

**INDIUM-CONTAINING ZSM-5 CATALYST FOR METHYLATION OF
BENZENE: EFFECT OF SILICA/ALUMINA RATIOS AND REACTION
CONDITIONS**

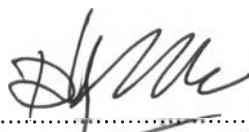
Nichapat Niyomthong

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
2013

128372670

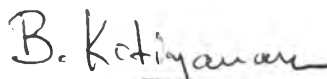
Thesis Title: Indium-Containing ZSM-5 Catalyst for Methylation of Benzene: Effect of Silica/Alumina Ratios and Reaction Conditions
By: Nichapat Niyomthong
Program: Petroleum Technology
Thesis Advisors: Asst. Prof. Boonyarach Kitiyanan

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



..... College Dean
(Asst. Prof. Pomthong Malakul)

Thesis Committee:



.....
(Asst. Prof. Boonyarach Kitiyanan)



.....
(Assoc. Prof. Apanee Luengnaruemitchai)



.....
(Dr. Tanate Danuthai)

ABSTRACT

5473010063: Petroleum Technology Program

Ms. Nichapat Niyomthong: Indium-Containing ZSM-5 Catalyst for Methylation of Benzene: Effect of Silica/Alumina Ratios and Reaction Conditions

Thesis Advisors: Asst. Prof. Boonyarach Kitiyanan, 81 pp.

Keywords: Benzene methylation/ Indium/ ZSM-5/ Silica to Alumina ratio

Catalytic conversion of methane to higher hydrocarbons is an attractive route for the utilization of methane. One possible way to convert methane is the direct methylation of benzene by methane in the presence of a catalyst. Indium-containing ZSM-5 catalyst has exhibited an ability to activate methane and convert benzene into toluene and xylenes. In this study, indium-containing ZSM-5 catalysts were prepared with varying $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios. The catalysts were characterized by temperature program reduction, temperature program desorption, X-Ray diffraction and UV-vis spectrophotometry. The In/HZSM-5 catalysts were treated in a hydrogen atmosphere prior to the reaction at 700 °C, this temperature was confirmed by the temperature program reduction method. Direct methylation could be achieved if oxygen was fed along with the feed at a reaction temperature of 350 °C. The effect of the reaction parameters; indium to aluminum ratio 1.0, methane to benzene feed ratio 104 and space velocity 2.8 h⁻¹ provided benzene conversion of 3% and greater than 95% toluene selectivity. $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios (23, 30, 50, 80 and 280) were also investigated and found that the highest benzene conversion was provided by a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 50.

บทคัดย่อ

นางสาวณิชาภัทร นิยมทอง : ตัวเร่งปฏิกิริยาอินเดียมบน ZSM-5 สำหรับปฏิกิริยาเมทิลเลชันของเบนซีน : การศึกษาผลของสัดส่วนซิลิกาต่ออลูมินาและสภาวะในการเกิดปฏิกิริยา (Indium-Containing ZSM-5 Catalyst for Methylation of Benzene: Effect of Silica/Alumina Ratios and Reaction Conditions) อ. ที่ปรึกษา : ผศ. ดร. บุนยรัชต์ กิตติยานันท์ 81 หน้า

กระบวนการเปลี่ยนมีเทนโดยการเร่งปฏิกิริยาเพื่อให้ได้ผลิตภัณฑ์ที่มีคุณค่าทางเศรษฐกิจสูงขึ้นเป็นวิธีการที่น่าสนใจในการใช้มีเทนให้เกิดประโยชน์ วิธีการหนึ่งที่เป็นไปได้ในการเปลี่ยนแปลงมีเทนคือปฏิกิริยาเมทิลเลชันโดยตรงของเบนซีนด้วยมีเทนและตัวเร่งปฏิกิริยาอินเดียมบน ZSM-5 ถูกเตรียมด้วยสัดส่วนซิลิกาต่ออลูมินาที่แตกต่างกัน ตัวเร่งปฏิกิริยาถูกวิเคราะห์ด้วยเทคนิค temperature program reduction, เทคนิค temperature program desorption, เทคนิคเอกซเรย์ดิฟแฟรกชันและเทคนิควัดการดูดกลืนแสง In/HZSM-5 ถูกเตรียมในสภาวะบรรยากาศแก๊สไฮโดรเจนที่อุณหภูมิ 700 องศาเซลเซียสซึ่งอุณหภูมินี้ถูกยืนยันโดยใช้เทคนิค temperature program reduction ปฏิกิริยาเมทิลเลชันเกิดขึ้นได้เมื่อแก๊สออกซิเจนถูกส่งเข้าทำปฏิกิริยาพร้อมกับสารตั้งต้นที่อุณหภูมิ 350 องศาเซลเซียส ในการทดลองยังมีการหาสภาวะที่เหมาะสมของตัวแปรต่างๆพบว่า สัดส่วนของอินเดียมต่ออลูมิเนียมเท่ากับ 1.0, สัดส่วนระหว่างมีเทนกับเบนซีนเท่ากับ 104, และความเร็วในการไหลของสารตั้งต้น 2.8 ต่อชั่วโมง ให้ค่าสัดส่วนการเปลี่ยนของเบนซีนไปเป็นผลิตภัณฑ์ 3 % และสัดส่วนการเกิดไปเป็นโทลูอินอยู่ที่ 95 % สัดส่วนซิลิกาต่ออลูมินา (23, 30, 50, 80 และ 280) ถูกศึกษาและพบว่าสัดส่วนซิลิกาต่ออลูมินาเท่ากับ 50 ให้ค่าสัดส่วนการเปลี่ยนของเบนซีนไปเป็นผลิตภัณฑ์สูงที่สุด

ACKNOWLEDGEMENTS

I gratefully take this opportunity to express my sincere gratitude to Asst. Prof. Boonyarach Kitiyanan, my thesis advisor, for his guidance, encouragement, suggestion, discussions and problem solving throughout of this work. I also acknowledge Assoc. Prof. Apanee Luengnaruemitchai and Dr. Tanate Danuthai for valuable information, comment and suggestion as thesis committees.

I am grateful for the scholarship and funding of this thesis work provided by the Petroleum and Petrochemical College and Center of Excellence on Petrochemical and Materials Technology, Thailand.

I would like to thank PTT Global Chemical Public Company Limited for the funding supports.

I also would like to thank all of the Petroleum and Petrochemical College's staff for the valuable knowledge and assistance. Lastly, I would like to thank my beloved parents, my friends and my seniors for their encouragement and suggestion without which this thesis would not be possible.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	ix
List of Figures	xiii
CHAPTER	
I INTRODUCTION	1
II LITERATURE REVIEW	3
2.1 Methane	3
2.1.1 Methane Activation	3
2.2 Intermediate of activated methane	4
2.2.1 Free radical	4
2.2.2 Alkyl species	5
2.2.3 Carbenium ion	5
2.3 Alkylation of aromatic	6
2.3.1 Free radical substitution mechanism	7
2.3.2 Electrophilic substitution mechanism	7
2.3.3 Nucleophilic substitution mechanism	8
2.4 Methylation of aromatic with methane	9
2.4.1 Methylation of naphthalene with methane	9
2.4.2 Methylation of toluene with methane	9
2.4.3 Methylation of benzene with methane	10
2.5 Zeolite	12
2.5.1 Zeolite structures	13
2.5.2 Acid sites	14

CHAPTER	PAGE
2.5.3 Zeolite SiO ₂ /Al ₂ O ₃	15
2.6 ZSM-5 Zeolite	15
2.7 Indium containing zeolite	18
2.7.1 The method of preparation of indium-containing zeolite	18
2.7.2 Catalytic activities of indium-containing zeolite	21
III EXPERIMENTAL	23
3.1 Materials	23
3.1.1 Chemicals	23
3.1.2 Gases	23
3.2 Experimental Procedures	24
3.2.1 Catalyst preparation	24
3.2.2 Catalyst characterization	25
3.2.3 Reaction Procedure	27
IV RESULTS AND DISCUSSION	29
4.1 Catalyst Characterization	29
4.1.1 Temperature program reduction (TPR)	29
4.1.2 X-ray diffraction spectroscopy (XRD)	31
4.1.3 X-ray fluorescence spectroscopy (XRF)	32
4.1.4 UV-visible spectroscopy	32
4.1.5 Surface Area Analysis	33
4.2 Catalytic activity measurement	35
4.2.1 Effect of treatment gas and treatment temperature	35
4.2.2 Effect of reaction temperature	40
4.2.3 Effect of oxidative reaction (carrier gas)	42
4.2.4 Effect of Indium to Aluminum Ratio	44
4.2.5 Effect of Methane to Benzene Feed Molar Ratio	46
4.2.6 Effect of Space Velocity (WHSV)	48

CHAPTER	PAGE
4.2.7 Effect of Silica to Alumina Ratio	49
V CONCLUSIONS AND RECOMMENDATIONS	53
5.1 Conclusions	53
5.2 Recommendations	54
REFERENCES	55
APPENDICES	60
Appendix A Calculation of catalysts composition	60
Appendix B Calibration data and feed flow adjustment	62
Appendix C Raw data of reaction results	67
Appendix D Raw data of catalysts characterization	78
CURRICULUM VITAE	80

LIST OF TABLES

TABLE		PAGE
4.1	XRF of H-ZSM-5 with different SiO ₂ /Al ₂ O ₃ ratios and In/Al ratios	32
4.2	BET surface area of HZSM-5 catalysts	34
4.3	BET surface area of physical mixing catalysts	34
4.4	BET surface area of In/HZSM-5 catalysts with different atmospheres	35
4.5	Temperature program desorption (TPD) results of catalysts with various indium loading ratios	44
4.6	Temperature program desorption (TPD) results of catalysts with various SiO ₂ /Al ₂ O ₃ ratios	51
A1	The ingredients of prepared catalysts	61
B1	The response factor calculated from calibration curve of each substances	65
B2	Flow controller adjustment and catalyst weight in various reaction condition	66
C1	The results of the reaction with O ₂ treatment at 350 °C and N ₂ carrier using SiO ₂ /Al ₂ O ₃ ratio 50, In/Al ratio 0.5, WHSV 2.8 h ⁻¹ and methane to benzene feed ratio 70 at reaction temperature 350 °C	67
C2	The results of the reaction with H ₂ treatment at 700 °C and N ₂ carrier using SiO ₂ /Al ₂ O ₃ ratio 50, In/Al ratio 0.5, WHSV 2.8 h ⁻¹ and methane to benzene feed ratio 70 at reaction temperature 350 °C	67
C3	The results of the reaction with H ₂ treatment at 700 °C followed by O ₂ treatment at 350 °C and N ₂ carrier using SiO ₂ /Al ₂ O ₃ ratio 50, In/Al ratio 0.5, WHSV 2.8 h ⁻¹ and methane to benzene feed ratio 70 at reaction temperature 350 °C	68

TABLE	PAGE	
C4	The results of the reaction with H ₂ treatment at 600 °C followed by O ₂ treatment at 350 °C and N ₂ carrier using SiO ₂ /Al ₂ O ₃ ratio 50, In/Al ratio 0.5, WHSV 2.8 h ⁻¹ and methane to benzene feed ratio 70 at reaction temperature 350 °C	68
C5	The results of the reaction with H ₂ treatment at 800 °C followed by O ₂ treatment at 350 °C and N ₂ carrier using SiO ₂ /Al ₂ O ₃ ratio 50, In/Al ratio 0.5, WHSV 2.8 h ⁻¹ and methane to benzene feed ratio 70 at reaction temperature 350 °C	69
C6	The results of the reaction with H ₂ treatment at 700 °C followed by O ₂ treatment at 350 °C and N ₂ carrier using SiO ₂ /Al ₂ O ₃ ratio 50, In/Al ratio 0.5, WHSV 2.8 h ⁻¹ and methane to benzene feed ratio 70 at reaction temperature 300 °C	69
C7	The results of the reaction with H ₂ treatment at 700 °C followed by O ₂ treatment at 350 °C and N ₂ carrier using SiO ₂ /Al ₂ O ₃ ratio 50, In/Al ratio 0.5, WHSV 2.8 h ⁻¹ and methane to benzene feed ratio 70 at reaction temperature 400 °C	70
C8	The results of the reaction with H ₂ treatment at 700 °C followed by O ₂ treatment at 350 °C and N ₂ carrier using SiO ₂ /Al ₂ O ₃ ratio 50, In/Al ratio 0.5, WHSV 2.8 h ⁻¹ and methane to benzene feed ratio 70 at reaction temperature 450 °C	70
C9	The results of the reaction with H ₂ treatment at 700 °C followed by O ₂ treatment at 350 °C and N ₂ carrier using SiO ₂ /Al ₂ O ₃ ratio 50, In/Al ratio 0.5, WHSV 2.8 h ⁻¹ and methane to benzene feed ratio 70 at reaction temperature 500 °C	71
C10	The results of the reaction with H ₂ treatment at 700 °C and O ₂ carrier using SiO ₂ /Al ₂ O ₃ ratio 50, In/Al ratio 0.5, WHSV 2.8 h ⁻¹ and methane to benzene feed ratio 70 at reaction temperature 350 °C	71

TABLE	PAGE
C11 The results of the reaction with H ₂ treatment at 700 °C and O ₂ carrier using SiO ₂ /Al ₂ O ₃ ratio 50, In/Al ratio 0.1, WHSV 2.8 h ⁻¹ and methane to benzene feed ratio 70 at reaction temperature 350 °C	72
C12 The results of the reaction with H ₂ treatment at 700 °C and O ₂ carrier using SiO ₂ /Al ₂ O ₃ ratio 50, In/Al ratio 0.3, WHSV 2.8 h ⁻¹ and methane to benzene feed ratio 70 at reaction temperature 350 °C	72
C13 The results of the reaction with H ₂ treatment at 700 °C and O ₂ carrier using SiO ₂ /Al ₂ O ₃ ratio 50, In/Al ratio 1.0, WHSV 2.8 h ⁻¹ and methane to benzene feed ratio 70 at reaction temperature 350 °C	73
C14 The results of the reaction with H ₂ treatment at 700 °C and O ₂ carrier using SiO ₂ /Al ₂ O ₃ ratio 50, In/Al ratio 1.0, WHSV 2.8 h ⁻¹ and methane to benzene feed ratio 23 at reaction temperature 350 °C	73
C15 The results of the reaction with H ₂ treatment at 700 °C and O ₂ carrier using SiO ₂ /Al ₂ O ₃ ratio 50, In/Al ratio 1.0, WHSV 2.8 h ⁻¹ and methane to benzene feed ratio 104 at reaction temperature 350 °C	74
C16 The results of the reaction with H ₂ treatment at 700 °C and O ₂ carrier using SiO ₂ /Al ₂ O ₃ ratio 50, In/Al ratio 1.0, WHSV 6.1 h ⁻¹ and methane to benzene feed ratio 104 at reaction temperature 350 °C	74
C17 The results of the reaction with H ₂ treatment at 700 °C and O ₂ carrier using SiO ₂ /Al ₂ O ₃ ratio 50, In/Al ratio 1.0, WHSV 12.3h ⁻¹ and methane to benzene feed ratio 104 at reaction temperature 350 °C	75

TABLE	PAGE
C18 The results of the reaction with H ₂ treatment at 700 °C and O ₂ carrier using SiO ₂ /Al ₂ O ₃ ratio 23, In/Al ratio 1.0, WHSV 2.8 h ⁻¹ and methane to benzene feed ratio 104 at reaction temperature 350 °C	75
C19 The results of the reaction with H ₂ treatment at 700 °C and O ₂ carrier using SiO ₂ /Al ₂ O ₃ ratio 30, In/Al ratio 1.0, WHSV 2.8 h ⁻¹ and methane to benzene feed ratio 104 at reaction temperature 350 °C	76
C20 The results of the reaction with H ₂ treatment at 700 °C and O ₂ carrier using SiO ₂ /Al ₂ O ₃ ratio 80, In/Al ratio 1.0, WHSV 2.8 h ⁻¹ and methane to benzene feed ratio 104 at reaction temperature 350 °C	76
C21 The results of the reaction with H ₂ treatment at 700 °C and O ₂ carrier using SiO ₂ /Al ₂ O ₃ ratio 280, In/Al ratio 1.0, WHSV 2.8h ⁻¹ and methane to benzene feed ratio 104 at reaction temperature 350 °C	77
D1 Desorption temperature and peak area of HZSM-5 catalysts	79
D2 Desorption temperature and peak area of HZSM-5 and In/HZSM with SiO ₂ /Al ₂ O ₃ 50	79

LIST OF FIGURES

FIGURE	PAGE
2.1 Methyl free radical.	4
2.2 Methyl carbanion.	5
2.3 Methyl carbenium ion.	6
2.4 The mechanism of methylation of benzene with methane on Ag/HZSM-5.	12
2.5 The tetrahedron structure.	13
2.6 Framework structure of zeolite ZSM-5 (MFI) illustrating the straight and sinusoidal pores and the pore intersections. A view of the complete structure down the straight pores is depicted in the lower left lower corner.	16
3.1 The catalytic measurement flow diagram.	27
4.1 H ₂ -TPR profiles of indium(II)oxide.	29
4.2 H ₂ -TPR profiles of physical mixing In ₂ O ₃ /HZSM-5 with SiO ₂ /Al ₂ O ₃ of HZSM-5 23, 30, 50, 80 and 280 and In/Al ratio 0.5.	30
4.3 X-ray diffraction patterns of HZSM-5, physical mixing In ₂ O ₃ /HZSM-5, In/HZSM-5 under hydrogen treatment, In/HZSM-5 under oxygen treatment, and In/HZSM-5 under hydrogen followed by oxygen treatment.	31
4.4 UV-Visible spectrum of In ₂ O ₃ physically mixed with ZSM-5 and In ₂ O ₃ /ZSM-5 treated in different atmosphere in the range of 200 to 900 nm.	33
4.5 Benzene conversion as a function of time on stream at different treatment atmosphere and treatment temperature.	36
4.6 Toluene selectivity as a function of time on stream at different treatment atmosphere and treatment temperature.	37

FIGURE	PAGE
4.7 Benzene conversion as a function of time on stream at different treatment atmosphere and treatment temperature.	39
4.8 Toluene selectivity as a function of time on stream at different treatment atmosphere and treatment temperature.	39
4.9 Thermodynamic calculation for benzene methylation reaction.	40
4.10 Benzene conversion as a function of time on stream at different reaction temperature.	41
4.11 Toluene selectivity as a function of time on stream at different reaction temperature.	42
4.12 Benzene conversion as a function of time on stream at different oxidative condition.	43
4.13 Toluene selectivity as a function of time on stream at different oxidative condition.	43
4.14 Benzene conversion as a function of time on stream at different indium to aluminum ratios.	45
4.15 Toluene selectivity as a function of time on stream at different indium to aluminum ratios.	45
4.16 Benzene conversion as a function of time on stream at different methane to benzene feed ratio.	47
4.17 Toluene selectivity as a function of time on stream at different methane to benzene feed ratio.	47
4.18 Benzene conversion as a function of time on stream at different space velocity (WHSV).	48
4.19 Toluene selectivity as a function of time on stream at different space velocity (WHSV).	49
4.20 Temperature program desorption (TPD) profiles of catalyst with various SiO ₂ /Al ₂ O ₃ ratios.	50
4.21 Benzene conversion as a function of time on stream at different silica to alumina ratios.	52

FIGURE		PAGE
4.22	Toluene selectivity as a function of time on stream at different silica to alumina ratios.	52
B1	Response area from GC FID as a function of injection volume of methane.	62
B2	Response area from GC FID as a function of injection volume of benzene.	63
B3	Response area from GC FID as a function of injection volume of toluene.	63
B4	Response area from GC FID as a function of injection volume of <i>p</i> -xylene.	64
B5	Response area from GC FID as a function of injection volume of <i>m</i> -xylene.	64
B6	Response area from GC FID as a function of injection volume of <i>o</i> -xylene.	65
D1	Temperature program desorption (TPD) profiles of catalyst with various In/Al ratios.	78