

***"SYNTHESIS OF MESOPOROUS MOLECULAR SIEVES
AND THEIR USE IN PARAFFINS
HYDROCONVERSIONS"***

A Thesis Submitted

***For the M. Sc. Degree (Chemistry)
(In Partial fulfillment)***

To

***The Department of Chemistry
Faculty of Science
Cairo University***

By

Samar Said Muhammed Abdelaal

۲۰۰۹

بسم الله الرحمن الرحيم

"يرفع الله الذين آمنوا منكم والذين أوتوا العلم درجات

والله بما تعملون خبير"

صدق الله العظيم

DEDICATED

TO

MY Mother

ACKNOWLEDGMENT

*All gratitude is due to **ALLAH** who guided and aided me to bring forth to light this thesis.*

I would like to express my gratitude to Prof. Dr. Fathy M. Abdelrazek, Professor of organic Chemistry Faculty of Science, Cairo University for his supervision and helpful suggestions.

I wish to express my sincere appreciation to Prof. Dr. Maged S. Ghattas, Professor of Catalysis, Refining Division, Egyptian Petroleum Research Institute for suggesting the research problem, encouragement, his continuous supervision and valuable discussion that made this work possible outcome in this form.

I would like to express my appreciation to Dr. H. M. Gobara, research of Catalysis, Refining Division, Egyptian Petroleum Research Institute for her careful guidance.

Also, I wish to express my sincere gratitude to International Center for Materials Nanoarchitectonics, National Institute for Materials Science group

Finally, I would like to express my sincere appreciation to the one who helped make possible the completion of this work and his valuable help. So really thanks "A .V".

APPROVAL SHEET FOR SUBMISSION

Title of the M. Sc. Thesis:

"Synthesis of mesoporous molecular sieves and their use in paraffins hydroconversions"

Name of the candidate: Samar Said Muhammed Abdelaal

This thesis has been approved for submission by the supervisors:-

١. **Prof. Dr. Fathy .M.Abdelrazek**

Signature:

٢. **Prof. Dr. Maged S. Ghattas**

Signature:

Prof. Dr. Mohamed Mohamed Shoukry

**Chairman,
Department of Chemistry,
Faculty of Science,
Cairo University.**

ABSTRACT

Name: Samar Said Muhammed Abdelaal

Title of thesis: "Synthesis of mesoporous molecular sieves and their use in paraffins hydroconversions".

Degree: M.sc., Faculty of Science, Cairo University, ٢٠٠٩

Nowadays, isomerization of n-paraffins plays an important role in the petroleum industry. Isomerization reaction generally takes place over bifunctional metal /acid catalysts.

Pure siliceous SBA-١٥ and AlSBA-١٥ of different n_{Si}/n_{Al} ratios (٥, ٧ and ١٤) were synthesized by well-known procedures and used as supports for preparation of Ni and Pt catalysts with different percentage. The catalysts were prepared by impregnation technique.

Supports and the prepared catalysts were characterized by X-ray diffraction (XRD), Nitrogen physisorption, Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA). The results showed that by Ni or Pt loading, both SBA-١٥ and AlSBA-١٥ supports preserve their hexagonal porous arrangement. All the samples are thermally stable up to ٦٠٠ °C. BET surface area, pore volume and pore diameter were decreased as the Ni or Pt loading increased, also the intensities of d, ... diffraction peaks were affected.

The catalytic activity and selectivity of the prepared catalysts were studied through the dehydrogenation of cyclohexane and through the hydroconversion (hydroisomerization and hydrocracking) of n-hexane in pulse flow system.

0.6 wt%Pt/SBA-10 and 0.3 wt%Pt/AlSBA-10(0) catalysts were active and selective toward cyclohexane dehydrogenation into benzene. Also the latter one showed high activity for n-hexane isomerization. Whereas Ni/SBA-10 and Ni/AlSBA-10 catalysts showed high activity for cyclohexane and n-hexane hydrocracking.

Keywords: SBA-10; AlSBA-10; Pt catalysts; Ni catalysts; hydroconversion; Dehydrogenation; n-hexane; cyclohexane.

Supervisors:

1. Prof. Dr. Fathy .M. Abdelrazek

2. Prof. Dr. Maged S. Ghattas

Prof. Dr. Mohamed Mohamed Shoukry

Chairman of chemistry Department,
Faculty of science, Cairo University.

CONTENTS

List of Tables.	i
List of Figures.	ii
<u>CHAPTER I</u>	1
(INTRODUCTION)	1
I.1. Porous materials.	1
I.2. Ordered mesoporous molecular sieves.	3
I.3. Behavior of surfactant molecules in an aqueous solution.	5
I.4. Synthesis of ordered mesoporous molecular sieves.	6
I.5. Control of local environment and morphology.	7
I.6. Mesoporous Santa Barbara Amorphous-10 (SBA-10) molecular sieves.	9
I.7. Mechanism of formation of SBA.	10
I.8. The incorporation of aluminum into SBA.	12
I.9. Mechanism of formation of AISBA-10.	14
I.10. Paraffins hydroconversions.	15
I.11. Catalytic application of metal supported SBA-10 and AISBA-10.	17
<u>CHAPTER II</u>	19
(EXPERIMENTAL)	19
II.1. Catalyst preparation.	19
II.1.1. Synthesis of the support.	19
(a) Siliceous SBA-10.	19
(b) AISBA-10 material.	19
II.1.2. Loading of metallic part.	20
(a) Loading of platinum.	20
(b) Loading of nickel.	20
II.2. Catalyst characterization.	21
II.2.1. X-ray diffraction analysis (XRD).	21
II.2.2. Nitrogen physisorption.	21
II.2.3. Thermal Analysis.	22
II.2.4. Catalytic Activity.	22
<u>CHAPTER III</u>	26
(RESULTS AND DISCUSSION)	26
III.1. SBA-10 system (pure silica).	26

III.1.1. X-ray diffraction analysis (XRD).	26
III.1.1.1 Small-angle XRD studies.	26
III.1.1.2. Wide-angle XRD studies.	31
III.1.2.Surface Characteristics.	32
III.1.3.Thermal Analysis.	36
III.1.4.Catalytic Activity.	39
III.1.4.1.Catalytic activity of Pt/SBA-10 catalysts.	39
(A) Cyclohexane conversion.	39
(B) n-hexane conversion.	39
III.1.4.2.Catalytic activity of Ni/SBA-10 catalysts.	42
(A) Cyclohexane conversion.	42
(B) n-hexane conversion.	42
III.2. AlSBA-10 system.	46
III.2.1. X-ray diffraction analysis (XRD).	46
III.2.1.1. Small-angle XRD studies.	46
III.2.1.2.Wide-angle XRD studies.	53
III.2.2. Surface Characteristics.	55
III.2.3.Thermal Analysis.	60
III.2.3.1. Nickel loaded over AlSBA.	66
III.2.3.2. Platinum loaded over AlSBA.	66
III.2.4.Catalytic Activity.	71
III.2.4.1. Catalytic activity of Pt/AlSBA-10(α) catalysts.	71
(A) Cyclohexane conversion.	71
(B) n-hexane conversion.	74
III.2.4.2. Catalytic activity of Ni/AlSBA-10 (α) catalysts.	74
(A) Cyclohexane conversion.	74
(B) n-hexane conversion.	77
III.2.4.3. Catalytic activity of Pt/AlSBA-10 (γ) catalysts.	77
(A) Cyclohexane conversion.	77
(B) n-hexane conversion.	80
III.2.4.4.Catalytic activity of Ni/AlSBA-10 (γ) catalysts.	80
(A) Cyclohexane conversion.	80
(B) n-hexane conversion.	80
III.2.4.5. Catalytic activity of Pt/AlSBA-10 (δ) catalysts.	83

(A) Cyclohexane conversion.	٨٣
(B) n-hexane conversion.	٨٣
III.٢.٤.٦. Catalytic activity of Ni/AlSBA-١٥ (١٤) catalysts.	٨٦
(A) Cyclohexane conversion.	٨٦
(B) n-hexane conversion.	٨٦
<u>Conclusion</u>	٩٠
<u>References</u>	٩٣
<u>Arabic Summary</u>	١٠١

LIST OF TABLES

Table 1. Textural parameters of SBA-10, Ni and Pt-supported SBA-10 catalysts.	30
Table 2. DSC and TGA of SBA-10, Ni and Pt-supported SBA-10 catalysts.	38
Table 3. Catalytic conversion of cyclohexane over Pt / SBA-10 catalysts: (A) 0.3 wt%Pt and (B) 0.6 wt%Pt.	41
Table 4. Catalytic conversion of cyclohexane over Ni/SBA-10 catalysts: (A) 0 wt% Ni (B) 10 wt% Ni and (C) 10 wt%Ni.	41
Table 5. Catalytic conversion of n-hexane over Ni /SBA-10 catalysts: (A) 0 wt%Ni (B) 10 wt%Ni and (C) 10 wt% Ni.	44
Table 6. Textural parameters of AISBA-10 (0, 5 and 10), Ni and Pt-supported catalysts.	54
Table 7. DSC and TGA of AISBA-10(0, 5 and 10), Ni and Pt-supported AISBA-10 catalysts.	70
Table 8. Catalytic conversion of cyclohexane over Pt /AISBA-10 (0) catalysts: (A) 0.3 wt%Pt and (B) 0.6 wt%Pt.	73
Table 9. Catalytic conversion of n-hexane over Pt /AISBA-10 (0) catalysts: (A) 0.3 wt%Pt and (B) 0.6 wt%Pt.	73
Table 10. Catalytic conversion of cyclohexane over Ni /AISBA-10 (0) catalysts: (A) 10 wt%Ni and (B) 10 wt%Ni.	76
Table 11. Catalytic conversion of n-hexane over Ni /AISBA-10 (0) catalysts: (A) 10 wt%Ni and (B) 10 wt%Ni.	76
Table 12. Catalytic conversion of cyclohexane over Pt /AISBA-10 (5) catalysts: (A) 0.3 wt%Pt and (B) 0.6 wt%Pt.	79
Table 13. Catalytic conversion of n-hexane over Pt /AISBA-10 (5) catalysts: (A) 0.3 wt%Pt and (B) 0.6 wt%Pt.	79
Table 14. Catalytic conversion of cyclohexane over Ni /AISBA-10 (5) catalysts: (A) 10 wt%Ni and (B) 10 wt%Ni.	82
Table 15. Catalytic conversion of n-hexane over Ni /AISBA-10 (5) catalysts: (A) 10 wt%Ni and (B) 10 wt%Ni.	82
Table 16. Catalytic conversion of cyclohexane over Pt /AISBA-10 (10) catalysts: (A) 0.3 wt%Pt and (B) 0.6 wt%Pt.	85
Table 17. Catalytic conversion of n-hexane over Pt /AISBA-10 (10) catalysts: (A) 0.3 wt%Pt and (B) 0.6 wt%Pt.	85

Table 18. Catalytic conversion of cyclohexane over Ni /AlSBA-100 (1%) catalysts: (A) 1.0 wt%Ni and (B) 0.5 wt%Ni.	88
Table 19. Catalytic conversion of n-hexane over Ni /AlSBA-100 (1%) catalysts: (A) 1.0 wt%Ni and (B) 0.5 wt%Ni.	88

LIST OF FIGURES

Fig.1 Structures of mesoporous MCM-S materials: a) MCM-41 (2D hexagonal, space group $p6mm$), b) MCM-48 (cubic, space group $la\bar{3}d$) and c) MCM-50 (lamellar, space group $P6$).	4
Fig.2 Phase sequence of surfactant – water binary system	5
Fig.3 Interaction between the inorganic species and the head group of the surfactant	7
Fig.4 The synthesis stages of the formation of mesoporous SBA-100	10
Fig.5 SBA-100	11
Fig.6 Brønsted acid form of AlSBA-100	14
Fig.7 Micro Catalytic Reactor	23
Fig.8 Pulse micro catalytic unit	25
Fig.9 (A) low angle XRD pattern and (B) wide angle XRD pattern of SBA-100 and Pt -supported catalysts	27
Fig.10 (A) low angle XRD pattern and (B) wide angle XRD pattern of Ni-supported catalysts	28
Fig.11 (A) the Nitrogen adsorption - desorption isotherms and (B) Pore Size Distribution curves of SBA-100 and Ni/SBA-100 catalyst	33
Fig.12 (A) the Nitrogen adsorption - desorption isotherms and (B) Pore Size Distribution curves of Ni/SBA-100 catalysts	34
Fig.13 (A) Nitrogen adsorption-desorption isotherms of and (B) Pore Size Distribution curves of Pt/SBA-100 catalysts	35
Fig.14 (A) DSC and (B) TGA curves of SBA-100 and Ni /SBA-100 catalysts	37
Fig.15 (A) DSC and (B) TGA curves of SBA-100 and Pt /SBA-100 catalysts	37

Fig. 16 The catalytic conversion of cyclohexane over Pt / SBA-10 catalysts: (A) 0.3 wt% Pt and (B) 0.6 wt% Pt	40
Fig. 17 The catalytic conversion of (A) cyclohexane (B) n-hexane over 0 wt% Ni/SBA-10.	40
Fig. 18 The catalytic conversion of (A) cyclohexane (B) n-hexane over 10 wt% Ni / SBA-10.	43
Fig. 19 The catalytic conversion of (A) cyclohexane (B) n-hexane over 10 wt% Ni / SBA-10.	43
Fig. 20 (A) low angle XRD pattern and (B) wide angle XRD pattern of AlSBA-10(0) and Ni- supported catalysts	47
Fig. 21 (A) low angle XRD pattern and (B) wide angle XRD pattern of Pt- supported AlSBA-10(0) catalysts.	48
Fig. 22 (A) low angle XRD pattern and (B) wide angle XRD pattern of AlSBA-10(V) and Ni- supported catalysts.	49
Fig. 23 (A) low angle XRD pattern and (B) wide angle XRD pattern of Pt- supported AlSBA-10(V) catalysts.	50
Fig. 24 (A) low angle XRD pattern and (B) wide angle XRD pattern of AlSBA-10(14) and Ni- supported catalysts.	51
Fig. 25 (A) low angle XRD pattern and (B) wide angle XRD pattern of Pt- supported AlSBA-10(14) catalysts.	52
Fig. 26 (A) the Nitrogen adsorption - desorption isotherm and (B) Pore Size Distribution curve of Al SBA-10(0).	56
Fig. 27 (A) the Nitrogen adsorption - desorption isotherms and (B) Pore Size Distribution curves of Ni/Al SBA-10(0) catalysts.	57
Fig. 28 (A) the Nitrogen adsorption - desorption isotherms and (B) Pore Size Distribution curves of Pt/Al SBA-10(0) catalysts	58
Fig. 29 (A) the Nitrogen adsorption - desorption isotherm and (B) Pore Size Distribution curve of Al SBA-10(V).	59
Fig. 30 (A) the Nitrogen adsorption - desorption isotherms and (B) Pore Size Distribution curves of Ni/Al SBA-10(V) catalysts.	60
Fig. 31 (A) the Nitrogen adsorption - desorption isotherms and (B) Pore Size Distribution curves of Pt/Al SBA-10(V) catalysts.	61
Fig. 32 (A) the Nitrogen adsorption - desorption isotherm and (B) Pore Size Distribution curve of Al SBA-10(14).	62
Fig. 33 (A) the Nitrogen adsorption - desorption isotherms and (B) Pore Size Distribution curves of Ni/Al SBA-10(14) catalysts.	63

Fig. 34 (A) the Nitrogen adsorption - desorption isotherms and (B) Pore Size Distribution curves of Pt/Al SBA-10(14) catalysts.	64
Fig. 35 (A) DSC and (B) TGA curves of AlSBA-10(0) and Ni /AlSBA-10(0).	67
Fig. 36 (A) DSC and (B) TGA curves of AlSBA-10(0) and Pt /AlSBA-10(0).	67
Fig. 37 (A) DSC and (B) TGA curves of AlSBA-10(7) and Ni /AlSBA-10(7).	68
Fig. 38 (A) DSC (B) TGA curves of AlSBA-10(7) and Pt /AlSBA-10(7).	68
Fig. 39 (A) DSC and (B) TGA curves of AlSBA-10(14) and Ni /AlSBA-10(14).	69
Fig. 40 (A) DSC and (B) TGA curves of AlSBA-10(14) and Pt /AlSBA-10(14).	69
Fig. 41 The catalytic conversion of (A) cyclohexane (B) n-hexane over 0.3 wt% Pt/AlSBA-10(0).	72
Fig. 42 The catalytic conversion of (A) cyclohexane (B) n-hexane over 0.6 wt% Pt/AlSBA-10(0).	72
Fig. 43 The catalytic conversion of (A) cyclohexane (B) n-hexane over 2.0 wt% Ni / AlSBA-10(0).	75
Fig. 44 The catalytic conversion of (A) cyclohexane (B) n-hexane over 7.0 wt% Ni/AlSBA-10(0)	75
Fig. 45 The catalytic conversion of (A) cyclohexane (B) n-hexane over 0.3 wt% Pt/AlSBA-10(7).	78
Fig. 46 The catalytic conversion of (A) cyclohexane (B) n-hexane over 0.6 wt% Pt/AlSBA-10(7).	78
Fig. 47 The catalytic conversion of (A) cyclohexane (B) n-hexane over 2.0 wt % Ni/AlSBA-10(7).	81
Fig. 48 The catalytic conversion of (A) cyclohexane (B) n-hexane over 7.0 wt % Ni/AlSBA-10(7).	81
Fig. 49 The catalytic conversion of (A) cyclohexane (B) n-hexane over 0.3 wt% Pt/AlSBA-10(14).	84
Fig. 50 The catalytic conversion of (A) cyclohexane (B) n-hexane over 0.6 wt% Pt/AlSBA-10(14).	84
Fig. 51 The catalytic conversion of (A) cyclohexane (B) n-hexane over 2.0 wt% Ni/AlSBA-10(14).	87
Fig. 52 The catalytic conversion of (A) cyclohexane (B) n-hexane over 7.0 wt % Ni/AlSBA-10(14).	87

CHAPTER I

INTRODUCTION