

เอสเทอร์ฟิเคชันของกลีเซอรอลโดยใช้ตัวเร่งปฏิกิริยาซิลิกาฟรอนขนาดกลางชนิดกรด



นายนพัฐไชย ก้องเดชาวิวัฒน์



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต  
สาขาวิชาเคมี ภาควิชาเคมี  
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย  
ปีการศึกษา 2556  
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย



ESTERIFICATION OF GLYCEROL USING ACIDIC MESOPOROUS SILICA CATALYST

Mr. Napattchai Kongdechaviwat



A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Science Program in Chemistry

Department of Chemistry

Faculty of Science

Chulalongkorn University

Academic Year 2013

Copyright of Chulalongkorn University



นพฐไชย ก้องเดชาวิวัฒน์ : เอสเทอร์ฟิเคชันของกลีเซอรอลโดยใช้ตัวเร่งปฏิกิริยาซิลิกา  
 พรุณขนาดกลางชนิดกรด. (ESTERIFICATION OF GLYCEROL USING ACIDIC  
 MESOPOROUS SILICA CATALYST) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ดร.ดวงกมล ตุงคะ  
 สมิต, 112 หน้า.

ตัวเร่งปฏิกิริยาสีดำพรุณขนาดกลางโครงสร้างสี่เหลี่ยมลูกบาศก์ชนิด Ia-3d สามารถ  
 สังเคราะห์โดยตรงภายใต้ภาวะที่เป็นกรดด้วยวิธีไมโครเวฟและไฮโดรเทอร์มอลโดย  
 tetraethoxysilane (TEOS) และ 3-mercaptopropyltrimetoxysilane (MPTMS) เป็นแหล่ง  
 ของซิลิกอน ใช้ไตรบล็อกโคพอลิเมอร์ชนิด P123 (พอลิเอทิลีนออกไซด์20-พอลิโพรพิลีนออกไซด์  
 70-พอลิเอทิลีนออกไซด์20) เป็นสารชั้นนำโครงสร้าง องค์ประกอบของเจลของสารสังเคราะห์พรุณ  
 ขนาดกลางคือ 1.0 TEOS : 0.089 MPTMS : 0.018 P123 : 2.0 HCl : 148 H<sub>2</sub>O ในขั้นตอนการ  
 เตรียมพบว่าการเติมปริมาณ MPTMS ในช่วง 4.1-16.4% ของปริมาณซิลิกอนทั้งหมดจะให้เกิด  
 การเปลี่ยนโครงสร้างจากเฮกซะโกนัลของ SBA-15 เป็นโครงสร้างสี่เหลี่ยมลูกบาศก์ Ia-3d  
 ยิ่งกว่านั้นการเติม MPTMS ก่อนการแตกสลายด้วยน้ำของ TEOS ในสารละลายชั้นนำโครงสร้าง  
 เป็นปัจจัยที่ทำให้เกิดโครงสร้างสี่เหลี่ยมลูกบาศก์ Ia-3d เช่นกัน ในทางตรงกันข้ามถ้าเติม TEOS  
 ก่อน MPTMS จะเกิดโครงสร้างเฮกซะโกนัล ความเป็นผลึกของตัวเร่งปฏิกิริยาขึ้นอยู่กับระยะเวลา  
 ในการตกผลึกและอุณหภูมิที่ใช้ในการบ่มผลึก วิธีการเตรียมด้วยไมโครเวฟสามารถลดระยะเวลา  
 การตกผลึกซึ่งยังคงให้ความเป็นผลึกที่ดีภายในระยะเวลา 3 ชั่วโมง จากนั้นตรวจสอบ  
 ลักษณะเฉพาะของวัสดุที่สังเคราะห์ได้ด้วยเทคนิคการเลี้ยวเบนของรังสีเอกซ์ เทคนิคการดูดซับ  
 ไนโตรเจน กล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด กล้องจุลทรรศน์อิเล็กตรอนแบบส่องผ่าน  
 และการทดสอบความเป็นกรดด้วยเทคนิคการไทเทรต ทดสอบประสิทธิภาพของตัวเร่งปฏิกิริยาที่  
 มีหมู่โพรพิลซัลโฟนิคด้วยปฏิกิริยาเอสเทอร์ฟิเคชันของกลีเซอรอลด้วยกรดอะซิติก กรดแคปโร  
 ริก กรดลอริก และกรดโอเลอิก ซึ่งวิเคราะห์ด้วยเทคนิคแก๊สโครมาโตกราฟี (gas  
 chromatography) พบว่าโครงสร้างสี่เหลี่ยมลูกบาศก์ Ia-3d ที่มีเชื่อมโพรงแบบหลายมิติสามารถ  
 ใช้เป็นตัวเร่งปฏิกิริยาที่มีประสิทธิภาพมากกว่าการเชื่อมโพรงแบบสองมิติของโครงสร้างเฮกซะ  
 โกนัล อีกทั้งยังให้ประสิทธิภาพดีกว่าตัวเร่งปฏิกิริยาทางการค้า Amberyst-15

ภาควิชา เคมี

สาขาวิชา เคมี

ปีการศึกษา 2556

ลายมือชื่อนิสิต นพฐไชย ก้องเดชาวิวัฒน์

ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก ดร.ดวงกมล ตุงคะสมิต



# # 5472086623 : MAJOR CHEMISTRY

KEYWORDS: ESTERIFICATION / GLYCEROL / MESOPOROUS SILICA / IA-3D /  
TRIACETIN

NAPATTHACHAI KONGDECHAVIWAT: ESTERIFICATION OF GLYCEROL USING  
ACIDIC MESOPOROUS SILICA CATALYST. ADVISOR: DUANGAMOL  
TUNGASMITA, Ph.D., 112 pp.

The large pore cubic Ia-3d mesoporous silica have been synthesized in acidic condition by microwave and hydrothermal direct synthesis using tetraethoxysilane (TEOS) and 3-mercaptopropyltrimetoxysilane (MPTMS) as the silica in the presence of triblock copolymers Pluronic P123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>) as a structure directing agent. The gel composition of synthetic porous material was 1.0 TEOS : 0.089 MPTMS : 0.018 P123 : 2.0 HCl : 148 H<sub>2</sub>O. In the synthesis procedure, the amount of MPTMS in range of 4.1-16.4% of silicon sources exhibited the phase transition from 2d-hexagonal structure SBA-15 to the cubic Ia-3d structure. Moreover, MPTMS addition prior to TEOS hydrolysis in the surfactant solution can cause cubic Ia-3d structure. On the other hand, if TEOS was added before, the 2d-hexagonal structure would be formed. The crystallinity of catalyst depended on aging temperature and crystallization time. The microwave synthesis could reduce crystallization time with a good crystallinity, in a total processing time for 3 hr. The synthesized materials were characterized by X-ray diffraction, nitrogen adsorption-desorption, scanning electron microscopy, transmission electron microscopy and acid-base titration. The sulfonated catalyst was used in synthesis of triacetin from esterification of glycerol and acetic acid, caproic acid, lauric acid and oleic acid, which was analyzed by Gas Chromatography. The multi-dimensional cubic Ia-3d mesostructure was more efficient than 2d-hexagonal structure SBA-15 and commercial Amberlyst-15 catalyst.

439643815

Department: Chemistry

Student's Signature Napatthachai Kongdechawiat

Field of Study: Chemistry

Advisor's Signature D. Tungasmita

Academic Year: 2013

## ACKNOWLEDGEMENTS

The accomplishment of this thesis can be attributed to the extensive support and assistance from Dr. Duangamol Tungasmita, my thesis advisor. I would like to sincere gratitude to her for valuable advice and guidance in this research as well as extraordinary experiences throughout the work.

I would like to thank Assistant Professor Dr. Warinthrin Chavasiri, Assistant Professor Dr. Sumrit Wacharasindhu and Dr. Anurak Winitsorn as the chairman and member of this thesis committee, respectively, for all of their kindness and useful advice in the research.

I would like to appreciatively thank Department of Chemistry, Faculty of Science, Chulalongkorn University for supporting a teacher assistant fund and the valuable knowledge and experience. Furthermore, I would like to thank Thailand Japan Technology Transfer Project a loan supported by Japan Banks for International Cooperation (TJTTP-JBIC) for instrument support.

Many thanks go in particular to the members of Materials Chemistry and Catalysis Research Unit for their help and encouragement throughout the course of my research and study. Finally, I greatly thank to my family and all of my friends for their help and encouragement during my graduate study.

## CONTENTS

	Page
THAI ABSTRACT .....	iv
ENGLISH ABSTRACT .....	v
ACKNOWLEDGEMENTS .....	vi
CONTENTS .....	vii
LIST OF TABLES .....	xii
LIST OF FIGURES .....	xiv
LIST OF SCHEMES .....	xviii
LIST OF ABBREVIATIONS .....	xix
CHAPTER I INTRODUCTION.....	1
1.1 Background.....	1
1.2 Literature reviews .....	4
1.2.1 Catalysis synthesis .....	4
1.2.2 Esterification of glycerol with acetic acid .....	5
1.3 Objectives.....	6
1.4 Scopes of work.....	6
CHAPTER II THEORY .....	8
2.1 The Fischer Esterification.....	8
2.2 Free fatty acid.....	9
2.2.1 Unsaturated fatty acid .....	9
2.2.1.1 Oleic acid (C <sub>18</sub> ).....	10
2.2.2 Saturated fatty acid.....	10
2.2.2.1 Acetic acid (C <sub>2</sub> ) .....	10
2.2.2.2 Caproic acid (C <sub>6</sub> ).....	10
2.2.2.3 Lauric acid (C <sub>12</sub> ) .....	11
2.3 Catalysts.....	11
2.3.1 Type of catalyst .....	12
2.4 Porous molecular sieves .....	13



	Page
2.4.1 Shape Selectivity.....	14
2.5 Mesoporous materials .....	15
2.5.1 Synthesis schemes of mesoporous materials.....	17
2.5.1.1 The behavior of surfactant molecules in an aqueous solution ...	18
2.5.1.2 Interaction between inorganic species and surfactant micelles...	19
2.5.1.3 Formation mechanism of mesoporous materials.....	20
2.5.2 Synthesis strategy of mesoporous material using block-copolymer as structure directing agent .....	22
2.5.3 Hexagonal mesoporous silica SBA-15.....	24
2.5.3.1 Structure and properties .....	24
2.5.3.2 Synthesis of SBA-15 and formation mechanism .....	25
2.5.4 Cubic <i> Ia-3d </i> Mesoporous silica (MCA).....	28
2.5.5 Modification of catalyst by organic functionalization .....	30
2.5.5.1 Direct synthesis .....	30
2.5.5.2 Post synthesis .....	31
2.6 Microwaves energy .....	32
2.6.1 Microwave interaction with matter .....	33
2.6.2 Two principle mechanisms for interaction with matter .....	33
2.7 Microwave and conventional heats.....	34
2.7.1 Conventional heating methods .....	34
2.7.2 Microwave heating methods .....	34
2.7.3 Microwave effect.....	35
2.8 Characterization of materials.....	36
2.8.1 X-ray powder diffraction (XRD).....	36
2.8.2 Nitrogen adsorption-desorption technique .....	37
2.8.3 Scanning electron microscope (SEM).....	40
2.8.4 Transmission electron microscope (TEM) .....	41
2.8.5 Temperature-programmed desorption of ammonia (NH <sub>3</sub> -TPD).....	42





	Page
CHAPTER III EXPERIMENTS.....	43
3.1 Instruments and apparatus.....	43
3.1.1 Oven and furnace.....	43
3.1.2 X-ray powder diffractometer (XRD).....	43
3.1.3 Surface area analyzer.....	44
3.1.4 Scanning electron microscope (SEM).....	44
3.1.5 Gas chromatograph (GC).....	44
3.1.6 Ammonia temperature-program desorption (NH <sub>3</sub> -TPD).....	45
3.2 Chemicals.....	46
3.2.1 Chemicals for synthesis catalysts.....	46
3.2.2 Chemicals for esterification.....	46
3.2.3 Chemicals for reaction mixture analysis.....	46
3.3 Synthesis of cubic <i>1a-3d</i> mesoporous silica (MCA).....	47
3.3.1 Synthesis MCA by hydrothermal and microwave methods.....	47
3.3.2 Post Synthesis SBA-15 by hydrothermal method.....	49
3.4 Sulfonic functionalized mesoporous materials.....	50
3.5 Acid-base titration.....	51
3.6 Parameters affecting catalytic preparation.....	52
3.6.1 Effect of aging time.....	52
3.6.2 Effect of aging temperature.....	52
3.6.3 Effect of sequence of input material by direct synthesis.....	52
3.6.4 Effect of MPTMS and TEOS amount (mol).....	53
3.7 Procedure in esterification of glycerol.....	53
3.8 Parameters affecting esterification of glycerol.....	53
3.8.1 Effect of reaction time.....	53
3.8.2 Effect of temperature.....	53
3.8.3 Effect of catalytic amount.....	53



	Page
3.8.4 Effect of glycerol to carboxylic acid molar ratio .....	53
3.8.5 Effect of various catalysts .....	54
3.8.6 Effect of reused catalyst .....	54
3.8.7 Effect of chain length of carboxylic acid .....	54
CHAPTER VI RESULTS AND DISCUSSION .....	55
4.1 Synthesis of cubic <i>1a-3d</i> mesoporous silica .....	55
4.1.1 The physico-chemical properties of sulfonic functionalized MCA synthesized by hydrothermal method .....	55
4.1.1.1 XRD results.....	55
4.1.1.2 Sorption properties .....	56
4.1.1.3 SEM images .....	58
4.1.1.4 TEM images .....	59
4.1.2 Effect of crystallization time.....	60
4.1.3 Effect of aging temperature .....	61
4.1.4 Effect of amount of Si sources (MPTMS and TEOS) .....	63
4.1.5 Effect of sequence of Si sources addition (TEOS and MPTMS).....	66
4.1.6 The physico-chemical properties of sulfonic functionalized MCA synthesized by microwave method.....	68
4.1.6.1 XRD results.....	68
4.1.6.2 Sorption properties .....	69
4.1.6.3 SEM images .....	71
4.1.6.4 TEM images .....	72
4.1.7 Effect of aging time by using microwave radiation .....	72
4.2 Post synthesis of hexagonal mesostructure SBA-15.....	74
4.2.1 The physico-chemical properties of SBA-15 materials .....	74
4.2.1.1 XRD results.....	74
4.2.1.2 Sorption properties .....	75
4.2.1.3 SEM images .....	76



	Page
4.3 Acidity from titration and pore size distribution of catalysts .....	77
4.4 Acidity from NH <sub>3</sub> -TPD .....	78
4.5 Thermal gravimetric Analysis (TGA).....	79
4.6 Catalytic activity of Amberlyst-15 in esterification of glycerol with acetic acid .	81
4.6.1 Effect of reaction times .....	82
4.6.2 Effect of catalytic amount .....	82
4.6.3 Effect of glycerol to acetic acid mole ratio.....	83
4.6.4 Effect of reaction temperature .....	84
4.7 Catalytic activity of cubic <i>1a-3d</i> mesoporous silica in esterification of glycerol with acetic acid.....	86
4.8 Esterification of glycerol with long chain carboxylic acid.....	89
CHAPTER V CONCLUSIONS .....	95
REFERENCES .....	96
APPENDIX.....	102
VITA.....	112



## LIST OF TABLES

Table	Page
Table 2.1 Properties of varied carbon chain carboxylic acid. ....	11
Table 2.2 Comparison of homogeneous and heterogeneous catalysts. ....	12
Table 2.3 IUPAC classification of porous materials. ....	13
Table 2.4 Various synthesis conditions of hexagonal mesoporous materials and the type of interaction between template and inorganic species. ....	16
Table 2.5 Properties of some hexagonal mesoporous materials.....	17
Table 2.6 Example routes for interactions between the surfactant and the inorganic soluble species. ....	19
Table 2.7 Comparison of two well-known mesoporous materials, MCM-41 and SBA-15 in their characteristic properties.....	25
Table 2.8 Various synthesis conditions of hexagonal mesoporous materials and the type of interaction between template and inorganic species.....	26
Table 2.9 Surface properties of MCA and MCM-48. ....	30
Table 2.10 Heating mechanism comparison between conventional and microwave process.....	35
Table 2.11 Features of adsorption isotherms.....	39
Table 4.1 Textural properties of synthesized materials by hydrothermal method. ....	57
Table 4.2 Textural properties of synthesized materials by microwave method. ....	70
Table 4.3 Surface properties of microwave catalysts varied aging times. ....	73
Table 4.4 Textural properties of SBA-15 and Sulfonic functionalized SBA-15.....	76
Table 4.5 The acid value and pore size of catalysts. ....	77
Table 4.6 Acidic properties of catalysts measured by NH <sub>3</sub> -TPD. ....	79
Table 4.7 Comparison of catalyst stability.....	81
Table 4.8 Effect of reaction time on product yields and selectivity over Amberlyst-15. ....	82
Table 4.9 Effect of catalyst amount on product yields and selectivity over Amberlyst-15. ....	83



Table 4.10 Effect of mole ratio on product yields and selectivity over Amberlyst-15. .....	83
Table 4.11 Effect of temperature and time on product yields and selectivity over Amberlyst-15. ....	85
Table 4.12 Esterification of acetic acid with different catalysts at 105°C.....	87
Table 4.13 Esterification of acetic acid with different catalysts at 115°C.....	88
Table 4.14 Size of acylated products structure estimated from Hyper-chem program. .....	89
Table 4.15 Esterification of glycerol with caproic acid.....	91
Table 4.16 Esterification of glycerol with lauric acid. ....	92
Table 4.17 Esterification of glycerol with oleic acid. ....	93



## LIST OF FIGURES

Figure	Page
Figure 1.1 The amount of biodiesel production over the past three years.....	1
Figure 1.2 World marketed energy consumption, 1990-2035 .....	2
Figure 1.3 Esterification of glycerol with acetic acid. ....	4
Figure 2.1 The Fisher esterification mechanism .....	9
Figure 2.2 The relationship between activation energy ( $E_a$ ) and enthalpy ( $\Delta H$ ) of the reaction with and without a catalyst.....	12
Figure 2.3 Three types of selectivity in zeolites: reactant, product and transition state shape selectivity .....	14
Figure 2.4 Types of silica surface Si-O species.....	15
Figure 2.5 A schematic presentation of three inorganic-surfactant mesostructures: (a) the hexagonal phase, (b) the cubic phase, and (c) the lamellar phase. ....	16
Figure 2.6 Phase sequence of the surfactant-water binary system .....	18
Figure 2.7 Schematic representation of the different types of silica-surfactant interfaces. Dashed line corresponded to H-bonding interactions.....	20
Figure 2.8 Mechanism of mesoporous formation .....	21
Figure 2.9 Block copolymer used in mesostructured generation.....	22
Figure 2.10 Three possible structures of a HI composed by a nonionic polymer and an inorganic framework.....	23
Figure 2.11 Various types of interaction of surfactant head group with inorganic species: electrostatic in MCM-41 .....	27
Figure 2.12 PerBU in ANA (chain of 6-rings).....	28
Figure 2.13 Connection modes in ANA.....	29
Figure 2.14 Cell content of cubic $Im-3d$ structure was seen along $c$ . ....	29
Figure 2.15 In-situ oxidation synthesis strategy for the preparation of sulfonic acid-modified mesostructured materials .....	31
Figure 2.16 Comparison of functionalization via co-condensation or grafting.....	32
Figure 2.17 Diffraction of X-ray by regular planes of atoms .....	36



Figure 2.18 The IUPAC classification of adsorption isotherm .....	37
Figure 2.19 IUPAC classification of hysteresis loop.....	40
Figure 2.20 Schematic diagram of transmission electron microscope .....	42
Figure 3.1 The temperature program for the calcination of SBA-15.....	43
Figure 3.2 The GC heating condition for short fatty acid analysis.....	44
Figure 3.3 The GC heating condition for long fatty acid analysis .....	45
Figure 4.1 XRD patterns of as-synthesized, extracted and oxidized MCA which synthesized by hydrothermal method. ....	56
Figure 4.2 N <sub>2</sub> adsorption-desorption isotherm and BJH-pore size distribution of MCAex synthesized by hydrothermal method. ....	57
Figure 4.3 N <sub>2</sub> adsorption desorption isotherm and BJH-pore size distribution of MCAox synthesized by hydrothermal method. ....	58
Figure 4.4 SEM images of (a) MCAex and (b) MCAox synthesized by hydrothermal method.....	59
Figure 4.5 TEM images of MCAox synthesized by hydrothermal method.....	60
Figure 4.6 XRD patterns of MCAox synthesized by hydrothermal method with different crystallization time (a) 24 hr. and (b) 48 hr. ....	61
Figure 4.7 XRD patterns of extracted and oxidized catalyst with varied aging temperature (a) MCAex-40, (b) MCAox-40, (c) MCAex-60, (d) MCAox-60, (e) MCAex-80 and (f) MCAox-80. ....	62
Figure 4.8 The expanding of hydrophobic core PPO block when increasing aging temperature.....	62
Figure 4.9 SEM images of MCAox synthesized by hydrothermal method varied aging temperature (a) 40°C, (b) 60°C and (c) 80°C.....	63
Figure 4.10 XRD patterns of MCAox with various the mol ratio of silicon source 1.089-x TEOS and x MPTMS by mole. ....	65
Figure 4.11 Phase transformation from from high-curvature 2d-hexagonal to low-curvature <i>1a-3d</i> structure by adding MPTMS. ....	65
Figure 4.12 SEM images of MCAox synthesized by hydrothermal method with varied Si mole ratio 1.089-x TEOS : x MPTMS (a) x=0.045, (b) x=0.067, (c) x=0.089, (d) x=0.111, (E) x=0.134, and (f) x=0.179.....	66



Figure 4.13 XRD Pattern of catalyst with varied sequence of input material by direct synthesis (a) MPTMS+TEOS 0 min, (b) MPTMS+TEOS 15 min, (c) MPTMS+TEOS 30 min, (d) TEOS+MPTMS 15 min, (e) TEOS+MPTMS 30 min, (f) TEOS+MPTMS 60 min and (g) TEOS+MPTMS 120 min.....	67
Figure 4.14 XRD patterns of XRD patterns of as-synthesized, extracted and oxidized MCA synthesized by microwave method using aging time 1 hr.....	68
Figure 4.15 XRD patterns of comparison extracted catalyst between hydrothermal and microwave method.....	69
Figure 4.16 N <sub>2</sub> adsorption desorption isotherm and BJH-pore size distribution of MCA <sub>ex</sub> synthesized by microwave method using aging time 1 hr.....	70
Figure 4.17 N <sub>2</sub> adsorption desorption isotherm and BJH-pore size distribution of MCA <sub>ox</sub> synthesized by microwave method using aging time 3 hr.....	70
Figure 4.18 SEM images of oxidized MCA <sub>ox</sub> synthesized by microwave method using aging time 1 hr.....	71
Figure 4.19 TEM images of MCA <sub>ox</sub> synthesized by microwave method.....	72
Figure 4.20 XRD patterns of synthesized materials by microwave method with varied aging temperature from 0.5-4.0 hr.....	73
Figure 4.21 XRD patterns of synthesized SBA-15.....	74
Figure 4.22 N <sub>2</sub> adsorption-desorption isotherm and BJH-pore sized distribution of SBA-15.....	75
Figure 4.23 N <sub>2</sub> adsorption-desorption isotherm and BJH-pore sized distribution of SBA-15-Pr-SO <sub>3</sub> H.....	75
Figure 4.24 SEM images of (a) SBA-15 and (d) SBA-15-Pr-SO <sub>3</sub> H.....	76
Figure 4.25 NH <sub>3</sub> -TPD profile profiles of synthesized catalyst and commercial catalyst.....	78
Figure 4.26 Thermal gravimetric profile of MCA <sub>ox</sub> -HT.....	80
Figure 4.27 Thermal gravimetric profile of Post-SBA-15-Pr-SO <sub>3</sub> H.....	80
Figure 4.28 Thermal gravimetric profile of Amberlyst-15.....	81
Figure A-1 Calibration curve of glycerol using dodecane as I.S. and column CP-8....	105
Figure A-2 Calibration curve of triacetin using dodecane as I.S. and column CP-8....	105
Figure A-3 Calibration curve of glycerol using dodecane as I.S. with metal column.	106





Figure A-4 GC chromatogram of products from esterification of glycerol with acetic acid.....	107
Figure A-5 GC chromatogram of products from esterification of glycerol with caproic acid.....	108
Figure A-6 GC chromatogram of products from esterification of glycerol with lauric acid.....	109
Figure A-7 GC chromatogram of products from esterification of glycerol with oleic acid.3. Calculation of glycerol conversion.....	110



## LIST OF SCHEMES

Scheme	Page
Scheme 1.1 Reaction of biodiesel production.....	3
Scheme 2.1 Amorphous SiO <sub>2</sub> framework.....	24
Scheme 2.2 Synthesis of SBA-15.....	25
Scheme 2.3 The formation process of the mesoporous material in acidic condition.....	28
Scheme 2.4 Post synthesis procedure for the preparation of sulfonic acid modified mesostructured materials.....	32
Scheme 3.1 Preparation diagram for GC analysis.....	45
Scheme 3.2 Preparation diagram for MCA by hydrothermal method.....	48
Scheme 3.3 Preparation diagram for MCA by microwave method.....	49
Scheme 3.4 Preparation diagram for SBA-15 by hydrothermal method.....	50
Scheme 3.5 Preparation diagram for oxidized materials.....	51
Scheme 3.6 Diagram for acid-base titration.....	52
Scheme 4.1 Mechanism of acetal formation by acid catalysts.....	85
Scheme 4.2 Mechanism of acrolein formation by acid catalysts.....	85



## LIST OF ABBREVIATIONS

Å	Angstrom
a.u.	Arbitrary unit
BET	Brunauer-Emmett-Teller
BJH	Barret, Joyner and Halenda
°C	Degree Celsius
GC	Gas chromatography
g	Gram (s)
hr.	Hour (s)
min	Minute (s)
µm	Micrometer (s)
ml	Milliliter (s)
MPTMS	(3-mercaptopropyl)trimethoxysilane
MCA	Mesoporous cubic amorphous
MCM	Mobile content management
MSTFA	N-Methyl-N-(trimethylsilyl) trifluoroacetamide
M	Molarity
nm	Nanometer (s)
%	Percentage
SBA-15	Santa barbara amorphous
SEM	Scanning electron microscopy
TPD	Temperature Programming desorption
TEM	Transmission electron microscopy
TEOS	Tetraethyl orthosilicate
XRD	X-Ray diffraction

