

***n*-ALKANES AROMATIZATION OVER Pt-CONTAINING ZEOLITE
CATALYSTS**



Ms. Siriporn Jongpatiwut

A Dissertation Submitted in Partial Fulfilment of the Requirements
for the Degree of Doctor of Philosophy
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 974-17-1366-5

Thesis Title : *n*-Alkanes Aromatization over Pt-Containing Zeolite Catalysts
By : Ms. Siriporn Jongpatiwut
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 Doctor of Philosophy.

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

Thesis Committee:

K. Bunyakiat
.....
(Assoc. Prof. Kunchana Bunyakiat)

Boonyarach Kitiyanan
.....
(Dr. Boonyarach Kitiyanan)

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

Vissanu Meeyoo
.....
(Asst. Prof. Vissanu Meeyoo)

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

W. E. ALVAREZ
.....
(Asst. Prof. Walter E. Alvarez)

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

ABSTRACT

4291003063 : PETROCHEMICAL TECHNOLOGY PROGRAM

Ms. Siriporn Jongpatiwut: *n*-Alkanes Aromatization over Pt-Containing Zeolite Catalysts.

Thesis Advisors: Prof. Daniel E. Resasco, Prof. Somchai Osuwan, and Asst. Prof. Thirasak Rirksomboon, 125 pp. ISBN 974-17-1366-5

Keywords : *n*-Hexane aromatization/ *n*-Octane aromatization/ Pt/K-LTL/ Pt/SiO₂/ Pt/K-BEA/ Pt/K-MAZ/ Pt/K-FAU/ Pt/VPI-5/ Vapor phase impregnation/ DRIFTS/ XANES/ EXAFS/ TPO/ TPD/ Hydrogen chemisorption/ XRD/ SEM/ Catalyst deactivation/ Sulfur tolerance/ Water resistance/ Diffusional effects on selectivity/ Cerium/ Ytterbium

The aromatization of *n*-hexane was investigated on 1% Pt-containing L-zeolite catalysts under clean, sulfur-, and water-containing feeds whereas the aromatization of *n*-octane was studied only under clean feed on different Pt-containing large-pore zeolite catalysts. In the studies of *n*-hexane, Pt/KL and Pt/KL-containing rare earth (RE; Ce and Yb) catalysts were prepared by vapor phase impregnation (VPI) method. Pt/KL was also prepared by incipient wetness impregnation (IWI) method. The influence of RE promoters to catalytic performance under clean, sulfur-, and water-containing feeds was studied. It was found that the addition of rare earth element could enhance the catalytic activity in the presence of sulfur. Morphology of platinum clusters in the catalysts was investigated by a combination of characterization techniques i.e. FT-IR of adsorbed CO, hydrogen chemisorption, and EXAFS.

The Pt/KL prepared by VPI method was also tested for the aromatization of *n*-octane. The results indicate that the activity was low and it quickly dropped after a few hours on stream. The product distribution obtained shows benzene and toluene as the dominant aromatic compounds, with small amount of ethylbenzene and *o*-xylene, which are the expected products from the direct closure of six-member

ring. The analysis of the product evolution as a function of conversion indicates that the benzene and toluene obtained are secondary products resulting from the hydrogenolysis of ethylbenzene and *o*-xylene. Temperature programmed oxidation and sorption studies on spent catalysts demonstrate that the rapid deactivation is due to pore blocking by coke formation.

The aromatization of *n*-octane was further studied on 1%Pt-containing other large pore zeolite catalysts, which are Pt/K-BEA, Pt/K-MAZ, and Pt/K-FAU catalysts. The Pt/KL, still, exhibits unique property among the zeolite catalysts. The results from FT-IR of adsorbed CO, hydrogen chemisorption and temperature programmed desorption of ammonia indicate that the superior property of Pt/KL is due to high Pt dispersion stabilized inside zeolite channel and lacking of high acid strength. Product distribution and coke formation were also discussed.

Finally, the preliminary study of *n*-octane aromatization over Pt-containing unidimensional, extra-large pore aluminophosphate zeolite (Pt/VPI-5) was investigated. The VPI-5 zeolite was synthesized and the resultant was verified by XRD and SEM techniques. Pt/VPI-5 catalyst prepared was tested for activity and aromatic selectivity of *n*-octane aromatization.

บทคัดย่อ

ศิริพร จงผาคิวดี : การศึกษาการเกิดปฏิกิริยาอะโรมาไทเซชันของนอร์มัล-อัลเคนบนตัวเร่งปฏิกิริยาชนิดแพลทินัมบนซีโอไลต์ (*n*-Alkanes Aromatization over Pt-Containing Zeolite Catalysts) อ. ที่ปรึกษา : ศ. ดร. แคนเน็ล อี ริชส์โก ศ.ดร. สมชาย โอสุวรรณ และ ผศ.ดร. ชีรศักดิ์ ฤกษ์สมบูรณ์ 125 หน้า ISBN 974-17-1366-5

ตัวเร่งปฏิกิริยาชนิดแพลทินัมบนซีโอไลต์แอลซึ่งมีประจุบวกเป็นโพแทสเซียม (Pt/KL) ถือว่าเป็นตัวเร่งปฏิกิริยาที่มีความสำคัญอย่างยิ่งต่อปฏิกิริยาอะโรมาไทเซชันของนอร์มัล-เฮกเซน เนื่องจากตัวรองรับชนิดนี้ไม่มีคุณสมบัติที่เป็นกรดซึ่งจะทำให้เกิดปฏิกิริยาแตกตัว และเปลี่ยนโครงสร้างเป็นไอโซเมอร์ อย่างไรก็ตามพบว่าตัวเร่งปฏิกิริยาชนิดนี้จะเสื่อมอย่างรวดเร็วในสภาวะที่มีซัลเฟอร์เจือเพียงเล็กน้อยเท่านั้น งานวิจัยนี้ได้ศึกษาการเพิ่มความต้านทานซัลเฟอร์โดยการเติมธาตุในอนุกรมแลนทาไนด์ ซีเรียม (Ce) และ อิทเรียม (Yb) งานวิจัยนี้เตรียมตัวเร่งปฏิกิริยา Pt/KL Pt/Ce-KL และ Pt/Yb-KL โดยวิธีระเหิดสารประกอบโลหะแพลทินัมเข้าไปยังโพรงของซีโอไลต์ (vapor phase impregnation) และนำตัวเร่งปฏิกิริยาชนิดต่าง ๆ มาศึกษาความว่องไวและความเฉพาะเจาะจงในการเกิดเป็นสารอะโรมาติกส์จากนอร์มัล-เฮกเซน ภายใต้สภาวะต่าง ๆ ได้แก่ สารตั้งต้นบริสุทธิ์ สารตั้งต้นที่มีซัลเฟอร์เจือ และ สารตั้งต้นที่มีไอน้ำเจือ นอกจากนี้ยังนำตัวเร่งปฏิกิริยา Pt/KL มาศึกษาการเกิดปฏิกิริยาอะโรมาไทเซชันของนอร์มัล-ออกเทน เปรียบเทียบกับตัวเร่งปฏิกิริยาที่เตรียมขึ้นจากซีโอไลต์ที่มีโพรงขนาดใหญ่อื่น ๆ เช่น ซีโอไลต์เบต้า (β; BEA) ซีโอไลต์โอเมกา (Ω; MAZ) ซีโอไลต์วาย (Y; FAU) และ ซีโอไลต์วีพีโอ-ไฟว์ (VPI-5; VFI) พบว่า การเติมธาตุ Ce หรือ Yb สามารถเพิ่มความต้านทานซัลเฟอร์ได้มากขึ้น แม้ว่าภายใต้สภาวะสารตั้งต้นบริสุทธิ์ การเติมธาตุจำพวกนี้ทำให้ความว่องไวลดลงก็ตาม และได้นำตัวเร่งปฏิกิริยา Pt/KL Pt/Ce-KL และ Pt/Yb-KL มาวิเคราะห์คุณสมบัติด้วยเทคนิคต่าง ๆ ได้แก่ ความสามารถในการดูดซับแก๊สไฮโดรเจน สเปกตรัม FT-IR ของโมเลกุลคาร์บอนมอนอกไซด์ซึ่งถูกดูดซับอยู่บนกลุ่มของแพลทินัม และ EXAFS เพื่ออธิบายการกระจายตัวของแพลทินัมบนตัวเร่งปฏิกิริยาชนิดต่าง ๆ

จากการศึกษาปฏิกิริยาอะโรมาไทเซชันของนอร์มัล-ออกเทน โดยใช้ตัวเร่งปฏิกิริยา Pt/KL พบว่า ความว่องไวและความเฉพาะจงในการเกิดสารอะโรมาติกส์ต่ำ และความว่องไวลดลงอย่างรวดเร็วเมื่อเทียบกับปฏิกิริยาของนอร์มัล-เฮกเซน อะโรมาติกส์ส่วนใหญ่ที่ได้จากปฏิกิริยา คือ เบนซีนและ โทลูอิน จากการศึกษานี้ที่อุณหภูมิ และเวลาต่าง ๆ รวมถึงการใช้สาร

พาราฟิน และอะโรมาติกส์ต่าง ๆ เป็นสารตั้งต้น พบว่า เบนซีนและโทลูอินที่พบเกิดขึ้นจากปฏิกิริยาไฮโดรจิโนไลซิสของ ออโต-ไซลีน และ เอทิลเบนซีน ซึ่งสารสองชนิดนี้เกิดจากการปิดวงแหวนอะโรมาติกส์โดยตรงจากนอร์มัล-ออกเทน ผลจากการศึกษาปริมาณโค้กและการแพร่ของไอโซบิวเทนบนตัวเร่งปฏิกิริยาที่ใช้งานแล้ว ชี้ให้เห็นว่าปริมาณโค้กที่เกิดมากขึ้นไปอุดตันโพรงของซีโอไลต์ ทำให้สารตั้งต้นเข้าไปทำปฏิกิริยาภายในโพรงของซีโอไลต์ได้น้อยลงจึงทำให้ความว่องไวลดลงอย่างรวดเร็ว อย่างไรก็ตามการอุดตันนี้ยังมีผลต่อการเลือกเกิดเป็นสารอะโรมาติกส์ชนิดต่าง ๆ อีกด้วย

ในการศึกษาการเกิดปฏิกิริยาอะโรมาไทเซชันของนอร์มัล-ออกเทนบนตัวเร่งปฏิกิริยาที่มีตัวรองรับเป็นซีโอไลต์ที่มีโพรงขนาดใหญ่ชนิดอื่น ๆ พบว่า Pt/KL ยังคงให้ผลในการเกิดปฏิกิริยานี้ดีที่สุดที่สุด เมื่อเทียบกับตัวเร่งปฏิกิริยา Pt/K-BEA Pt/K-MAZ และ Pt/K-FAU จากเทคนิคการวิเคราะห์ความสามารถในการดูดซับแก๊สไฮโดรเจน และ สเปกตรัม FT-IR ของโมเลกุลคาร์บอนมอนอกไซด์ซึ่งถูกดูดซับอยู่บนกลุ่มของแพลทินัม พบว่า ข้อดีของตัวเร่งปฏิกิริยา Pt/KL คือภายใต้สภาวะรีดักชัน แพลทินัมยังคงกระจายตัวได้ดีในโพรงของซีโอไลต์ในขณะที่แพลทินัมบนตัวเร่งปฏิกิริยาชนิดอื่น ๆ จะรวมกลุ่มกันอยู่ภายนอกโพรงของซีโอไลต์ นอกจากนี้ยังได้ทำการศึกษาการเกิดปฏิกิริยาอะโรมาไทเซชันของนอร์มัล-ออกเทน บนตัวเร่งปฏิกิริยาแพลทินัมบนซีโอไลต์ที่มีโพรงขนาดใหญ่พิเศษ (Pt/VPI-5) ซีโอไลต์ VPI-5 ได้ถูกสังเคราะห์และวิเคราะห์โดยเทคนิค XRD และ SEM การกระจายตัวของสารผลิตภัณฑ์ของปฏิกิริยาได้ถูกศึกษาเปรียบเทียบกับตัวเร่งปฏิกิริยา Pt/KL และตัวเร่งปฏิกิริยาแพลทินัมบนซิลิกา (Pt/SiO₂)

ACKNOWLEDGEMENTS

First of all, I would like to express my deep gratitude to my advisors, Dr. Somchai Osuwan, Prof. Daniel E. Resasco, and Asst. Prof. Thirasak Rirksomboon for their guidance. Prof. Somchai gave me opportunity of doing my Ph.D. under the Royal Golden Jubilee Ph.D. Project. He has kindly guided and set up an excellent plan for my study. He brought me to work with my US-advisor, Dr. Resasco. Dr. Resasco is a devoted researcher. I really appreciate working with him. His advice is invaluable and very useful. I also really appreciate the hospitality he and his family have shown me during my stay in Norman. Dr. Thirasak always helps me solve problems in the PPC laboratory. He is a big source of basic knowledge. He encourages me to invent many tools myself. It is actually very useful practice. I will always esteem all my advisors.

I would like to thank everybody in the PPC Catalysis Group especially, Banchong Lertrojanachosit, Thitiporn Thongsrikate, Paneeya Sackamduang, Benjawan Chanajaranwit for their contributions; Jirapon Leerat, Korada Supat, Siriphong Roatleuchai, and Apanee Luengnaruemitchai for their help and friendship. Thanks are also due to everybody in the OU Heterogeneous Catalysis Group, particularly Walter E. Alvarez and Jose Herrera for their helps and friendship. They willingly supervised me using several characterization instruments when I started doing research at the University of Oklahoma.

Also, I would like to thank a number of PPC staff for their contributions, particularly Chaturong Tiamsiri for all mechanical piecework e.g. making glove box, box for FTIR instrument, and repairing DRIFTS cell. His work is always nicer than I expected. I also thank C. P. O. Poon Arjpru for all electronic piecework e.g. making furnaces and temperature controller; Sanit Prinakorn for glassware piecework. I also want to acknowledge Syed Khalid at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory for help with the EXAFS works; Arisara Suthasut at the Petroleum Authority of Thailand for help with the TPD characterization.

I would like to acknowledge Assoc. Prof. Kunchana Bunyakiat, Asst. Prof. Walter E. Alvarez, Asst. Prof. Vissanu Meeyoo, and Dr. Boonyarach Kitiyanan for serving on my thesis committee and for their comments.

I sincerely acknowledge the Thailand Research Fund (TRF) for providing stipend and budget for doing research including airfare and stipend for doing research at the university of Oklahoma, USA during November 2000–April 2001 and January 2002–March 2002. TRF also supports my work presentation in the AIChE Annual Meeting 2000 in Los Angeles, USA during 12-17 November 2000. I also acknowledge the Oklahoma Center for Advancement of Science and Technology (OCAST) for providing research fund for all experiments at the University of Oklahoma, airfare and allowance for doing EXAFS experiments at the NSLS, New York during 14-18 February 2001 and 16-21 February 2002. I would like to thank the Petroleum and Petrochemical College (PPC) for partial supporting tuition fee. PPC also partially supports my work presentation in the AIChE Spring Meeting 2002 in New Orleans, USA during 10-14 March 2002. Here, I am deeply grateful Dr. Somchai who personally supports the round-trip airfare from Oklahoma to New Orleans.

I would like to express my gratitude to the PPG-Siam Silica Co. for donating silica support in this work. I also acknowledge Condea Vista Co., TX, U.S.A. for kindly donating and shipping Catapal B (Al_2O_3) to Thailand for the synthesis of VPI-5 zeolite.

I sincerely thank my parents, sisters, and brother for their encouragement. Lastly, I would like to acknowledge my lovely husband, Winai Sow, for being a permanent consultant for me. He has given me the strongest encouragement when I encountered serious problems.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	v
Acknowledgements	vii
Table of Contents	ix
List of Tables	xii
List of Figures	xiv
Abbreviations	xxiii
List of Symbols	xxv
 CHAPTER	
I INTRODUCTION	1
Motivation	1
Historical Perspective	3
Scope of Work	4
II SULFUR- AND WATER-TOLERANCE OF Pt/KL AROMATIZATION CATALYSTS PROMOTED WITH Ce AND Yb	6
Abstract	7
Introduction	8
Experimental	9
Results and Discussion	13
Conclusions	33
Acknowledgements	34
References	34
III <i>n</i>-OCTANE AROMATIZATION ON A Pt/KL CATALYST PREPARED BY VAPOR-PHASE IMPREGNATION	37

CHAPTER	PAGE
Abstract	38
Introduction	39
Experimental	40
Results	43
Discussion	59
Conclusions	62
Acknowledgements	62
References	62
IV <i>n</i>-OCTANE AROMATIZATION ON Pt-CONTAINING ZEOLITES I. LARGE PORE ALUMINOSILICATE MOLECULAR SIEVES	64
Abstract	65
Introduction	65
Experimental	66
Results	69
Discussion	76
Conclusions	77
Acknowledgements	77
References	77
V <i>n</i>-OCTANE AROMATIZATION ON Pt-CONTAINING ZEOLITES II. EXTRA-LARGE PORE ALUMINOPHOSPHATE VPI-5	80
Abstract	81
Introduction	81
Experimental	82
Results and Discussion	84
Conclusions	90
Acknowledgements	91
References	91

CHAPTER		PAGE
VI	CONCLUSIONS AND RECOMMENDATIONS	92
	REFERENCES	93
	APPENDICES	94
	Appendix A Information of zeolites	94
	Appendix B Dual-function mechanism for catalytic reforming	101
	Appendix C Experimental data	102
	Appendix D Equipment	115
	CURRICULUM VITAE	123

LIST OF TABLES

TABLE		PAGE
CHAPTER II		
1	Product distribution of <i>n</i> -hexane aromatization on Pt/KL and Pt/Ce-KL catalysts using clean and 2.5 ppm sulfur-containing feeds, after 9 h on stream. Reaction conditions: 500°C, H ₂ : <i>n</i> -C ₆ ratio 6:1, WHSV 5 h ⁻¹	18
2	Hydrogen chemisorption data on fresh (reduced) catalysts	20
3	Structural parameters obtained from the fitting of the EXAFS data	28
CHAPTER III		
1	Analysis data of fresh and spent Pt/KL catalysts	45
2	Product distribution of <i>n</i> -hexane and <i>n</i> -octane aromatization over different catalysts. Reaction conditions: 500°C, H ₂ / <i>n</i> -C ₆ (or <i>n</i> -C ₈) molar ratio 6:1, WHSV 5 h ⁻¹	47
3	Product distribution of <i>n</i> -octane aromatization over Pt/KL-VPI at various reaction temperatures. Reaction conditions: H ₂ / <i>n</i> -C ₈ molar ratio 6:1, WHSV 5 h ⁻¹	52
4	Product distribution of <i>n</i> -octane aromatization over Pt/KL-VPI at various WHSV. Reaction conditions: 500°C, H ₂ / <i>n</i> -C ₈ molar ratio 6:1	53
5	Product distribution of different feeds over Pt/KL-VPI catalysts. Reaction conditions: 500°C, H ₂ /reactant molar ratio 6:1, WHSV 5 h ⁻¹	54
6	Diffusibility of different aromatics into channel of L zeolite	56

TABLE		PAGE
CHAPTER IV		
1	Formulas and channel structures of different zeolites	67
2	Analysis data of different catalysts and supports	70
3	Product distribution of <i>n</i> -octane aromatization on Pt/SiO ₂ and Pt/zeolite catalysts, after 10 h on stream. Reaction conditions; 500°C, H ₂ : <i>n</i> -C8 ratio 6:1, WHSV 5 h ⁻¹	74
CHAPTER V		
1	Product distribution of <i>n</i> -octane aromatization on Pt/SiO ₂ , Pt/KL, and Pt/VPI-5 catalysts, after 10 h on stream. Reaction conditions; 500°C, H ₂ : <i>n</i> -C8 ratio 6:1, WHSV 5 h ⁻¹	89
APPENDIX C		
1	AAS data of Pt containing in different catalysts	102
2	AAS data of Si/Al, K/Al, and Na of K-exchanged zeolites	102

LIST OF FIGURES

FIGURE		PAGE
CHAPTER I		
1	Sources of benzene in the United States in the early 1990s.	1
2	Major uses of benzene in the United States in the early 1990s.	2
CHAPTER II		
1	<i>n</i> -Hexane conversion (a) and benzene selectivity (b) vs. time on stream under clean <i>n</i> -hexane feed over various Pt/KL and rare earth-promoted Pt/KL catalysts. Reaction conditions: WHSV= 5 h ⁻¹ ; H ₂ / <i>n</i> -hexane molar ratio = 6; temperature = 500°C.	14
2	<i>n</i> -Hexane conversion (a) and benzene selectivity (b) vs. time on stream under 2.5 ppm sulfur containing feed. Reaction conditions: WHSV= 5 h ⁻¹ ; H ₂ / <i>n</i> -hexane molar ratio = 6; temperature = 500°C.	15
3	Hexenes selectivity (a) and C5 selectivity (b) vs. time on stream under 2.5 ppm sulfur containing feed. Reaction conditions: WHSV= 5 h ⁻¹ ; H ₂ / <i>n</i> -hexane molar ratio = 6; temperature = 500°C.	17
4	<i>n</i> -Hexane conversion (a) and benzene selectivity (b) vs. time on stream first 9 h in clean <i>n</i> -hexane feed, then in the presence of 3 mol. % water vapor containing <i>n</i> -hexane feed for 1 h, and then continue in clean <i>n</i> -hexane feed. Reaction conditions: WHSV = 5 h ⁻¹ ; H ₂ / <i>n</i> -hexane molar ratio = 6; temperature = 500°C.	19

FIGURE		PAGE
5	DRIFTS of CO adsorbed on fresh catalysts reduced in situ at 300°C after an ex situ reduction at 500°C. The reduced catalysts were exposed to a flow of 3% CO in He for 30 min at room temperature and purged in He for 30 min.	22
6	DRIFTS of CO adsorbed on (a) Pt/KL and (b) Pt/Ce-KL fresh and after reaction with 2.5 ppm sulfur containing feed for 30 h. Each sample was reduced in situ at 300°C. The reduced catalysts were exposed to a flow of 3% CO in He for 30 min at room temperature and purged in He for 30 min.	23
7	TPO profiles of (a) Pt/KL and (b) Pt/Ce-KL spent catalysts after reaction at 500°C for different times on stream, using feed containing 2.5 ppm S. A sample run with a clean feed is included for each catalyst. The calculated amount of coke is included for each curve.	24
8	TPO profiles of (a) Pt/KL and (b) Pt/Ce-KL spent catalyst after reaction at 500°C for different times on stream, using feed containing 3 mol. % H ₂ O. The calculated amount of coke is included for each curve.	26
9	Carbon deposits (wt. %) as calculated from integration of the TPO profiles of Fig. 8 expressed as a function of time on stream in (a) feed containing 2.5 ppm S and (b) feed containing 3 mol. % H ₂ O over Pt/KL and Pt/Ce-KL catalysts.	27
10	Fourier transforms corresponding to the k ³ -weighted Pt L ₃ -edge EXAFS spectra obtained at liquid nitrogen temperature on in situ reduced Pt/KL and Pt/Ce-KL catalysts.	28

FIGURE		PAGE
11	XANES spectra of the Pt L ₃ and L ₂ edges obtained at liquid nitrogen temperature over a Pt foil, and Pt/KL and Pt/Ce-KL catalysts. Each set of spectra were aligned and normalized in order to match the EXAFS oscillations. The spectra of the catalysts were obtained after in situ reduction and flushing in He.	29
12	Comparison for the XANES spectra of the (a) Pt L ₂ and (b) Pt L ₃ edges obtained in He at liquid nitrogen temperature after in situ reduction at 500°C over the catalysts Pt/KL and Pt/Ce-KL. Inset emphasizes the differences in the white lines for the two catalysts.	31
13	XANES spectra of the Pt L ₃ edges obtained under hydrogen as a function of temperature. More than 10 spectra were obtained for each sample at different temperatures (they are included in Fig. 14) but only five are shown here for the sake of clarity.	32
14	Variation of the area under the first peak in the XANES spectra (white line) as a function of reduction temperature. The decrease in the size of the white line indicates the reduction of Pt.	32

CHAPTER III

1	DRIFTS spectra of CO adsorbed on Pt/KL-VPI, Pt/KL-IWI, and Pt/SiO ₂ catalysts reduced in situ at 500°C. The reduced catalysts were exposed to a flow of 3%CO in He for 30 min at room temperature and purged in He for 30 min.	45
---	---	----

FIGURE		PAGE
2	(a) Total conversion of <i>n</i> -hexane (open symbols) and <i>n</i> -octane (full symbols) as a function of time on stream (b) Selectivity to total aromatics as a function of time on stream. Catalysts: Pt/KL-VPI (triangles), Pt/KL-IWI (squares), and Pt/SiO ₂ (circles). Reaction conditions: 500°C, H ₂ / <i>n</i> -C ₆ (<i>n</i> -C ₈) molar ratio 6:1, WHSV 5 h ⁻¹ .	46
3	Benzene to C ₈ -aromatics product ratio during <i>n</i> -octane aromatization as a function of time on stream over Pt/KL-VPI, Pt/KL-IWI, and Pt/SiO ₂ catalysts. Reaction conditions: 500°C, H ₂ / <i>n</i> -C ₈ molar ratio 6:1, WHSV 5 h ⁻¹ .	48
4	Ethylbenzene: <i>o</i> -xylene (EB/OX) ratio during <i>n</i> -octane aromatization over Pt/KL-VPI, Pt/KL-IWI, and Pt/SiO ₂ catalysts. Reaction conditions: 500°C, H ₂ / <i>n</i> -C ₆ (<i>n</i> -C ₈) molar ratio 6:1, WHSV 5 h ⁻¹ . Included for comparison are data adapted from ref. [2].	49
5	Steady-state product selectivity as a function of conversion during <i>n</i> -octane aromatization. (a) Conversion varied by increasing temperature from 300 to 500 °C, at a fixed WHSV=5 h ⁻¹ . (b) Conversion varied by changing the WHSV from 9 to 1 h ⁻¹ , at a fixed temperature, 500°C. circles: C ₈ -aromatics; triangles: toluene; squares: methane.	50
6	Ethylbenzene: <i>o</i> -xylene (EB/OX) ratio during <i>n</i> -octane aromatization over the Pt/KL-VPI catalyst as a function of space velocity. Reaction conditions: 500°C, H ₂ / <i>n</i> -C ₆ (<i>n</i> -C ₈) molar ratio 6:1, 10 h on stream.	51
7	Total conversion of different hydrocarbons over the Pt/KL-VPI catalyst as a function of time on stream. Reaction conditions: 500°C, H ₂ /hydrocarbon molar ratio 6:1, WHSV 5 h ⁻¹ .	56

FIGURE		PAGE
8	Temperature programmed oxidation (TPO) profiles of coke deposits left over the Pt/KL-VPI catalyst after 9 h on stream during <i>n</i> -hexane (thin line) and <i>n</i> -octane aromatization (heavier line). Reaction conditions: 500°C, H ₂ / <i>n</i> -C ₆ (or <i>n</i> -C ₈) molar ratio 6:1, WHSV 5 h ⁻¹ .	57
9	(a) Total <i>n</i> -octane conversion before and after regeneration in air at 400°C as a function of time on stream. Open symbols: first reaction cycle; full symbols: reaction cycle after regeneration. (b) Left axis: Selectivity to total aromatics; Right axis: Ethylbenzene: <i>o</i> -xylene (EB/OX) ratio.	58
CHAPTER IV		
1	DRIFTS spectra of CO adsorbed on fresh catalysts reduced in situ at 500°C. The reduced catalysts were exposed to a flow of 3%CO in He for 30 min at room temperature and purged in He for 30 min. (a) Pt/SiO ₂ , (b) Pt/K-LTL, (c) Pt/K-BEA, (d) Pt/K-MAZ, and (e) Pt/K-FAU.	71
2	TPD profiles of ammonia adsorbed on catalyst supports (a) SiO ₂ , (b) K-LTL, (c) K-BEA, (d) K-MAZ, and (e) K-FAU. The supports were exposed to a flow of 10%NH ₃ /He at 100°C for 30 min and purged by He for 30 min.	72
3	(a) <i>n</i> -Octane conversion and (b) Total aromatics selectivity (mole basis) vs. time on stream over Pt/SiO ₂ and Pt/zeolite catalysts. Reaction conditions: 500°C, H ₂ / <i>n</i> -C ₆ (or <i>n</i> -C ₈) molar ratio 6:1, WHSV 5 h ⁻¹ .	73
4	TPO profiles of coke deposits on (a) Pt/SiO ₂ , (b) Pt/K-LTL, (c) Pt/K-BEA, (d) Pt/K-MAZ, and (e) Pt/K-FAU, after reaction at 500°C for 10 h on stream.	75

FIGURE		PAGE
CHAPTER V		
1	XRD pattern of synthesized VPI-5. (Asterisk is due to AlPO ₄ -5 pattern.)	85
2	SEM images of different morphologies of synthesized VPI-5 (a) needle-like, (b) needle-like aggregate into bundles, and (c) needle-like aggregate into spherulites.	85
3	TPD profiles of ammonia adsorbed on catalyst supports (a) SiO ₂ , (b) KL, and (c) VPI-5. The supports were exposed to a flow of 10%NH ₃ /He at 100°C for 30 min and purged by He for 30 min.	86
4	XRD patterns of (a) synthesized VPI-5, (b) Pt/VPI-5, and (c) spent Pt/VPI-5, after reaction at 500°C for 20 h. (Asterisks are due to AlPO ₄ -8 pattern.)	87
5	(a) <i>n</i> -Octane conversion and (b) Total aromatics selectivity (mole basis) vs. time on stream over Pt/SiO ₂ , Pt/KL, and Pt/VPI-5 catalysts. Reaction conditions: 500°C, H ₂ / <i>n</i> -C ₆ (or <i>n</i> -C ₈) molar ratio 6:1, WHSV 5 h ⁻¹ .	88
6	TPO profiles of coke deposits on (a) Pt/SiO ₂ , (b) Pt/KL, and (c) Pt/VPI-5, after reaction at 500°C for 10 h on stream. The calculated amount of coke is included in each curve.	90
APPENDIX A		
1	Structure of LTL zeolite. (viewed normal to [001])	94
2	Referable XRD pattern for LTL zeolite, x-axis is 2θ, y-axis is intensity.	94
3	Structure of BEA zeolite. (viewed along to [100])	95
4	Referable XRD pattern for BEA zeolite, x-axis is 2θ, y-axis is intensity.	95

FIGURE	PAGE
5 Structure of MAZ zeolite. (viewed along to [001])	96
6 Referable XRD pattern for MAZ zeolite, x-axis is 2θ , y-axis is intensity.	96
7 Structure of FAU zeolite. (viewed along to [111])	97
8 Referable XRD pattern for FAU zeolite, x-axis is 2θ , y-axis is intensity.	98
9 Structure of VFI zeolite. (viewed along to [001])	99
10 Referable XRD pattern for VFI zeolite, x-axis is 2θ , y-axis is intensity.	99
11 Structure of AET zeolite. (viewed along to [001])	100
12 Referable XRD pattern for AET zeolite, x-axis is 2θ , y-axis is intensity.	100

APPENDIX B

1 Dual-function mechanism for catalytic reforming.	101
--	-----

APPENDIX C

1 SEM images of Catapal B, Al_2O_3 source of VPI-5 synthesis.	103
2 SEM images of Pt/VPI-5 catalyst.	103
3 SEM images of Pt/KL catalyst.	104
4 XRD pattern of K-LTL.	104
5 XRD patterns of MAZ zeolite, before and after exchanged to K-MAZ and after calcination at $400^\circ C$ for 5 h.	105
6 XRD patterns of FAU zeolite, before and after exchanged to K-FAU and after calcination at $400^\circ C$ for 5 h.	105
7 XRD patterns of BEA zeolite, before and after exchanged to K-BEA and after calcination at $400^\circ C$ for 5 h.	106

FIGURE		PAGE
8	XRD patterns of VPI-5 zeolite; fresh, after BET measurement (heated at 300°C for 5h, under vacuum), and after TGA-DSC measurement (heated to 1,000°C in the presence of air).	107
9	DRIFTS of CO molecules and CO adsorbed over Pt/KL and Pt/KY (FAU) catalysts reduced in situ at 500°C. The catalysts were exposed to 3%CO/He for 30 min at room temperature and purging by He for 30 min. The spectra were collected before and after purging by He.	108
10	TGA and DSC curves of synthesized VPI-5. The zeolite was heated to 1000°C (10°C/min) in the presence of air.	109
11	TPD profiles of adsorbed ammonia on NaH-BEA, K-exchanged BEA, and H-exchanged BEA. The samples were exposed to 10%NH ₃ /He for 30 min and purged by He for 30 min.	110
12	TPD profiles of adsorbed ammonia on K-LTL and Pt/K-LTL. The samples were exposed to 10%NH ₃ /He for 30 min and purged by He for 30 min.	110
13	TPD profiles of adsorbed ammonia on K-BEA and Pt/K-BEA. The samples were exposed to 10%NH ₃ /He for 30 min and purged by He for 30 min.	111
14	TPD profiles of adsorbed ammonia on K-MAZ and Pt/K-MAZ. The samples were exposed to 10%NH ₃ /He for 30 min and purged by He for 30 min.	112
15	TPD profiles of adsorbed ammonia on K-FAU and Pt/K-FAU. The samples were exposed to 10%NH ₃ /He for 30 min and purged by He for 30 min.	113
16	TPD profiles of adsorbed ammonia on SiO ₂ and Pt/SiO ₂ . The samples were exposed to 10%NH ₃ /He for 30 min and purged by He for 30 min.	114

FIGURE		PAGE
APPENDIX D		
1	Schematic diagram of overall reaction testing system.	115
2	Schematic diagram of auto-sampling system.	116
3	Electronic connection designed for auto-sampling-controlled system.	117
4	Schematic diagram of hydrogen chemisorption system.	118
5	Schematic diagram of temperature programmed oxidation (TPO) system.	119
6	Image of DRIFTS cell (Spectra-Tech 0030-103; high temperature/vacuum chamber).	120
7	Image of EXAFS cell.	121
8	Images of equipment and tools for VPI-5 synthesis. (a) Microwave oven, (b) Assemblies of Teflon vessel set, (c) Teflon vessel set, and (d) Cross-section of Teflon vessel set.	122

ABBREVIATIONS

2MP	2-Methyl pentane
3MP	3-Methyl pentane
AAS	Atomic absorption spectroscopy
BET	Brunauer, Emmett, and Teller
CN	Coordination number
DRIFTS	Diffuse reflection infrared Fourier transform spectroscopy
DSC	Differential scanning calorimetry
DTGS	Deuterated triglycene sulfate
EB	Ethylbenzene
EXAFS	Extended x-ray absorption fine structure
FID	Flame ionization detector
FT-IR	Fourier transform infrared spectrometer
GC	Gas chromatograph
IWI	Incipient wetness impregnation
MCP	Methylcyclopentane
MCT	Mercury-cadmium-telluride
OX	<i>o</i> -Xylene
ppm	Part per million (weight basis)
RE	Rare earth
SEM	Scanning electron microscope
TCD	Thermal conductivity detector
TEM	Transmission electron microscope
TGA	Thermo-gravimetric analysis
TPD	Temperature programmed desorption
TPO	Temperature programmed oxidation
VPI	Vapor phase impregnation

WHSV	Weight hourly space velocity
XANES	X-ray absorption near edge spectroscopy
XRD	X-ray diffraction

LIST OF SYMBOLS

E_0	Inner potential
σ^2	Mean-squared displacement of atoms in the sample
χ	EXAFS function
E_F	Fermi energy
ΔVB	Empty valence band levels
k	Wave number of photoelectron
R	Inter-atomic distance