## AROMATIZATION OF *n*-OCTANE OVER Pt-Sn/KL CATALYSTS: ACTIVITY AND REGENERATION

1

1. 1. 11

A CHARTER CALLER

Worarat Charoennam

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 2008

# 512011

Thesis Title:	Aromatization of <i>n</i> -Octane over Pt-Sn/KL Catalysts:
	Activity and Regeneration
Program:	Petroleum Technology
Thesis Advisors:	Dr. Siriporn Jongpatiwut
	Assoc. Prof. Thirasak Rirksomboon
	Prof. Somchai Osuwan
	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.

Nantaya Sknunet College Director

(Assoc. Prof. Nantaya Yanumet)

Thesis Committee:

J. hin /

(Dr. Siriporn Jongpatiwut)

.....

(Prof. Somchai Osuwan)

1. Speett eft.

(Dr. Thammanoon Sreethawong)

ull

(Assoc. Prof. Thirasak Rirksomboon)

(Prof. Daniel E. Resasco)

.....

(Assoc. Prof. Tawan Sooknoi)

## บทคัดย่อ

วรรัตน์ เจริญนาม : อะโรมาไทเซชันของนอร์มัลออกเทนบนโลหะแพลททินัมและคีบุก บนตัวรองรับซีโอไลต์แอล: ความสามารถในการเกิดปฏิกิริยาและการนำกลับมาใช้ไหม่ (Aromatization of *n*-Octane over Pt-Sn/KL Catalysts: Activity and Regeneration) อ. ที่ปรึกษา : คร. ศิริพร จงผาติวุฒิ ศ. แดเนียล อีรีซัสโก รศ.คร. ธีรศักดิ์ ฤกษ์สมบูรณ์ และ ศ. สมชาย โอสุวรรณ 84 หน้า

ตัวเร่งปฏิกิริยาแพลททินัมบนซีโอไลต์แอล (Pt/KL) 🦯 เป็นตัวเร่งปฏิกิริยาที่มี ประสิทธิภาพสุงสำหรับปฏิกิริยาอะโรมาไทเซชันของนอร์มัลเฮกเซนเป็นเบนซีน แต่มี ประสิทธิภาพไม่ดีสำหรับนอร์มัลออกเทน เพราะให้ผลิตภัณฑ์ที่เป็นอะโรเมติกส์ที่มีอะตอม คาร์บอน 8 อะตอมน้อยแต่มีปริมาณเบนซีนและ โทลอีนมาก ซึ่งเป็นผลิตภัณฑ์ที่ไม่ต้องการที่เกิด ้จากปฏิกิริยาไฮโครจึโนไลซีส จากการศึกษาที่ผ่านมาพบว่าการใช้ซีโอไลต์แอลที่มีขนาคเล็กระดับ นาโนเมตร (NCL) และการเติมโลหะดีบุกจะทำให้ความว่องไวในการเป็นตัวเร่งปฏิกิริยาและมี ความเลือกเฉพาะกับผลิตภัณฑ์อะโรเมติกส์ที่มีอะตอมการ์บอน 8 อะตอมดีขึ้น การใช้ซีโอไลต์แอล ้ขนาดเล็กระดับนาโนเมตรสามารถลดข้อจำกัดการแพร่ของผลิตภัณฑ์ในขณะที่การเติมโลหะดีบุก จะช่วยแยกกลุ่มก้อนของแพลททินัมโดยการเกิด PtSn อัลลอยค์ ซึ่งทำให้ปฏิกิริยาไฮโครจีโนไล ซีสถูกขับขั้ง อย่างไรก็ตาม PtSn อัลลอยค์อาจจะถูกทำลายระหว่างการเผาโค้กในขั้นตอนการนำ กลับมาใช้ใหม่ คังนั้น งานวิจัยนี้จะเป็นการรวมระหว่างซีโอไลต์ขนาคเล็กระคับนาโนเมตรเป็นตัว รองรับกับการเติมโลหะดีบุกบนแพลททินัมบนซีโอไลต์แอล ผลการศึกษาพบว่าการเติมโลหะ ดีบุกจะช่วยปรับปรุงความสามารถในการเกิดปฏิกิริยาและความเลือกเฉพาะกับผลิตภัณฑ์ของ ้ตัวเร่งปฏิกิริยา Pt/COM และ Pt/NCL ใม่ว่าอย่างไรก็ตาม PtSn/COM ให้อะโรเมติกส์ที่มี อะตอมการ์บอน 8 อะตอมมากกว่า PtSn/NCL เพราะ PtSn/COM มีจำนวน PtSn อัลลอยค์ มากกว่า PtSn/NCL นอกจากนี้ยังมีการศึกษาผลกระทบของอุณหภูมิ (300-500 องศาเซลเซียส) เวลา (15 นาที-2 ชั่วโมง) และความเร็วของอากาศ (10-40 มิลลิลิตร/นาที) ที่มีต่อ PtSn อัลลอยค์ บนตัวรองรับ COM ผลการศึกษาพบว่าสภาวะที่เหมาะสมที่สุดของการนำกลับมาใช้ใหม่ของ ตัวเร่งปฏิกิริยา คือ 400 องศาเซลเซียส 1 ชั่วโมง และ 20 มิลลิลิตร/นาที โดยที่สภาวะนี้มีปริมาณ ที่เหลืออยู่ของ PtSn อัลลอยค์สูงสุดและมีโค้กอยู่ในปริมาณที่ต่ำ ซึ่งส่งผลให้ความสามารถในการ ้เกิดปฏิกิริยาและความเลือกเฉพาะกับผลิตภัณฑ์ของตัวเร่งปฏิกิริยาสูงสุดในการใช้งานอีกครั้งหนึ่ง โดยใกล้เดียงกับ Pt-Sn/COM ที่ไม่ได้ผ่าบการใช้งาบบา

#### ABSTRACT

4973011063 Petroleum Technology
Worarat Charoennam: Aromatization of *n*-Octane over Pt-Sn/KL
Catalysts: Activity and Regeneration
Thesis Advisors: Dr. Siriporn Jongpatiwut, Prof. Daniel E. Resasco,
Assoc. Prof. Thirasak Rirksomboon and Prof. Somchai Osuwan, 84
pp.

Keywords: *n*-Octane Aromatization/ Pt-Sn Catalyst/ Catalyst Regeneration

Platinum supported on KL zeolite (Pt/KL) is an efficient catalyst for the aromatization of *n*-hexane into benzene, but is not as effective for *n*-octane aromatization. The product distribution shows small quantities of C8-aromatics but high amounts of benzene and toluene, which are undesired products from the secondary hydrogenolysis reaction. In previous studies, using nano-crystalline KL zeolite (NCL) and the addition of Sn enhanced the activity and selectivity toward C8 aromatics. The advantage of using the NCL is to reduce the diffusion limitations while that of the Sn addition is to break the Pt ensemble by forming the Pt-Sn alloy phase; hence, the hydrogenolysis reaction is inhibited. However, the Pt-Sn alloy may be destroyed during the catalyst regeneration. Therefore, in this work, the combination of using NCL zeolite with the addition of Sn on Pt/KL was studied. It was found that the addition of Sn improved the catalytic activity and selectivity on both Pt/COM and Pt/NCL. However, the PtSn/COM gave higher C8 aromatics than PtSn/NCL. This could be because PtSn/COM has higher fraction of PtSn alloy phase than PtSn/NCL. The effects of regeneration temperature (300-500°C), time (15 min-2 h) and air flow rate (10-40 ml/min) on Pt-Sn alloy over COM were also studied. Among the conditions tested, the catalyst regenerated with an air flow rate of 20 ml/min at 400°C for 1 h exhibits the highest degree of PtSn alloy and low residual coke contents, leading to the highest catalytic activity and selectivity in the 2<sup>nd</sup> cycle which is close to the those observed on the fresh Pt-Sn/COM catalyst.

#### ACKNOWLEDGEMENTS

This thesis work is partially funded by the Petroleum and Petrochemical College; the National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Thailand; and the Grant for Development of New Faculty Staff, Chulalongkorn University.

I would like to express my greatest appreciation to Dr. Siriporn Jongpatiwut, Assoc. Prof. Thirasak Rirksomboon, Prof. Somchai Osuwan, and Prof. Daniel E. Resasco for their guidance, assistance, and the opportunity to do research at the University of Oklahoma. Their professionalism and expertise has inspired me in many ways while writing throughout my research. I would also like to thank all friends and staff at the PPC for their help and support.

It is my pleasure to acknowledge Dr. Supak Trakarnroek and Dr. Pisan Chungchamroenkit for giving me priceless knowledge and helping me with the problems that I have stumbled upon during my research. I would also like to thank Mr. Robert Wright for his valuable advice in writing papers and thesis. Special thanks also go to Jongpatiwut's group for helping me operate the laboratory.

My deepest appreciation goes to Air, Q, and Phueng for making my transition from Thailand to United States as smooth as possible and giving excellent suggestion. My appreciation also goes to Kitti and Emma for their allowing me to stay in their home during my stay at the University of Oklahoma. I would also like to thank Ming for showing me the American culture as well as fine tuning my English speaking and writing skills.

Special gratitude goes to all of my family who have supported me throughout my life, these people have been with me through great and bad times and shared every moment that I have encountered. Without these special people, I would not have been able to achieve my Master's degree in Petroleum Technology. I am grateful for everything they have given me.

### **TABLE OF CONTENTS**

					PAGE	
	Title	Page			i	
	Abst	ract (in English)			iii	
	Abst	ract (in Thai)			iv	
	Ackı	nowledgement			v	
	Tabl	e of Contents			vi	
	List	of Tables			x	
	List of Figures					
Cl	HAPTE	R	•			
a.	I	INTRODUCTION			i	
	П	LITERATURE REVIEW			4	
		2.1 Catalytic Reforming			4 ·	
		2.1.1 <i>o</i> -Xylene			5	
		2.1.2 Ethybenzene			5.	
		2.2 Catalysts for Aromatization of n-Alka	ne		6.	
		2.2.1 Molecular Die (geometric) Effe	cts		6	
		2.2.2 Preorganization of <i>n</i> -Hexane for	r Ring			
		Closure			6	
		2.2.3 Electronic Effects			6	
		2.2.4 Inhibition of Bimolecular Pathw	ay		7	
		2.2.5 Stabilization of Small Pt Cluster	rs		7	
		2.3 The Structure of LTL Zeolite			8	
		2.4 Synthesis of KL Zeolites			9	
		2.5 The Effect of Additional Promoter into	o Pt/KL			
		Catalyst			11	
		2.6 Catalyst Deactivation			16	

ine. P

### CHAPTER

Ш

2.	6.1	Poison	ing	17
		2.6.2	Fouling	18
			2.6.2.1 Coking	18
			2.6.2.2 Metal Deposition	21
		2.6.3	Thermal Degradation	22
			2.6.3.1 Sintering of Metals	22
			2.6.3.2 Sintering of Supports	23
			2.6.3.3 Thermal Degradation of Supported	
			Catalysts	23
		2.6.4	Loss of Catalytic Phase by Vapour Transport	24
		2.6.5	Mechanical Failure of Catalysts	24
	2.7	Preve	ention of Catalyst Deactivation	24
	2.8	Regen	neration of Deactivated Catalysts	26
		2.8.1	Regeneration Parameters	27
			2.8.1.1 Temperature	27
			2.8.1.2 Heating Rate	29
			2.8.1.3 Time	· 29
	EX	PERI	MENTAL	31
	3.1	Mater	rial	31
		3.1.1	Chemicals	31
		3.1.2	Gases	31
	3.2	Equip	oment	32
	3.3	Meth	odology	32
		3.3.1	Synthesis of the Nano-crystalline KL Zeolites	32
		3.3.2	Catalyst Preparation	33
		3.3.3	Characterization of Synthesized KL Zeolites	
			and Catalyst	34
			3.3.3.1 X-Ray Diffraction (XRD)	34

PAGE

### CHAPTER

### PAGE

. .

		3.3.3.2	Dynamic Light Scattering (DLS)	34
		3.3.3.3	Hydrogen Chemisorption	35
		3.3.3.4	Transmission Electron Microscopy	
			(TEM)	35
		3.3.3.5	Temperature Programmed Reduction	
			(TPR)	35
		3.3.3.6	X-Ray Photoelectron Spectroscopy	
			(XPS)	36
		3.3.3.7	Temperature Programmed Oxidation	
			(TPO)	. 36
		3.3.4 Catalyt	ic Activity Testing	37
6499-X		3.3.5 Regene	ration in Air	38
		3.3.5.1	Pretreatment	. 38
		3.3.5.2	Coke Oxidation	• 39
		3.3.5.3	Final Reduction	39
		3.3.6 The Pro	oduct of <i>n</i> -Octane Aromatization	
		Analys	is	39
IV	RE	SULTS AND	DISCUSSION	40
	4.1	Synthesis of t	he Nano-crystalline KL Zeolites	40
	4.2	Characterizat	ion of the Fresh Catalysts	42
	4.3	Catalytic Acti	vity Testing: n-Octane Aromatization	48
	4.4	Regeneration	in Air of deactivated 1Pt1Sn/COM Catalysts	54
		4.4.1 Effect of	of Regeneration Temperature	54
		4.4.1.1	Catalytic Activity Measurement	54
		4.4.1.2	Characterization of Catalysts	59
		4.4.2 Effect of	of Regeneration Time	65
		4.4.1.1	Catalytic Activity Measurement	65
		4.4.1.2	Characterization of Catalysts	67

ix

	4.4.3 Effect of Regeneration Air Flow Rate	69
	4.4.3.1 Catalytic Activity Measurement	69
	4.4.3.2 Characterization of Catalysts	72
V	CONCLUSIONS AND RECOMMENDATIONS	75
	REFERENCES	76
	CURRICULUM VITAE	84
	and the second	

#### LIST OF TABLES

TABLI	E	PAGE
2.1	Prevention of catalyst deactivation	25
3.1	List of mono- and bi- metallic Pt-Sn/KL catalysts investigated	34
3.2	Regeneration Conditions	38
4.1	The comparison between the particle size of COM and NCL	
	measured by DLS method	41
4.2	Analysis of Fresh and Spend Catalysts	43
4.3	Deconvolution of TPR profile of bimetallic Pt-Sn/KL	
	catalysts	45
4.4	Binding energies and relative intensities of different species	
	from curve-fitted XPS spectra of various catalysts	47
4.5	n-Octane conversion and product distribution over 1Pt/COM,	
	1Pt/NCL, 1Pt1Sn/COM, 1Pt1Sn/NCL, and 1Pt0.6Sn/NCL	
	catalysts tested for <i>n</i> -octane aromatization after 550 min time	
	on stream; Reaction condition: temperature = 500°C,	
	pressure = 1 atm, WHSV = 5 $h^{-1}$ , H <sub>2</sub> :HC = 6:1	49
4.6	Binding energies and relative intensities of different species	
	from curve-fitted XPS spectra of various catalysts	63
4.7	TPO analysis of spent and regenerated 1Pt1Sn/COM	
	catalysts at different regeneration temperatures	64
4.8	TPO analysis of spent and regenerated 1Pt1Sn/COM	
	catalysts at different regeneration times	69
4.9	TPO analysis of spent and regenerated 1Pt1Sn/COM	
	catalysts at different regeneration air flow rates	73

#### LIST OF FIGURES

FIGURE		PAGE
		-
2.1	Schematic of <i>o</i> -xylene.	5
2.2	Schematic of phthalic anhydride.	5
2.3	Schematic of dehydrogenation of ethylbenzene	6
2.4	Schematic of L zeolite structure.	8
2.5	SEM image of hockeypuck KL zeolite with the size of	
	40,000 times (Verduijn et al, 2001).	10
2.6	Conceptual model of fouling, crystallite encapsulation and	
	pore plugging of a supported metal catalyst due to carbon	
	deposition.	19
2.7	Relationship between catalyst activity loss and coke	
	deposition with during of run.	20
2.8	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 condition: 500°C, H <sub>2</sub> /n-C6 (or n-C8)	
	molar ratio 6:1, WHSV 5 h <sup>-1</sup> .	21
3.1	Schematic diagram of the experimental set-up for n-alkane	
	aromatization.	37
4.1	XRD patterns of nano-crystalline KL zeolite (NCL) and	
	commercial KL zeolite (COM).	40
4.2	TEM image of synthesized nano-crystalline KL zeolite	
	(NCL) at 175°C for 8 h.	41
4.3	FTIR spectra of nano-crystalline KL zeolites obtained at	
	aging time of 17 h and crystallization time of 8 h	
	synthesized by microwave hydrothermal treatment compared	
	to that of commercial KL zeolite (COM).	42

### FIGURE

TEM images of metal size distribution obtained by TEM of	
the mono- and bi- metallic Pt-Sn/KL catalysts.	43
TPR profiles of the different Sn/Pt ratio of bimetallic Pt-Sn	
catalysts prepared by vapor phase co-impregnation.	45
Pt4f XPS spectra of 1Pt/COM and 1Pt1Sn/COM after	
hydrogen treatment for 1 h at 500°C (reduced).	47
The variations of (a) <i>n</i> -octane conversion (b) total aromatics	
selectivity and (c) C8-aromatics selectivity with time on	
stream (Catalyst: 1Pt/COM and 1Pt/NCL. Reaction	
condition; temperature = 500°C, pressure = 1 atm, WHSV =	
$5 h^{-1}, H_2:HC = 6:1.$	50
The variations of <i>n</i> -octane conversion and C8-aromatics	
selectivity on mono- and bi- metallic Pt-Sn supported on (a),	
(c) COM and (b),(d) NCL with time on stream. (Reaction	
condition; temperature = $500^{\circ}$ C, pressure = 1 atm, WHSV =	
$5 h^{-1}$ , H <sub>2</sub> :HC = 6:1).	52
The variation of <i>n</i> -octane conversion at 500°C without	
regeneration in air.	56
The <i>n</i> -octane conversion after 370 min on stream of	
regenerated catalysts at various regeneration temperatures	
(300-500°C).	55
The C8-aromatics selectivity after 370 min on stream of	
regenerated catalysts at various regeneration temperatures	
(300-500°C).	57
The total aromatics selectivity after 370 min on stream of	
regenerated catalysts at various regeneration temperatures	
(300-500°C).	58
	TEM images of metal size distribution obtained by TEM of the mono- and bi- metallic Pt-Sn/KL catalysts. TPR profiles of the different Sn/Pt ratio of bimetallic Pt-Sn catalysts prepared by vapor phase co-impregnation. Pt4f XPS spectra of 1Pt/COM and 1Pt1Sn/COM after hydrogen treatment for 1 h at 500°C (reduced). The variations of (a) <i>n</i> -octane conversion (b) total aromatics selectivity and (c) C8-aromatics selectivity with time on stream (Catalyst: 1Pt/COM and 1Pt/NCL. Reaction condition; temperature = 500°C, pressure = 1 atm, WHSV = 5 h <sup>-1</sup> , H <sub>2</sub> :HC = 6:1. The variations of <i>n</i> -octane conversion and C8-aromatics selectivity on mono- and bi- metallic Pt-Sn supported on (a), (c) COM and (b),(d) NCL with time on stream. (Reaction condition; temperature = 500°C, pressure = 1 atm, WHSV = 5 h <sup>-1</sup> , H <sub>2</sub> :HC = 6:1). The variation of <i>n</i> -octane conversion at 500°C without regeneration in air. The <i>n</i> -octane conversion at 500°C without regenerated catalysts at various regeneration temperatures (300-500°C). The C8-aromatics selectivity after 370 min on stream of regenerated catalysts at various regeneration temperatures (300-500°C). The total aromatics selectivity after 370 min on stream of regenerated catalysts at various regeneration temperatures (300-500°C).

PAGE

#### FIGURE

xiii

PAGE

4.13	The EB/OX ratio after 370 min on stream of regenerated	
	catalysts at various regeneration temperatures (300-500°C).	59
4.14	TPR profiles of regenerated catalysts at various regeneration	
	temperatures (300-500°C).	60
4.15	Pt4f XPS spectra of 1Pt/COM, 1Pt1Sn/COM and	
	regenerated 1Pt1Sn/COM catalyst in air at 400°C after	
	hydrogen treatment for 1 h at 500°C (reduced).	62
4.16	The <i>n</i> -octane conversion after 370 min on stream of	
	regenerated catalysts at various regeneration times (15-120	
	min).	65
4.17	The C8-aromatics selectivity after 370 min on stream of	
	regenerated catalysts at various regeneration times (15-120-	
	min).	66
4.18	The total aromatics selectivity after 370 min on stream of	
	regenerated catalysts at various regeneration times (15-120	
	min).	66
4.19	The EB/OX ratio after 370 min on stream of regenerated	
	catalysts at various regeneration times (15-120 min).	67
4.20	TPR profiles of regenerated catalysts at various regeneration	
	times (15-120 min).	68
4.21	The n-octane conversion after 370 min on stream of	
	regenerated catalysts at various regeneration air flow rates	
	(10-40 ml/min).	70
4.22	The C8-aromatics selectivity after 370 min on stream of	
	regenerated catalysts at various regeneration air flow rates	
	(10-40 ml/min).	70

4.23	The total aromatics selectivity after 370 min on stream of	
	regenerated catalysts at various regeneration air flow rates	
	(10-40 ml/min).	71
4.24	The EB/OX ratio after 370 min on stream of regenerated	
	catalysts at various regeneration air flow rates (10-40	
	ml/min).	71
4.25	TPR profiles of regenerated catalysts at various regeneration	
	air flow rates (10-40 ml/min).	72

PAGE

utra je