

**OXIDATIVE COUPLING OF METHANE TO HIGHER
HYDROCARBONS OVER ZEOLITE IN AC ELECTRIC DISCHARGES**

Ms. Pornpilai Viriyasiripongkul

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,
and Case Western Reserve University

2001

ISBN 974-13-0681-4

Thesis Title : Oxidative Coupling of Methane to Higher
Hydrocarbons over Zeolite in AC Electric Discharges
By : Ms. Pornpilai Viriyasiripongkul
Program : Petrochemical Technology
Thesis Advisors : Prof. Richard G. Mallinson
Assoc. Prof. Sumaeth Chavadej

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

K. Bunyakit.
..... College Director
(Assoc. Prof. Kunchana Bunyakit)

Thesis Committee:

Richard G. Mallinson
.....
(Prof. Richard G. Mallinson)

Sumaeth Chavadej
.....
(Assoc. Prof. Sumaeth Chavadej)

Piya Ouraipryvan
.....
(Mr. Piya Ouraipryvan)

ABSTRACT

4271017063 : PETROCHEMICAL TECHNOLOGY PROGRAM
Pornpilai Viriyasiripongkul : Oxidative Coupling of
Methane to Higher Hydrocarbons over Zeolite in AC
Electric Discharges.

Thesis Advisors: Prof. Richard G. Mallinson
and Assoc. Prof. Sumaeth Chavadej, 66 pp
ISBN 974-13-0681-4

Keywords : Methane Conversion/Plasma/AC Electric Discharges/
Corona discharge

The objective of this study was to investigate the oxidative coupling of methane to produce higher hydrocarbons by using a combination of AC electric discharges and zeolite catalyst at ambient conditions. It was found that with an increase in voltage, methane, oxygen and ethane conversions as well as yields of C₂ hydrocarbons (ethylene and acetylene) increased. The conversions of methane, oxygen and ethane, including yields of C₂ hydrocarbons decreased with increasing either frequency or flow rate. An increase in ethane partial pressure resulted in decreasing the conversions of methane and ethane. Pt/NaOH treated Y led to more significant methane and ethane conversions, while the highest oxygen conversion was obtained with Pt/KL and Pt/NaX. The results showed that the maximum yield of C₂ hydrocarbons was approximately 23 % when the system was operated over Pt/KL at 8,000 V, of 500 Hz, 50 ml/min flow rate of and methane to oxygen to ethane ratio of 4:2:1. The presence of Pt/KL zeolite also enhanced the conversion of oxygen and the selectivity of ethylene while, for the non-catalytic system, hydrogen and carbon monoxide were main products.

บทคัดย่อ

พรพิไล วิริยะศิริพงศ์กุล : ปฏิกริยาออกซิเดทีปคัปปลิงของมีเทนเพื่อผลิตก๊าซไฮโดรคาร์บอนโมเลกุลใหญ่บนตัวเร่งปฏิกริยาซีโอไลต์ภายใต้สนามไฟฟ้ากระแสสลับ (Oxidative Coupling of Methane to Higher Hydrocarbons over Zeolite in AC Electric Discharges) อ. ที่ปรึกษา : ศ. ริชาร์ด จี แมลลินสัน (Prof. Richard G. Mallinson) และ รศ. สุเมธ ชวเดช เอกสารจำนวน 66 หน้า ISBN 974-13-0681-4

วัตถุประสงค์ของงานศึกษานี้เพื่อศึกษาปฏิกริยาออกซิเดทีปคัปปลิงของมีเทนเพื่อผลิตก๊าซไฮโดรคาร์บอนโมเลกุลใหญ่บนตัวเร่งปฏิกริยาซีโอไลต์และภายใต้สนามไฟฟ้าแรงสูงกระแสสลับที่อุณหภูมิห้องและความดันบรรยากาศ จากการศึกษาพบว่า เมื่อทำการเพิ่มความต่างศักย์ไฟฟ้า ประสิทธิภาพการเปลี่ยนแปลงของก๊าซมีเทน, ออกซิเจนและอีเทนเพิ่มสูงขึ้นและประสิทธิภาพการผลิตก๊าซไฮโดรคาร์บอน(เอทิลีนและเอเซทิลีน)สูงขึ้นด้วย ประสิทธิภาพการเปลี่ยนก๊าซมีเทน, ออกซิเจนและอีเทนรวมทั้งประสิทธิภาพการผลิตก๊าซไฮโดรคาร์บอนลดลง เมื่อเพิ่มความถี่หรืออัตราการไหลของก๊าซเข้า หรือเพิ่มอัตราส่วนของก๊าซอีเทนในก๊าซเข้า มีผลทำให้การเปลี่ยนแปลงของก๊าซมีเทนและอีเทนลดลง ตัวเร่งปฏิกริยาแพลตินัมบนพื้นผิวโซเดียมไฮดรอกไซด์ที่รีดิวซ์โอไลต์ช่วยให้การเปลี่ยนแปลงของก๊าซมีเทนและอีเทนที่เด่นชัดกว่า ในขณะที่การเปลี่ยนแปลงของก๊าซออกซิเจนสูงสุดเกิดบนตัวเร่งปฏิกริยาแพลตินัมบนพื้นผิวโพแทสเซียมซีโอไลต์แอลและโซเดียมซีโอไลต์เอ็กซ์ ผลการทดลองยังแสดงว่าประสิทธิภาพการผลิตสูงสุดของสารไฮโดรคาร์บอนที่มีคาร์บอน 2 ตัวประมาณ 23 เปอร์เซ็นต์ เมื่อระบบถูกควบคุมบนตัวเร่งปฏิกริยาแพลตินัมบนพื้นผิวโพแทสเซียมซีโอไลต์แอล ที่แรงดันไฟฟ้า 8,000 โวลต์, ความถี่ 500 เฮิรซ์ และอัตราการไหลของก๊าซเข้า 50 ลูกบาศก์เซนติเมตรต่อนาที และที่อัตราส่วนของก๊าซมีเทน, ต่อออกซิเจนต่ออีเทนเท่ากับ 4:2:1 ตัวเร่งปฏิกริยาแพลตินัมบนพื้นผิวโพแทสเซียมซีโอไลต์แอลยังช่วยเพิ่มการเปลี่ยนแปลงของก๊าซออกซิเจนและประสิทธิภาพการเกิดจำเพาะของเอทิลีนให้สูงขึ้น ในขณะที่ปฏิกริยาแบบไม่ใช้ตัวเร่งปฏิกริยา ผลิตภัณฑ์หลักคือไฮโดรเจนและคาร์บอนมอนอกไซด์

ACKNOWLEDGEMENTS

This work can not be successful without the participation of the following individuals and organizations.

First of all, I would like to express my utmost appreciation and deepest gratitude to my thesis advisors, Professor Richarge G. Mallinson and Associate Professor Sumaeth Chavadej for their constructive guidance, time spent discussing and assistance devotedly throughout my graduate work.

I would like to extend my sincere thanks to CPO. Poon Arjpru who helped me set up experimental equipment and Ms. Korada Supat who made me perceptible and wonderful throughout my thesis work.

It is a pleasure to acknowledge the Petroleum and Petrochemical College for the support in laboratory facilities and all of the staffs of the college for their helpful assistance.

Very special thanks are forwarded to all of my friends and Ph.D. students for making my two years of study at the college most memorable and enjoyable.

Finally, I would like to express whole-hearted gratitude to my family for their love, understanding and measureless support.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	x
List of Figures	xiv
CHAPTER	
I INTRODUCTION	1
II LITERATURE SURVEY	3
2.1 Physical and Chemical Properties of Methane	3
2.2 Gaseous Plasmas for Activating Methane Molecules	5
2.2.1 Fundamental Properties of Plasmas	5
2.2.2 Generation of Plasmas	6
2.3 Types of Non-Equilibrium Plasmas	10
2.3.1 Radio Frequency Discharge	11
2.3.2 Microwave Discharge	11
2.3.3 Glow Discharge	11
2.3.4 Corona Discharge	12
2.3.5 Dielectric Barrier Discharge	12
2.4 Related Research Work	13

CHAPTER	PAGE	
III	EXPERIMENTAL SECTION	19
3.1	Materials	19
3.1.1	Catalyst Preparation Materials	19
3.1.2	Gaseous Reactant Materials	19
3.2	Catalyst Preparation	20
3.3	Experimental Setup	21
3.3.1	Reactant Gases Mixing Section	21
3.3.2	Reaction Section	21
3.3.2.1	Power Supply Unit	21
3.3.2.2	Reactor Unit	24
3.3.3	Analysis Section	25
3.4	Experimental Procedure	26
3.4.1	The Plasma System	26
3.4.1.1	Study of Ethane Partial Pressure Effect	26
3.4.1.2	Study of Flow Rate Effect	27
3.4.1.3	Study of Frequency Effect	27
3.4.1.4	Study of Voltage Effect	27
3.4.2	The Catalytic Plasma System	28
3.4.2.1	Catalyst Reduction Procedure	28
3.4.2.2	Study of Frequency Effect	28
3.4.2.3	Study of Voltage Effect	28
3.4.2.4	Study of Catalyst Types	29
IV	RESULTS AND DISCUSSION	30
4.1	The Plasma System with the Absence of Catalyst	30

CHAPTER	PAGE
4.1.1 Effect of Ethane Partial Pressure on Conversions and Yield	31
4.1.2 Effect of Ethane Partial Pressure on Products Selectivities	32
4.1.3 Effect of Flow Rate on Conversions and Yield	34
4.1.4 Effect of Flow Rate on Products Selectivities	36
4.1.5 Effect of Frequency on Conversions and Yield	37
4.1.6 Effect of Frequency on Products Selectivities	39
4.1.7 Effect of Applied Voltage on Conversions and Yield	40
4.1.8 Effect of Applied Voltage on Products Selectivities	43
4.2 The Plasma System with the Presence of Catalyst	44
4.2.1 Effect of Frequency on Conversions and Yield over Pt/KL	44
4.2.2 Effect of Frequency on Products Selectivities over Pt/KL	45
4.2.3 Effect of Applied Voltage on Conversions and Yield over Pt/KL	46
4.2.4 Effect of Applied Voltage on Products Selectivities over Pt/KL	48

CHAPTER		PAGE
	4.2.5 Plasma Catalytic Oxidative Conversion of Methane over Different Zeolites	49
V	CONCLUSIONS AND RECOMMENDATIONS	51
	5.1 Conclusions	51
	5.2 Recommendations	52
	REFERENCES	53
	APPENDICES	55
	CURRICULUM VITAE	66

LIST OF TABLES

TABLE	PAGE
2.1 Average chemical bond energy of some covalent bonds	4
2.2 The first ionization potential of some common gases	4
2.3 Collision mechanisms in the gases	9
4.1 Comparison of non-catalytic and catalytic over the Different zeolites system on conversions and yield at CH ₄ :O ₂ :C ₂ H ₆ ratio = 4:2:1. Applied voltage: 6000 V. Flow rate: 50 ml/min. Gap width: 1.3 cm. Frequency: 500 Hz.	50
4.2 Comparison of non-catalytic and catalytic over the different zeolites system on products selectivities at CH ₄ :O ₂ :C ₂ H ₆ ratio = 4:2:1. Applied voltage: 6000 V. Flow rate: 50 ml/min. Gap width: 1.3 cm. Frequency: 500 Hz.	50
B.1 Ethane partial pressure on partial pressure of effluent gases at total flow rate 100 ml/min, gap width 1.3 cm, applied voltage 8,000 V and frequency 400 Hz	57
B.2 Ethane partial pressure on conversions and yield at total flow rate 100 ml/min, gap width 1.3 cm, applied voltage 8,000 V and frequency 400 Hz	57
B.3 Ethane partial pressure on product selectivities at total flow rate 100 ml/min, gap width 1.3 cm, applied voltage 8,000 V and frequency 400 Hz	58

TABLE	PAGE
B.4 Flow rate on partial pressure of effluent gases at methane, oxygen and ethane ratio 4:2:1, gap width 1.3 cm, applied voltage 8,000 V and frequency 400 Hz	58
B.5 Flow rate on conversions and yield at methane, oxygen and ethane ratio 4:2:1, gap width 1.3 cm, applied voltage 8,000 V and frequency 400 Hz	59
B.6 Flow rate on product selectivities at methane, oxygen and ethane ratio 4:2:1, gap width 1.3 cm, applied voltage 8,000 V and frequency 400 Hz	59
B.7 Frequency on partial pressure of effluent gases at methane, oxygen and ethane ratio 4:2:1, gap width 1.3 cm, applied voltage 8,000 V and total flow rate 50 ml/min	60
B.8 Frequency on conversions and yield at methane, oxygen and ethane ratio 4:2:1, gap width 1.3 cm, applied voltage 8,000 V and total flow rate 50 ml/min	60
B.9 Frequency on current at methane, oxygen and ethane ratio 4:2:1, gap width 1.3 cm, applied voltage 8,000 V and total flow rate 50 ml/min	60
B.10 Frequency on product selectivities at methane, oxygen and ethane ratio 4:2:1, gap width 1.3 cm, applied voltage 8,000 V and total flow rate 50 ml/min	61
B.11 Voltage on partial pressure of effluent gases at methane, oxygen and ethane ratio 4:2:1, gap width 1.3 cm, frequency 500 Hz and total flow rate 50 ml/min	61

TABLE	PAGE
B.12 Voltage on conversions and yield at methane, oxygen and ethane ratio 4:2:1, gap width 1.3 cm, frequency 500 Hz and total flow rate 50 ml/min	62
B.13 Voltage on current at methane, oxygen and ethane ratio 4:2:1, gap width 1.3 cm, frequency 500 Hz and total flow rate 50 ml/min	62
B.14 Voltage on product selectivities at methane, oxygen and ethane ratio 4:2:1, gap width 1.3 cm, frequency 500 Hz and total flow rate 50 ml/min	62
B.15 Frequency on partial pressure of effluent gases at methane, oxygen and ethane ratio 4:2:1, gap width 1.3 cm, applied voltage 8,000 V and total flow rate 50 ml/min	63
B.16 Frequency on conversions and yield at methane, oxygen and ethane ratio 4:2:1, gap width 1.3 cm, applied voltage 8,000 V and total flow rate 50 ml/min	63
B.17 Frequency on current at methane, oxygen and ethane ratio 4:2:1, gap width 1.3 cm, applied voltage 8,000 V and total flow rate 50 ml/min	64
B.18 Frequency on product selectivities at methane, oxygen and ethane ratio 4:2:1, gap width 1.3 cm, applied voltage 8,000 V and total flow rate 50 ml/min	64
B.19 Voltage on partial pressure of effluent gases at methane, oxygen and ethane ratio 4:2:1, gap width 1.3 cm, frequency 500 Hz and total flow rate 50 ml/min	64

TABLE	PAGE
B.20 Voltage on conversions and yield at methane, oxygen and ethane ratio 4:2:1, gap width 1.3 cm, frequency 500 Hz and total flow rate 50 ml/min	65
B.21 Voltage on current at methane, oxygen and ethane ratio 4:2:1, gap width 1.3 cm, frequency 500 Hz and total flow rate 50 ml/min	65
B.22 Voltage on product selectivities at methane, oxygen and ethane ratio 4:2:1, gap width 1.3 cm, frequency 500 Hz and total flow rate 50 ml/min	65

LIST OF FIGURES

FIGURE	PAGE
2.1 Alternative methods of charged particles generation	7
3.1 Flow diagram of plasma reactor system	22
3.2 Schematic diagram of power supply unit	23
3.3 The corona discharge reactor	24
4.1 Effect of ethane partial pressure on partial pressure of effluent gases. Flow rate: 100 ml/min. Applied voltage: 8000 V. Frequency: 400 Hz. Gap width: 1.3 cm	31
4.2 Effect of ethane partial pressure on conversions and yield. Flow rate: 100 ml/min. Applied voltage: 8000 V. Frequency: 400 Hz. Gap width: 1.3 cm.	31
4.3 Effect of ethane partial pressure on products selectivities. Flow rate: 100 ml/min. Applied voltage: 8000 V. Frequency: 400 Hz. Gap width: 1.3 cm.	32
4.4 Effect of flow rate on partial pressure of effluent gases. CH ₄ :O ₂ :C ₂ H ₆ =4:2:1. Applied voltage: 8000 V. Frequency: 400 Hz. Gap width: 1.3 cm.	35
4.5 Effect of flow rate on conversions and yield. CH ₄ :O ₂ :C ₂ H ₆ =4:2:1. Applied voltage: 8000 V. Frequency: 400 Hz. Gap width: 1.3 cm.	35
4.6 Effect of flow rate on products selectivities. CH ₄ :O ₂ :C ₂ H ₆ =4:2:1. Applied voltage: 8000 V. Frequency: 400 Hz. Gap width: 1.3 cm.	36

FIGURE	PAGE
4.7 Effect of frequency on partial pressure of effluent gases. CH ₄ :O ₂ :C ₂ H ₆ = 4:2:1. Applied voltage: 8000 V. Flow rate: 50 ml/min. Gap width: 1.3 cm.	37
4.8 Effect of frequency on conversions and yield. CH ₄ :O ₂ :C ₂ H ₆ = 4:2:1. Applied voltage: 8000 V. Flow rate: 50 ml/min. Gap width: 1.3 cm.	38
4.9 Effect of frequency on current. CH ₄ :O ₂ :C ₂ H ₆ = 4:2:1. Applied voltage: 8000 V. Flow rate: 50 ml/min. Gap width: 1.3 cm.	38
4.10 Effect of frequency on products selectivities. CH ₄ :O ₂ :C ₂ H ₆ = 4:2:1. Applied voltage: 8000 V. Flow rate: 50 ml/min. Gap width: 1.3 cm.	40
4.11 Effect of voltage on partial pressure of effluent gases. CH ₄ :O ₂ :C ₂ H ₆ = 4:2:1. Frequency: 500 Hz. Flow rate: 50 ml/min. Gap width: 1.3 cm.	41
4.12 Effect of voltage on conversions and yield. CH ₄ :O ₂ :C ₂ H ₆ = 4:2:1. Frequency: 500 Hz. Flow rate: 50 ml/min. Gap width: 1.3 cm.	42
4.13 Effect of voltage on current. CH ₄ :O ₂ :C ₂ H ₆ = 4:2:1. Frequency: 500 Hz. Flow rate: 50 ml/min. Gap width: 1.3 cm.	42
4.14 Effect of voltage on products selectivities. CH ₄ :O ₂ :C ₂ H ₆ = 4:2:1. Frequency: 500 Hz. Flow rate: 50 ml/min. Gap width: 1.3 cm.	43

FIGURE	PAGE
4.15 Effect of frequency on partial pressure of effluent gases over Pt/KL system. CH ₄ :O ₂ :C ₂ H ₆ ratio = 4:2:1. Applied voltage: 8000 V. Flow rate: 50 ml/min. Gap width: 1.3 cm.	44
4.16 Effect of frequency on conversions and yield over Pt/KL system. CH ₄ :O ₂ :C ₂ H ₆ ratio = 4:2:1. Applied voltage: 8000 V. Flow rate: 50 ml/min.	45
4.17 Effect of frequency on products selectivities over Pt/KL system. CH ₄ :O ₂ :C ₂ H ₆ ratio = 4:2:1. Applied voltage: 8000 V. Flow rate: 50 ml/min.	46
4.18 Effect of voltage on conversions and yield over Pt/KL system. CH ₄ :O ₂ :C ₂ H ₆ ratio = 4:2:1. Frequency : 500 Hz. Flow rate: 50 ml/min.	47
4.19 Effect of voltage on conversions and yield over Pt/KL system. CH ₄ :O ₂ :C ₂ H ₆ ratio = 4:2:1. Frequency : 500 Hz. Flow rate: 50 ml/min.	47
4.20 Effect of voltage on products selectivities over Pt/KL system. CH ₄ :O ₂ :C ₂ H ₆ ratio = 4:2:1. Frequency : 500 Hz. Flow rate: 50 ml/min.	49