



College of Women's for Arts,  
Science and Education  
Ain Shams University

# **Mesoporous materials: synthesis, characterization and possible applications**

**Thesis Submitted**

*By*

**Mohamed Ahmad Hassan Betiha**

**(M. Sc., 2007)**

Assistance Researcher

Petroleum Reefing Division

Egyptian Petroleum Institute

(EPRI)

**For Doctor of Philosophy**

**(Chemistry)**

**Chemistry Department**

**College of Women's for Arts, Science and Education  
Ain Shams University**

**2010**



**This thesis has not submitted for any degree at this  
or any other university.**

Mohamed Ahmad Hassan Betiha



## **Ph.D. Thesis**

**Name:** Mohamed Ahmad Hassan Betiha

**Title:** Mesoporous materials: synthesis, characterization  
and possible applications

**Degree:** Doctor of Philosophy in Chemistry

### **Supervised by**

**1. Dr. Essam Mohamed Ezzo**

Professor of physical chemistry, Faculty of Girls

Ain Shams University

**2. Dr. Mohamed Fathy Monoufy**

Professor of petroleum refining (EPRI)

**3. Dr. Maged Samir Ghattus**

Professor of catalysis (EPRI)

**4. Dr. Hussien Abd Elazziz El-said**

Researcher (EPRI)



## **Approval sheet**

Ph.D. Thesis

Entitled

**Mesoporous materials: synthesis, characterization and  
possible applications**

**Approved**

**Signature**

Dr. Essam Mohamed Ezzo

Dr. Mohamed Fathy Monoufy

Dr. Maged Samir Ghattus

Dr. Hussien Abd Elazziz El-said

Date   /   /2010



## ABSTRACT

The formation of liquid-crystal-like arrays made up of molecular complex formed between molecular inorganic species (TEOS) and neutral, cationic, non-ionic, and linear anionic surfactants are convenient approach for the synthesis of mesostructure materials. Mesoporous silicates structure with controlled pore sizes (2- 17 nm) were successfully synthesized from tetraethoxysilane (TEOS) or sodium silicate using previous organic materials mixture as template. By adjusting the initial molar ratio of surfactants/TEOS, pore sizes of the final disordered or ordered hexagonal mesoporous silicas could be precisely tuned in the ranges of 2-17 nm. Incorporation of  $\text{Al}^{3+}$  into silica framework using direct method has been successfully prepared in high acidic medium.

Results show that the materials have high surface area, narrow pore size distribution and high total pore volume. The mesoporous materials were characterized and confirmed by using X-ray,  $\text{N}_2$  sorption, SEM, TEM, AFM, FTIR, pyridine-FTIR, TGA, DSC, TPR and  $\text{NH}_3$ -TPD.

The activity of different supports and catalysts were carried out on paraffinic wax, cumene cracking, n- heptane, n-hexane and cyclohexane hydroconversion, which gave great catalytic activities toward catalytic cracking, hydrocracking and hydroisomerization.

**Key words:** mesoporous materials; Al-mesoporous materials; HMS; AlHMS; SBA-15; AlSBA-15; MCM-41; AlMCM-41; anionic surfactants; paraffinic wax cracking; cumene cracking; isomerization.



## SUMMARY

Nanoporous materials have become more and more important in either science or technology. They can be grouped into three classes based on their pore diameter ( $d$ ): microporous,  $d < 2.0$  nm; mesoporous,  $2.0 < d < 50$  nm; macroporous,  $d > 50$  nm. Among them, mesoporous materials have attracted more attention due to tailoring ability of the pore structure over a wide range, and the potential applications in catalysis.

Designing a heterogeneous catalyst involves both the proper control of the surface chemistry and a rigorous control of the surface geometry at the micro-, meso- and macroscales. This is because high surface areas or high active phase dispersions as well as fast mass transfer of the reactants that are required from any active catalyst.

Four groups of ordered and disordered hexagonal structural mesoporous molecular sieves Si-HMS, Si-SBA-15, Si-MCM-41, Si-MFG and have been prepared and successfully controlled by optimizing the gel compositions using tetraethylorthosilicate and sodium silicate have been used as silica sources while aluminium isopropoxide is used as alumina source. In addition, decylamine, nonionic (poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) triblock copolymer Pluronic P123 ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ , Mwt = 5800), cationic cetyltrimethylammonium bromide, and commercial alkylbenzene sulphonic acid have been used as structure directing agents (templates).

HMS molecular sieve has been synthesized via hydrogen bonding self-assembly in microemulsion of ethanol/water, dioxane/water and benzene/water mixtures in order to obtain the hexagonal mesoporous materials. Homogeneous solutions of the structure directing surfactant in water/ethanol and water/dioxin co-solvents completely dissolve the



surfactant and allow for the formation of HMS derivatives with high textural mesoporosity. The pore size distribution and particle size of the final disordered hexagonal mesoporous silicas could be precisely tuned depending on nature of solvent and TEOS/DA ratios.

ALSBA-15 materials with different  $n\text{Si}/n\text{Al}$  ratio have been synthesized by simply adjusting the molar water to hydrochloric acid ratio ( $n\text{H}_2\text{O}/n\text{HCl}$ ).

MCM-41 and AlMCM-41 have been synthesized from low cost sodium silicate and sodium aluminate via cationic templating. Substitution of high cost silica sources by low cost sodium silicate is the first target of this work.

Large-pore mesoporous silica and silica-alumina with 3D wormhole framework structures (denoted as MFG) have been prepared using novel and inexpensive commercially available linear alkylbenzene sulphonic without using both acid catalyzed hydrolysis of silica source pathway and swelling agents for core micelle. Substitution of high cost templates by inexpensive, low toxicity and locally commercial is the second target of this work.

Direct incorporation of heteroatoms ( $\text{Al}^{3+}$ ) has a negative effect on structure ordering, total pore volume and pore size distribution. The negative effect is directly proportion to amount of  $\text{Al}^{3+}$  incorporated. On the other hand, incorporation of  $\text{Al}^{3+}$  has a positive effect on enhancement of acidity, dispersion of  $\text{NiMoO}_3$ . The acidity and dispersion of active phases is directly proportional to amount  $\text{Al}^{3+}$ . The loading of Mo in highly acidic medium preserve the mesostructure ordering. The preservation of structure ordering after Mo loading is the third target of this work.



The physical and chemical compositions of the prepared materials have been characterized by adequate analysis that proves the physical and chemical composition is identical for mesoporous materials.

The high performance catalytic activity of mesoporous material have been studies on different petroleum fraction such as, wax cracking, cumene cracking and hydroconversion of n-heptane, n-hexane and cyclohexane.



## ACKNOWLEDGEMENTS

I am most grateful to **Almighty God, the Most Gracious and Most Merciful**, for supporting me to complete my thesis.

Thanks to **Dr. Essam M. Ezzo**, professor of inorganic chemistry, Chemistry Department, Faculty of women's for Arts, Science and Education, Ain Shams University, for his thoughtful guidance and support throughout my research.

I would like to express my deep and sincere thanks to my supervisor, **Dr. Mohammed F. Menoufy**, professor of petroleum refining, Refining Division, Egyptian Petroleum Research Institute (EPRI), for his helpful guidance, inspiration during his continuity and suggestions for completion of this thesis. In addition, I am grateful for his time and efforts taken by him to read and correct the written materials.

Thanks also go to my thesis supervisor **Dr. Maged S. Ghattus**, professor of catalysis, Catalysis Division, Egyptian Petroleum Research Institute (EPRI), for his advice, which are beneficial to perform my work.

My sincere thanks go to **Dr. Ahmad M. Al-Sabagh**, Head of the Egyptian Petroleum Research Institute (EPRI) and professor of physical chemistry for his helpful guidance, advice and critical comments.

My appreciation also go to all my colleagues and friends in EPRI for their helpfully cooperation in different types of analysis.

Last but the most important, I would like to express my deepest gratitude and appreciation to my wife (God's special gift to me) my daughters, my son and other family members for their enduring love, encouragement and support during the past years.



*Mohamed A. Betiha*

*Dedicated*

*To the two most important people in the world, my parents Ahmad and Fatma, who sacrificing their lives to provide me with everything that I wished.*

*They have instilled in me the qualities that have brought me to where I am today.*

*”رب ارحمهما كما ربياني صغير“*

*"My Lord! Bestow on them your Mercy even as they cherished me in childhood. " (The Holly Quran, Chapter 17, Verse 24)*



## CONTENTS

Pages

1. <b>INTRODUCTION</b> .....	1
1.1. General background.....	2
1.2. Chemistry of silicates/aluminosilicates in an Alkaline and acidic Aqueous Solution.....	4
1.3. Synthesis of mesoporous materials sieves (MMS).....	5
1.3.1. Synthesis of Mobil composite material (MCM-41).....	6
1.3.2. Synthesis of hexagonal mesoporous silica (HMS).....	6
1.3.3. Synthesis of Santa Barbara Amorphous-15 (SBA-15).....	6
1.3.4. Synthesis of acidic MMS .....	7
1.4. Formation mechanism of mesoporous silica.....	13
1.4.1. Liquid crystal templating (LCT) mechanism..	14
1.4.2. Charge density matching.....	16
1.4.3. Folded sheet mechanism.....	16
1.4.4. Silicotropic liquid crystals.....	18
1.4.5. Generalized liquid crystal templating mechanism.....	18
1.5. Control of crystal size, pore size and morphology....	21
1.5.1. Effect of swelling agent.....	23
1.5.2. Effect of temperature.....	23
1.6. Catalytic application.....	25



1.7.	Aim of the work.....	31
<b>2.</b>	<b>MATERIALS AND METHODS.....</b>	<b>32</b>
2.1.	Chemicals.....	32
2.2.	Materials synthesis.....	33
2.2.1	Synthesis of CTAB.....	33
2.2.2.	Synthesis of nanoporous materials.....	34
2.2.2.1.	Synthesis of Si-HMS.....	34
2.2.2.2.	Synthesis of AlHMS.....	36
2.2.2.3.	Synthesis of Si-SBA-15.....	36
2.2.2.4.	Synthesis AlSBA-15.....	36
2.2.2.5.	Synthesis of Si-MCM-41.....	37
2.2.2.6.	Synthesis of AlMCM-41.....	37
2.2.2.6.1.	Synthesis of H-MCM-41.....	38
2.2.2.7.	Synthesis Si-MFG-x.....	38
2.2.2.8.	Synthesis AlMFG-8.....	39
2.3.	Preparation of different catalysts .....	40
2.3.1.	Preparation of NiMo/(AlHMS, SBA-15, AlSBA-15, MFG-8 and AlMFG-8) catalyst.....	40
2.3.2	Preparation of CoMo-MCM-41 catalyst... ..	40
2.3.3.	Preparation of Pt/(MFG-8 and AlMFG-8) catalyst.....	41
2.3.3.1	Hydrochlorination of Pt/catalysts.....	41
2.4.	Analytical methods.....	42
2.4.1.	X-Ray diffraction.....	42



2.4.1.1.	Theory.....	42
2.4.1.2.	Bragg diffraction.....	43
2.4.2.	N <sub>2</sub> Sorption isotherms.....	46
2.4.2.1	N <sub>2</sub> sorption in mesoporous materials.....	49
2.5.	Catalytic test reactions.....	52
2.6.	Instruments.....	53
<b>3.</b>	<b>RESULTS AND DISCUSSION.....</b>	<b>61</b>
3.1.	Synthesis.....	61
3.1.1.	Synthesis of CTAB.....	61
3.1.2.	Synthesis of HMS.....	61
3.1.3.	Synthesis of SBA-15 and AlSBA-15.....	63
3.1.4.	Synthesis of MCM-41 and AlMCM-41...	65
3.1.5.	Synthesis of MFG and AlMFG.....	66
3.1.5.1.	Packing constraint considerations.....	67
3.1.5.2.	The formation mechanism.....	69
3.1.6.	Synthesis of purely Si-mesoporous and Al-mesoporous materials.....	70
3.1.7.	Preparation of NiMoO <sub>3</sub> -catalysts.....	71
3.2.	Characterization.....	72
3.2.1.	XRD analysis.....	72
3.2.1.1	XRD of HMS.....	72
3.2.1.2.	XRD analysis of pure AlHMS, NiMoO <sub>3</sub> /AlHMS-7&NiMoO <sub>3</sub> /AlHMS-14..	79
3.2.1.3.	XRD analysis of pure SBA-15, AlSBA-15(x), NiMoO <sub>3</sub> /SBA-15 and	



	NiMoO <sub>3</sub> /AlSBA-15(7).....	84
3.2.1.4.	XRD analysis of pure MCM-41, AlMCM-41(x), CoMoO <sub>3</sub> /MCM-41 and CoMoO <sub>3</sub> /AlMCM-41(7).....	89
3.2.1.5.	XRD analysis of pure MFG, AlMFG(x), NiMoO <sub>3</sub> /MFG and NiMoO <sub>3</sub> /MFG(x).....	93
3.2.1.6.	XRD analysis of pure Pt/MFG-8 and Pt/AlMFG-8(x).....	96
3.2.2.	N <sub>2</sub> Sorption isotherms.....	101
3.2.2.1.	N <sub>2</sub> sorption isotherms of HMS .....	101
3.2.2.2.	N <sub>2</sub> sorption isotherms of AlHMS-7B, AlHMS7I, AlHMS-14I, NiMoO <sub>3</sub> /AlHMS-7 and NiMoO <sub>3</sub> /AlHMS-14.....	109
3.2.2.3.	N <sub>2</sub> sorption isotherms of SBA-15, AlSBA-15(x), NiMoO <sub>3</sub> /SBA-15(7) and NiMoO <sub>3</sub> /AlSBA-15(7).....	116
3.2.2.4.	N <sub>2</sub> sorption isotherms of MCM-41, AlMCM-41(7&14), CoMoO <sub>3</sub> /MCM-41 and CoMoO <sub>3</sub> /AlMCM-41(7).....	121
3.2.2.5.	N <sub>2</sub> sorption isotherms of MFG, AlMFG-8(x) and CSi/Al.....	126
3.3.	Fourier transform infrared spectroscopy.....	134
3.3.1.	FT-IR of pure supports.....	134
3.3.2.	FT-IR of NiMo supported catalysts.....	136
3.4.	Surface acidity of AlMMS material.....	144
3.4.1.	Generation of active sites in Al-mesoporous	144



materials.....	
3.4.2. Surface acidity of the supports determined by pyridine-FTIR.....	148
3.4.3. Surface acidity of the supports determined by NH <sub>3</sub> -TPD.....	152
3.4.4. Surface acidity of the supports determined by Pyr-TGA .....	154
3.5. Temperature programmed reduction (TPR) analysis..	160
3.6. Morphology studies.....	169
3.6.1. SEM studies.....	169
3.6.2. AFM studies.....	171
3.6.3. TEM studies.....	187
3.7. Catalytic activity tests.....	199
3.7.1. Catalytic activity of supports.....	199
3.7.1.1. Cumene hydrocracking.....	199
3.7.1.2. Paraffinic wax cracking.....	206
3.7.2. Catalytic activity of metal loaded supports.	215
3.7.2.1. Hydroconversion of n-heptane.....	216
3.7.2.2. Hydroconversion of n-hexane.....	226
3.7.2.3. Hydroconversion of cyclohexane.....	233
<b>4. CONCLUSIONS.....</b>	<b>239</b>
<b>REFERENCES.....</b>	<b>242</b>
الملخص العربي	