

ผลของตัวเร่งปฏิกิริยาเชื้อโรคในชีวนบนตัวรองรับ MCM-41 ชนิดไบมอดูลสำหรับการโคลอเจนรีเรเซ็น
ของเขตลีนกับหนึ่งของที่น

นางสาวศรินลักษณ์ บรรจงธุระการ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาบริหารเครื่อง ภาควิชาบริหารเครื่อง
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2549
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

EFFECT OF BIMODAL MCM-41-SUPPORTED ZIRCONOCENE CATALYST FOR
ETHYLENE / 1-OCTENE COPOLYMERIZATION

Miss Sirinlak Bunchongturakarn

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering

Department of Chemical Engineering

Faculty of Engineering

Chulalongkorn University

Academic year 2006

Copyright of Chulalongkorn University

490748

Thesis Title EFFECT OF BIMODAL MCM-41-SUPPORTED
 ZIRCONOCENE CATALYST FOR ETHYLENE / 1-OCTENE
 COPOLYMERIZATION

By Miss Sirinlak Bunchongturakarn

Field of Study Chemical Engineering

Thesis Advisor Bunjerd Jongsomjit, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial
Fulfillment of the Requirements for the Master's Degree

Direk Lavansiri Dean of the Faculty of Engineering
(Professor Direk Lavansiri, Ph.D.)

THESIS COMMITTEE

Piyasan Praserthdam Chairman
(Professor Piyasan Praserthdam, Dr.Ing.)

Bunjerd Jongsomjit Thesis Advisor
(Assistant Professor Bunjerd Jongsomjit, Ph.D.)

ML Supakanok Thongyai Member
(Associate Professor ML. Supakanok Thongyai, Ph.D.)

M. Phisalaphong Member
(Assistant Professor Muenduen Phisalaphong, Ph.D.)

N. Intaragamjon Member
(Nawaporn Intaragamjon, D.Eng.)

ศิรินลักษณ์ บรรจงธุระการ: ผลของตัวเร่งปฏิกิริยาเซอร์โคโนชีนบนตัวรองรับ
MCM-41 ชนิดไบมอดอลสำหรับการโคพอลิเมอร์ เชิงของเอทิลีนกับหนึ่งออกทีน
(EFFECT OF BIMODAL MCM-41-SUPPORTED ZIRCONOCENE
CATALYST FOR ETHYLENE /1-OCTENE COPOLYMERIZATION)
อ.ที่ปรึกษา : ผศ.ดร. บรรเจิด งามจิตร, 156 หน้า

ความสนใจในการใช้ตัวเรื่องปฏิกริยาเมทัลโลซีนสำหรับการเกิดพอลิเมอร์ในอุตสาหกรรมพอดี โอลีฟินมีมากขึ้น และสาเหตุนี้อาจทำให้มีการค้นคว้าวิจัยเกี่ยวกับการใช้ตัวเรื่องปฏิกริยาเมทัลโลซีนให้มีประสิทธิภาพ อย่างไรก็ตามระบบตัวเรื่องปฏิกริยาเมทัลโลซีนแบบเอกพันธ์มีข้อเสียอย่างชัดเจนอยู่สองข้อคือ ไม่สามารถควบคุมโครงสร้างของพอลิเมอร์และเกิดปัญหาการสูญเสียพอลิเมอร์ที่สังเคราะห์ได้เนื่องจากการติดอยู่ข้างถังปฏิกรณ์ ดังนั้นวิธีการอันหนึ่งที่จะปรับปรุงตัวเรื่องปฏิกริยาเมทัลโลซีนเพื่อแก้ปัญหาดังกล่าว สามารถทำได้โดยการนำสารประกอบแมทัลโลซีนมาเข้าด้วยกันด้วยวิธีการรับฟัง สำหรับงานวิจัยในครั้งนี้จะมุ่งเน้นการพัฒนาและปรับปรุงตัวเรื่องปฏิกริยาเมทัลโลซีนที่มีตัวรองรับโดยเลือกใช้ตัวรองรับ MCM-41 ที่มีโครงสร้างของรูพรุนต่างกัน นั่นคือ โครงสร้างของรูพรุนแบบบูนิ monocotol และไบมอเดล โดยจะแบ่งการศึกษาออกเป็น 2 ส่วน ในส่วนแรกจะทำการศึกษาผลของตัวเรื่องปฏิกริยาเซอร์โคลโนเซ็นบนตัวรองรับ MCM-41 ที่มีโครงสร้างของรูพรุนต่างกันในการเตรียมปฏิกริยาโดย พอลิเมอร์ไตรีเซียนของเอทิลีนกับหนึ่งออกทีน และการในส่วนที่สองจะทำการศึกษาผลของโคลโนโนเมอร์ที่ใช้ในการเตรียมปฏิกริยาโดยพอลิเมอร์ไตรีเซียนของเอทิลีนแอลฟ่าโอลีฟินนั้นคือ 1-เอกซีน และ 1-ಡอกซีน ซึ่งพบว่าในปฏิกริยาการโดยพอลิเมอร์ไตรีเซียนของเอทิลีน/1-ออกทีน และ เอทิลีน/1-ಡอกซีน โดยใช้ตัวรองรับ MCM-41 ที่มีโครงสร้างแบบไบมอเดลที่ถูกปรับปรุงด้วยคราฟโนดิฟายเมทิกโลโซลูมินอกเซน จะให้ค่าความว่องไวในการเกิดปฏิกริยาสูงกว่าการใช้ตัวรองรับ MCM-41 ที่มีโครงสร้างแบบบูนิมอเดล ในขณะที่ปฏิกริยาการโดยพอลิเมอร์ไตรีเซียนของเอทิลีน/1-เอกซีนโดยใช้ตัวรองรับ MCM-41 ที่มีโครงสร้างแบบไบมอเดลจะให้ค่าความว่องไวในการเกิดปฏิกริยาต่ำกว่าบูนิมอเดล และในงานวิจัยนี้ได้มีการศึกษาคุณสมบัติอื่นๆ ของโดยพอลิเมอร์ เช่น มวลโมเลกุล อุณหภูมิหลอมเหลว อีกค้วบ

ภาควิชา..... วิศวกรรมเคมี..... ลายมือชื่อนักศึกษา.....
สาขาวิชา..... วิศวกรรมเคมี..... ลายมือชื่ออาจารย์ที่ปรึกษา.....
ปีการศึกษา..... 2549.....

##4870488021 : MAJOR CHEMICAL ENGINEERING

KEY WORD : SUPPORTED METALLOCENE CATALYST / COPOLYMERIZATION
OF ETHYLENE/1-OCTENE / ZIRCONOCENE

SIRINLAK BUNCHONGTURAKARN : EFFECT OF BIMODAL MCM-41-SUPPORTED ZIRCONOCENE CATALYST FOR ETHYLENE /1-OCTENE COPOLYMERIZATION. THESIS ADVISOR : ASST. PROF. BUNJERD JONGSOMJIT, Ph.D., 156 pp.

Due to the commercial interest of using metallocene catalysts for olefin polymerization, it has led to extensive efforts to utilize metallocene catalysts efficiently. However, it was found that homogeneous metallocene catalysts have two major disadvantages; (i) the lack of morphology control and (ii) reactor fouling. Therefore, binding these metallocene catalysts onto inorganic supports as supported metallocene catalysts can overcome those drawbacks. This research proposed the development and improvement of metallocene catalyst system by using MCM-41 supports with various pore structures such as unimodal and bimodal. This study were divided into two parts. In the first part, impact of various MCM-41 supported zirconocene/dMMAO on the catalytic activities during copolymerization of ethylene/1-octene was investigated. In the second part, the impact of comonomers (1-hexene and 1-decene) employed under the corresponding condition as mentioned in the first part was further investigated. It was found that the bimodal MCM-41-supported zirconocene/dMMAO showed higher activity during copolymerization of ethylene/1-octene and ethylene/1-decene with the bimodal support whereas the lower activity during copolymerization of ethylene/1-hexene was found using the bimodal. The obtained copolymers with various pore structures of MCM-41 supports such as molecular weight , melting temperature were further characterized and discussed.

Department....Chemical Engineering..... Student's signature.....Sirinlak Bunchongturaekarn
Field of study...Chemical Engineering.... Advisor's signature.....Bunjerd Jongsomjit
Academic year.....2006.....

ACKNOWLEDGEMENTS

I would like to express my gratitude to Assistant Professor Dr. Bunjerd Jongsomjit, my advisor, for his invaluable suggestions, encouragement during my study, useful discussions throughout this research. His advice is always worthwhile and without him this work could not be possible.

I cannot miss to thanks Assiatant Professor Dr. Joongjai Panpranot for the assistance with MCM-41 preparation and valuable guidance of this study.

I wish to thank Professor Dr. Piyasan Praserthdam, Associate Professor Dr. ML. Supakanok Thongyai, Assistant Professor Dr. Muenduen Phisalaphong and Dr. Nawaporn Intaragamjon as a chairman and members of this thesis committee for their valuable guidance and revision throughout my thesis, respectively.

Sincere thanks are given to the Thailand Research Fund (TRF), and The Graduate School of Chulalongkorn University (90th Aniversary of Chulalongkorn University) for the financial support of this work

Finally, the author wishes to thank the members of the Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University for friendship and their assistance, who have provided me with support and encouragement throughout this study, please be assured that I thinks of you.

CONTENTS

	Page
ABSTRACT (IN THAI)	iv
ABSTRACT (IN ENGLISH).....	v
ACKNOWLEDGMENTS.....	vi
CONTENTS.....	vii
LIST OF TABLES.....	xi
LIST OF FIGURES.....	xii
CHAPTER I INTRODUCTION.....	1
1.1 Objective of the Thesis.....	3
1.2 Scope of the Thesis.....	3
CHAPTER II LITERATURE REVIEWS.....	5
2.1 Polymerization of olefins.....	5
2.2 Mechanisms of homogeneous, catalytic olefin polymerization.....	7
2.2.1 Chain transfer - molecular weight and molecular weight distribution.....	8
2.3 Background on Polyolefin Catalysts	11
2.3.1 Catalyst Structure.....	11
2.3.2 Polymerization mechanism.....	14
2.3.3 Cocatalysts.....	17
2.3.4 Catalyst Activity.....	20
2.3.5 Copolymerization.....	21
2.4 Metallocene Catalysts.....	25
2.4.1 Olefin Polymerization with Metallocene Catalysts.....	25
2.4.2 Catalyst Systems for Olefin Polymerization.....	26
2.5 Heterogenous Systems.....	27
2.5.1 Catalyst Chemistry.....	28
2.5.2 Supporting Methods.....	29
2.5.2.1 Direct Supporting of Inert Material.....	30
2.5.2.2 Supporting Catalyst on Material Treated with Alkyaluminum.....	32
2.5.2.3 Chhemically Anchoring catalyst on Support.....	34

2.5.2.4 Supporting on other Supports.....	37
2.6 Mesoporour material.....	39
2.6.1 MCM-41.....	39
CHAPTER III EXPERIMENTAL.....	41
3.1 Chemicals.....	41
3.2 Equipments.....	42
3.2.1 Cooling System.....	42
3.2.2 Inert Gas Supply.....	42
3.2.3 Magnetic Stirrer and Heater.....	43
3.2.4 Reactor.....	43
3.2.5 Schlenk Line.....	43
3.2.6 Schlenk Tube.....	44
3.2.7 Vacuum Pump.....	45
3.2.8 Polymerization line.....	45
3.3 Characterizing Instruments.....	45
3.3.1 Differential Scanning Calorimetry (DSC).....	45
3.3.2 Gel Permeation Chromatography (GPC).....	46
3.3.3 N ₂ physisorption.....	46
3.3.4 Nuclear Magnetic Rasonance (NMR).....	46
3.3.5 Scanning Electron Microscope (SEM) and Energy dispersive x-ray spectroscopy (EDX).....	46
3.3.6 Thermogravimetric analysis (TGA).....	46
3.3.7 Raman spectroscopy.....	47
3.3.8 X-ray diffraction (XRD).....	47
3.3.9 X-ray photoelectron spectroscopy (XPS).....	47
3.4 Supporting Procedure.....	47
3.4.1 Preparation of dried-MMAO (dMMAO).....	47
3.4.2 Preparation of various MCM-41 supports.....	48
3.4.3 Preparation of MCM-41-supported dMMAO.....	48
3.5 Ethylene and α -olefins Copolymerization Procedure.....	49
3.6 Research methodology.....	50
3.7 Characterization of supports and catalyst precursor	51

3.7.1 Pore size and pore size distribution	51
3.7.2 Morphology and elemental distribution	51
3.7.3 The Amount of Al on Catalyst Precursors.....	51
3.8 Characterization of Ethylene/ α -olefins Copolymer products.....	51
3.8.1 Chemical Structure Determination.....	51
3.8.2 Melting Temperature (T_m).....	51
3.8.3 Average Molecular Weight and Molecule Weight Distribution.....	51
CHAPTER IV RESULTS AND DISCUSSIONS.....	53
4.1 Characterization of supports and catalyst precursors.....	53
4.1.1 Characterization of supports with N_2 physisorption.....	53
4.1.2 Characterization of supports and catalyst precursors with X-ray diffraction (XRD).....	54
4.1.3 Characterization of supports and catalyst precursors with Raman spectroscopy.....	55
4.1.4 Characterization of supports and catalyst precursors with X-ray photoelectron spectroscopy (XPS).....	56
4.1.5 Characterization of supports and catalyst precursors with Scanning electron microscope SEM) and energy dispersive X-ray spectroscopy (EDX).....	57
4.2 Effect of various MCM-41 supports in ethylene/1-octene Copolymerization system.....	59
4.2.1 The effect of various MCM-41 supports on the catalytic activity.....	59
4.2.2 The effect of various MCM-41 supports on the molecular weight of copolymers.....	62
4.2.3 The effect of various MCM-41 supports on the melting temperatures of copolymers.....	62
4.2.4 The effect of various MCM-41 supports on the incorporation of copolymers.....	63
4.3 Effect of various MCM-41 supports with different comonomers.....	64
4.3.1 The effect of various MCM-41 supports with different comonomers on the catalytic activity.....	64

4.3.2 The effect of various MCM-41 supports with different comonomers on the molecular weight of copolymers.....	66
4.3.3 The Effect of various MCM-41 supports on the melting temperatures of copolymers with different comonomers.....	67
4.3.4 The effect of various MCM-41 supports on incorporation of copolymers the with different comonomers	68
CHAPTER V CONCLUSION & RECOMMENDATIONS	71
5.1 Conclusion.....	71
5.2 Recommendations	71
REFERENCES.....	72
APPENDICES.....	81
APPENDIX A.....	82
APPENDIX B.....	89
APPENDIX C.....	96
APPENDIX D.....	103
APPENDIX E.....	107
APPENDIX F.....	118
APPENDIX G.....	121
APPENDIX H.....	126
VITA.....	156

LIST OF TABLES

Table	Page
2.1 Representative examples of metallocenes.....	12
4.1 BET surface area and average pore diameter of various MCM-41 Supports Catalytic activity of different ratio mixed oxide in ethylene/1-octene.....	53
4.2 XPS results for different supports.....	57
4.3 Catalytic activities of various MCM-41-supported dMMAO with zirconocene catalyst during ethylene/1-octene copolymerization.....	60
4.4 Molar weight (MW) and molecular weight distribution (MWD) of polymers obtained from various MCM-41-supported dMMAO with zirconocene catalyst.....	62
4.5 Melting temperatures % crystallinity of copolymers obtained various MCM-41 supports.....	63
4.6 ^{13}C NMR analysis of ethylene/1-octenecopolymer.....	64
4.7 Reactivity ratios of ethylene and 1-octene monomer.....	64
4.8 Catalytic activities of various MCM-41-supported dMMAO with zirconocene catalyst during ethylene/ α -olefin copolymerization.....	65
4.9 Molar weight (MW) and molecular weight distribution (MWD) of copolymers obtained from various MCM-41-supported dMMAO with zirconocene catalyst.....	66
4.10 Melting temperatures % crystallinity of copolymers using various MCM-41 supports with different comonomer.....	67
4.11 ^{13}C NMR analysis of ethylene/ α -olefins copolymer.....	69
4.12 Reactivity ratios of ethylene and α -olefin monomers.....	69

LIST OF FIGURES

Figure	page
2.1 Examples of polyethenes: LDPE, HDPE and LLDPE (copolymer of ethene and 1-hexene).....	6
2.2 Common polymer tacticities.....	6
2.3 Scheme of migratory insertion mechanism, in which the metal-bound alkyl group migrates to the alkene.....	8
2.4 Scheme of termination reactions by β-H, β-CH₃ and H-transfer to monomer.....	10
2.5 Scheme of chain transfer to aluminum.....	10
2.6 Molecular structure of metallocene.....	11
2.7 Some of zirconocene catalyst structure.....	12
2.8 Scheme of the different metallocene complex Figure structure.....	13
2.9 Cossee mechanism for Ziegler-Natta olefin polymerization.....	14
2.10 The propagation step according to the trigger mechanism.....	15
2.11 Propagation mechanism in polymerization.....	15
2.12 Chain transfer via β-H elimination.....	16
2.13 Chain transfer via β-CH₃ elimination.....	16
2.14 Chain transfer to aluminum.....	17
2.15 Chain transfer to monomer.....	17
2.16 Chain transfer to hydrogen.....	17
2.17 Early structure models of MAO.....	18
2.18 Representation of MAO showing the substitution of one bridging methylgroup by X ligand extracted from racEt(Ind)₂ZrCl₂ (X = Cl, NMe₂, CH₂Ph).....	19
2.19 Structure of Et[Ind]₂ZrCl₂ supported on silica.....	30
2.20 Structure of Et[Ind]₂ZrCl₂ supported on alumina.....	31
2.21 Reaction of silica and metallocene during catalyst supporting.....	31
2.22 Alkylation of supported metallocene MAO.....	32
2.23 Effect of surface hydroxyl groups on ionic metallocene catalysts.....	33

Figure	page
2.24 Structure of some silica supported metallocene catalysts.....	35
2.25 Mechanism for supporting metallocene catalysts on silica using Spacer molecules.....	36
2.26 Modification of silica with Cp(CH ₂) ₃ Si(OCH ₂ CH ₃) ₃ and preparation of supported metallocene catalyst.....	37
3.1 Inert gas supply system.....	43
3.2 Schlenk. line.....	44
3.3 Schlenk tube.....	44
3.4 Diagram of system in slurry phase polymerization.....	45
4.1 Pore size distribution of various MCM-41 supports.....	54
4.2 XRD patterns of various MCM-41 supports.....	55
4.3 Raman spectra of various MCM-41 supports.....	56
4.4 SEM micrographs of various MCM-41 supports.....	58
4.5 EDX mapping of various MCM-41 supports after dMMAO impregnation.....	59
4.6 TGA profiles of [Al] _{dMMAO} on various MCM-41 supports.....	61
A-1 GPC curve of ethylene/1-hexene copolymer produce with homogenous.....	83
A-2 GPC curve of ethylene/1-hexene copolymer produce with MCM41(UMD).....	83
A-3 GPC curve of ethylene/1-hexene copolymer produce with MCM-41(BMD1)	84
A-4 GPC curve of ethylene/1-hexene copolymer produce with MCM-41(BMD2)	84
A-5 GPC curve of ethylene/1-octene copolymer produce with homogenous.....	85
A-6 GPC curve of ethylene/1-octene copolymer produce with MCM41(UMD).....	85

Figure	page
A-7 GPC curve of ethylene/1-octene copolymer produce with MCM-41(BMD1).....	86
A-8 GPC curve of ethylene/1-octene copolymer produce with MCM-41(BMD2).....	86
A-9 GPC curve of ethylene/1-decene copolymer produce with homogenous.....	87
A-10 GPC curve of ethylene/1-decene copolymer produce with MCM41(UMD).....	87
A-11 GPC curve of ethylene/1-decene copolymer produce with MCM-41(BMD1).....	88
A-12 GPC curve of ethylene/1-decene copolymer produce with MCM-41(BMD2).....	88
B-1 DSC curve of ethylene/1-hexene copolymer produce with homogenous.....	90
B-2 DSC curve of ethylene/1-hexene copolymer produce with MCM-41(UMD).....	90
B-3 DSC curve of ethylene/1-hexene copolymer produce with MCM-41(BMD1).....	91
B-4 DSC curve of ethylene/1-hexene copolymer produce with MCM-41(BMD2).....	91
B-5 DSC curve of ethylene/1-octene copolymer produce with homogenous.....	92
B-6 DSC curve of ethylene/1-octene copolymer produce with MCM-41(UMD).....	92
B-7 DSC curve of ethylene/1-octene copolymer produce with MCM-41(BMD1).....	93
B-8 DSC curve of ethylene/1-octene copolymer produce with MCM-41(BMD2).....	93
B-9 DSC curve of ethylene/1-decene copolymer produce with homogenous.....	94

Figure	page
B-10 DSC curve of ethylene/1-decene copolymer produce with MCM-41(UMD).....	94
B-11 DSC curve of ethylene/1-decene copolymer produce with MCM-41(BMD1).....	95
B-12 DSC curve of ethylene/1-decene copolymer produce with MCM-41(BMD2).....	95
C-1 ^{13}C -NMR spectrum of ethylene/1-hexene copolymer produce with homogenous.....	97
C-2 ^{13}C -NMR spectrum of ethylene/1-hexene copolymer produce with MCM-41(UMD).....	97
C-3 ^{13}C -NMR spectrum of ethylene/1-hexene copolymer produce with MCM-41(BMD1).....	98
C-4 ^{13}C -NMR spectrum of ethylene/1-hexene copolymer produce with MCM-41(BMD2).....	98
C-5 ^{13}C -NMR spectrum of ethylene/1-octene copolymer produce with homogenous.....	99
C-6 ^{13}C -NMR spectrum of ethylene/1-octene copolymer produce with MCM-41(UMD).....	99
C-7 ^{13}C -NMR spectrum of ethylene/1-octene copolymer produce with MCM-41(BMD1).....	100
C-8 ^{13}C -NMR spectrum of ethylene/1-octene copolymer produce with MCM-41(BMD2).....	100
C-9 ^{13}C -NMR spectrum of ethylene/1-decene copolymer produce with homogenous.....	101
C-10 ^{13}C -NMR spectrum of ethylene/1-decene copolymer produce with MCM-41(UMD).....	101
C-11 ^{13}C -NMR spectrum of ethylene/1-decene copolymer produce with MCM-41(BMD1).....	102
C-12 ^{13}C -NMR spectrum of ethylene/1-decene copolymer produce with MCM-41(BMD2).....	102

Figure	page
D-1 The TGA profiles MCM-41(UMD) supports.....	104
D-2 The TGA profiles MCM-41(BMD1) supports.....	104
D-3 The TGA profiles MCM-41(BMD2) supports.....	105
D-4 The TGA profiles of $[Al]_{dMMAO}$ on MCM-41(UMD) supports.....	105
D-5 The TGA profiles of $[Al]_{dMMAO}$ on MCM-41(BMD1) supports.....	106
D-6 The TGA profiles of $[Al]_{dMMAO}$ on MCM-41(BMD2) supports.....	106
E-1 The typical XPS profile for dMMAO exhibited the identical binding energy (BE) of Al 2p.....	108
E-2 The typical XPS profile for dMMAO exhibited the identical binding energy (BE) of Al 2s.....	108
E-3 The typical XPS profile for dMMAO exhibited the identical binding energy (BE) of C 1s.....	109
E-4 The typical XPS profile for dMMAO exhibited the identical binding energy (BE) of O 1s.....	109
E-5 The typical XPS profile for MCM-41(UMD)-supported dMMAO exhibited the identical binding energy (BE) of Al 2p.....	110
E-6 The typical XPS profile for MCM-41(UMD)-supported dMMAO exhibited the identical binding energy (BE) of Al 2s.....	110
E-7 The typical XPS profile for MCM-41(UMD)-supported dMMAO exhibited the identical binding energy (BE) of C 1s.....	111
E-8 The typical XPS profile for MCM-41(UMD)-supported dMMAO exhibited the identical binding energy (BE) of O 1s.....	111
E-9 The typical XPS profile for MCM-41(UMD)-supported dMMAO exhibited the identical binding energy (BE) of Si 2p.....	112
E-10 The typical XPS profile for MCM-41(BMD1)-supported dMMAO exhibited the identical binding energy (BE) of Al 2p.....	112
E-11 The typical XPS profile for MCM-41(BMD1)-supported dMMAO exhibited the identical binding energy (BE) of Al 2s.....	113
E-12 The typical XPS profile for MCM-41(BMD1)-supported dMMAO exhibited the identical binding energy (BE) of C 1s.....	113

Figure	page
E-13 The typical XPS profile for MCM-41(BMD1)-supported dMMAO exhibited the identical binding energy (BE) of O 1s	114
E-14 The typical XPS profile for MCM-41(BMD1)-supported dMMAO exhibited the identical binding energy (BE) of Si 2p.....	114
E-15 The typical XPS profile for MCM-41(BMD2)-supported dMMAO exhibited the identical binding energy (BE) of Al 2p.....	115
E-16 The typical XPS profile for MCM-41(BMD2)-supported dMMAO exhibited the identical binding energy (BE) of Al 2s.....	115
E-17 The typical XPS profile for MCM-41(BMD2)-supported dMMAO exhibited the identical binding energy (BE) of C 1s.....	116
E-18 The typical XPS profile for MCM-41(BMD2)-supported dMMAO exhibited the identical binding energy (BE) of O 1s.....	116
E-19 The typical XPS profile for MCM-41(BMD2)-supported dMMAO exhibited the identical binding energy (BE) of Si 2p.....	117
F-1 EDX profiles of $[Al]_{dMMAO}$ on MCM-41(UMD) supports.....	119
F-2 EDX profiles of $[Al]_{dMMAO}$ on MCM-41(BMD1) supports.....	119
F-3 EDX profiles of $[Al]_{dMMAO}$ on MCM-41(BMD2) supports.....	120