ROLES OF Zn SPECIES IN Zn-PROMOTED HZSM-5 CATALYSTS ON THE AROMATIZATION ACTIVITY

Sikarin Tamiyakul

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
2016

I 28368307

580002

Thesis Title: Roles of Zn Species in Zn–Promoted HZSM–5 Catalysts on the Aromatization Activity
By: Sikarin Tamiyakul
Program: Petrochemical Technology
Thesis Advisors: Assoc. Prof. Siriporn Jongpatiwut
Prof. Lance L. Lobban
Assoc. Prof. Tawan Sooknoi

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

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

Thesis Committee:

....
(Asst. Prof. Pomthong Malakul)

....
(Assoc. Prof. Siriporn Jongpatiwut)

....
(Assoc. Prof. Tawan Sooknoi)

B. Kitiyanan
....
(Assoc. Prof. Boonyarach Kitiyanan)

....
(Prof. Thirasak Rirksomboon)

....
(Assoc. Prof. Metta Chareonpanich)

ABSTRACT

5581001063: Petrochemical Technology Program
Sikarin Tamiyakul: Roles of Zn Species in Zn–Promoted HZSM-5 Catalysts on the Aromatization Activity.
Thesis Advisors: Assoc. Prof. Siriporn Jongpatiwut, Assoc. Prof. Tawan Sooknoi, and Prof. Lance L. Lobban 126 pp.

Keywords: Zn species/ HZSM–5/ Aromatization/ Glycerol/ Palm fatty acid distillate (PFAD)/ *p*–Xylene

The roles of Zn species in Zn/HZSM-5 catalyst on the aromatization of palm fatty acid distillate (PFAD), glycerol, and *n*-pentane were investigated. The amounts of Zn loading and preparation methods strongly affect the Zn species on HZSM-5 support. The Zn species strongly depended on the method of introducing Zn. Compared with ZnO, the higher dehydrogenation activity of $(ZnOH)^+$ showed the higher aromatization of glycerol. However, using PFAD as a feedstock, even the $(ZnOH)^+$ species is essential for improving the aromatization. The ZnO also plays a key role in the deoxygenation of PFAD, shifting the deoxygenation pathway from decarbonylation on Brønsted acid site to decarboxylation on ZnO, thus preserving the Brønsted acid site for aromatization. The evolution of Zn species upon different thermal treatments was studied by XPS and IPA–TPD. Under H_2 atmosphere, hydrodehydroxylation of $(ZnOH)^+$ species generated $(ZnH)^+$, further dissociated H_2 molecule, forming $(ZnH_3)^+$ species. The presence of $(ZnH_3)^+$ was found to improve the aromatics selectivity. Even the $(ZnH_3)^+$ species is not stable, it can be recovered upon H_2 treatment. In order to improve the *p*–xylene selectivity, silicalite–1 was later coated on Zn/HZSM–5 catalyst. Even the selectivity of *p*–xylene was improved, the aromatics yield was found to be traded with *p*–xylene selectivity. To increase aromatics yield, Zn(II)ions was grafted on silicalite–1 layer. Due to its high dehydrogenation activity, *n*–pentane feedstock was firstly converted to olefins on Zn(II)ions/Sil–1 then further aromatized in Zn/HZSM–5 catalyst, thus improving *p*–xylene yield.

บทคัดย่อ

ศิขริน เตมียกุล : บทบาทของสังกะสีแต่ละสปีชีส์บนตัวเร่งปฏิกิริยาแซทเอสเอ็ม–5 ที่ได้รับการเติมแต่งสังกะสี ต่อการเกิดปฏิกิริยาอะโรมาไทเซชัน (Roles of Zn Species in Zn–Promoted HZSM–5 Catalysts on the Aromatization Activity)
อาจารย์ที่ปรึกษา : รศ. ดร. ศิริพร จงผาติวุฒิ รศ. ดร. ตะวัน สุขน้อย
และ ศ. ดร. ลานซ์ แอล ล็อบแบน 126 หน้า

งานวิจัยนี้ศึกษาบทบาทของสังกะสีแต่ละสปีชีส์บนตัวเร่งปฏิกิริยาแซทเอสเอ็ม–5 ที่ได้รับการเติมแต่งสังกะสีต่อการเปลี่ยน กลีเซอรอล กรดไขมันปาล์ม และเอ็นเพนเทน เป็นสารอะโรเมติกส์ จากการทดลองพบว่า วิธีการเตรียมตัวเร่งปฏิกิริยาส่งผลต่อการเกิดสปีชีส์ที่แตกต่างกันของสังกะสี ในปฏิกิริยาอะโรมาไทเซชัน สังกะสีที่มีสปีชีส์เป็น $(ZnOH)^+$ มีความว่องไวและความเจาะจงในการเกิดสารอะโรเมติกส์สูงกว่า ZnO อย่างไรก็ตามเมื่อใช้กรดไขมันปาล์มเป็นสารตั้งต้นพบว่า ตัวเร่งปฏิกิริยาที่ประกอบด้วยสังกะสีทั้งสองสปีชีส์ส่งผลให้อัตราการเกิดผลิตภัณฑ์อะโรเมติกส์สูงขึ้น โดย $(ZnOH)^+$ ช่วยเร่งปฏิกิริยาอะโรมาไทเซชัน ในขณะที่ ZnO ช่วยเร่งกระบวนการดีออกซิจิเนชันผ่านปฏิกิริยาดีคาร์บอกซิเลชั่น การศึกษาผลของการให้ความร้อนภายใต้แก๊สไฮโดรเจนของตัวเร่งปฏิกิริยาสังกะสีบนแซทเอสเอ็ม–5 พบว่าปฏิกิริยาไฮโดรดีไฮดรอกซิเดชั่นระหว่าง $(ZnOH)^+$ และแก๊สไฮโดรเจนทำให้ สปีชีส์ของสังกะสีเกิดการเปลี่ยนแปลงจาก $(ZnOH)^+$ เป็น $(ZnH)^+$ ซึ่งภายใต้สภาวะที่มีแก๊สไฮโดรเจน การดูดซับทางเคมีของโมเลกุลไฮโดรเจนบน $(ZnH)^+$ ทำให้สปีชีส์ของสังกะสีเกิดการเปลี่ยนแปลงเป็น $(ZnH_3)^+$ เมื่อเปรียบเทียบความว่องไวและความเจาะจงในการเกิดสารอะโรเมติกส์ของสังกะสีทั้งสามสปีชีส์พบว่า $(ZnH_3)^+$ มีความสามารถสูงสุดในปฏิกิริยาอะโรมาไทเซชันของเอ็นเพนเทน ถึงแม้ว่าสปีชีส์ดังกล่าวจะไม่เสถียรในภาวะที่ปราศจากแก๊สไฮโดรเจน แต่สามารถเกิดขึ้นใหม่ได้โดยการให้ความร้อนภายใต้แก๊สไฮโดรเจน เพื่อเพิ่มความจำเพาะต่อการเกิดผลิตภัณฑ์พาราไซลีน ตัวเร่งปฏิกิริยาสังกะสีบนบนแซทเอสเอ็ม–5 ได้ถูกเคลือบด้วยซิลิคาไลท์–1 จากการปรับปรุงผิวด้านนอกของตัวเร่งปฏิกิริยาส่งผลให้ความจำเพาะต่อพาราไซลีนมากขึ้น แต่ความว่องไวในการเกิดปฏิกิริยาลดลง อย่างไรก็ตามหลังจากเติมสังกะสีลงบนผิวด้านนอกของซิลิคาไลท์–1 สปีชีส์ของสังกะสีที่เกิดขึ้นคือ Zn(II)ions ซึ่งมีความสามารถสูงในปฏิกิริยาดีไฮโดรจีเนชัน ส่งผลให้ตัวเร่งปฏิกิริยามีอัตราการเกิดปฏิกิริยาอะโรมาไทเซชันและความจำเพาะต่อพาราไซลีนสูงขึ้น

ACKNOWLEDGEMENTS

Firstly, I would like to express my deepest gratitude to my advisor Assoc. Prof. Siriporn Jongpatiwut for giving me the greatest opportunity of studying in this Ph.D. program. I have been amazingly fortunate to have an advisor who allowed me the freedom to study on my own and at the same time provided the guidance in every problem that I have met. During the past four years, working with her broadened my vision and attitude in my work.

My great honours and appreciations also go to my co-advisor, Assoc. Prof. Tawan Sooknoi. He is one of the best teachers that I have ever had. Many complicated topics that he simplified made it easy for me to understand. I am deeply grateful to him for every discussion that helped me understand the chemistry views of my work.

My sincere thanks also go to Prof. Lance L. Lobban, Prof. Daniel E. Resasco and Dr. Duangamol N. Tungasmita, who provided me a numerous discussion and lectures related on my works. Without their precious suggestions, it would not be possible to conduct this research.

I would like to thank Asst. Prof. Pomthong Malakul, Prof. Thirasak Rirksomboon, Assoc. Prof. Boonyarach Kitiyanan, and Assoc. Prof. Metta Chareonpanich for all the questions and suggestions during my preliminary examination and the PETROMAT meetings (Sustainable Petrochemical Group). Their suggestions helped me get understand in my work and enriched my ideas.

I am grateful for the scholarship and funding supported for my Ph.D. research, provided by the Petroleum and Petrochemical Collage and the Center of Excellence on Petrochemical and Materials Technology (Thailand). I would also like to thank all the PPC faculties and staffs for their contributions throughout my study.

Special thanks to Asst. Prof. Piya Ouraipryvan, his support, advice, and care helped me overcome setbacks and stay focused on the research. I thank all members in SP group and my Ph.D. friends for the fun we have had in the four years.

Most importantly, all of the success would have been impossible without the love, support, and patience of my family. I would like to dedicate this dissertation to my parents, who will always be the strength of my life.

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 xiii

CHAPTER

I INTRODUCTION 1

II THEORETICAL BACKGROUND AND LITERATURE REVIEW 3

2.1 Palm Fatty Acid Distillate (PFAD) 3

2.2 Glycerol from Biodiesel 4

2.3 Production of Aromatics 6

2.3.1 Catalytic Reforming 6

2.3.2 Cyclar Process 7

2.4 Aromatization 8

2.4.1 Dehydrogenation 9

2.4.2 Dehydrocyclization 9

2.5 Lewis and Brønsted Acid Concepts 11

2.6 Zeolite 11

2.6.1 ZSM–5 Zeolite 12

2.6.2 Zeolite Acidity 12

2.6.3 Shape Selectivity of HZSM–5 Zeolite 14

2.6.3.1 Reactant Selectivity 14

CHAPTER **PAGE**

2.6.3.2 Product Selectivity 15
2.6.3.3 Restricted Transition State Selectivity 16
2.6.4 Production of Zeolites 16
2.7 The Catalytic Activity of HZSM–5 Catalysts 17
2.8 The Roles of Zn Species on Zn/HZSM–5 Catalysts 19
2.9 Modified HZSM–5 Catalysts for Highly Selective *p*–Xylene Formation 22

III **EXPERIMENTAL** 24
3.1 Materials 24
3.1.1 Chemicals 24
3.1.2 Gases 24
3.2 Experimental Procedure 25
3.3 Catalyst Characterization 30

IV **CONVERSION OF GLYCEROL TO AROMATIC HYDROCARBONS OVER Zn–PROMOTED HZSM–5** 33
4.1 Abstract 33
4.2 Introduction 34
4.3 Experimental 36
4.4 Results and Discussion 37
4.5 Conclusions 54
4.6 Acknowledgements 55
4.7 References 55

CHAPTER PAGE

V THE EFFECT OF Ga AND Zn OVER HZSM–5 ON THE TRANSFORMATION OF PALM FATTY ACID DISTILLATE (PFAD) TO AROMATICS 58
- 5.1 Abstract 58
- 5.2 Introduction 58
- 5.3 Experimental 59
- 5.4 Results and Discussion 61
- 5.5 Conclusions 71
- 5.6 Acknowledgements 72
- 5.7 References 72

VI GENERATION OF $(ZnH_3)^+$ SPECIES OVER HYDROGEN–TREATED Zn/HZSM–5 CATALYSTS FOR *n*–PENTANE AROMATIZATION 75
- 6.1 Abstract 75
- 6.2 Introduction 75
- 6.3 Experimental 77
- 6.4 Results and Discussion 78
- 6.5 Conclusions 91
- 6.6 Acknowledgements 92
- 6.7 References 92

VII IMPROVED *n*–PENTANE CONVERSION AND *p*–XYLENE SELECTIVITY USING Zn(II)IONS/SILICALITE–1 COATED ON Zn/HZSM–5 CATALYSTS 95
- 7.1 Abstract 95

CHAPTER PAGE

7.2 Introduction 95
7.3 Experimental 97
7.4 Results and Discussion 99
7.5 Conclusions 109
7.6 Acknowledgements 110
7.7 References 110

VIII CONCLUSIONS AND RECOMMENDATIONS 112
8.1 Conclusions 112
8.2 Recommendations 113

REFERENCES 115

APPENDIX 119

CURRICULUM VITAE 124

LIST OF TABLES

TABLE **PAGE**

CHAPTER II

2.1 Free fatty acid composition of palm fatty acid distillate 3
2.2 Kinetic diameters of some reactants and pore size diameter of zeolite 15

CHAPTER III

3.1 Description of flow diagram 27

CHAPTER IV

4.1 Analysis of Zn loadings, textural properties, and acidity of HZSM–5 and Zn/HZSM–5 catalysts prepared by aqueous phase ion–exchange (IE) and incipient wetness impregnation (IWI) methods 43
4.2 Acidic properties of HZSM–5 (30) and Zn containing HZSM–5 prepared by aqueous phase ion–exchange (IE) and incipient wetness impregnation (IWI) methods 54

CHAPTER V

5.1 Fatty acid composition of palm fatty acid distillate (PFAD) 62
5.2 Analysis of Zn loading, textural properties, and acidity of parent HZSM–5, Ga/HZSM–5, and Zn/HZSM–5 catalysts 63

CHAPTER VI

6.1 Analysis of Zn loadings and textural properties of HZSM–5 and Zn/HZSM–5 catalysts 79

TABLE **PAGE**

6.2 Acidic properties of HZSM–5 and Zn/HZSM–5 catalysts investigated under inert and H_2 atmospheres 81

6.3 Product distribution of *n*–Pentane transformation over HZSM–5 and Zn/HZSM–5 catalysts with and without the H_2 pre–treatment 89

CHAPTER VII

7.1 Total surface area and micropore volume of HZSM–5, ZnHZSM–5, Sil–1/ZnHZSM–5, and Zn(II)ions/Sil–1/ZnHZSM–5 catalysts 100

7.2 Surface composition of Zn(II)ions/Sil–1, ZnHZSM–5, Sil–1/ZnHZSM–5, and Zn(II)ions/Sil–1/ZnHZSM–5 catalysts 101

7.3 The total acidity, detected by NH_3–TPD of HZSM–5, ZnHZSM–5, Sil–1/ZnHZSM–5, and Zn(II)ions/Sil–1/ZnHZSM–5 catalysts 104

7.4 The total Brønsted acidity, detected by IPA–TPD of HZSM–5, ZnHZSM–5, Sil–1/ZnHZSM–5, and Zn(II)ions/Sil–1/ZnHZSM–5 catalysts. 106

7.5 Product distribution of *n*–pentane transformation over HZSM–5, ZnHZSM–5, Sil–1/ZnHZSM–5, Zn(II)ions/Sil–1, and Zn(II)ions/Sil–1/ZnHZSM–5 catalysts 108

APPENDIX

A1 Response factors of each substance in the reference standard 120

TABLE **PAGE**

A2 The product yields and conversion of glycerol obtained over the HZSM–5 with various SiO_2/Al_2O_3 ratios. (Reaction conditions: 400 °C, 300 psig, W/F= 1 h, and TOS=3 h) 121

A3 Product yield and acetaldehyde conversion over HZSM–5 with SiO_2/Al_2O_3 of 80 (Reaction conditions: 400 °C, 300 psig, and TOS = 3 h) 122

LIST OF FIGURES

FIGURE **PAGE**

CHAPTER II

2.1 Transesterification reaction. 4
2.2 Methods for the conversion of glycerol into useful products. 5
2.3 Major reactions in catalytic reforming of naphtha. 7
2.4 Schematic representation of UOP Cyclar Process. 8
2.5 Schematic of cyclohexane dehydrogenation to benzene. 9
2.6 Schematic of *n*–hexane dehydrocyclization to benzene. 10
2.7 A stepwise dehydrocyclization of *n*–hexane. 10
2.8 A mechanism of *n*–octane dehydrocyclization. 10
2.9 Structure of ZSM–5 zeolite. 12

CHAPTER III

3.1 A schematic flow diagram of experimental setup. 26

CHAPTER IV

4.1 Product yield of glycerol conversion over HZSM–5 with SiO_2/Al_2O_3 ratio of 80 as a function of space time (W/F). Reaction conditions: 300 psig, 400 °C, and TOS = 3 h. 38
4.2 Proposed reaction pathway for converting glycerol to aromatics. 40
4.3 Effect of SiO_2/Al_2O_3 ratios of HZSM–5 zeolite on the glycerol conversion and aromatics yield. Reaction conditions: 300 psig, 400 °C, WHSV = 1 h^{-1}, and TOS = 3 h. 41
4.4 TPO profiles of spent HZSM–5 with SiO_2/Al_2O_3 ratios of a) 280, b) 23, c) 80, d) 50, and e) 30 42

FIGURE PAGE

4.5 XRD patterns of HZSM–5 and Zn/HZSM–5 zeolites prepared by aqueous phase ion–exchange (IE) and incipient wetness impregnation (IWI) methods. 44

4.6 Isopropylamine–TPD (IPA–TPD) profiles of parent HZSM–5 and Zn/HZSM–5 (IE). The mass monitored was propylene (m/e = 41). 45

4.7 Isopropylamine–TPD (IPA–TPD) profiles of Zn/HZSM–5 prepared by incipient wetness impregnation (0.88Zn/HZSM–5 (IWI)) and aqueous phase ion–exchange methods (0.64Zn/HZSM–5 (IE)). The mass monitored was propylene (m/e = 41). 46

4.8 Ammonia–TPD (NH3–TPD) profiles of Zn/HZSM–5 prepared by incipient wetness impregnation (0.88Zn/HZSM–5 (IWI)) and aqueous phase ion–exchange methods (0.64Zn/HZSM–5 (IE)). The mass monitored was ammonia (m/e = 17). 46

4.9 XPS spectra of Zn (2p3/2) of 0.88Zn/HZSM–5 (IWI), 0.64Zn/HZSM–5 (IE), and ZnO. 48

4.10 EXAFS of Zn K–edge radial distributions of 0.64Zn/HZSM–5 (IE), 0.88Zn/HZSM–5 (IWI), ZnO powder, and metallic Zn foil. 49

4.11 Temperature programmed reduction (TPR) profiles of 0.88Zn/HZSM–5 (IWI), 0.64Zn/HZSM–5 (IE), 0.59Zn/HZSM–5 (IE), 0.48Zn/HZSM–5 (IE), 0.45Zn/HZSM–5 (IE), and HZSM–5. 49

FIGURE PAGE

4.12 Glycerol conversion and aromatics yield as a function of Zn loading by aqueous phase ion–exchange (IE) method. Reaction conditions: 300 psig, 400 °C, WHSV = 1 h^{-1}, and TOS = 3 h. 51

4.13 The relationship between aromatics and light paraffins yields as a function of Zn loading by aqueous phase ion–exchange (IE) method. Reaction conditions: 300 psig, 400 °C, WHSV = 1 h^{-1}, and TOS = 3 h. 52

4.14 Glycerol conversion and aromatics yield as a function of preparation methods, 0.64Zn/HZSM–5 (IE) and 0.88Zn/HZSM–5 (IWI). Reaction conditions: 300 psig, 400 °C, WHSV = 3.33 h^{-1}, and TOS = 3 h. 53

CHAPTER V

5.1 (a) Products yield of PFAD conversion over HZSM–5 as a function of space time (W/F). Reaction conditions: 500 °C, atmospheric pressure, and TOS = 3 h. (b) Proposed reaction pathway for the transformation of palm fatty acid distillate (PFAD) to aromatics. 61

5.2 (a) PFAD conversion and products yield over parent HZSM–5 as a function of SiO2/Al2O3 ratios, (b) Products yield of PFAD conversion over parent HZSM–5, 3Ga/HZSM–5 and 3Zn/HZSM–5 catalysts, and (c) Products yield of PFAD conversion over parent HZSM–5, 1Zn/HZSM–5, 3Zn/HZSM–5, 5Zn/HZSM–5 and 7Zn/HZSM–5 catalysts. Reaction conditions: atmospheric pressure, 500 °C, WHSV = 5 h^{-1}, TOS = 3 h. 64

FIGURE PAGE

5.3 Isopropylamine–TPD (IPA–TPD) profiles of parent HZSM–5, 3Ga/HZSM–5, 1Zn/HZSM–5, 3Zn/HZSM–5, 5Zn/HZSM–5, and 7Zn/HZSM–5 catalysts. The mass monitored was propylene (m/e = 41). 65

5.4 XPS spectra; (a) Ga (2p3/2) of 3Ga/HZSM–5 and (b) Zn (2p3/2) of 1Zn/HZSM–5, 3Zn/HZSM–5, 5Zn/HZSM–5, and 7Zn/HZSM–5 catalysts. 67

5.5 UV–vis absorption spectra of 1Zn/HZSM–5, 3Zn/HZSM–5, 5Zn/HZSM–5, and 7Zn/HZSM–5 catalysts. 69

5.6 Proposed the effect of Zn species on Zn/HZSM–5 catalyst to the reaction pathway for the transformation of palm fatty acid distillate (PFAD) to aromatics. 70

CHAPTER VI

6.1 XRD patterns of HZSM–5 and Zn/HZSM–5 catalysts. 79

6.2 Isopropylamine–TPD (IPA–TPD) profiles of HZSM–5, Zn/HZSM–5 investigated under inert and H2 atmospheres. The mass monitored was propylene (m/e = 41). 81

6.3 XPS (Zn (2p3/2)) spectra of standard ZnO (a), As–prepared Zn/HZSM–5 (b), Zn/HZSM–5 catalysts treated under inert atmosphere at 125 °C (c), 500 °C (d), and 500 °C following with exposed to atmosphere at room temperature for 1 h (e). 83

6.4 Zn K–edge X–ray absorption near edge structures of metallic Zn foil, ZnO, and As–prepared Zn/HZSM–5 catalyst at room temperature. 84

6.5 XPS (Zn (2p3/2)) spectra of As–prepared Zn/HZSM–5 (a), hydrogen treated Zn/HZSM–5 at different temperature: 125 °C (b), 150 °C (c), 300 °C (d), and 500 °C (e). 86

FIGURE **PAGE**

6.6 *n*-Pentane conversion and BTX selectivity over HZSM-5 and Zn/HZSM-5 catalysts with different treatments. Reaction conditions: atmospheric pressure, 500 °C, catalyst = 50 mg, 0.025 mL of *n*-pentane gas, 180 mL/min of He). 90

CHAPTER VII

7.1 XRD patterns of HZSM–5, ZnHZSM–5, Sil–1/ZnHZSM–5, Zn(II)ions/Sil–1/ZnHZSM–5, and Zn(II)ions/Sil–1 catalysts. 99

7.2 XPS (Zn ($2p_{3/2}$)) spectra of ZnO, Zn(II)ions/Sil–1, ZnHZSM–5, Sil–1/ZnHZSM–5, and Zn(II)ions/Sil–1/ZnHZSM–5 catalysts. 102

7.3 Ammonia–TPD (NH_3–TPD) profiles of HZSM–5, ZnHZSM–5, Sil–1/ZnHZSM–5, and Zn(II)ions/Sil–1/ZnHZSM–5 catalysts. The mass monitored was ammonia (*m/e*=17). 104

7.4 Isopropylamine–TPD (IPA–TPD) profiles of HZSM–5, ZnHZSM–5, Sil–1/ZnHZSM–5, and Zn(II)ions/Sil–1/ZnHZSM–5 catalysts. The mass monitored was ammonia (*m/e*=41). 106

APPENDIX

A1 Chromatogram of standard gas mixture. 119

A2 Chromatogram of standard liquid mixture. 120

A3 XRD patterns of HZSM–5 (23), HZSM–5 (30), HZSM–5, and (50) catalysts. 123

A4 Isopropylamine–TPD profile of the parent HZSM–5 catalysts with SiO_2/Al_2O_3 ratios of 23, 30, 50, 80, and 280. 123