of Ni/HZSM-5 Catalysts	23
	3.3.2 Catalyst Characterization	23
	3.3.3 Catalytic Activity Testing	25

CHAPTER		PAGE
IV	**RESULTS AND DISCUSSION**	27
	4.1 Catalyst Characterization	27
	4.1.1 X-ray Diffraction (XRD)	27
	4.1.2 X-ray Fluorescence (XRF)	28
	4.1.3 Scanning Electron Microscope (SEM)	30
	4.1.4 Surface Area Measurements	32
	4.1.5 Temperature Program of Reduction (H_2-TPR)	34
	4.1.6 TPD of Isopropylamine (IPA-TPD)	35
	4.2 Catalytic Activity Testing	37
	4.2.1 Effect of Ni loading	37
	4.2.2 Effect of Hydrofluorination	40
	4.2.3 Effect of Reaction Temperature	42
	4.2.4 Effect of Methane Concentration	43
VI	**CONCLUSIONS AND RECOMMENDATIONS**	45
	5.1 Conclusions	45
	5.2 Recommendations	45
	REFERENCES	46
	APPENDICES	50
	Appendix A Calibration Curves for Methane and Gas Product	50
	Appendix B Calibration Curves for Flow Meter	51
	Appendix C Experimental Data of Catalytic Activity Tests for Methane Dehydrogenation and Coupling to Ethylene	52
	Appendix D Calculation of Carbon Balanced of Methane	56
	CURRICULUM VITAE	58

LIST OF TABLES

TABLE		PAGE
2.1	Thermodynamic data, Change of Free Energy, ΔG°, for methane transformation	8
4.1	Chemical composition of prepared catalysts	29
4.2	Textural properties of the catalysts studied	33
4.3	Metal dispersion of all loaded catalysts	33
4.4	Gas product selectivity for HZSM-5 and various Ni/HZSM-5 (reaction temperature 750 °C, 20% CH_4, GHSV = 1500 ml/g/h)	38
4.5	Gas product selectivity for unloaded HZSM-5 (HF) and loaded HZSM-5 at reaction temperature 750 °C, 20% methane, GHSV =1500 ml/g/h, and TOS = 180 min	42
4.6	Coke formation of the catalyst at different methane concentration in feed	44
C1	Catalytic activity test of HZSM-5 catalyst using 20% methane as a feed at reaction temperature 750 °C, with GHSV 1500 ml/g/h under atmospheric pressure	52
C2	Catalytic activity test of 1%Ni/HZSM-5 catalyst using 20% methane as a feed at reaction temperature 750 °C, with GHSV1500 ml/g/h under atmospheric pressure	52

TABLE **PAGE**

C3	Catalytic activity test of 3%Ni/HZSM-5 catalyst using 20% methane as a feed at reaction temperature 750 °C, with GHSV1500 ml/g/h under atmospheric pressure	53
C4	Catalytic activity test of 1%Ni/HZSM-5 catalyst using 20% methane as a feed at reaction temperature 800 °C, with GHSV1500 ml/g/h under atmospheric pressure	53
C5	Catalytic activity test of HZSM-5 (HF) catalyst using 20% methane as a feed at reaction temperature 750 °C, with GHSV1500 ml/g/h under atmospheric pressure	54
C6	Catalytic activity test of 1%Ni/HZSM-5 (HF) catalyst using 20% methane as a feed at reaction temperature 750 °C, with GHSV1500 ml/g/h under atmospheric pressure	54
C7	Catalytic activity test of 3%Ni/HZSM-5 (HF) catalyst using 20% methane as a feed at reaction temperature 750 °C, with GHSV1500 ml/g/h under atmospheric pressure	55
C8	Catalytic activity test of 1%Ni/HZSM-5 catalyst using pure methane as a feed at reaction temperature 750 °C, with GHSV1500 ml/g/h under atmospheric pressure	55
D1	The amount of C in methane reaction using HZSM-5	56

LIST OF FIGURES

FIGURE		PAGE
2.1	Classification of organic compounds.	4
2.2	The structure of a.) methane and b.) ethylene.	5
2.3	Schematic of comparison of indirect and direct routes for methane conversion.	5
2.4	Schematic of olefin production processes.	6
2.5	Thermodynamics of direct conversion of CH_4 under non-oxidative conditions.	8
2.6	Schematic Mechanism of C–C Coupling and elimination of molecular hydrogen and ethylene on zeolite-supported Mo carbides.	11
2.7	a.) Chemical structure of zeolite b.) Primary building unit of zeolite structure.	17
2.8	Schematic of ZSM-5 zeolite consisting of an intersecting two-dimensional pore structure. There are two types of pores, both formed by 10-membered oxygen rings. One is straight with an elliptical cross section, while the second type of circular cross-section pores intersects the straight pores at right angles in a zig-zag pattern. The effective pore diameter is 0.59 nm.	17
2.9	Top-down and Bottom-up approach for nanomaterial synthesis.	19
3.1	Schematic of the experimental system: (1) N_2, (2) CH_4, (3) Air zero, (4) H_2, (5) Mass flow rate controller for CH_4, (6) Mass flow rate controller for N_2 or H_2, (7) Gas mixer, (8) K-Type Thermocouple, (9) Temperature controller, (10) Furnace, (11) Quartz tube reactor, (12) Quartz wool, (13) Catalyst bed, (14) Gas Chromatography, (15) Computer.	27

FIGURE **PAGE**

4.1	XRD patterns of prepared catalysts.	28
4.2	SEM images of unmodified HZSM-5.	30
4.3	SEM images of fresh 1%Ni/HZSM-5.	31
4.4	SEM images of the 1%Ni/HZSM-5 at reaction temperature 750 °C.	31
4.5	SEM images of the 1%Ni/HZSM-5 at reaction temperature 800 °C.	32
4.6	TPR profiles of the prepared catalysts.	34
4.7	IPA-TPD profiles of HZSM-5 and HZSM-5 (HF).	35
4.8	IPA-TPD profiles of HZSM-5 and Ni/HZSM-5.	36
4.9	IPA-TPD profiles of HZSM-5 (HF) and Ni/HZSM-5 (HF).	36
4.10	The relative amounts of the Brönsted acid sites in the absence and presence of Ni loading on (■) HZSM-5 and (▪) HZSM-5(HF).	37
4.11	Methane conversion profiles for HZSM-5 and various Ni/HZSM-5 (750 °C, 20% CH_4 balanced in N_2, GHSV = 1500 ml/g/h	38
4.12	Methane conversion profiles over HZSM-5 and HZSM-5 (HF) (750 °C, 20% CH_4 balanced in N_2, GHSV = 1500 ml/g/h.	40
4.13	Methane conversion profiles over 1%Ni/HZSM-5 and 1%Ni/HZSM-5(HF) (750 °C, 20% CH_4 balanced in N_2, GHSV = 1500 ml/g/h.	41
4.14	Methane conversion profiles over 3%Ni/HZSM-5 and 3%Ni/HZSM-5 (HF) (750 °C, 20% CH_4 balanced in N_2, GHSV = 1500 ml/g/h.	41
4.15	Catalytic activity testing over 1%Ni/HZSM-5 (750 and 800 °C, at 20% CH_4 balanced in N_2, GHSV = 1500 ml/g/h).	43
4.16	Catalytic activity testing over 1%Ni/HZSM-5 for different CH_4 concentration at 750 °C, GHSV = 1500 ml/g/h, 60-80 mesh.	43

FIGURE **PAGE**

4.17	TPO profiles of the catalysts studied.	44
A1	The relationship between methane concentration (CH_4) and peak area.	48
A2	The relationship between volume of ethylene (C_2H_4) and peak area.	48
A3	The relationship between volume of propylene (C_3H_6) and peak area.	49
B1	The relationship between bubble flow meter and methane air flow meter.	49