

การเตรียมคอมพิวเตอร์ของยางธรรมชาติและซิลิกาที่มีหมู่ฟังก์ชันด้วยกรดซัลโฟนิกและการประยุกต์
เป็นตัวเร่งปฏิกิริยาในเอสเทอร์ฟิเคชัน



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PREPARATION OF NATURAL RUBBER AND SILICA COMPOSITES FUNCTIONALIZED
WITH SULFONIC ACID GROUP AND THEIR APPLICATION AS CATALYSTS IN
ESTERIFICATION

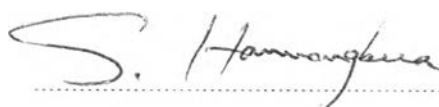
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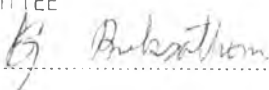
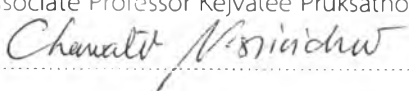
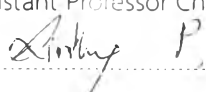
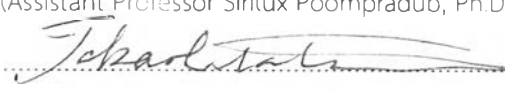
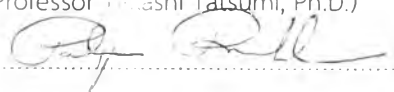


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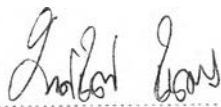


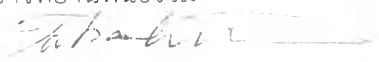
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ศักดิ์นันท์ นันตัง : การเตรียมคอมพอสิตของยางธรรมชาติและซิลิกาที่มีหมู่ฟังก์ชันด้วยกรดซัลโฟนิกและการประยุกต์เป็นตัวเร่งปฏิกิริยาในเอสเทอร์ฟิเคชัน (PREPARATION OF NATURAL RUBBER AND SILICA COMPOSITES FUNCTIONALIZED WITH SULFONIC ACID GROUP AND THEIR APPLICATION AS CATALYSTS IN ESTERIFICATION) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร. ขวลิต งามจรสศรีวิชัย, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ.ดร. ศิริลักษณ์ พุ่มประดับ, ศ.ดร. Takashi Tatsumi, 136 หน้า

งานวิจัยนี้มีจุดประสงค์เพื่อศึกษาการเตรียมคอมพอสิตของยางธรรมชาติและซิลิกาที่มีหมู่ฟังก์ชันด้วยกรดซัลโฟนิก ผ่านวิธีอินซิทู โซล-เจล ร่วมกับการฟังก์ชันด้วยหมู่กรดซัลโฟนิก และการประยุกต์เป็นตัวเร่งปฏิกิริยาในเอสเทอร์ฟิเคชัน เริ่มต้นด้วยการศึกษาการเตรียมคอมพอสิตของยางธรรมชาติและเฮกซะโกนอลเมโซพอร์ซิลิกา (NR/HMS) ที่สังเคราะห์ผ่านวิธีอินซิทู โซล-เจล ในตัวทำละลายเตตระไฮโดรฟูแรน (THF) โดยใช้เตตระเอทิลอโทซิลิเกต (TEOS) เป็นวัตถุดิบซิลิกา จากนั้นนำคอมพอสิตที่เตรียมได้ไปวิเคราะห์ลักษณะสมบัติทางกายภาพและเคมีโดยใช้เทคนิควิเคราะห์ขั้นสูงต่างๆ นอกจากนี้ยังศึกษาผลกระทบของสัดส่วนของผสมในการเตรียมคอมพอสิตต่อลักษณะโครงสร้างและสมบัติความพรุน จากผลวิเคราะห์ที่ได้พบว่า NR/HMS แสดงค่าพื้นที่ผิวที่สูง ปริมาตรรูพรุนสูง การกระจายตัวขนาดรูพรุนแคบ และการจัดเรียงตัวของโครงสร้างแบบเฮกซะโกนอลที่มีความเป็นระเบียบสูง รวมถึงแสดงสมบัติความไม่ชอบน้ำ ต่อจากนั้นทำการศึกษากการเตรียมคอมพอสิตของยางธรรมชาติและเฮกซะโกนอลเมโซพอร์ซิลิกาที่มีหมู่ฟังก์ชันด้วยกรดซัลโฟนิก (NR/HMS-SO₃H) ซึ่งเตรียมโดยใช้สัดส่วนผสมของ 3-เมอร์แคปโตโพรพิลไตรเมทอกซีไซเลน (MPTMS) ต่อเตตระเอทิลอโทซิลิเกต (TEOS) หลายสัดส่วน จากนั้นทำการศึกษาลักษณะสมบัติทางกายภาพและเคมี ลักษณะโครงสร้างและสมบัติความพรุน ของ NR/HMS-SO₃H คอมพอสิตที่เตรียมขึ้นเปรียบเทียบกับเฮกซะโกนอลเมโซพอร์ซิลิกาที่มีหมู่ฟังก์ชันด้วยกรดซัลโฟนิก (HMS-SO₃H) จากผลวิเคราะห์ที่ได้พบว่า NR/HMS-SO₃H มีความเป็นกรดสูง และแสดงข้อดีของลักษณะความพรุนแบบเมโซพอร์ร่วมกับสมบัติความไม่ชอบน้ำจากการคอมพอสิตกับยางธรรมชาติ สุดท้ายทำการศึกษาศรรณนะเชิงเร่งปฏิกิริยาของคอมพอสิตที่เตรียมได้ในเอสเทอร์ฟิเคชันกับกรดคาร์บอกซิลิกหลายชนิดกับเอทานอล จากผลการศึกษาพบว่า ตัวเร่งปฏิกิริยาชนิดคอมพอสิต NR/HMS-SO₃H มีความว่องไวในการเร่งเอสเทอร์ฟิเคชันที่เหนือกว่า HMS-SO₃H และคอมพอสิตของแนฟิออนและซิลิกา (SAC-13) นอกจากนี้ NR/HMS-SO₃H ยังมีความสามารถในการกลับมาใช้ซ้ำสำหรับการเร่งเอสเทอร์ฟิเคชันอย่างน้อย 4 รอบ

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SAKDINUN NUNTANG: PREPARATION OF NATURAL RUBBER AND SILICA COMPOSITES FUNCTIONALIZED WITH SULFONIC ACID GROUP AND THEIR APPLICATION AS CATALYSTS IN ESTERIFICATION. ADVISOR: ASST. PROF. CHAWALIT NGAMCHARUSSRIVICHAI, Ph.D., CO-ADVISOR: ASST. PROF. SIRILUX POOMPRADUB, Ph.D., PROF. TAKASHI TATSUMI, Ph.D., 136 pp

The main objectives of this study were the preparation propylsulfonic acid-functionalized mesoporous composites based on natural rubber (NR) and hexagonal mesoporous silica (HMS) via the in situ sol-gel technique and the simultaneous functionalization with organo-sulfonic acid groups, in order to use them as catalysts in esterification. Firstly, a series of NR/HMS composites was prepared in tetrahydrofuran (THF) via an in situ sol-gel process using tetraethylorthosilicate (TEOS) as a silica precursor. The physicochemical properties of the composites were characterized by various techniques. In addition, the effects of the gel composition on the structural and textural properties of the NR/HMS composites were investigated. NR/HMS exhibited the high BET surface area, large pore volume, narrow pore size distribution and high order hexagonal structure, including hydrophobicity. After that, the propylsulfonic acid functionalized mesoporous composites based on natural rubber and hexagonal mesoporous silica (NR/HMS-SO₃H) were prepared by varying 3-mercaptopropyl trimethoxysilane (MPTMS) to tetraethylorthosilicate (TEOS) molar ratio. The physicochemical, textural and structural properties of acidic composites were compared with acidic hexagonal mesoporous silica (HMS-SO₃H). The acidic composites possessed high acidity, high mesoporosity of HMS and the hydrophobicity of the NR. Finally, their catalytic activities were tested in the esterification of various carboxylic acids with ethanol. The NR/HMS-SO₃H catalysts possessed a superior specific activity to HMS SO₃H and silica-supported Nafion® catalyst (SAC-13). Moreover, NR/HMS-SO₃H catalysts exhibited reusability in esterification at least 4 cycles.

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CONTENTS

	Page
THAI ABSTRACT	iv
ENGLISH ABSTRACT	v
ACKNOWLEDGEMENTS	vi
CONTENTS	vii
LIST OF TABLES	xii
LIST OF FIGURES	xiv
ABBREVIATIONS.....	xviii
NOMENCLATURE	xix
CHAPTER I INTRODUCTION	1
1.1 Motivation	1
1.2 Objectives.....	3
1.3 Scope of this work.....	3
CHAPTER II THEORY AND LITERATURE REVIEWS	6
2.1 Mesoporous materials	6
2.2 Sol-gel process for the synthesis mesoporous silica.....	9
2.3 Mesoporous silica with hexagonal structure.....	11
2.3.1 General features of mesoporous silica with hexagonal structure	11
2.3.2 Synthesis method of mesoporous silica with hexagonal structure	13
2.3.2.1 Ionic surfactant and ionic inorganic precursor	13
2.3.2.2 Neutral surfactant and inorganic precursor.....	15
2.3.2.3 Using amphiphilic di- and tri-block copolymer	16
2.4 Hexagonal mesoporous silica (HMS).....	17
2.5 Surface modification of mesoporous silicas.....	18
2.5.1 Post synthesis method	19
2.5.2 Co-condensation method.....	20
2.6 Organic esters	22
2.6.1 General features.....	22



	Page
2.6.2 Synthesis of esters.....	24
2.7 Acid catalyzed esterification.....	25
2.7.1 Homogeneous acid catalysts.....	26
2.7.2 Heterogeneous acid catalysts	27
2.7.2.1 Supported catalysts	28
2.7.2.2 Bulk catalysts.....	28
2.7 Natural rubber	31
2.8 Natural rubber/silica composites.....	32
2.9 Literature reviews	34
2.9.1 Synthesis of natural rubber/silica composites via <i>in situ</i> sol-gel reaction	34
2.9.2 Functionalization of silica with sulfonic acid group.....	34
2.9.3 Esterification over heterogeneous acid catalysts	35
CHAPTER III EXPERIMENTAL AND ANALYTICAL METHOD	38
3.1 Materials	38
3.1.1 Chemical for synthesis mesoporous materials and composites	38
3.1.2 Commercial catalyst.....	38
3.1.3 Chemical for esterification	39
3.1.4 Chemicals for reaction product analysis.....	39
3.2 Instruments and equipment.....	39
3.3 Preparation of mesoporous silica and composites with NR	40
3.3.1 Hexagonal mesoporous silica (HMS) synthesis	40
3.3.2 Natural rubber and hexagonal mesoporous silica composites (NR/HMS) synthesis	41
3.3.3 Propylsulfonic acid-functionalized hexagonal mesoporous silica (HMS- SO ₃ H) synthesis.....	42
3.3.4 Propylsulfonic acid-functionalized natural rubber and hexagonal mesoporous silica composites (NR/HMS-SO ₃ H) synthesis	42
3.4 Material characterization procedure	43



	Page
3.4.1 Compositional and elemental analysis.....	43
Thermogravimetric/differential thermal analysis (TG/DTA).....	43
Carbon, Hydrogen, Nitrogen and Sulfur (CHNS) analysis	43
3.4.2 Surface functional groups analysis.....	44
Fourier-transform infrared spectroscopy (FTIR).....	44
Solid-state ²⁹ Si magic angle spinning nuclear magnetic resonance (²⁹ Si MAS NMR).....	44
3.4.3 Structural analysis.....	45
X-ray Powder diffraction (XRD).....	45
3.4.4 Textural properties and hydrophobicity measurement.....	46
N ₂ adsorption-desorption measurement	46
H ₂ O adsorption-desorption measurement	48
3.4.5 Electron microscopy	48
Scanning electron microscope (SEM)	48
Transmission electron microscopy (TEM)	48
3.4.6 Particle size analysis.....	49
3.4.7 Acidity measurement.....	49
3.5 Esterification carboxylic acids and alcohols over acidic mesoporus silicas and composites.....	49
3.5.1 Study on the effect of type of acidic mesoporous catalysts.....	49
3.5.2 Study on the effect of catalyst amount	50
3.5.3 Study on the effect of H ₂ O on catalytic activity	50
3.6 Catalyst reusability of NR/HMS-SO ₃ H composite	51
3.7 Reaction product analysis.....	51
CHAPTER IV SYNTHESIS AND CHARACTERIZATION OF NR/HMS COMPOSITES.....	53
4.1 Thermogravimetric analysis (TGA)	53
4.2 FTIR spectroscopy.....	55
4.3 Solid state ²⁹ Si MAS NMR studies	56



	Page
4.4 XRD analysis.....	58
4.5 Transmission electron microscopy (TEM).....	61
4.6 Scanning electron microscopy (SEM).....	65
4.7 Particle size analysis.....	68
4.8 N ₂ adsorption-desorption measurement.....	69
4.9 H ₂ O adsorption-desorption measurement.....	75
4.10 Pathway for the formation of NR/HMS composite.....	77
CHAPTER V SYNTHESIS AND CHARACTERIZATION OF NR/HMS-SO ₃ H COMPOSITES.....	79
5.1 Thermogravimetric analysis (TGA).....	79
5.2 XRD analysis.....	81
5.3 FTIR spectroscopy.....	84
5.4 Solid state ²⁹ Si MAS NMR studies.....	85
5.5 Sulfur content and acidity measurement.....	87
5.6 N ₂ adsorption-desorption measurement.....	88
5.7 Electron microscopy.....	92
5.8 H ₂ O adsorption-desorption measurement.....	95
5.9 Pathway for the formation of NR/HMS-SO ₃ H composite.....	97
CHAPTER VI ESTERIFICATION OF CARBOXYLIC ACID WITH ALCOHOL OVER ACIDIC MESOPOROUS SILICAS AND NATURAL RUBBER/MESOPOROUS SILICA COMPOSITES.....	99
6.1 Study on esterification of various carboxylic acids with ethanol over acidic catalysts.....	99
6.1.1 Esterification of acetic acid with ethanol.....	99
6.1.2 Esterification of octanoic acid with ethanol.....	102
6.1.3 Esterification of lauric acid with ethanol.....	105
6.2 Effect of catalyst amount on esterification.....	107
6.3 Effect of H ₂ O on catalytic activity.....	109
6.4 Reusability of NR/HMS-SO ₃ H composite.....	112
6.4.1 Effect of organic solvent for washing spent NR/HMS-SO ₃ H composite...	112



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	Page
6.4.2 Reusability of NR/HMS-SO ₃ H in the esterification of octanoic acid with ethanol.....	114
CHAPTER VII CONCLUSIONS AND RECOMMANDATIONS.....	116
7.1 Conclusions.....	116
7.2 Recommendation and future works.....	117
REFERENCES.....	118
APPENDIX A.....	128
Appendix B.....	134
Appendix C.....	135
VITA.....	136



LIST OF TABLES

Table 2.1 Pore-size systems and representative porous inorganic materials.	6
Table 2.2 Possible pathways for the synthesis of mesoporous silicas with hexagonal structure.	8
Table 2.3 Various synthesis conditions of mesoporous silica with hexagonal structure and the types of interaction between templates and inorganic species.	12
Table 2.4 Properties of some mesoporous silicas with hexagonal structure.	13
Table 2.5 Summary of advantage and disadvantage of two organic functionalized modification methods.	21
Table 2.6 Examples of organic esters are used in the manufacturing.	23
Table 3.1 The physicochemical properties of Nafion [®] SAC-13.	38
Table 3.2 Synthesis molar composition of HMS-E and HMS-T.	40
Table 3.3 Synthesis molar composition of NR/HMS composites.	41
Table 3.4 Synthesis molar composition of HMS-SO ₃ H materials.	42
Table 3.5 Synthesis molar composition of NR/HMS-SO ₃ H composites.	43
Table 3.6 Reaction condition of esterification carboxylic acids and alcohols.	50
Table 3.7 GC conditions for determination of residual carboxylic acid and ester content.	51
Table 4.1 Silica content of NR/HMS composites synthesized under various conditions.	54
Table 4.2 Relative intensity of the Q ⁿ group of the ²⁹ Si MAS NMR.	57
Table 4.3 Structural properties of pure silica HMSs and NR/HMS composites synthesized under various conditions.	59
Table 4.4 Textural properties of pure silica HMS-E and HMS-T.	70
Table 4.5 Textural properties of pure silica HMS-T and NR/HMS-1 to -3 composites.	71
Table 4.6 Textural properties of pure silica HMS-T and NR/HMS-4 to -6 composites.	73
Table 4.7 Textural properties of pure silica HMS-T and NR/HMS-1, -7 and -8 composites.	75
Table 5.1 Silica content of HMS-T, HMS-SO ₃ H and NR/HMS-SO ₃ H composites synthesized under various conditions.	81
Table 5.2 Structural properties of HMS-T, HMS-SO ₃ H and NR/HMS-SO ₃ H composites synthesized under various conditions.	83



Table 5.3 Relative intensities of the T^m and Q^n groups from ^{29}Si MAS NMR and the sulfur contents of HMS-T, HMS-SO ₃ H and NR/HMS-SO ₃ H composites synthesized under various conditions.....	87
Table 5.4 Sulfur contents and acidity of HMS-SO ₃ H and NR/HMS-SO ₃ H composites synthesized under various conditions.....	88
Table 5.5 Textural properties of mesoporous and acidic mesoporous materials synthesized under various conditions.....	90
Table 6.1 Esterification of acetic acid with ethanol over acidic mesoporous catalysts.....	101
Table 6.2 Esterification of octanoic acid with ethanol over acidic mesoporous catalysts.....	104
Table 6.3 Esterification of lauric acid with ethanol over acidic mesoporous catalysts.....	107
Table 6.4 Effect of catalyst loading in catalytic esterification of octanoic acid with ethanol over SAC-13, HMS-SO ₃ H catalysts and NR/HMS-SO ₃ H composites.....	109
Table 6.5 Effect of H ₂ O addition in catalytic esterification of octanoic acid with ethanol over SAC-13, HMS-SO ₃ H (0.2) catalyst and NR/HMS-SO ₃ H (0.2) catalyst.....	110
Table 6.6 Elemental composition (C,H,N,S contents) of fresh NR/HMS-SO ₃ H and spent NR/HMS-SO ₃ H after used at 1 st cycle in esterification.	113
Table 6.7 Elemental composition (C,H,N,S contents) of fresh NR/HMS-SO ₃ H and spent NR/HMS-SO ₃ H after the 5 th cycle in the esterification of octanoic acid with ethanol.....	115
Table C- 1 Textural properties of SAC-13.....	135



LIST OF FIGURES

Figure 1.1 Experimental framework of this study.	5
Figure 2.1 Schematic diagram of the M41S materials, MCM-50 (layered), MCM-41 (hexagonal) and MCM-48 (cubic).	7
Figure 2.2 Phase sequence of surfactant-water binary system	8
Figure 2.3 Sol-gel general reaction scheme.	9
Figure 2.4 Effect of catalyst on hydrolysis and condensation.	11
Figure 2.5 Effect of pH on hydrolysis and condensation rates.	11
Figure 2.6 Schematic representation of the different types of silica-surfactant interfaces.	14
Figure 2.7 Schematic representative of the synthesis of MCM-41	15
Figure 2.8 Primary amine used in mesostructured generation.	15
Figure 2.9 Block copolymer used in mesostructured generation.	16
Figure 2.10 TEM image and SEM image of HMS.	17
Figure 2.11 Schematic representation of the $S^{\circ}I^{\circ}$ template mechanism of formation of HMS mesoporous silica	18
Figure 2.12 Diagram illustrating unmodified pore wall and the presence of functional group on the pore wall.	19
Figure 2.13 Functionalization of inner walls of mesoporous silicas by post synthesis method	19
Figure 2.14 <i>In-situ</i> oxidation synthesis strategy for the preparation of organo-sulfonic acid group modified hexagonal mesoporous material.	21
Figure 2.15 Examples of organic ester molecules.	22
Figure 2.16 Pathway for preparation of organic esters.	24
Figure 2.17 Esterification of carboxylic acid with alcohol.	25
Figure 2.18 Mechanism of acid catalyzed esterification.	25
Figure 2.19 Conventional process for synthesis of ester lubricants via esterification. .	27
Figure 2.20 Classification of the heterogeneous acid catalysts.	28
Figure 2.21 Brønsted and Lewis acid sites in zeolites.	29
Figure 2.22 The polymer structure of Amberlyst-15.	30
Figure 2.23 Chemical formula of Nafion.	30
Figure 2.24 Conceptual scheme of composite materials of mesoporous silica with organic components.	31
Figure 2.25 Isoprene structure of natural rubber.	32
Figure 2.26 SEM image of natural rubber/silica composites.	33



Figure 2.27 Possible reaction mechanism for the acetic acid esterification with methanol over propylsulfonic acid-functionalized SBA-15	37
Figure 3.1 Diffraction of X-ray by regular planes of atoms.	45
Figure 3.2 The IUPAC classification of adsorption isotherm.	47
Figure 3.3 Temperature program of GC condition for acetic acid determination.....	52
Figure 3.4 Temperature program of GC condition for octanoic acid and ethyl octanoate determination.....	52
Figure 3.5 Temperature program of GC condition for lauric acid and ethyl laurate determination.....	52
Figure 4.1 Weight loss and DTG curves of NR/HMS-1 composite.....	54
Figure 4.2 Weight loss and DTG curves of pure NR.	55
Figure 4.3 FTIR spectra of mesoporous silica HMS-E, HMS-T and NR/HMS-1 composite.	56
Figure 4.4 ²⁹ Si MAS NMR spectra of HMS-T and NR/HMS-1 composite.	57
Figure 4.5 XRD patterns of pure silica HMS-E and pure silica HMS-T	58
Figure 4.6 XRD patterns of pure silica HMS-T and NR/HMS composites.....	60
Figure 4.7 TEM images and the simulated 2D and 3D TEM images of HMS-E.	62
Figure 4.8 TEM image and the simulated 2D and 3D TEM images of HMS-T.....	63
Figure 4.9 TEM image and the simulated 2D and 3D TEM images of NR/HMS-1 composite.	64
Figure 4.10 Simulated 2D TEM images of HMS-T and NR/HMS-1 composite.	65
Figure 4.11 FE-SEM images of HMS-T.....	66
Figure 4.12 FE-SEM images of NR/HMS-1 composite.....	67
Figure 4.13 Particle size distribution of the pure silica HMS-T and NR/HMS-1 composite.	68
Figure 4.14 N ₂ adsorption-desorption isotherms and BJH pore size distribution of pure silica HMS-E and HMS-T.....	69
Figure 4.15 N ₂ adsorption-desorption isotherms and BJH pore size distribution of pure silica HMS-T and NR/HMS-1 to -3 composites.....	71
Figure 4.16 N ₂ adsorption-desorption isotherms and BJH pore size distribution of pure silica HMS-T and NR/HMS-4 to -6 composites.....	72
Figure 4.17 N ₂ adsorption-desorption isotherms and BJH pore size distribution of pure silica HMS-T and NR/HMS-1, -7 and -8 composites.	74
Figure 4.18 H ₂ O adsorption-desorption isotherms of HMS-T and NR/HMS composites.	76
Figure 4.19 Pathway for the formation of NR/HMS composite.	78



Figure 5.1 Weight loss and DTA curves of HMS-SO ₃ H (0.1) and NR/HMS-SO ₃ H (0.1) composite.....	80
Figure 5.2 XRD patterns of pure silica HMS-T, HMS-SO ₃ H, NR/HMS-8 and NR/HMS-SO ₃ H composites.....	82
Figure 5.3 FTIR spectra of the pure silica HMS-T, HMS-SO ₃ H (0.1), NR/HMS-8 and NR/HMS-SO ₃ H (0.1).	85
Figure 5.4 ²⁹ Si MAS NMR spectra of pure silica HMS-T, functionalized HMSs, NR/HMS-8 composite and functionalized NR/HMS composites.....	86
Figure 5.5 N ₂ adsorption-desorption isotherms and BJH pore size distribution of the pure silica HMS-T and functionalized HMSs.....	89
Figure 5.6 N ₂ adsorption-desorption isotherms (a) and BJH pore size distribution (b) of pure silica HMS-T, NR/HMS and functionalized NR/HMS composites.....	91
Figure 5.7 Formation of the hexagonal array of silicate micellar rods and NR in the presence of MPTMS.	92
Figure 5.8 FE-SEM images of HMS-SO ₃ H (0.1) and NR/HMS-SO ₃ H (0.1) composite.....	93
Figure 5.9 STEM images of HMS-SO ₃ H (0.1) and NR/HMS-SO ₃ H (0.1) composite.....	94
Figure 5.10 H ₂ O adsorption-desorption isotherms of pure silica HMS-T, functionalized HMSs, NR/HMS-8 and functionalized NR/HMS composites.....	96
Figure 5.11 Pathway for the formation of NR/HMS-SO ₃ H composite.....	98
Figure 6.1 Esterification of acetic acid with ethanol over acidic mesoporous catalysts.....	100
Figure 6.2 Esterification of octanoic acid with ethanol over acidic mesoporous catalysts.....	103
Figure 6.3 Esterification of lauric acid with ethanol over acidic mesoporous catalysts.....	106
Figure 6.4 Effect of catalyst loading in esterification of octanoic acid with ethanol.....	108
Figure 6.5 Effect of H ₂ O on catalytic esterification of octanoic acid with ethanol over acidic mesoporous catalysts.....	111
Figure 6.6 FTIR spectra of fresh NR/HMS-SO ₃ H and spent NR/HMS-SO ₃ H after 1 st cycle in esterification.....	112
Figure 6.7 Reusability of NR/HMS-SO ₃ H (0.2) in esterification of octanoic acid with ethanol.....	114
Figure A-1 Chromatogram of acetic acid by using <i>n</i> -octane as internal standard.....	128
Figure A-2 Chromatogram of octanoic acid and ethyl octanoate by using <i>n</i> -decane as internal standard.....	129



Figure A-3 Chromatogram of lauric acid and ethyl laurate by using <i>n</i> -decane as internal standard.....	130
Figure A-4 The standard curves of acetic acid by using <i>n</i> -octane as internal standard.	131
Figure A-5 The standard curves of octanoic acid and ethyl octanoate by using <i>n</i> -decane as internal standard.....	132
Figure A-6 The standard curves of lauric acid and ethyl laurate by using <i>n</i> -decane as internal standard.....	133
Figure C-1 N ₂ adsorption-desorption isotherms and BJH pore size distribution of SAC-13.	135



ABBREVIATIONS

BET	=	Brunner-Eller-Teller
BJH	=	Barret-Joyner-Halenda
DDA	=	Dodecylamine
DTA	=	Differential Thermal Analysis
FTIR	=	Fourier Transform Infrared Spectroscopy
GC	=	Gas chromatography
HMS	=	Hexagonal Mesoporous Silica
MPTMS	=	3-mercaptopropyltrimethoxysilane
MAS	=	Magic Angle Spinning
NMR	=	Nuclear Magnetic Resonance
NR	=	Natural Rubber
SEM	=	Scanning Electron Microscope
TEM	=	Transmission Electron Microscopy
TEOS	=	Tetraethylorthosilicate or tetraethoxysilane
TGA	=	Thermo Gravimetric Analysis
THF	=	Tetrahydrofuran
XRD	=	X-Ray Diffraction



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NOMENCLATURE

$^{\circ}\text{C}$	=	Degree Celsius
g	=	Gram
mL	=	Milliliter
min	=	Minute
h	=	Hour
cm^{-1}	=	Unit of wavenumber
a_0	=	The repeat distance between pore centers of the hexagonal structure
d_{100}	=	d-spacing of plane (100)
S_{BET}	=	BET specific surface area ($\text{m}^2 \text{g}^{-1}$)
S_{ext}	=	External surface area ($\text{m}^2 \text{g}^{-1}$)
D_p	=	Pore diameter (nm)
V_p	=	Total pore volume ($\text{cm}^3 \text{g}^{-1}$)
V_p	=	Mesopore volume ($\text{cm}^3 \text{g}^{-1}$)
V_m	=	Monolayer adsorbed volume ($\text{cm}^3 \text{g}^{-1}$)

