

**N-OCTANE AROMATIZATION ON PLATINUM OVER VARIOUS
SUPPORTS PREPARED BY VAPOR PHASE IMPREGNATION METHOD**



Ms. Benjawan Chanajaranwit

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

2002

ISBN 974-03-1558-5

Thesis Title : n-Octane Aromatization on Platinum over Various Supports Prepared by Vapor Phase Impregnation Method
By : Benjawan Chanajaranwit
Program : Petrochemical Technology
Thesis Advisors : Prof. Somchai Osuwan
Asst. Prof. Thirasak Rirksomboon
Prof. Daniel E. Resasco

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:

A. Osuwan
.....
(Prof. Somchai Osuwan)

Thirasak Rirksomboon
.....
(Asst. Prof. Thirasak Rirksomboon)

Daniel Resasco
.....
(Prof. Daniel E. Resasco)

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

Sirirat Jitkarnka
.....
(Dr. Sirirat Jitkarnka)

ABSTRACT

4371004063 : PETROCHEMICAL TECHNOLOGY PROGRAM

Benjawan Chanajaranwit: n-Octane Aromatization on Platinum over Various Supports Prepared by Vapor-Phase Impregnation (VPI) Method.

Thesis Advisors: Prof. Somchai Osuwan, Asst. Prof. Thirasak Rirkksomboon and Prof. Daniel E. Resasco, 43 pp. ISBN 974-03-1558-5

Keywords : Aromatization/ n-Octane/ Naphtha reforming/ Dehydrocyclization

Aromatization is one of the most important industrial processes for the production of intermediate aromatics. Since bifunctional catalysts such as Pt/Al₂O₃ give poor selectivity to aromatics, monofunctional catalysts such as Pt/KBeta, Pt/KL, Pt/KOmega, Pt/KY and Pt/SiO₂ were studied. These catalysts were chosen because they lack acid sites which can cause undesirable side reactions. Pt/KL is known to be an effective catalyst for n-hexane aromatization. However, it has much lower catalytic activity when used for n-octane aromatization. The objectives of this work were to study the effects of various supports such as Beta, L, Omega and Y zeolites, and SiO₂, and determine the optimum amount of Pt loading in the range of 0.5-1.5% for n-octane aromatization. The catalysts were prepared by the vapor-phase impregnation method. The catalytic performances of such catalysts on n-octane aromatization were investigated. It was found that 1%Pt/KL and 1%Pt/SiO₂ showed somewhat higher catalytic performance in both conversion and selectivity.

บทคัดย่อ

เบญจวรรณ ชนะจรัญวิทย์ : การศึกษาปฏิกิริยาอะโรมาไทเซชันของนอร์มัลออกเทนบนตัวเร่งปฏิกิริยาแพลตินัม/ตัวรองรับซึ่งเตรียมด้วยวิธีระเหิดสารเข้าไปในโพรงของตัวรองรับ (n-Octane Aromatization on Platinum over Various Supports Prepared by Vapor-Phase Impregnation Method) อ. ที่ปรึกษา: ศ.ดร. สมชาย โอสุวรรณ ผศ. ดร. ชिरศักดิ์ ฤกษ์สมบูรณ์ และ ศ.ดร. แดเนียล อี รีซัสโก (Prof. Daniel E. Resasco) 43 หน้า ISBN 974-03-1558-5

ปฏิกิริยาอะโรมาไทเซชันเป็นปฏิกิริยาสำคัญปฏิกิริยาหนึ่งในการผลิตสารอะโรมาติก ตัวเร่งปฏิกิริยาชนิดฟังก์ชันคู่ (Bifunctional Catalyst) ให้ค่าความเฉพาะเจาะจงในการเลือกทำปฏิกิริยา (Selectivity) ต่ำ จึงมีการนำตัวเร่งปฏิกิริยาชนิดฟังก์ชันเดี่ยว (Monofunctional Catalyst) มาประยุกต์ใช้ เนื่องจากตัวเร่งปฏิกิริยาชนิดนี้ไม่มีฟังก์ชันที่เป็นกรดทำให้เกิดปฏิกิริยาที่ไม่ต้องการลดลง ตัวเร่งปฏิกิริยาชนิดแพลตินัมบนพื้นผิวโพแทสเซียมซีโอไลต์แอล (Pt/KL) ได้รับการยอมรับว่าเป็นตัวเร่งปฏิกิริยาที่เหมาะสมสำหรับนอร์มัลเฮกเซน (n-Hexane) อย่างไรก็ตามเมื่อนำตัวเร่งปฏิกิริยาชนิดนี้มาใช้สำหรับนอร์มัลออกเทน (n-Octane) พบว่าความสามารถในการเป็นตัวเร่งปฏิกิริยาลดลง การทดลองนี้ทำการศึกษาอิทธิพลของตัวรองรับดังนี้ ซีโอไลต์เบตา (Beta zeolite) ซีโอไลต์แอล (L zeolite) ซีโอไลต์โอเมก้า (Omega zeolite) ซีโอไลต์วาย (Y zeolite) และซิลิกา (SiO₂) ต่อความสามารถในการเร่งปฏิกิริยาของตัวเร่งปฏิกิริยาชนิดแพลตินัมบนพื้นผิวของตัวรองรับ (Pt/Supports) ของปฏิกิริยาอะโรมาไทเซชัน (Aromatization) ของนอร์มัลออกเทน โดยทำการเตรียมตัวเร่งปฏิกิริยาด้วยวิธีระเหิดสารเข้าไปในโพรงของตัวรองรับ (Vapor-phase Impregnation, VPI) ผลการศึกษาแสดงในรูปความสามารถในการเปลี่ยนแปลง (Conversion) และความเฉพาะเจาะจงในการเลือกทำปฏิกิริยา ซึ่งให้เห็นว่าตัวเร่งปฏิกิริยาชนิดแพลตินัมบนพื้นผิวโพแทสเซียมซีโอไลต์แอลและตัวเร่งปฏิกิริยาแพลตินัมบนพื้นผิวซิลิกามีความว่องไวในการทำปฏิกิริยาอะโรมาไทเซชันมากกว่าตัวเร่งปฏิกิริยาชนิดอื่น สำหรับการศึกษอิทธิพลของปริมาณแพลตินัมที่มีในตัวเร่งปฏิกิริยาพบว่า ตัวเร่งปฏิกิริยาที่มีปริมาณแพลตินัมเท่ากับหนึ่งเปอร์เซ็นต์ให้ค่าความเฉพาะเจาะจงในการเลือกทำปฏิกิริยาสูงที่สุด

ACKNOWLEDGEMENTS

This thesis could not have been completed without all invaluable supports of the following individuals and organizations.

First of all, I would like to express my gratitude to Professor Daniel E. Resasco, my US advisor, Professor Somchai Osuwan and Assistant Professor Thirasak Rirksomboon, my Thai advisors, for their helpful guidance, useful advises and encouragement throughout the course of this research.

My thankfulness is also dedicated to Associate Professor Sumaeth Chavadej and Dr. Sirirat Jitkarnka for serving on my thesis committees and providing beneficial suggestions.

I am obliged to all professors who taught me and helped to establish the knowledge through their courses. And I also wish to express my gratefulness for PPC's staff who contributed knowledge for me.

I would like to express my sincere thanks to all Ph.D. students, especially Ms. Siriporn Jongpatiwut for profitable comments and for performing H₂ chemisorption testing at University of Oklahoma.

Unforgettable thanks are for all my friends for their understanding, cheerful and encouragement especially for the wonderful life time in these two years. All of them deserve these whole-heart thanks.

Finally, I would like to express my deepest gratitude for my beloved family for their unconditional love, support and understanding. All of them play the greatest role on my success.

TABLE OF CONTENTS

	PAGE
Title Page	i
Acceptance Page	ii
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 SURVEY	3
2.1 Catalyst for n-Octane Aromatization	3
2.2 Existing Catalyst for n-Octane Aromatization	4
2.3 Catalyst Preparation	5
2.4 The Addition of Rare Earth	6
2.5 Catalyst Deactivation	7
2.5.1 Catalyst Deactivation by Sintering	7
2.5.2 Catalyst Deactivation by Poisoning	7
2.5.3 Catalyst Deactivation by Fouling	8
III EXPERIMENTAL	9
3.1 Materials	9
3.1.1 Chemicals	9
3.1.2 Gases	9
3.2 Catalyst Preparation	10

CHAPTER	PAGE
3.2.1 Ion Exchange Procedure	10
3.2.2 Vapor Phase Impregnation method	10
3.2.2.1 Calcination of Alkaline Zeolite	10
3.2.2.2 Pt loading	10
3.2.2.3 Pretreatment	10
3.3 Reaction Testing	11
3.3.1 Reduction the Catalyst	11
3.3.2 Reaction Testing	11
3.3.3 The Product of n-Octane Aromatization Analysis	11
3.4 Characterization of Catalyst	12
3.4.1 Fourier Transform Infrared Spectroscopy of CO adsorbed	12
3.4.2 Temperature Programmed Oxidation	12
3.4.3 Surface Area Measurement	13
3.4.4 X-ray Diffraction	13
3.5 Apparatus	14
 IV RESULTS AND DISCUSSION	 15
4.1 Effect of Various supports on n-octane aromatization	15
4.1.1 Ion Exchange Step	15
4.1.2 BET Results	17
4.1.3 Catalytic Activity Measurement	18
4.1.3 Catalyst Characterizations	21
4.1.3.1 FT-IR adsorbed CO	21
4.1.3.2 Temperature Programmed Oxidation	25
4.2 Effect of the percentage of Pt loading	28
4.2.1 Pt/KL Study	28
4.2.1.1 Catalytic Activity Measurement	28
4.2.1.2 Catalyst Characterizations	30

CHAPTER		PAGE
IV	4.2.1.2.1 FT-IR adsorbed CO	30
	4.2.1.2.2 Temperature Programmed Oxidation	31
	4.2.2 Pt/SiO ₂ Study	33
	4.2.2.1 Catalytic Activity Measurement	33
	4.2.2.2 Catalyst Characterizations	35
	4.2.2.2.1 FT-IR adsorbed CO	35
	4.2.2.2.2 Temperature Programmed Oxidation	36
V	CONCLUSIONS AND RECOMMENDATIONS	39
	5.1 Conclusions	39
	5.2 Recommendations	39
	REFERENCES	40
	CURRICULUM VITAE	43

LIST OF TABLES

TABLE		PAGE
4.1	AAS results of zeolite composition after ion-exchange	15
4.2	BET results of various supports	18

LIST OF FIGURES

FIGURE		PAGE
3.1	Experimental set up	14
4.1	XRD patterns of NaHBeta (before ion-exchange), KBeta (after ion-exchange) and calcined KBeta (after calcination)	16
4.2	XRD patterns of NaY (before ion-exchange), KY (after on-exchange) and calcined KY (after calcination)	16
4.3	XRD patterns of NaOmega (before ion-exchange), KOmega (after on-exchange) and calcined KOmega (after calcination)	17
4.4	The variation of n-octane conversion with time on stream of various support catalysts prepared by VPI method on n-octane aromatization	19
4.5	The variation of total aromatics selectivity with time on stream of various support catalysts prepared by VPI method on n-octane aromatization	20
4.6	The variation of total aromatics yield with time on stream of various support catalysts prepared by VPI method on n-octane aromatization	20
4.7	FT-IR adsorbed CO spectra of various support catalysts	21
4.8	FT-IR adsorbed CO spectra of Pt/KBeta prepared by VPI method with 1%Pt loading presented in fresh and spent catalyst form	22
4.9	FT-IR adsorbed CO spectra of Pt/KL prepared by VPI method with 1%Pt loading presented in fresh and spent catalyst form	23
4.10	FT-IR adsorbed CO spectra of Pt/KOmega prepared by VPI method with 1%Pt loading presented in fresh and spent	

FIGURE		PAGE
	catalyst form	23
4.11	FT-IR adsorbed CO spectra of Pt/KY prepared by VPI method with 1%Pt loading presented in fresh and spent catalyst form	24
4.12	FT-IR adsorbed CO spectra of Pt/SiO ₂ prepared by VPI method with 1%Pt loading presented in fresh and spent catalyst form	24
4.13	TPO profile for 1% Pt/KBeta catalyst after spent in n-octane aromatization for 20 hours on stream	25
4.14	TPO profile for 1% Pt/KL catalyst after spent in n-octane aromatization for 20 hours on stream	26
4.15	TPO profile for 1% Pt/KOmega catalyst after spent in n-octane aromatization for 20 hours on stream	26
4.16	TPO profile for 1% Pt/KY catalyst after spent in n-octane aromatization for 20 hours on stream	27
4.17	TPO profile for 1% Pt/SiO ₂ catalyst after spent in n-octane aromatization for 20 hours on stream	27
4.18	The variation of n-octane conversion with time on stream of Pt/KL VPI catalysts with varying % Pt loading on n-octane aromatization	29
4.19	The variation of total aromatics selectivity with time on stream of Pt/KL VPI catalysts with varying % Pt loading on n-octane aromatization	29
4.20	The variation of total aromatics yield with time on stream of Pt/KL VPI catalysts with varying % Pt loading on n-octane aromatization	30
4.21	FT-IR adsorbed CO spectra of Pt/KL prepares by VPI method with varying % Pt loading at 0.5,1 and 1.5%	31

FIGURE		PAGE
4.22	TPO profile for 0.5% Pt/KL catalyst after spent in n-octane aromatization for 20 hours on stream	32
4.23	TPO profile for 1% Pt/KL catalyst after spent in n-octane aromatization for 20 hours on stream	32
4.24	TPO profile for 1.5% Pt/KL catalyst after spent in n-octane aromatization for 20 hours on stream	33
4.25	The variation of n-octane conversion with time on stream of Pt/SiO ₂ catalysts prepared by VPI method on n-octane aromatization	34
4.26	The variation of total aromatics selectivity with time on stream of Pt/SiO ₂ VPI catalysts with varying % Pt loading on n-octane aromatization	34
4.27	The variation of total aromatics yield with time on stream of Pt/SiO ₂ VPI catalysts with varying % Pt loading on n-octane aromatization	35
4.28	FT-IR adsorbed CO spectra of Pt/SiO ₂ prepared by VPI method with varying %Pt loading at 0.5,1,1.5 %	36
4.29	TPO profile for 0.5% Pt/SiO ₂ catalyst after spent in n-octane aromatization for 20 hours on stream	37
4.30	TPO profile for 1% Pt/SiO ₂ catalyst after spent in n-octane aromatization for 20 hours on stream	37
4.31	TPO profile for 1.5% Pt/SiO ₂ catalyst after spent in n-octane aromatization for 20 hours on stream	38