



Women's Faculty for Arts,
Science and Education .

***Role of Rice Husk Ash for Heterogeneous Catalytic
Conversion of Some Organic Compounds and of Its
Effect on Some Environmental Hazards***

A Thesis

*Submitted to the Chemistry Department,
Women's Faculty, Ain Shams University.*

*In Partial Fulfillment of the Requirements for the **Ph.D.**
Degree in Science.
(Physical Chemistry)*

Presented by

Amira Said Hassan Mohamed
(M.Sc., 2015)

Supervised by

Prof. Dr. Essam Mohamed Ezzo

*Prof. of Physical Chemistry
Women's Faculty,
Ain Shams University, Cairo - Egypt*

Dr. Suzan Ahmad Hassan
*Ass .Prof. of Physical Chemistry
Women's Faculty,
Ain Shams University,
Cairo- Egypt*

Dr. Magda Abdel Basset El-kherbawi
*Lecturer of Physical Chemistry
Women's Faculty,
Ain Shams University,
Cairo - Egypt*

(2019)



Women's Faculty for Arts,
Science and Education ,
Chemistry Department.

APPROVAL SHEET

***Role of Rice Husk Ash for Heterogeneous Catalytic
Conversion of Some Organic Compounds and of Its Effect
on Some Environmental Hazards***

A Thesis
Submitted for the Ph. D. Degree in Chemistry
(Physical Chemistry)

By

Amira Said Hassan Mohamed

Board of Advisors Approved

Prof. Dr. Essam Mohamed Ezzo _____

Ass. Prof .Suzan Ahmad Hassan _____

Dr. Magda Abdel Basset El-kherbawi _____

Head of Chemistry Department

Prof. Dr. Mansoura Ismail Mohamed

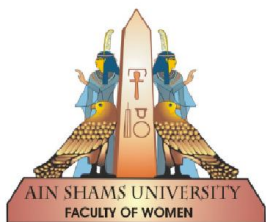
بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

قَالَ

سَبَّحَانَكَ لَا إِلَهَ إِلَّا مَا عَلَّمْتَنَا إِنَّكَ أَنْتَ
الْعَلِيمُ الْعَظِيمُ

صدق الله العظيم

سورة البقرة الآية: ٣٢



Qualification

Student Name : *Amira Said Hassan Mohamed*

Scientific Degree : *M.Sc. (physical Chemistry)*

Department : *Chemistry*

Faculty : *Faculty of Women*

University : *Ain Shams University*

B.Sc. Graduation Date : *2011*

M.Sc. Graduation Date : *2015*



Acknowledgement

In the name of Allah, I start by thanking him for giving me the strength and patience to complete this study. Words are on real assistance to express my deepest gratitude and thanks to Prof. Dr. Essam Mohamed Ezzo Professor of Physical Chemistry, Chemistry Department, Women's Faculty for Arts, Science and Education , Ain Shams University. I would like to thank him for his guidance , patience and mentorship .in addition to his technical knowledge , his support has made it easier to go through the ups and downs of research .

Also, I am indebted to express my sincere thank to Dr. Suzan Ahmad Hassan and Dr Magda Abdel Basset for their encouragement continuous help and careful guidance, through the accomplishment of this work

Finally, my deep thanks to all staff members at my department for their encouragement and moral support

Amira Said

Dedication

*Toprofessor Dr . Essam Mohammed Ezzo
for his great supervision and continuous advices.*

*ToMy husband for his patience ,encouragement and
love .*

*ToMy family for love and moral support im my
whole life .*

*ToAll my friends and colleagues for their kindness and
support.*



CONTENTS

	<i>Page</i>
LIST OF TABLES.....	IV
LIST OF FIGURES.....	XII
ABBREVIATIONS	XIV
AIM OF WORK.....	XVII
CHAPTER I.....	1
I. INTRODUCTION.....	1
I.A. Heterogeneous Catalysis.....	1
I.B. Catalyst Supports.....	2
I.B.i. Silica as Support Material.....	4
I.B.i.a. Amorphous silica derived from rice husk ash	5
I.B.i.b. Nano-structured silica	7
I.B.i.c. Transition metal-based catalysts.....	8
I.B.i.d . Metal based catalysts	8
I.B.i.e. Silica aerogels.....	9
I.B.i.f. Current and future progress	10
I.C. Supported Metal Catalysts Preparation.....	11
I.C.i. Impregnation method.....	11
I.C.ii. Sol- gel process.....	12
I.D. Heterogeneous Kinetic Study of Catalytic Conversion of Alcohols	13
I.E. Removal of Environmental Hazards	19
I.E.i.. Types and sources of pollution	20
I.E.ii. Variable activity in micro-organisms.....	22
I.E.ii.a. Bacteria.....	22
I.E.ii.b. Fungi.....	24
CHAPTER II.....	27
II. EXPERIMENTAL.....	27
II. A. STARTING MATERIALS	27
II.A.i. Reagents	27
II.A.ii. Preparation.....	28
II.B. PHYSICAL STUDIES.....	30

	<i>Page</i>
II.B.i. Textural Characteristics(BET).....	30
II.B.ii. X-Ray Diffraction (XRD)	40
II.B.iii. Transmission Electron Microscope(TEM).....	40
II.B.iv. Thermogravimetric Analysis (TGA and DTA).....	44
II.B.v. Differential Scanning Calorimetry (DSC).....	44
II.C. KINETIC STUDY OF THE HETEROGENEOUS CATALYTIC CONVERSION OF BENZYLOL OVER Ni/SiR AND Ni/SiG CATALYSTS IN FLOW SYSTEM	46
II.C.i. Catalytic Apparatus of Flow Type.....	47
II.C.ii. Calibration of the Micro – Dose Pump.....	49
II.C.iii. Analysis of the Liquid Product by GL Chromatograph.....	49
II.C.iv. Determination of the Order of Reaction.....	49
II.C.v. Determination of Apparent Activation Energy.....	51
II.C.vi. Determination of the Change in Weight of the Catalysts.....	51
II.D. REMOVAL OF ENVIRONMENTAL HAZARDS.....	53
II.D.i. Pigments Removal.....	53
II.D.ii. Microbial Removal.....	54
III. CHAPTER III.....	57
III. RESULTS AND DISCUSSION.....	57
III.A.PHYSICOCHEMICAL PROPERTIES OF THE Ni/SiR AND Ni/SiG SOLIDS.....	57
III.A.i. Surface and Textural Characteristics.....	57
III.A.i.a Adsorption- desorption isotherms.....	57
III.A.i.b. BET surface area.....	60
III.A.i.c. The V_L -t plots.....	62
III.A.i.d. Pore size distribution.....	64
III.A.ii. XRD.....	66
III.A.iii. TEM.....	70
III.A.iv. TGA and DTA.....	72
III.A.v. DSC.....	77
III.B. KINETICS OF HETEROGENEOUS CATALYTIC CONVERSION IN FLOW SYSTEM OVER THE Ni/SiR AND Ni/SiG SOLIDS.....	80

	<i>Page</i>
II.B.i. Determination of the Rate of Conversion of Over Ni/SiR Catalysts.....	81
II.B.ii. Determination of the Rate of Conversion of Over Ni/SiG Catalysts.....	102
III.B.iii. Determination of the Apparent Activation Energy for the Catalytic Conversion Over Ni/SiR Catalysts.....	122
III.B.iv. Determination of the Apparent Activation Energy for the Catalytic Conversion Over Ni/SiG Catalysts.....	139
III.B.v. Determination of the Catalytic Activity and Selectivity for the Catalytic over Ni/SiR and Ni/SiG Catalysts.....	156
III.B.vi. Reaction Mechanism for the Catalytic Conversion of Benzylol over Ni/SiR and Ni/SiG Catalysts	158
III.B.v. Thermodynamic Parameters for the Catalytic Conversion of Benzylol over Ni/SiR and Ni/SiG Catalysts.....	165
III.C.REMOVAL OF ENVIRONMENTAL HAZARDS	167
III.C.i. Removal of Pigments by Adsorption.....	167
III.C.i.a. Effect of pH.....	168
III.C.i.b. Effect of adsorbent dose.....	171
III.C.i.c. Effect of contact time.....	171
III.C.i.d. Effect of temperature.....	175
III.C.i.e. Effect of initial concentration.....	175
III.C.i.f. Adsorption isotherms.....	177
III.C.ii. Microbial Removal.....	181
Summary and Conclusions	183
References.....	186
Arabic Summary.....	

LIST OF TABLES

<i>Table No.</i>	<i>Title</i>	<i>Page</i>
1a	Example for support used in selected catalytic reactions.	3
1b	The chemical composition of RHA after burning out at 973K for 6h.	6
2	An overview of the prepared solid catalysts and their pretreatments conditions.	29
3a	Adsorption - desorption isotherm for nitrogen at 77K on Ni/SiRI.	34
3b	Adsorption - desorption isotherm for nitrogen at 77K on Ni/SiRII.	35
3c	Adsorption - desorption isotherm for nitrogen at 77K on Ni/SiRIII.	36
3d	Adsorption - desorption isotherm for nitrogen at 77K on Ni/SiGI.	37
3e	Adsorption - desorption isotherm for nitrogen at 77K on Ni/SiGII.	38
3f	Adsorption - desorption isotherm for nitrogen at 77K on Ni/SiGIII.	39
4a	The value of d-spacing of Ni/SiRI solid.	42
4b	The value of d-spacing of Ni/SiRII solid.	42
4c	The value of d-spacing of Ni/SiRIII solid.	42
4d	The value of d-spacing of Ni/SiGI solid.	42
4e	The value of d-spacing of Ni/SiGII solid.	43
4f	The value of d-spacing of Ni/SiGIII solid.	43
5	Textural characteristic of the samples investigated.	59
6	The X- ray parameters of the prepared solids.	69
7	The TGA and DTA data for the prepared solids.	74
8	The DSC data of the investigated solids.	78
9	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiRI catalyst in flow system under normal pressure at 593 K.	87
10	Effect of space velocity on the catalytic conversion	88

<i>Table No.</i>	<i>Title</i>	<i>Page</i>
	of benzylol over Ni/SiRI catalyst in flow system under normal pressure at 613 K.	
11	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiRI catalyst in flow system under normal pressure at 633 K.	89
12	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiRI catalyst in flow system under normal pressure at 653K.	90
13	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiRI catalyst in flow system under normal pressure at 637K.	91
14	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiRII catalyst in flow system under normal pressure at 593 K.	92
15	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiRII catalyst in flow system under normal pressure at 613 K.	93
16	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiRII catalyst in flow system under normal pressure at 633 K.	94
17	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiRII catalyst in flow system under normal pressure at 653K.	95
18	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiRII catalyst in flow system under normal pressure at 637K.	96
19	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiRIII catalyst in flow system under normal pressure at 593 K.	97
20	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiRIII catalyst in flow system under normal pressure at 613 K.	98
21	Effect of space velocity on the catalytic conversion	99

<i>Table No.</i>	<i>Title</i>	<i>Page</i>
	of benzylol over Ni/SiRIII catalyst in flow system under normal pressure at 633 K.	
22	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiRIII catalyst in flow system under normal pressure at 653K.	100
23	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiRIII catalyst in flow system under normal pressure at 637K.	101
24	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiGI catalyst in flow system under normal pressure at 593 K.	107
25	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiGI catalyst in flow system under normal pressure at 613 K.	108
26	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiGI catalyst in flow system under normal pressure at 633 K.	109
27	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiGI catalyst in flow system under normal pressure at 653K.	110
28	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiGI catalyst in flow system under normal pressure at 637K.	111
29	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiGII catalyst in flow system under normal pressure at 593 K.	112
30	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiGII catalyst in flow system under normal pressure at 613 K.	113
31	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiGII catalyst in flow system under normal pressure at 633 K.	114
32	Effect of space velocity on the catalytic conversion	115

Table No.	Title	Page
	of benzylol over Ni/SiGII catalyst in flow system under normal pressure at 653K.	
33	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiGII catalyst in flow system under normal pressure at 637K.	116
34	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiGIII catalyst in flow system under normal pressure at 593 K.	117
35	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiGIII catalyst in flow system under normal pressure at 613 K.	118
36	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiGIII catalyst in flow system under normal pressure at 633 K.	119
37	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiGIII catalyst in flow system under normal pressure at 653K.	120
38	Effect of space velocity on the catalytic conversion of benzylol over Ni/SiGIII catalyst in flow system under normal pressure at 673K.	121
39	Effect of temperature on the catalytic conversion of benzylol on Ni/SiRI catalyst in flow system under normal pressure on catalyst sample 0.5 h in benzylol vapour.	124
40	Effect of temperature on the catalytic conversion of benzylol on Ni/SiRI catalyst in flow system under normal pressure on catalyst sample 1 h in benzylol vapour.	125
41	Effect of temperature on the catalytic conversion of benzylol on Ni/SiRI catalyst in flow system under normal pressure on catalyst sample 1.5 h in benzylol vapour.	126

<i>Table No.</i>	<i>Title</i>	<i>Page</i>
42	Effect of temperature on the catalytic conversion of benzylol on Ni/SiRI catalyst in flow system under normal pressure on catalyst sample 2 h in benzylol vapour.	127
43	Effect of temperature on the catalytic conversion of benzylol on Ni/SiRI catalyst in flow system under normal pressure on catalyst sample 2.5 h in benzylol vapour.	128
44	Effect of temperature on the catalytic conversion of benzylol on Ni/SiRII catalyst in flow system under normal pressure on catalyst sample 0.5 h in benzylol vapour.	129
45	Effect of temperature on the catalytic conversion of benzylol on Ni/SiRII catalyst in flow system under normal pressure on catalyst sample 1 h in benzylol vapour.	130
46	Effect of temperature on the catalytic conversion of benzylol on Ni/SiRII catalyst in flow system under normal pressure on catalyst sample 1.5 h in benzylol vapour.	131
47	Effect of temperature on the catalytic conversion of benzylol on Ni/SiRII catalyst in flow system under normal pressure on catalyst sample 2 h in benzylol vapour.	132
48	Effect of temperature on the catalytic conversion of benzylol on Ni/SiRII catalyst in flow system under normal pressure on catalyst sample 2.5 h in benzylol vapour.	133
49	Effect of temperature on the catalytic conversion of benzylol on Ni/SiRIII catalyst in flow system under normal pressure on catalyst sample 0.5 h in benzylol vapour.	134

<i>Table No.</i>	<i>Title</i>	<i>Page</i>
50	Effect of temperature on the catalytic conversion of benzylol on Ni/SiR ^{III} catalyst in flow system under normal pressure on catalyst sample 1 h in benzylol vapour.	135
51	Effect of temperature on the catalytic conversion of benzylol on Ni/SiR ^{III} catalyst in flow system under normal pressure on catalyst sample 1.5 h in benzylol vapour.	136
52	Effect of temperature on the catalytic conversion of benzylol on Ni/SiR ^{III} catalyst in flow system under normal pressure on catalyst sample 2 h in benzylol vapour.	137
53	Effect of temperature on the catalytic conversion of benzylol on Ni/SiR ^{III} catalyst in flow system under normal pressure on catalyst sample 2.5 h in benzylol vapour.	138
54	Effect of temperature on the catalytic conversion of benzylol on Ni/SiG ^I catalyst in flow system under normal pressure on catalyst sample 0.5 h in benzylol vapour	141
55	Effect of temperature on the catalytic conversion of benzylol on Ni/SiG ^I catalyst in flow system under normal pressure on catalyst sample 1 h in benzylol vapour.	142
56	Effect of temperature on the catalytic conversion of benzylol on Ni/SiG ^I catalyst in flow system under normal pressure on catalyst sample 1.5 h in benzylol vapour.	143
57	Effect of temperature on the catalytic conversion of benzylol on Ni/SiG ^I catalyst in flow system under normal pressure on catalyst sample 2 h in benzylol vapour.	144