

Preparation and characterization of amorphous silica and metal modified silica catalyst from rice husk

A Thesis Submitted to the
National Institute of Technology, Rourkela
In Partial Fulfillment of the Requirements
For the Degree of

Master of Technology
in
Chemical Engineering

By
Ms. G.V.V.Gowthami
213 CH 1118

Under the Guidance of
Dr.(Mrs.) Abanti Sahoo



Department of Chemical Engineering
National Institute of Technology
Rourkela
2015

Certificate



Department of Chemical Engineering
National Institute of Technology
Rourkela -769008, India

This is to certify that, G.V.V.Gowthami, a student of M.Tech, 4th Semester, Chemical Engineering Department, NIT Rourkela bearing Roll No. 213CH1118 has completed her final project on the topic "*Preparation and Characterization of amorphous Silica and metal modified silica from Rice Husk*" under my guidance successfully. She has shown an authentic work with valid results and submitted a complete thesis of the work as required according to the curriculum in partial fulfillment for the award of M. Tech. degree.

Date:

.....

Dr. A. Sahoo.
Associate Professor,
Chemical Engineering Department,
NIT Rourkela.

ACKNOWLEDGEMENTS

A project can never be completed without the help of a lot of people and the sound knowledge they provide in various aspects. The persons in the list that follows are the people who had some contribution for completing this work.

First and foremost, I am sincerely grateful for the continuous support, insight and patience of my supervisor, Dr. Abanti Sahoo, without whose constant trust and, sometimes, gentle prodding, this thesis would not have been completed.

I am indebted to the Department of Chemical Engineering for providing the necessary equipment and materials required to fulfill this project. I also would like to thank the Head of the Department of Chemical Engineering, Prof. Rath for providing the platform to fulfill this work. I would extend my regards to the Chemistry Department, Metallurgy and Materials Engineering Department and the Ceramic Engineering Department for providing the various facilities and equipment to conduct parts of my research.

I would also like to thank Technical Assistant Mr. Mohanty and Laboratory Attendant Mr. Jhajo Nayak for providing the lab facilities and their time to assist me in various ways. Finally, I would like to acknowledge the support of my family, friends and college-mates without whose moral support and inspirations this work would not have seen this stage.

Date:.....

.....

G.V.V.Gowthami
213 CH 1118
NIT Rourkela

Contents

Chapter No	Title	Page no
	<i>Certificate</i>	<i>i</i>
	<i>Acknowledgments</i>	<i>ii</i>
	<i>Contents</i>	<i>iii-iv</i>
	<i>List of Figures</i>	<i>v-viii</i>
	<i>List of Tables</i>	<i>ix</i>
	<i>Nomenclature</i>	<i>x</i>
	Abstract	<i>xi</i>
Chapter 1	INTRODUCTION	
1.1	Overview	1
1.2	Properties of rice husk	2
1.3	Potential and current uses of rice husk ash and amorphous silica	3
1.4	Rice Husk Silica as Catalyst	3
1.5	Objective	4
Chapter 2	LITERATURE REVIEW	
2.1	General Outline	5
2.2	Amorphous Silica Extraction	6
2.3	Silica Aerogels	7
2.4	Transition metal modified catalyst from rice husk	8
2.5	Silica Zeolites	10
Chapter 3	EXPERIMENTATION	
3.1	Amorphous Silica Extracted from Rice Husk	11
	3.1.1 Water Washing	11
	3.1.2 Acid Washing/Leaching	11
	3.1.3 Rice Husk Pyrolysis	11
	3.1.4 Extraction of Amorphous Silica	11
3.2	Metal-Modified Silica Catalyst Extracted from Rice Husk	12
	3.2.1 Water Washing	12

	3.2.2. Acid Washing/Leaching	12
	3.2.3. Rice Husk Pyrolysis	13
	3.2.4. Preparation of Metal Modified Silica Catalyst	13
3.3	Oxidation of Styrene in Liquid phase	14
Chapter 4	RESULTS AND DISCUSSION	
4.1	Structural Features of Rice husk ash, Silica from Rice Husk and Metal Modified Silica Catalyst	16
	4.1.1 XRD Analysis of Pyrolysed Char	16
	4.1.2. XRD Analysis of Silica Obtained from RHA	19
	4.1.3. XRD Analysis of Transition Metal Modified Silica Catalyst Obtained from Rice Husk Ash	23
4.2	FESEM Images and EDX Analysis of RHA, Silica from RH and Metal Modified Silica Catalyst	29
	4.2.1. SEM and EDX of RHA (pyrolyzed)	29
	4.2.2 FESEM and EDX Analysis of Silica Derived from Pyrolysed RHA	31
4.3	Nitrogen Sorption Analysis	35
	4.3.1. N ₂ Adsorption-Desorption of silica derived from RH	35
	4.3.2. N ₂ Adsorption-Desorption of metal Modified Silica Catalyst derived from RH	37
4.4	Oxidation of Styrene in the Liquid Phase	40
Chapter 5	EPILOGUE	
5.1	Conclusions	42
5.2	Future scope	43
	References	44

List of Figures

Figure No.	Description of Figure	Page No.
2.1	The formation of Si-N bond on silica surface	9
3.1	Experimental setup for liquid phase oxidation of styrene	15
4.1	XRD analysis of RHA pyrolysed at 650°C treated with oxalic acid	16
4.2	XRD analysis of RHA pyrolysed at 650°C treated with HNO ₃	17
4.3	XRD analysis of RHA pyrolysed at 750°C treated with Oxalic acid	17
4.4	XRD analysis of RHA pyrolyzed at 750°C treated with HNO ₃	18
4.5	XRD analysis of RHA pyrolyzed at 850°C treated with Oxalic acid	18
4.6	XRD analysis of RHA pyrolyzed at 850°C treated with Oxalic acid	19
4.7	XRD analysis of silica at 650°C treated with Oxalic acid	20
4.8	XRD analysis of silica at 650°C treated with HNO ₃	21
4.9	XRD analysis of silica at 750°C treated with Oxalic acid	21
4.10	XRD analysis of RHA pyrolyzed at 750°C treated with HNO ₃	22
4.11	XRD analysis of Metal Modified Silica Catalyst with 10%Cr – 5%Cu from RHA extracted at pH of 10	23
4.12	XRD analysis of Metal Modified Silica Catalyst with 10%Cr – 5%Cu from RHA extracted at pH of 7	24
4.13	XRD analysis of Metal Modified Silica Catalyst with 10%Cr – 5%Cu from RHA extracted at pH of 3	25
4.14	XRD analysis of Metal Modified Silica Catalyst with 10%Cr – 10%Cu from RHA extracted at pH of 10	26
4.15	XRD analysis of Metal Modified Silica Catalyst with 10%Cr – 10%Cu from RHA extracted at pH of 7	26
4.16	XRD analysis of Metal Modified Silica Catalyst with 10%Cr – 10%Cu from RHA extracted at pH of 3	27

4.17	XRD analysis of Metal Modified Silica Catalyst with 10%Cr – 5%Cu from RHA extracted at pH of 10 treated with oxalic acid	29
4.18	FESEM image of RHA (inner surface)	30
4.19	FESEM image of RHA outer surface	30
4.20	EDX pattern of rice husk ash at 650°C and leached with oxalic acid	30
4.21	EDX pattern of RHA at 650°C without acid washed	30
4.22	FESEM image of RHA 650°C	31
4.23	FESEM image of RHA at 750°C	31
4.24	FESEM image of silica from RHA Without acid washed at 650°C	32
4.25	Silica from RHA without acid washed at 750°C	32
4.26	FESEM image of silica from RHA washed with HNO ₃ at 650°C	32
4.27	Silica from RHA Washed with HNO ₃ at 750°C	32
4.28	FESEM image of silica from RHA with oxalic acid (650°C)	33
4.29	Silica from RHA acid washed with Oxalic acid at 750°C.	33
4.30	EDX pattern of silica at 650°C obtained from rice husk leached with HNO ₃	33
4.31	EDX pattern of silica at 650°C obtained from rice husk leached with oxalic acid	33
4.32	FESEM image of metal modified silica at 650°C	34
4.33	Metal modified silica at 750°C	34
4.34	EDX Pattern of metal modified silica obtained from RHA (650°C) with oxalic acid	34
4.35	The N ₂ Adsorption-Desorption analysis of Silica from RH leached with HNO ₃ at different temperatures.	35
4.36	The N ₂ Adsorption-Desorption analysis of Silica from RH leached with Oxalic acid at different temperatures	36
4.37	The N ₂ Adsorption-Desorption analysis of Metal Modified Silica Catalyst from RH extracted at different pH	39

4.38	The N ₂ Adsorption-Desorption analysis of Metal Modified Silica Catalyst from RH extracted at different pH	39
------	---	----

List of Tables

Table No.	Description of Table	Page No.
1.1	Compositional analysis of rice husk ash	2
4.1	Peak list of RHA at 750°C treated with oxalic acid	17
4.2	Peak List of RHA pyrolyzed at 750°C	18
4.3	Peak List of RHA pyrolyzed at 850°C treated with Oxalic acid	19
4.4	Peak List of RHA pyrolyzed at 850°C treated with HNO ₃	19
4.5	Pattern List of Silica from RH Pyrolysed at 650°C treated with oxalic acid	20
4.6	Pattern List of Silica at 650°C and treated with Oxalic acid	20
4.7	Pattern List: Silica at 750°C and treated with Oxalic acid	21
4.8	Peak List of silica from RHA Pyrolysed at 750°C treated with Oxalic acid	22
4.9	Pattern List of Silica from RH Pyrolysed at 750°C treated with HNO ₃	22
4.10	Peak List of silica at 750°C treated with HNO ₃	22
4.11	Peak List of 10% Cr – 5% Cu modified Silica extracted at pH of 10	24
4.12	Pattern List of 10% Cr – 5% Cu modified Silica extracted at pH of 10	24
4.13	Peak List of 10% Cr – 10% Cu modified Silica extracted at pH of 10	25
4.14	Pattern List of 10% Cr – 10% Cu modified Silica extracted at pH of 10	25
4.15	Peak List of 10% Cr – 10% Cu modified Silica extracted at pH of 3	28
4.16	Pattern List: 10%Cr – 10%Cu modified Silica extracted at pH of 3	28
4.17	The N ₂ Adsorption-Desorption Analysis Parameters of Silica Based on BET Calculations	36
4.18	The N ₂ Adsorption-Desorption Analysis Parameters of Silica (treated with oxalic acid) Based on BET Calculations	37

4.19	The N ₂ Adsorption-Desorption Analysis Parameters of Metal modified Silica Catalyst based on BET Calculations	38
4.20	The N ₂ Adsorption-Desorption Analysis Parameters of Silica (RH treated with oxalic acid) Catalyst based on BET Calculation	40
4.21	The effect of preparation pH of catalyst on the product selectivity during oxidation of styrene	41
4.22	The effect of copper loading in the catalyst on the product selectivity and conversion.	41

Nomenclature

RH	Rice Husk
RHA	Rice Husk Ash
CTAB	Cetyl Tetramethyl Ammonium Bromide
SDA	Structural Directing Agent
Rh Si	Rice Husk Silica
Rh Si-Cr/Cu	Rice Husk Silica Impregnated with Copper and Chromium
GC-MS	Gas Chromatography Mass Spectroscopy
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscope
EDX	Energy Dispersive X-ray
BET	Brunauer–Emmett–Teller Surface Area Measurement
TEOS	Tetra Ethyl Ortho Silicate
TMOS	Tetra Methyl Ortho Silicate
PEDS	Poly EthoxyDisiloxane
UNEP	United Nations Environment Programme
MCM	Mobil Composition of Matter

Abstract

Rice husk ash, an agricultural waste material obtained from rice mills. It is a low-density material that causes disposal problems but is rich in amorphous chemically reactive silica (>90% ash). Alkaline extraction of Pyrolysed rice husk ash followed by acid precipitation led to the production of amorphous silica having high surface area and very less mineral contaminants. In the present work, pyrolysis of controlled burning conditions and later leaching alkali is used to produce amorphous silica. After pre-treatment of rice husk with different acids were Pyrolysed at different temperatures in a furnace and then leached with alkali NaOH. The obtained sodium silicate was titrated with HCl to produce silica. Metal modified silica was also prepared by incorporating the metals chromium and copper into silica matrix. This leads to the production of metal modified silica catalyst. Both the catalysts were sent for characterization of BET, SEM, EDX and XRD analysis. The amorphous nature of silica was confirmed by XRD analysis. The average surface area and total pore volume were obtained by using N₂ adsorption-desorption calculations by BET analysis. High surface areas were obtained. The amorphous nature and percentage of silica were determined from SEM and EDX analysis. Oxidation of styrene was performed by using metal modified catalyst at different pH. The products formed were analysed by GC-MS. A better conversation was found at lower pH.

Keywords:

Rice Husk, Rice Husk Ash, Amorphous Silica, Metal Modified Silica Catalyst, pyrolysis, leaching, Oxidation of styrene, SEM, XRD, BET and GC-MS analysis.

CHAPTER 1

INTRODUCTION

1.1 Overview

Water shortage and contamination rank equal to environmental changes as the most critical natural turmoil. Globalization advancement and metropolitan development has many negative effects on many ecosystems and seriously threatens the human health and environment. Without a doubt, horticultural waste biomass is in the blink of an eye a standout amongst the most demanding topics, which is gaining serious considerations during the past several decades. In perspective, rice husk ash, an agro-based waste collected from rice mill boilers, has emerged to be an invaluable source. Many researchers have drastically been addressed and confronted for the conversion of rice husk biomass into the high value-added and useful income-generating products. The present work aims at providing a concise utilization of rice husk ash as renewable sources (especially in accessing an ideal adsorption system) [1]

475 million tons of rice is produced every year. It is one of the important food crops and covers 1% surface area of the earth. 20% of rice paddy consists of waste named as rice husk. Rice husk is an agricultural waste material abundantly available in rice-producing countries. They are the regular sheaths that frame on rice grains during their growth. A substantial amount of husk, which is famous to have a fibrous material with an excessive silica content material, is available as waste from rice industries. In many countries, the rice husk produced from the processing of rice is either burnt or dumped as a waste, causing environmental pollution and disposal problems. Due to highproduction of rice husk, it has been used as fuel to generate steamforheating. Rice husk is used as substitute for firewood and coal for domestic uses. Due to the requirement of conservation of energy and resources, researchers have madesomeefforts to produce high-quality products from rice huskwaste by burning it under controlled conditions. The burning of rice husk results in the formation of rice husk ash with a content of silica that varies from 85% to 98% depending on the burning conditions, the furnace type, the rice variety, the rice husk moisture content, the climate and the geographic area [2].Uncontrolled burning results in highly crystalline products that are of low reactivity. Theconditions (temperature and duration of incineration) significantly change the final quality of the ash. The ash produced can be used as semiconductor, abrasive, insulating boardsand as a catalyst. Some small amounts of inorganic impurities are always present in the ash along with unburned carbon. The unburned carbon can remove from the ash by further heating

treatments at high temperatures, but this usually leads to the crystallization of the amorphous silica to cristobalite and tridymite. The crystallization of the contained silica of the ash also occurs when the burning conditions of the husk are uncontrolled. This crystallization is a disadvantage towards the preparation of silicon-based materials because the silica ash is rendered inactive in its crystalline form.

Table 1.1: Compositional analysis of rice husk ash

Constituents	Mass fraction (%)
Silica (SiO ₂)	80 – 90
Alumina (Al ₂ O ₃)	1 – 2.5
Ferric oxide (Fe ₂ O ₃)	0.5
Calcium oxide (CaO)	1 – 2
Magnesium oxide (MgO)	0.5 – 2.0
Sodium oxide (Na ₂ O)	0.2 – 0.5
Potash	0.2
Titanium dioxide (TiO ₂)	Nil
Loss on Ignition	10 – 20

1.2 Properties of Rice Husk

The utilisation of rice husk either in its crude form or ash form is numerous. Rice husk from the industry after milling is either burnt or dumped as waste in open fields. Very small amounts are used as fuel for boilers, electricity generation, heat generation, etc.,

The outer layer of rice husk composed of rectangular elements, which consists mostly of silica coated with a thick cuticle and surface hairs. The inner region and inner epidermis contain little silica. So, the amorphous silica is concentrated more at the outer surface of the rice husk and not within the husk.

Rice husk contains cellulose 40-50%, lignin 25-30%, ash 15-20% and moisture 8-15%. The white ash obtained from the combustion of this raw material at moderate temperature contains 87±97% silica in an amorphous form and some amount of metallic impurities. Many authors have concluded that rice husks are an excellent source of high-grade amorphous silica. This silica has been shown to be a good material for the synthesis of very pure silicon, silicon nitride, silicon carbide and

magnesium silicide [3]. After burning of rice husk, all the evaporable components are lost and only silicates remains. Rice husk is only able to preserve such a large proportion of silica in it.

Plants absorb silicates and various minerals from soil into their body. Inorganic materials, especially silicates are present mainly in annually grown plants, like rice, wheat, sunflower, etc.. Inorganic materials are present in the form of free salts and particles of cationic groups combined with the anionic groups of fibers into the plants [Basha et al., 2005].

1.3 Potential and current uses of rice husk ash and amorphous silica

Two main uses have been identified, as an insulator in the steel industry and as a pozzolan in the cement industry and mainly in the production of silica.

RHA has many uses:

- Steel Industry.
- Cement Industry.
- In the manufacture of silicon chips.
- Because of its insulating properties it has been used in the manufacturing of bricks and insulating boards.

Amorphous silica is also used for:

- Microelectronic devices mainly in semiconductors because of its high mechanical resistance and high dielectric strength
- Silica has been used in the manufacture of chips, telescope glasses and optical fibres.
- Silica has been used as food additive because of its hygroscopic nature
- Silica is also used in the extraction of DNA and RNA due to its ability to bind to the nucleic acids under the presence of chaotropes.
- It is also used in pharmaceutical products, cosmetics
- Silica aerogels is used in spacecraft.

1.4 Rice Husk Silica as Catalyst

Silica has been found to exist in form of gel, crystal and also in amorphous forms. SiO_2 structure is found to be based on the SiO_4 tetrahedral. Each Silicon atom is bonded to four oxygen atoms with each oxygen atom in turn getting attached to two silicon atoms. The silica surface consists of two types of functional groups, namely silanol (Si-O-H) and siloxane (Si-O-Si), with silanol being the more reactive one and with more adsorptive properties. Commercial silica is manufactured in a process

involving multiple steps which involves high temperatures and pressure. This makes such a process less cost effective and not very environmentally friendly. Mobil Oil Company developed the mesoporous material and it led to a huge research on such material and various metals incorporated on them. The inertness of silica and its ability to be custom tailored led to publication of around 3000 papers on mesoporous materials. The most common method for extraction of silica is solvent extraction. It is achieved either directly from the husk or the ash produced after pyrolysis of the husk. Better results are obtained on extraction of silica from the RHA instead of RH. Combustion at temperatures ranging from 550-800°C leads to formation of silica on which metal can be impregnated, with higher temperature resulting formation of crystalline silica and reducing the available surface area.

Various types of synthesis procedures for preparation of mesoporous silica from rice husk and metals incorporation, have been reported by several researchers. Aluminum sulfate, aqueous ammonia and nickel nitrate have been used by Tsayet [4] to prepare Ni/RHA–Al₂O₃ via simple impregnation and ion exchange methods. Chen [5] have reported the preparation of copper impregnated RHA using the deposition–precipitation method followed by calcination at 673 K. Copper nitrate trihydrate has been used by Chang [6] as the copper source to produce copper impregnated silica. He achieved this via an incipient wetness impregnation method. Mesoporous molecular sieve materials have also been extensively studied in details. Grisdanuraket [7] have used CTAB as structure-directing agent (SDA) and synthesized MCM-41 mesoporous materials. Chlorinated volatile organic compounds were adsorbed and photocatalytic degradation of herbicide undergone using such materials developed. Manufacturing silica structural materials with desired pore size is influenced by varying parameters like silica source, type and concentration of surfactant, pH and the temperature of obtaining the silica precursor.

1.5 Objectives

- Characterisation of rice husk ash at different conditions.
- Preparation and Characterisation of amorphous silica.
- Preparation and characterisation of Metal modified silica at different conditions.
- Oxidation of styrene in liquid phase

CHAPTER 2

LITERATURE REVIEW

2.1 General Outline

Silica, although having a simple formula of SiO_2 , exists in different forms in nature. Each form of silica exhibits different physical and also chemical properties, existing in the form of gels, crystalline and amorphous forms. It is also found to exist with other elements in form of ores or minerals. Silica is found in abundant quantities on earth, still for most technological applications silica is prepared by synthetic methods. Synthetic silica possess huge surface area which allows it to be used as adsorbing material and as catalyst support. In general the SiO_2 structure is based upon a SiO_4 tetrahedron. Each silicon atom is bonded to four oxygen atoms and again each oxygen atom being bound to two silicon atoms. Two types of functional group: silanol groups (Si-O-H) and siloxane groups (Si-O-Si) are present on the silica surface. All the chemical processes and even the physical processes like adsorption takes place on the silanol sites, the siloxane sites on the surface being inert to most of the activities. Generally the SiO_2 is a part of the SiO_2 tetrahedron structure, where each Si atom is bonded to four oxygen atoms and each oxygen atom in turn bonded to two silicon atoms [8]. Silica has also been reported to be found in some dicotyledonous plankton their husks or seeds like rice husk and foxtail millet. Porous amorphous silica has been found to contains isolated, germinal and vicinal as the three types of silanol bonds on its surface [9]. Isolated silanols have been found to be the more reactive species among all the three types found. An increase of temperature makes the silica surface more hydrophobic. The surface hydroxyl groups condense and form siloxane bridges. Commercial silica manufacture involves high temperature and pressure which renders it as a less cost efficient and non-environmental compatible process [10]. Considerable attention has been laid in recent years to modify catalytic surfaces, making it more efficient for reactions. Alternatives to conventional heterogeneous catalyst are possible by such chemical modifications of the silica obtained from RH. Amorphous silica which is usually produced commercially is a high energy consuming process, thus leading researchers to look for alternatives. Biogenic silica from rice husk has been extensively studied and various techniques applied on it to modify it with transition metals, metals and organic substances to catalyze various reactions. Heterogeneous catalysts have been prepared by immobilization of transition metal complexes and their nature and mechanism has been studied and developed.

This has also helped to manipulate the metal particle size and the crystallinity helping to achieve various catalytic reactions [11]. Side chain oxidation of styrene to produce benzaldehyde and styrene oxide is of considerable industry importance. Benzaldehyde is widely used as a starting material for various compounds in the pharmaceutical, dyes, resins, additives, flavours and organic solvents. Tungsten modified rice husk silica has been found to give 100% conversion of styrene with very less byproducts [12]. Heterogeneous catalysts along with greener oxidant like H₂O₂ and molecular oxygen have been reported to overcome some limitations of other heterogeneous catalysts and have drawn some serious research implications [13]. Mobil Oil company developed mesoporous materials in the early 90's. Since then an extensive research was initiated in the silica field. Presently there are more than 3000 publications specifically in the area of mesoporous silica. Silica being chemically inert and the ease with which it can be structurally modified with metals and organic substances helped it to be widely considered as a catalyst support [14]. A vast amount of literature is available on amorphous silica, transition metal modified silica, heterogeneous catalyst on silica and rice husk derived silica which are briefly mentioned below.

2.2. Amorphous Silica Extraction

Rice husk is one of the agro waste materials. Rahman has reported that the main components of rice husk are 32.7wt% of cellulose, 20.5 wt% of hemi-cellulose and 21.8wt% of lignin, 15.1 wt% of silica, 2.8 wt % of soluble and 7.5 wt % of moisture. Aristidou and pentila have reported that due to having large amounts of organic components, rice husk is used for many purposes as the generation of energy. Protor [15] has investigated his work on rice husk ash which is rich in silica and is for the production of biogenic silica.

Many researchers have reported the importance of the leaching process before rice husk pyrolysis to produce good quality biogenic silica. Leaching treatments are the acid treatment of rice husk with inorganic acids like HNO₃, HCl and H₂SO₄ or with organic acids like oxalic acid and citric acid. Several researchers have tried basic treatment with NH₄OH, NaOH [16]. They have concluded that the leaching treatment with organic acids such as citric acid and oxalic acid were considered as friendly to the environment and harmless. Because of this treatment metal impurities were removed from rice husk. Umeda and Kondoh have reported that usage of inorganic acids for the removal of metal impurities from rice husk causes harm to both

environment and human life. It uses high amounts of water for the removal of acid after leaching process and also needs special disposal systems.

The extraction of porous silica from rice husks depends upon the chemical pre-treatment by using a special procedure consists of two steps. The two parameters temperature and time effects the leaching treatment. The burning of rice husk directly in the air causes environmental pollution. So the burning of leached or non-leached rice husk has to be conducted in the muffle furnace or N₂ atmospheric furnace at a heating rate of 10 Kmin⁻¹ or 5 Kmin⁻¹ to reach the minimum desired temperatures. Otherwise at lower temperatures than 650 leads to the production of carbon in the sample. With the non-leached rice husk also we can produce amorphous silica with controlled burning conditions but of poor quality. The leached rice husk improved the purity of amorphous silica. It has shown a significant improvement in the properties of ash after leaching. In addition pore size distribution also changes to macro and mesopores were reported.

Sanhuez [17] has reported the synthesis of value added porous biogenic silica through rice husk ash is better than the common water glass. Many researchers have investigated a study on the transformation of amorphous silica to ordered mesoporous MCM-41 or MCM-48 type silica by using the pseudomorphic transformations. An advantage of this method is to produce material with high specific surface area and highly ordered pore structure that can be used as stationary phase in liquid chromatography.

2.3 Silica Aerogels

Sol-gel followed with super critical drying is the method used to prepare silica aerogels. Organic silicon monomers, such as polyethoxydisiloxane (PEDS), tetramethyl orthosilicate (TMOS), sodium silicate solution and tetraethyl orthosilicate (TEOS) are used as precursors. These precursors are very costly and carcinogenic. So, the industrial production of silica aerogel is economically not possible. So, the researchers have investigated and found the cheapest way to produce silica. Kalapathy [18] has reported the usage of rice husk in the production of pure silica. Yalcin and Sevinc [19] investigated to produce pure activated silica from the rice hull ash for the preparation of silica aerogel by a sol - gel method combined with supercritical CO₂ drying.

Tang and Wang reported that the densities and pore volume of silica aerogels from rice husk and TEO'S are comparable. The surface area of rice husk ash aerogel

is less than the aerogel from TEO'S. Aerogel is having transparent color when produced from TEO'S and having white colour from rice husk [20-24].

Biocompatible silica aerogel microparticles are used in the drug delivery vehicles because of their large surface area and open pore structures. R.S.Kumar , M.Vinjamur and M.Mukhopadhyay has developed a process to prepare aerogel microparticles from rice husk ash. This process consists of (1) sol - gel process (2) aging of gel and (3) drying. They used water-in-oil emulsion for sol-gel method and aging in ethanol to strengthen gel network followed by drying with CO₂.

Hong and Yoon reported that the preparation of monolith which is having Nano particles with three dimensional open pore networks like aerogels is easier than direct synthesis of aerogel. Alnaief and Smirnova have reported that it is essential to prepare aerogel microparticles for drug delivery vehicles by direct method, which gives good control over physicochemical properties. Otherwise, aerogel may loss its textual properties when prepared from crushing of monoliths.

2.4 Transition Metal Modified Catalyst from Rice Husk

Transition metal incorporated silica was prepared by using the sol-gel technique. By using the sol-gel technique, a greater control over final properties of the catalyst is achieved because metal and molecular precursors mixed homogeneously. Metal ions are incorporated to occupy neighboring positions in a gel matrix. Cetyltrimethylammonium bromide (CTAB) as a structural directing agent was used.

Many researchers have reported different ways for the synthesis of metal incorporated silica catalysts. Adam [25] has incorporated chromium into silica matrix using the sol-gel method. Chang [26] has reported the incorporation of nickel nitrate into the silica matrix via an ion exchange method. Recently, Chen [16] used deposition–precipitation to incorporate the copper nitrate in RHA. In this technique, the metal salt was dissolved in urea solution and added rice husk ash to yield a suspension.

By using the sol-gel technique, chromium was impregnated into silica matrix. Silica chromium was used to test the oxidation of cyclohexanol cyclohexane and cyclohexene. Cyclohexane conversion was 27.13% when silica chromium catalyst used, and 12.69% was achieved while usage of calcined silica chromium catalyst was used. By incorporating the structural directing agent, the surface area can be increased thereby the conversion of cyclohexane also increased. Adam has studied the effect of

pH on chromium silica catalyst and found that at pH 7 the cyclohexane conversion was high and at pH 3 it was low. At pH 10, Si-O-Cr bond was formed due to the interaction of positive and negative charged particles.

Molybdenum has also been incorporated into silica matrix using the same preparation sol-gel method. The effect of pH has also studied at pH 3, 7 and 10. At pH 3 Mo(V) and Mo(VI) was obtained on the catalyst surface, and only Mo(VI) was detected while pH was 7 and 10. Catalysts prepared at low pH were found to be more active in catalyzing.

Tungsten has also inserted into the silica matrix using the same method and conditions as discussed above, i.e., sol-gel method. At pH 3 the concentration of tungsten was high and low when the catalyst was prepared at pH 10. The trend as pH decreases the concentration of tungsten increases related to the interaction between the tungsten species and silicate species.

Iron is non-toxic and very cheapest transition metal has also been impregnated into silica matrix to catalyze various organic reactions. Here 4-(methylamino) benzoic acid was used as SDA to increase catalyst surface area. The formation of the Si-N bond has been taken place and is shown in a figure 2.1.

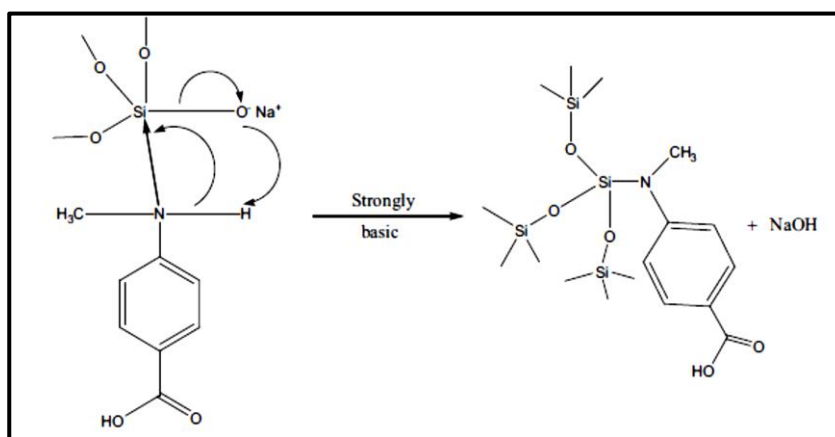


Figure 2.1: The formation of Si-N bond on silica surface

Cobalt catalysts were also prepared using rice husk silica. Most of the procedures reported in the literature were tedious, expensive and time-consuming. Adam [13] introduced a simple way to prepare cobalt-silica catalyst and nanoparticles using the sol-gel technique under mild conditions at a range of 2-15 nm.

2.5 Silica Zeolites:

Zeolites are microporous and crystalline alumina silicate minerals that are commonly used as adsorbents, ion exchangers and catalysts. Mobil co. reported the manufacturing process of the high silica zeolite of type ZSM-5 in 1972. It is a medium pore zeolite made by ten-membered rings that are having a pore size of 0.55-0.57 nm [1]. Many researchers have reported, the utilization of silica extracted from the rice husk ash in synthesizing MCM-41 (Mobil Composite Material number 41) type mesoporous silica. They studied deeply and once again they found that rice husk ash is the alternative source for the preparation of high value zeolites.

Due to having unique pore structure and shape, it is very much useful in the process of catalyzing of organic reactions. Researchers have carried out their work on synthesis and applications of ZSM-5. They synthesized ZSM-5 at a temperature of 120-180°C in an autoclave. They have also reported the possibility of synthesis at 90-100°C. In this process they used silica and alumina from chemical sources. They have made some efforts to use rice husk ash in the autoclave process for the synthesis of zeolites. Their efforts turned into success in production of amorphous zeolites from rice husk ash under atmospheric pressure.

Transition metal ions also incorporated into zeolites to arrange active sites required for some reactions. Metal modified zeolites ZSM-5 is prepared by incorporating the acids like phosphoric or boric acid led to the conversion from methanol to hydrocarbons, alkylation of benzene with ethanol etc. has been reported.

CHAPTER 3

EXPERIMENTATION

3.1 Amorphous Silica Extracted from Rice Husk

3.1.1 Water Washing

Rice husk was collected from a rice mill and at first it was sieved through a 20 mesh, and it is then cleaned and washed with water thoroughly to remove mud and dirt. After rice husk had washed, it was dried in a drier for 12 hours at 90-100°C. It was water washed rice husk and stored it for further usage.

3.1.2 Acid Washing/Leaching

Acid washing was used to remove small quantities of minerals from rice husk. A considerable amount of rice husk was taken and added to 500ml of 1N HNO₃ or oxalic acid and heated in a magnetic stirrer hot plate for one hour at 90-100°C. After that, the solution was let to cool, and the husk was washed with water thoroughly until the washout reaches pH of 7. The husk was vacuum filtered through a normal filter paper and dried it in an oven at 80-90°C for 10 hours. The rice husk obtained was light weight.

3.1.3 Rice Husk Pyrolysis

Rice husk pyrolysis was undertaken in a muffle furnace. A considerable amount of acid washed rice husk was taken in a crucible and put in a muffle furnace at a temperature of 650°C for 1 hour and after turnoff the furnace let the sample cool down. After cooling take the sample out and place it in a desiccator for overnight. This procedure was done at different temperatures 650°C, 750°C, 850°C for both the oxalic acid washed and HNO₃ acid washed rice husk and termed as acid washed rice husk ash.

3.1.4 Extraction of Amorphous Silica

A. Digestion

Take 5 grams of rice husk ash and added that to 150ml, 2.5N NAOH solution and heated on a magnetic stirrer cum heating plate with constant stirring at 85-95°C for 90 minutes. A dark-brown solution was obtained. The solution after cooling was filtered using whatman 41 ashless filter paper. The filtrate obtained was clear and glassy.

B. Precipitation

The filtrate i.e. sodium silicate solution obtained was titrated with concentrated HCL (35.4%) along with constant stirring. On addition of acid dropwise, white gelatinous precipitate starts to form which dissolves off on stirring. The precipitate keeps on forming till pH of 7 after which no further precipitate forms. This process was followed for sodium silicate obtained from all the rice husk ash produced at different temperatures treated with different acids.

C. Filtration

This suspension was aged for 24 hours and the precipitate settles to the bottom of the conical flask. The gelatinous precipitate of silica was vacuum filtered using whatman 41 filter paper. 50 ml of boiling water was added to the residue on the paper to remove any salt (NaCl) formed due to the acid base reaction.

D. Drying

The amorphous silica obtained was dried in a hot air oven at 90°C and separated from the filter paper and ground to powder using a motor-pestle and stored in air tight bottles for characterization and further usage.

3.2 Metal-Modified Silica Catalyst Extracted From Rice Husk

3.2.1 Water Washing

Rice husk was collected from a rice mill and at first it was sieved through a 20 mesh, and it is then cleaned and washed with water thoroughly to remove mud and dirt. After rice husk had washed, it was dried in a drier for 12 h at 90-100°C. It was water washed rice husk and stored it for further usage.

3.2.2 Acid Washing/Leaching

Acid washing was used to remove small quantities of minerals from rice husk. A considerable amount of rice husk was taken and added to 500ml of 1N HNO₃ or oxalic acid and heated in a magnetic stirrer hot plate for one hour at 90-100°C. After that, the solution was let to cool, and the husk was washed with water thoroughly until the washout reaches pH of 7. The husk was vacuum filtered through

a normal filter paper and dried it in an oven at 80-90°C for 10 hours. The rice husk obtained was light weight.

3.2.3 Rice Husk Pyrolysis

Rice husk pyrolysis was undertaken in a muffle furnace. A considerable amount of acid washed rice husk was taken in a crucible and put in a muffle furnace at a temperature of 650°C for 1 hour and after turnoff the furnace let the sample cool down. After cooling take the sample out and place it in a desiccator for overnight. This procedure was done at different temperatures 650°C, 750°C, 850°C for both the oxalic acid washed and HNO₃ acid washed rice husk and termed as acid washed rice husk ash.

3.2.4. Preparation of Metal Modified Silica Catalyst

A. Digestion

To prepare metal incorporated silica catalyst 4 grams of acid washed rice husk ash was taken and added to 150ml of 2.5N NaOH and 50ml of 0.01M CTAB solution. The solution thus prepared was heated and stirred on a magnetic stirrer at 85-95°C for 90 minutes. A brown solution was obtained, which was filtered using Whatman 41 filter paper to obtain a clear sodium silicate solution with CTAB as structural directing agent (SDA).

B. Precipitation:-

The solution obtained was titrated with 3M HNO₃ solution containing 10%(W/W) chromium and 10%(W/W) copper in the form of chromium nitrate and copper nitrate respectively.

This causes green precipitate to form which continues till the PH was 10,7 and 3. The pH was checked while the process was going on i.e., dropwise addition of acid to sodium silicate solution with stirring on magnetic stirrer. By adding high amount of acid, the pH goes on decreases. On reaching the desired pH, the addition of acid was stopped. The gelatinous precipitate which was loaded with metal ions was removed from the vessel. The gel formed is the metal incorporated silica.

The same procedure was also used to obtain bi-metal incorporated silica with 5%(w/w) copper loading and 10%(w/w) chromium loading along with 3M HNO₃.

The same procedure was used for both the HNO₃ washed rice husk and oxalic acid washed rice husk ash at different temperatures upto three different pH of 10,7 and 3.

C. Separation and Centrifugation:

The precipitate formed is in gel state. The gel initially needs to be aged for 24 h. After aging the solution mixture or suspension is put in 15ml centrifuge tubes and centrifuged at 5000 rpm for 10 minutes. The precipitate separated out at the bottom and the clear liquid above is decanted off. The tubes along with the precipitate were dried at 50°C for 3-4 hours and the precipitate which was solidified was taken out by a spatula and put on petri-dish. Again precipitate was further dried in a hot air oven at 100°C for 24 hours. After drying the green powdered material was ground to powder using mortar and pestle.

D. Calcination

The rice husk silica modified with Cr-Cu is ground to powder, contains the SDA (CTAB). In order to remove the CTAB, calcination is performed. The sample i.e. powder is put in a ceramic crucible and calcined at 500°C for 3 hours. The resulting silica modified with cr-cu ground to powder and stored it for further analysis.

3.3 Oxidation of Styrene in Liquid phase

Oxidation test of styrene can be performed in a 50 ml round bottom flask. 500ml beaker or paraffin oil bath, micropipette, condenser, vacuum pump, magnetic stirrer cum heating plate, sample collection bottles are the required equipment. 10 mmol styrene, 40 mmol of dilute H₂O₂ (30%), 20 ml acetonitrile, 100 mgs of catalyst, 5ml of m-xylene and paraffin oil bath are the required chemicals.

The reactants 20 ml of acetonitrile, 10 mmol of styrene and 100 mg of catalyst was taken in a 50ml round flask and mixed well and heated in a paraffin oil bath at 80°C. The reflux condenser was fitted on top of the flask to avoid loss of vapour. Once the reaction has reached the desired temperature, add 40m mol of dilute H₂O₂ (30%) to flask and reaction let to continue.

After 30 mins remove the catalyst and let the reaction to be continued with the filtrate for 3 hours. Remove 1ml of sample for every hour and add 5ml m-xylene and send to GC-MS analysis.

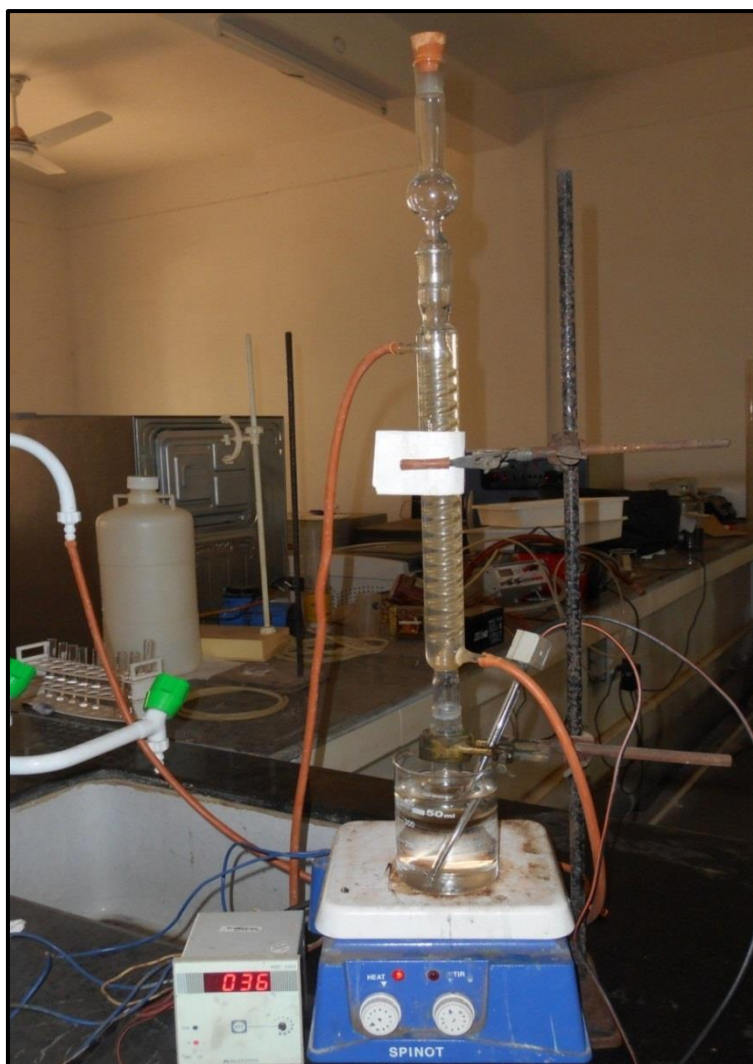


Figure 3.1: Experimental setup for liquid phase oxidation of styrene

CHAPTER 4

RESULTS and DISCUSSION

4.1 Structural Features of Rice husk ash, Silica from Rice Husk and Metal Modified Silica Catalyst

4.1.1 XRD Analysis of Pyrolysed Char

XRD analysis: The X-ray diffraction intensity of acid washed Pyrolysed rice husk ash, which was treated using two different acids and at three different temperatures is analysed. This was performed in an X'Pert Powder diffraction system. It was recorded at a range of 10-80° 2 θ Bragg's angle and a scanning speed of 3 deg/min. The figures below are showing the XRD pattern of ash treated with oxalic acid and HNO₃ at three different temperatures. The broad peaks at a range of 18-30° indicating the characteristic of the amorphous structure is observed. However, the small peaks at 20° and 29° of 850° shown in *fig. 4.5 and 4.6* and at 26° of 750° shown in *fig. 4.3 and 4.4* indicating crystalline quartz due to increasing temperatures. However, the presence of amorphous silica is confirmed by the broad range of peaks.

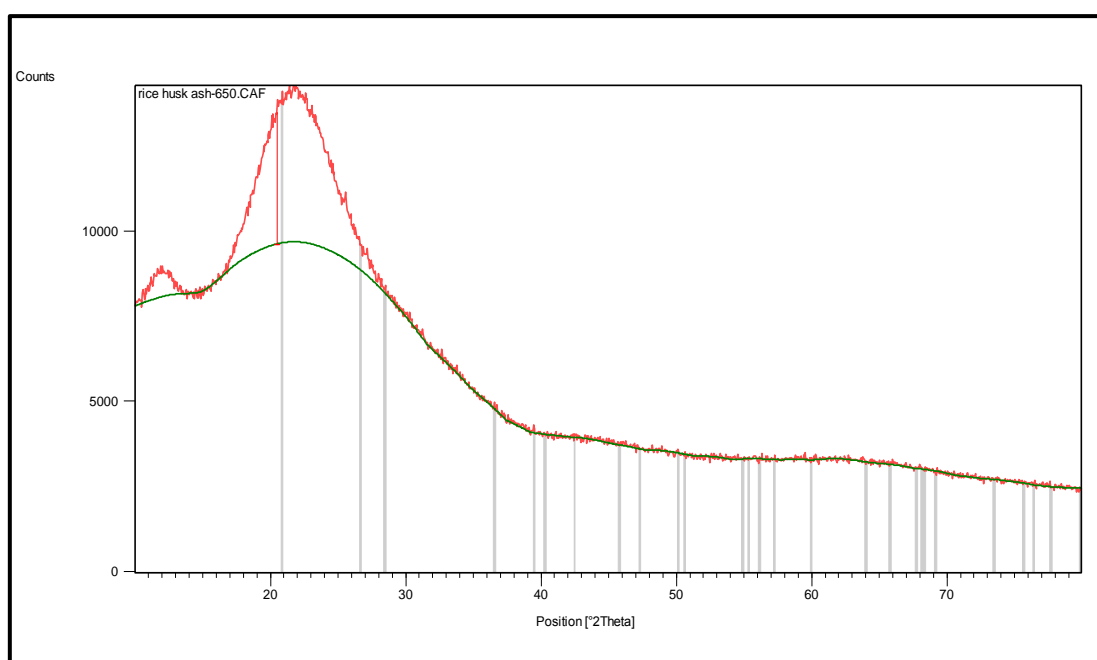


Figure 4.1:XRD analysis of RHA pyrolysed at 650°C treated with oxalic acid

Pyrolysed rice husk which is treated with oxalic acid and HNO₃ are showing the amorphous nature of silica. Both the leaching treatments are following the same pattern. But Oxalic acid treated husks are showing more sharp peaks between 18° and 30° at temperatures 750°C and 850°C. These peaks are due to small metallic impurities that are present after leaching. So, HNO₃ acid wash is the more effective leaching treatment. On increasing temperatures the crystalline quartz forms.

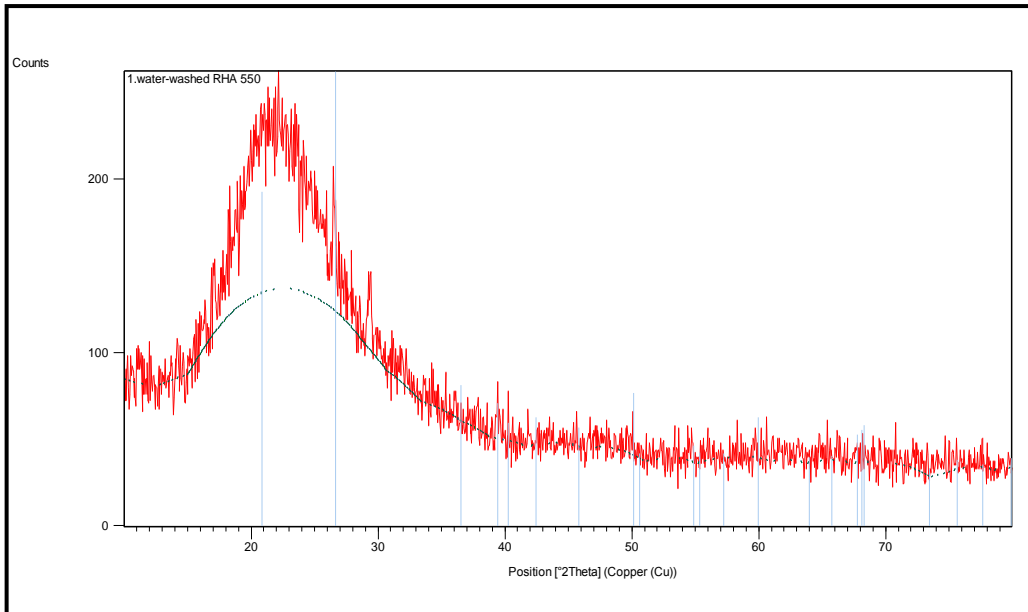


Figure 4.2:XRD analysis of RHA pyrolyzed at 650°C treated with HNO₃

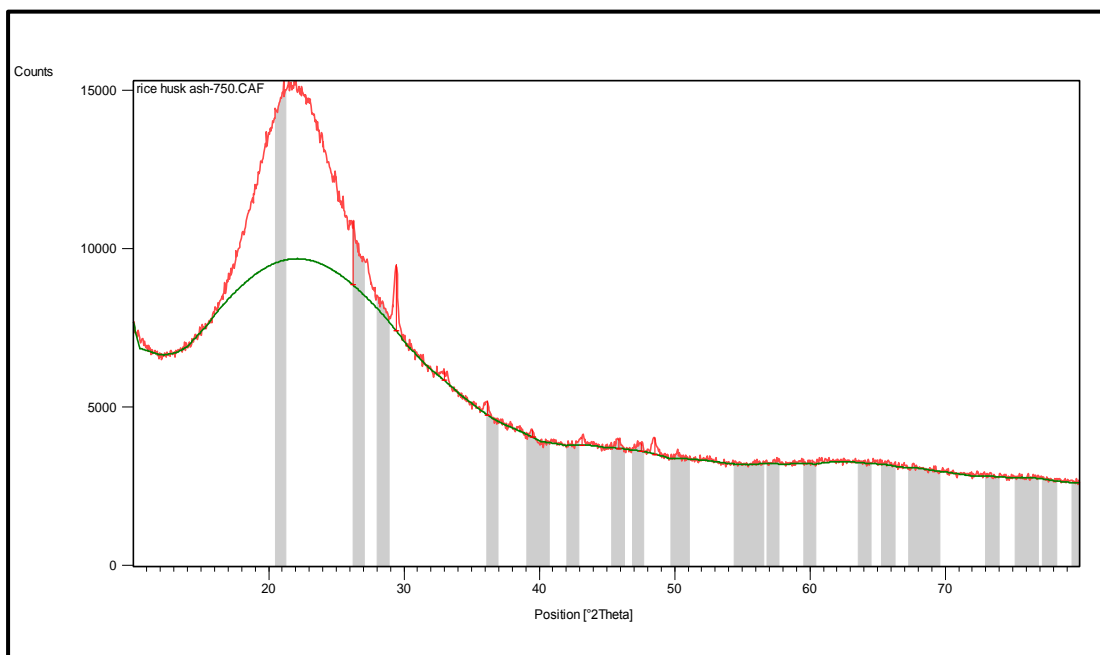


Figure4.3:XRD analysis of RHA pyrolyzed at 750°C treated with Oxalic acid

Table 4.1: Peak list of RHA at 750°C treated with oxalic acid

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
26.2345	2027.79	0.2952	3.39703	94.91
29.4479	2136.59	0.2460	3.03324	100.00

XRD scan of rice husk ash obtained from pyrolysis at 750°C and 850°C shows the presence of a single peak confirming presence of silica and quartz in the sample for both oxalic acid treated and HNO₃ treated husks.

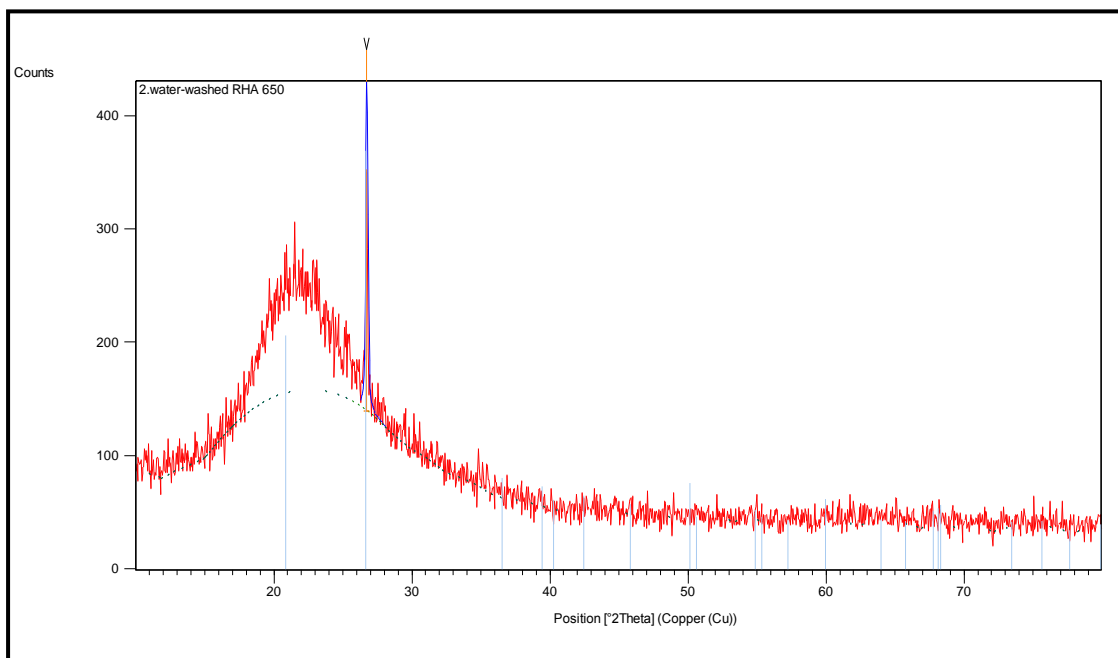


Figure 4.4: XRD analysis of RHA pyrolyzed at 750°C treated with HNO₃

Table 4.2: Peak List of RHA pyrolysed at 750°C

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
26.5500	110.20	0.1800	3.35459	100.00

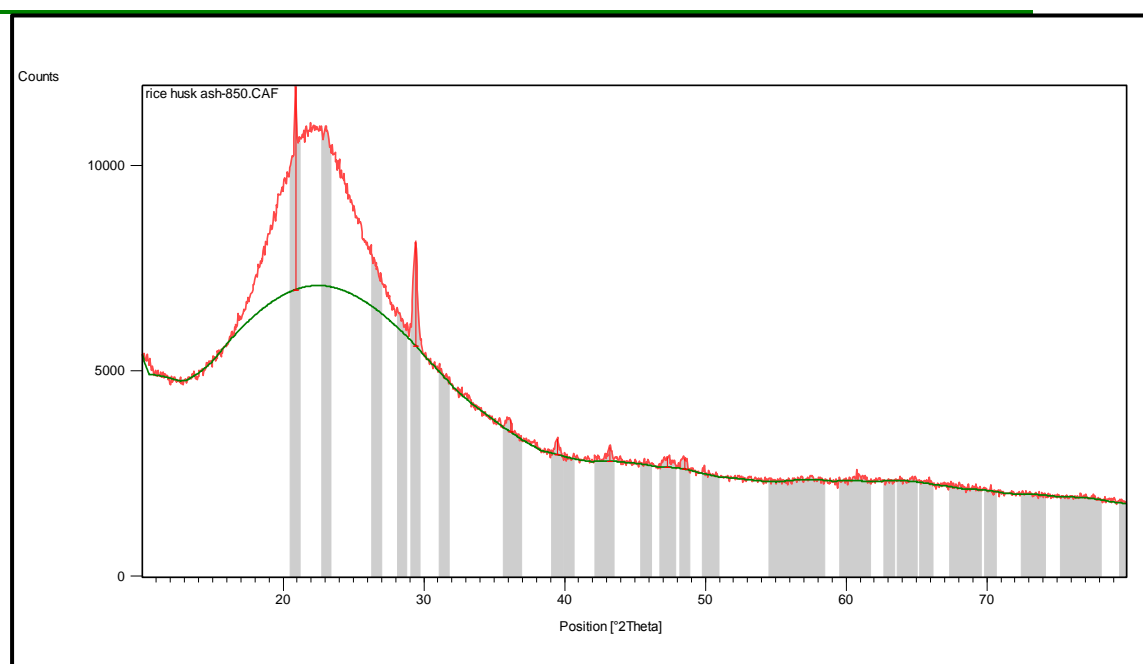
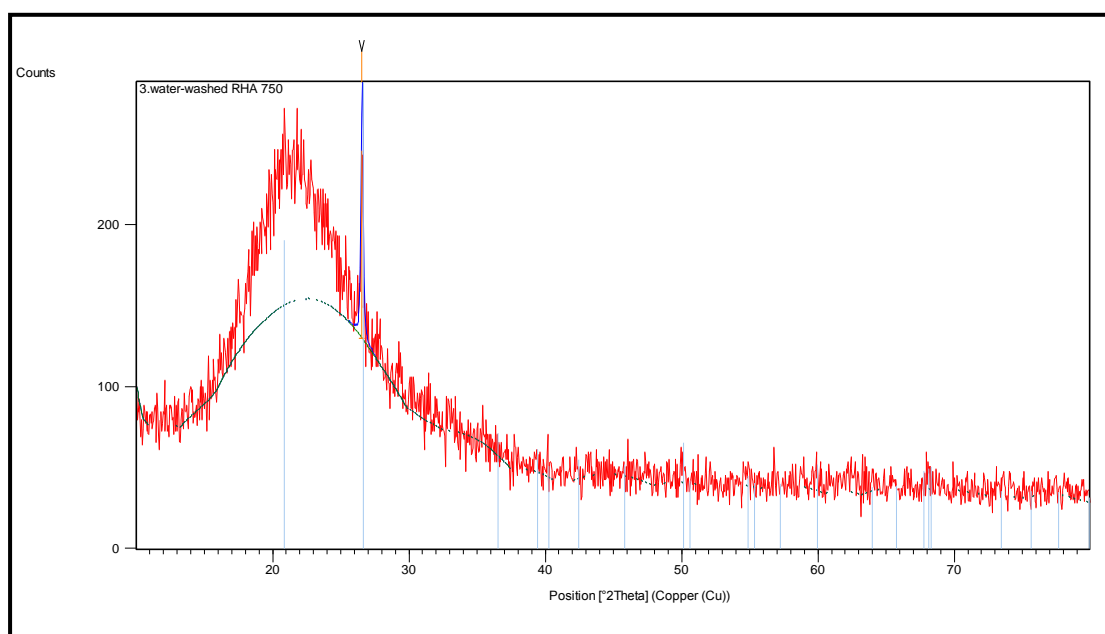


Figure 4.5: XRD analysis of RHA pyrolyzed at 850°C treated with Oxalic acid

Table 4.3: Peak List of RHA pyrolyzed at 850°C treated with Oxalic acid

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
20.9163	4961.79	0.1476	4.24718	100.00
29.4386	2573.75	0.2952	3.03419	51.87

**Figure 4.6:** XRD analysis of RHA pyrolyzed at 850°C treated with Oxalic acid**Table 4.4:** Peak List of RHA pyrolyzed at 850°C treated with HNO₃

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
26.5500	106.25	0.1800	3.35459	100.00

4.1.2. XRD Analysis of Silica Obtained from RHA

The X-ray diffraction intensity of silica obtained from Pyrolysed rice husk ash, which was treated using two different acids and at three different temperatures was also analysed using X-ray diffraction technique. This was performed in an XPanalytical X'Pert Powder diffraction system. It was also recorded at a range of 10-80° 2θ Bragg's angle and a scanning speed of 3 deg/min. The figures 4.7 - 4.10 are showing the XRD pattern of silica obtained at temperatures of 650°C, 750°C. A reference comparison with JCPDS data has shown presence of sodium and chlorine compounds. All the samples have shown the presence of amorphous structure of silica due to absence of peak near 26° 2θ which confirms the absence of cristoballite. The

other sharp peaks indicating the presence of Na and Cl formed during the titration process. The silica obtained from oxalic acid treated pyrolysed rice husk ash and HNO₃ treated also following the same trend.

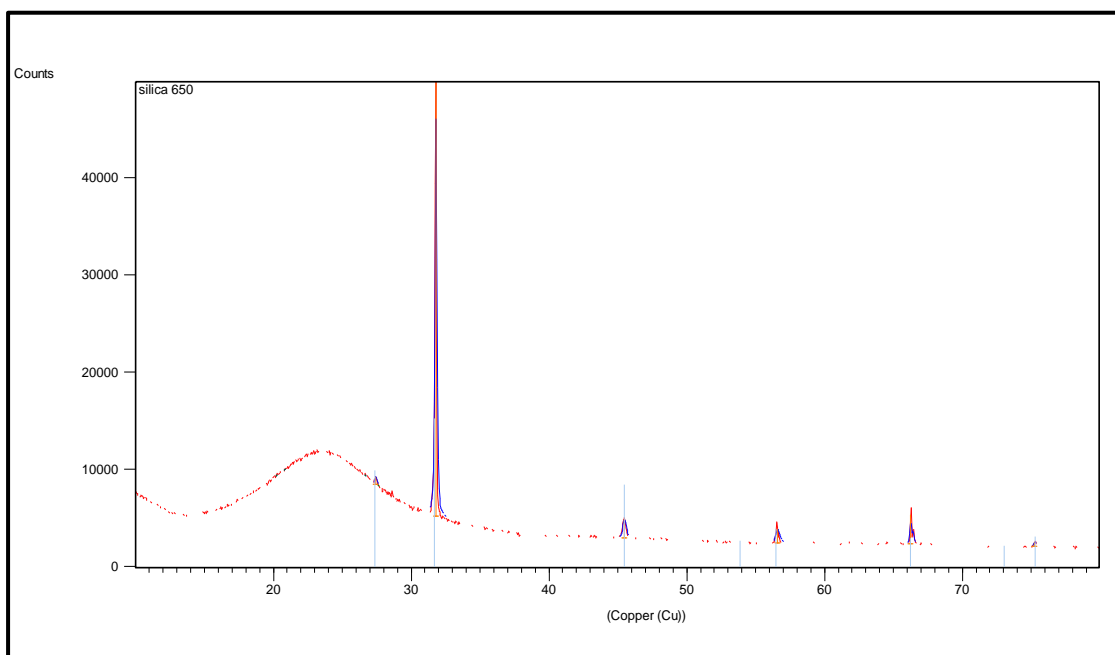


Figure 4.7: XRD analysis of silica at 650°C treated with Oxalic acid

Table 4.5: Pattern List of Silica from RH Pyrolysed at 650°C treated with oxalic acid

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	00-005-0628	68	Halite, syn	0.000	0.201	Na Cl

Table 4.6: Peak List of silica at 650°C treated with oxalic acid

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
27.4272	1359.24	0.1476	3.25196	3.02
31.7750	45080.21	0.1476	2.81622	100.00
45.4458	1916.03	0.2460	1.99583	4.25
56.5638	1498.59	0.2952	1.62710	3.32
66.2478	3015.19	0.1476	1.41081	6.69
75.2459	443.06	0.1800	1.26183	0.98

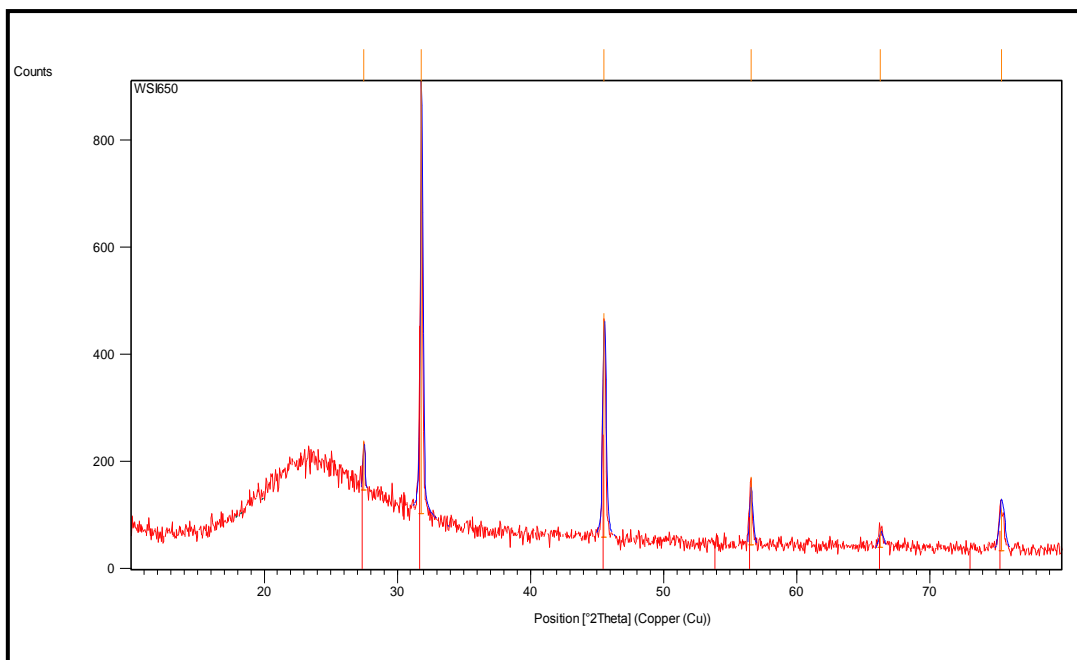


Figure 4.8: XRD analysis of silica at 650°C treated with HNO₃

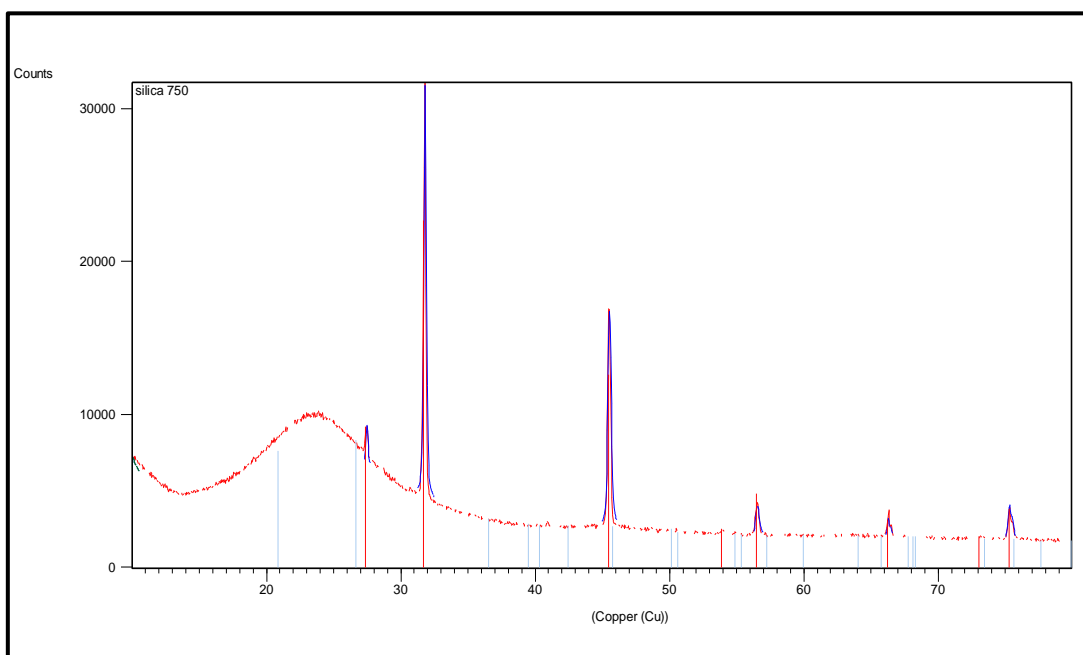


Figure 4.9: XRD analysis of silica at 750°C treated with Oxalic acid

Table 4.7: Pattern List: Silica at 750°C and treated with Oxalic acid

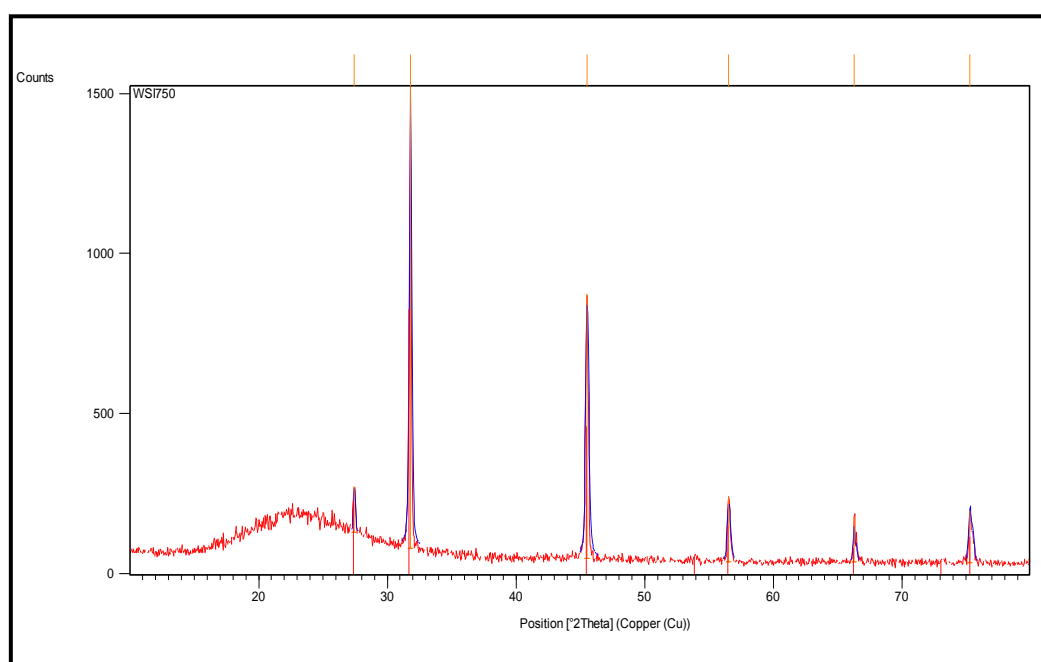
Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	00-005-0628	86	Halite, syn	0.000	0.572	Na Cl

Table 4.8: Peak List of silica from RHA pyrolysed at 750°C treated with Oxalic acid

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
27.4615	2536.81	0.1476	3.24798	9.16
31.7838	27699.79	0.1968	2.81545	100.00
45.5039	14626.98	0.2460	1.99341	52.81
53.9630	192.57	0.5904	1.69921	0.70
56.5151	2101.91	0.2460	1.62839	7.59
66.2835	1462.72	0.1476	1.41013	5.28
73.1076	110.01	0.5904	1.29444	0.40
75.3111	2040.54	0.2400	1.26090	7.37

Table 4.9: Pattern List: Silica from RH pyrolysed at 750°C treated with HNO₃

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	00-005-0628	77	Halite, syn	0.000	0.490	Na Cl

**Figure 4.10:** XRD analysis of RHA pyrolyzed at 750°C treated with HNO₃**Table 4.10:** Peak List of silica at 750°C treated with HNO₃

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
27.4280	145.65	0.1476	3.25187	9.96
31.7900	1462.81	0.1968	2.81492	100.00
45.5143	825.85	0.2460	1.99298	56.46
56.5219	202.89	0.2460	1.62821	13.87
66.2756	143.56	0.1476	1.41028	9.81
75.3009	162.78	0.2400	1.26104	11.13

4.1.3. XRD Analysis of Transition Metal Modified Silica Catalyst Obtained from Rice Husk Ash

The X-ray diffraction intensity of transition metal incorporated silica catalyst obtained from Pyrolysed rice husk ash by thermo chemical techniques was also analyzed by X-ray diffraction technique. This was performed in an XPanalytical X'Pert Powder diffraction system. It was also recorded at a range of 10-80° 2 θ Bragg's angle and a scanning speed of 3 deg/min. Both catalyst groups with 10%Cr –10% Cu and 10%Cr – 5%Cu prepared by sol-gel technique were analyzed and presence of Chromium and Copper were confirmed. Rice husk ash produced at temperature of 750°C which was treated with HNO₃ was used to obtain the silica. All the samples have shown the presence of ordered crystalline structure. This was due to the presence of chromium and copper species.

Fig 4.11, 4.12 and 4.13 show the XRD patterns of the metal incorporated silica with lower percentage of Copper loading, i.e. 5%Cu with the constant 10% Cr only extracted upto pH of 10, 7 and 3 respectively. The *Tables 4.11, 4.12, 4.13 and 4.14* show the Peak List and Pattern List of Metal Modified Silica Catalyst obtained at pH of 10 for the samples with 10%Cr and 5% Cu loading and for 10%Cr and 10%Cu loading. Rice husk which was treated with Oxalic acid was also taken at temperature of 750°C and produced Cr-Cu impregnated silica with at pH of 10 with loading 10% Cr and 10% Cu.

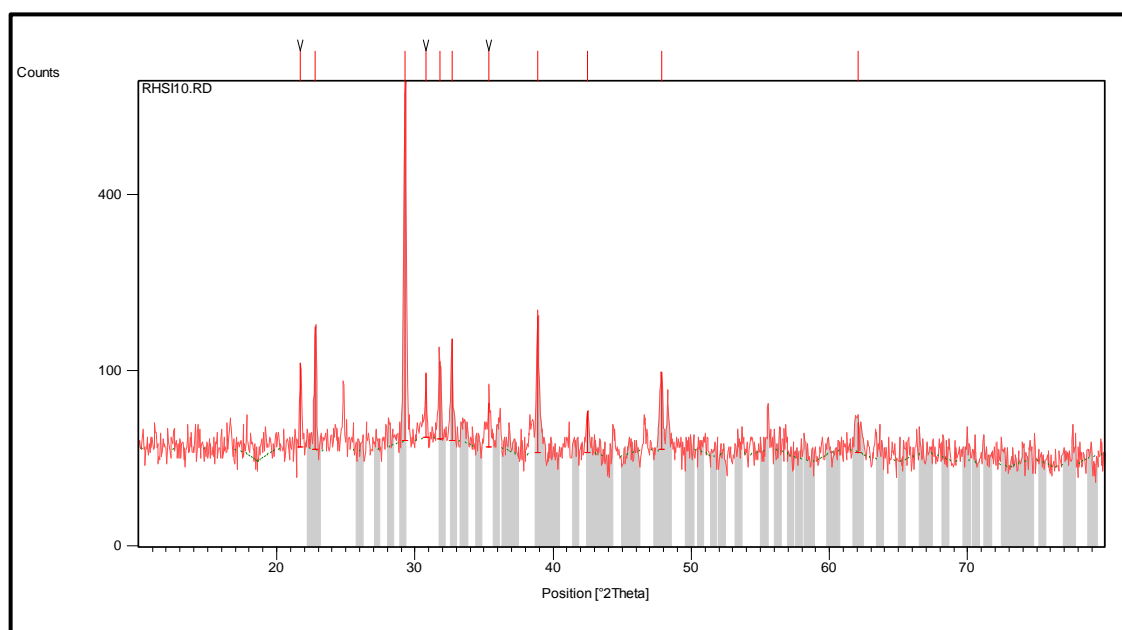


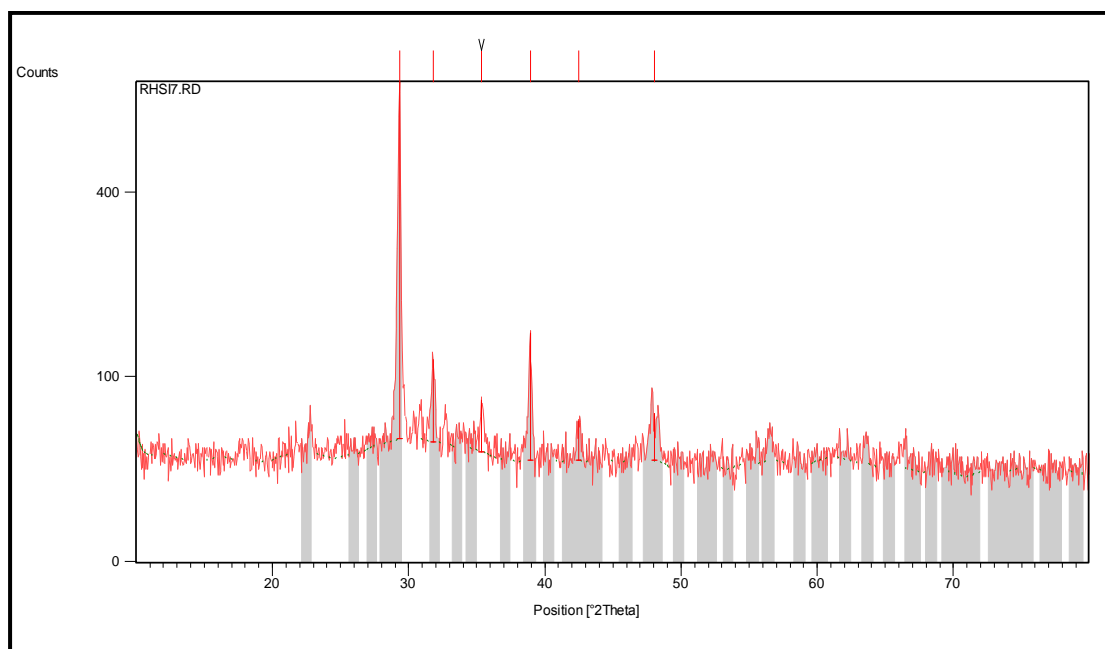
Fig 4.11:XRD analysis of Metal Modified Silica Catalyst with 10%Cr – 5%Cu from RHA extracted at pH of 10

Table 4.11: Peak List: 10%Cr – 5%Cu modified Silica extracted at pH of 10

Pos. [$^{\circ}2\theta$.]	Height [cts]	FWHM [$^{\circ}2\theta$.]	d-spacing [\AA]	Rel. Int. [%]
21.7258	76.57	0.1476	4.09074	11.48
22.7940	126.38	0.1476	3.90139	18.95
29.2985	666.99	0.1476	3.04837	100.00
30.8006	59.72	0.1476	2.90305	8.95
31.8053	73.94	0.1476	2.81360	11.09
32.6749	103.10	0.1476	2.74068	15.46
35.3292	34.54	0.3936	2.54062	5.18
38.9019	152.60	0.1476	2.31513	22.88
42.5007	30.94	0.2952	2.12705	4.64
47.8267	68.28	0.1968	1.90188	10.24
62.0475	21.91	0.7200	1.49458	3.28

Table 4.12: Pattern List: 10%Cr – 5%Cu modified Silica extracted at pH of 10

Visible	Ref. Code	Score	Compound Name	Displacement [$^{\circ}2\theta$.]	Scale Factor	Chemical Formula
*	76-1800	6	Copper Silicon	0.000	0.192	$\text{Cu}_{15}\text{Si}_4$
*	23-0223	5	Copper Silicon	0.000	0.040	$\text{Cu}_{0.83}\text{Si}_{0.17}$
*	39-0973	4	Silicon	0.000	0.032	Si
*	72-1326	3	Chromium Silicon	0.000	0.127	Cr Si

**Fig 4.12:** XRD analysis of Metal Modified Silica Catalyst with 10%Cr – 5%Cu from RHA extracted at pH of 7

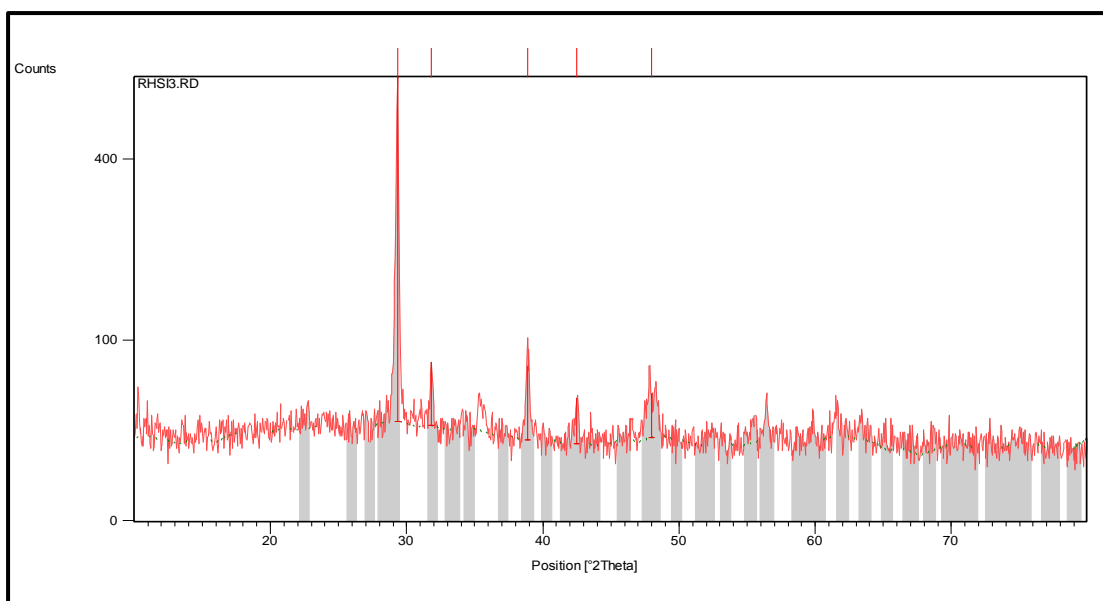


Fig 4.13:XRD analysis of Metal Modified Silica Catalyst with 10%Cr – 5%Cu from RHA extracted at pH of 3

Table 4.13: Peak List: 10%Cr – 10%Cu modified Silica extracted at pH of 10

Pos. [$^{\circ}$ 2Th.]	Height [cts]	FWHM [$^{\circ}$ 2Th.]	d-spacing [\AA]	Rel. Int. [%]
22.8864	43.18	0.2952	3.88584	12.30
29.3342	350.94	0.1968	3.04475	100.00
31.7947	48.99	0.2952	2.81451	13.96
35.3935	28.55	0.5904	2.53615	8.13
38.9713	77.54	0.2952	2.31117	22.10
47.9109	32.48	0.7200	1.89716	9.25

Table 4.14: Pattern List: 10%Cr – 10%Cu modified Silica extracted at pH of 10

Vis	Ref. Code	Score	Compound Name	Displacement [$^{\circ}$ 2Th.]	Scale Factor	Chemical Formula
*	76-1800	10	Copper Silicon	0.000	0.250	Cu ₁₅ Si ₄
*	39-0973	6	Silicon	0.000	0.537	Si
*	01-1261	4	Chromium	0.000	0.036	Cr
*	75-0841	4	Silicon	0.000	0.438	Si
*	03-0990	3	Copper Silicide	0.000	0.300	Cu ₄ Si
*	72-1326	4	Chromium Silicon	0.000	0.578	CrSi

Fig 4.10, 4.11 and 4.12 shows the XRD pattern of the group of metal modified rice husk silica catalyst loaded with 10%Cr and 10%Cu. The catalysts were extracted by sol-gel methods upto pH of 10, 7 and 3 respectively. The Tables 4.8 and 4.9 show the Peak List and Pattern List of Metal Modified Silica Catalyst obtained at pH of 3 for the samples with 10%Cr and 10% Cu loading only.

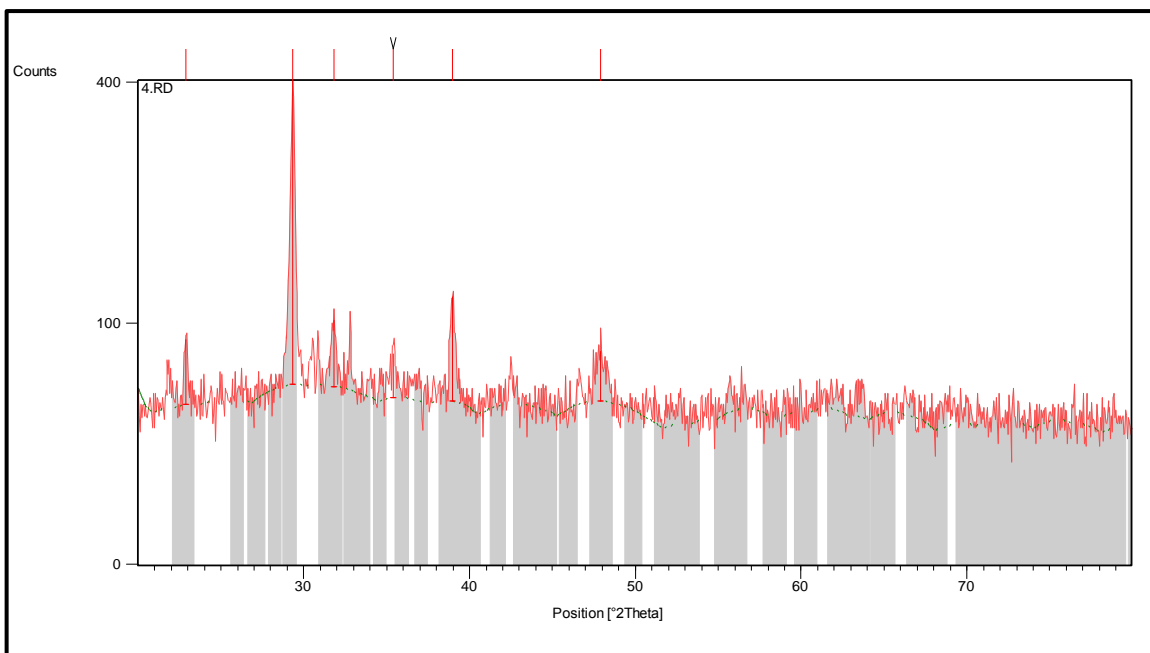


Fig 4.14:XRD analysis of Metal Modified Silica Catalyst with 10%Cr – 10%Cu from RHA extracted at pH of 10

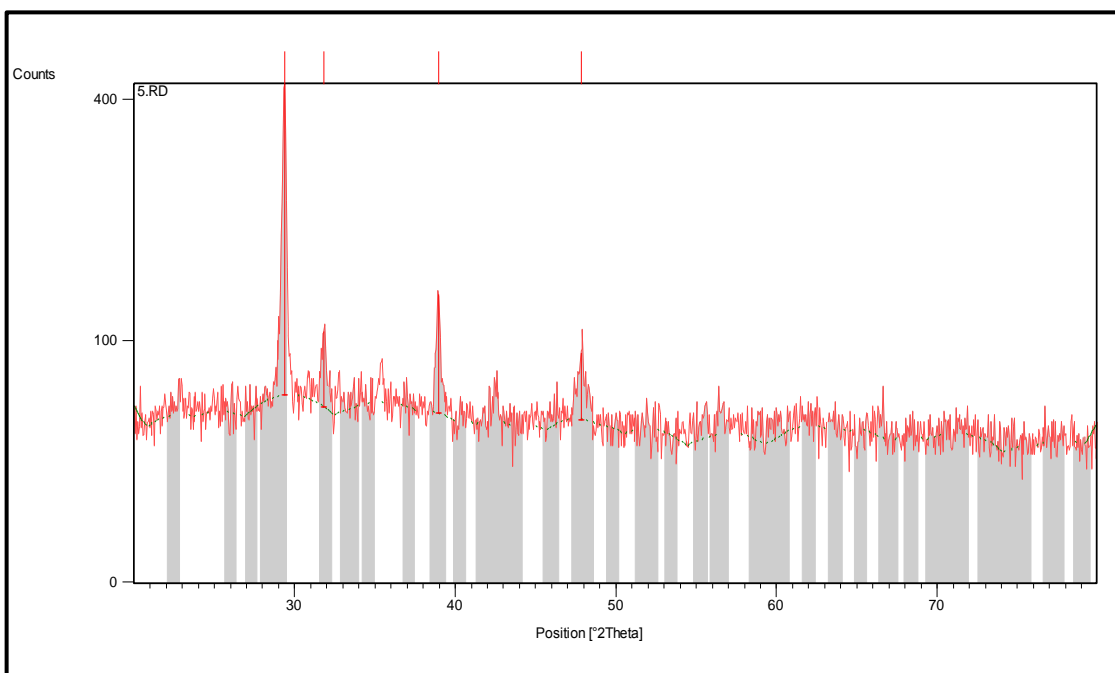


Fig 4.15:XRD analysis of Metal Modified Silica Catalyst with 10%Cr – 10%Cu from RHA extracted at pH of 7

A comparison with the XRD peak pattern of Silica obtained from RHA by alkaline extraction, wherein the RH is itself HNO₃ washed, with the XRD patterns of Cr-Cu modified silica from RH, with similar prior acid washing has shown a broad peak at $2\theta = 23^\circ$. The presence of these peaks suggests the presence of amorphous

silica in the catalyst sample. The absence of other peaks in the silica without transition metal impregnation in RHSi 550, RHSi 750 and RHSi 850 indicate that the Cr_2O_3 and CuO crystals did not form on the silica surface. The XRD patterns of metal modified silica also depicts that the Chromium and Copper species are evenly spread out on the silica matrix. The broad peaks at round $23^\circ 2\theta$ started to split and new peaks at 22, 29, 31, 38 and $47^\circ 2\theta$ began to on impregnation of transition metal and on reduction of the pH at which the metal modified silica catalysts were extracted. Peaks and pattern list of silica catalyst with higher metal loading extracted at pH of 3 is shown in *Tables 4.15* and *4.16*. Reduction of pH also led to more shift of the peaks toward the higher angle side, i.e. toward $45\text{-}47^\circ 2\theta$. Larger metal crystals are formed with pH reduction more amount of metal is being impregnated into the silica matrix which in turn causes phase segregation.

A comparison of the peaks for metal modified silica catalyst with lower amount on Copper loading, i.e. 10%Cr – 5%Cu, with the catalyst having higher amount of Copper loading, i.e. 10%Cr – 10%Cu, showed the split in peaks at 21, 30, 32, 42 and 62 converge at single peaks around them. This can be accounted for formation of complexes within Cr and Cu and their crystals on the silica surface, also higher amounts of Cu leaving a greater impression on the XRD patterns.

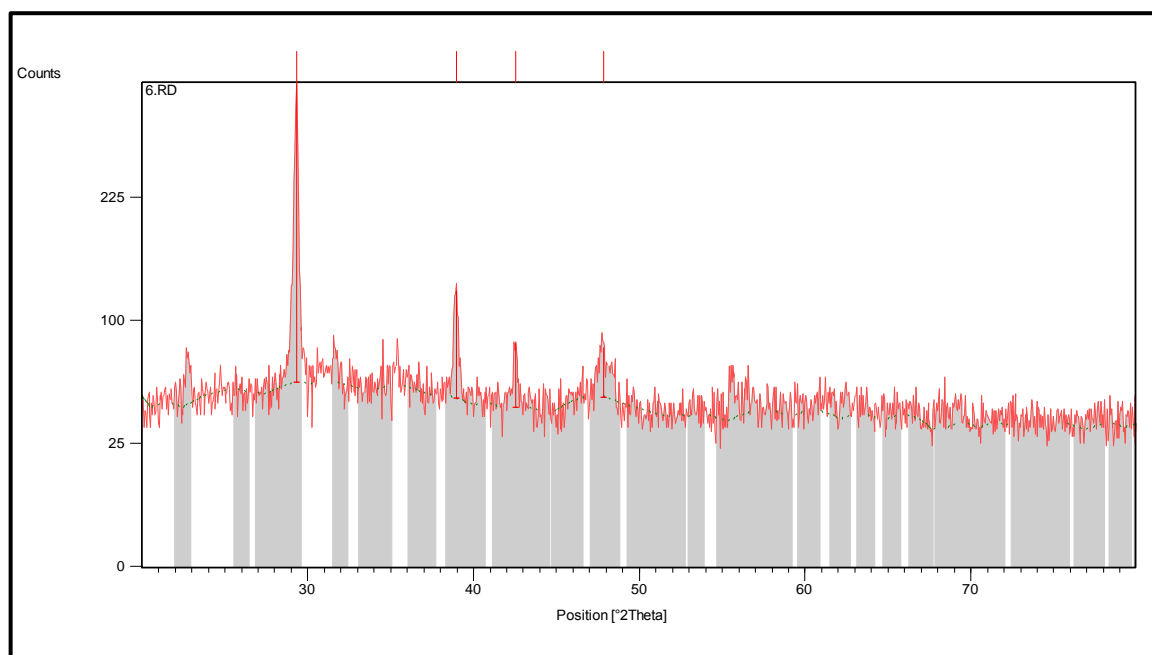


Fig 4.16:XRD analysis of Metal Modified Silica Catalyst with 10%Cr – 10%Cu from RHA extracted at pH of 3

Table 4.15: Peak List: 10%Cr – 10%Cu modified Silica extracted at pH of 3

Pos. [$^{\circ}2\theta$.]	Height [cts]	FWHM [$^{\circ}2\theta$.]	d-spacing [\AA]	Rel. Int. [%]
29.3042	329.39	0.1968	3.04779	100.00
38.9415	79.07	0.2460	2.31286	24.01
42.5261	40.87	0.2952	2.12584	12.41
47.8491	32.28	1.2000	1.89947	9.80

Table 4.16: Pattern List: 10%Cr – 10%Cu modified Silica extracted at pH of 3

Visible	Ref. Code	Score	Compound Name	Displacement [$^{\circ}2\theta$.]	Scale Factor	Chemical Formula
*	01-0791	15	Silicon	0.000	0.036	Si
*	23-0223	11	Copper Silicon	0.000	0.079	Cu _{0.83} Si _{0.17}
*	47-1186	13	Silicon	0.000	0.722	Si
*	03-0990	6	Copper Silicide	0.000	0.369	Cu ₄ Si
*	76-1800	9	Copper Silicon	0.000	0.195	Cu ₁₅ Si ₄
*	72-1326	4	Chromium Silicon	0.000	0.370	Cr Si

A comparison of the XRD peaks of metal impregnated silica obtained from rice husk ash leached with HNO₃ and Oxalic acid. 10% Cr and 5% Cu loaded catalysts were considered for the comparison at temperature of 750°C. For the HNO₃ leached catalyst the broad peak at around 23° 2θ started to split and new peaks at 22, 29, 31, 38 and 47° 2θ began to form on impregnation of transition metal and on reduction of the pH at which the metal modified silica catalysts were extracted. For Oxalic acid leached catalyst the peaks started to split from 15° 2θ up to higher angle side. This indicates that on oxalic acid leached catalyst, the formation of crystals is not proper. Very fine crystals are formed compared to HNO₃ leached rice husk metal impregnated catalyst.

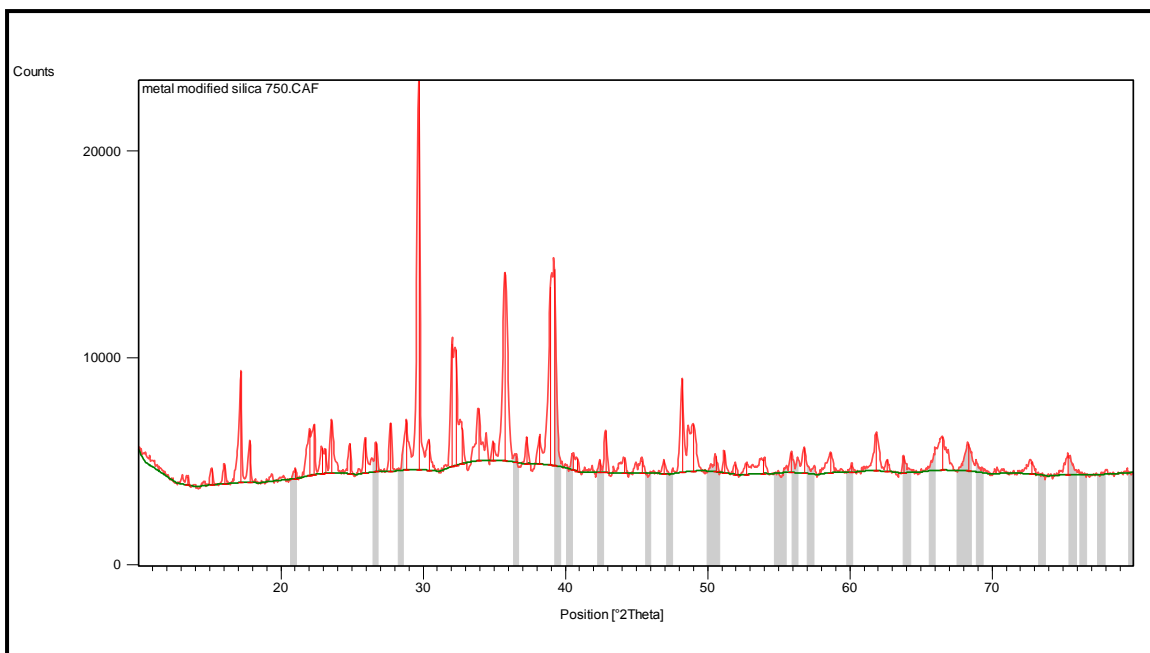


Fig 4.17:XRD analysis of Metal Modified Silica Catalyst with 10%Cr – 5%Cu from RHA extracted at pH of 10 treated with oxalic acid

4.2. FESEM Images and EDX Analysis of RHA, Silica from RH and Metal Modified Silica Catalyst

4.2.1. SEM and EDX of RHA (pyrolysed)

Pyrolysed rice husk, after acid wash with HNO_3 and pyrolysed at 750°C has been tested under FESEM and Energy Dispersive X-Ray technique was used to identify the components in the ash. The silica is mainly localized in the tough interlayer (epidermis) of the rice husk and also filling in the spaces between the epidermal cells. The FESEM images of the ash showing the pyrolysed condition of a single rice husk inner surface in 100X magnification, with a 500X magnification in the inset is shown in *Fig 4.18*. The EDX analysis confirmed the presence of silica and oxygen in the ash shown in *Fig 4.20*. Silica was found to be present in about 16.8% of the ash. The SEM image of the same ash but showing the outer shell of the husk with proturbances is shown in *Fig 4.19* and an EDX analysis shows 34% of silica on the outer part of the husk confirming that the amorphous silica in the husk lies mainly on the outer epidermis of the husk which is well organized and has a corrugated structure. The morphology is different for the outer and inner surfaces of rice husk.

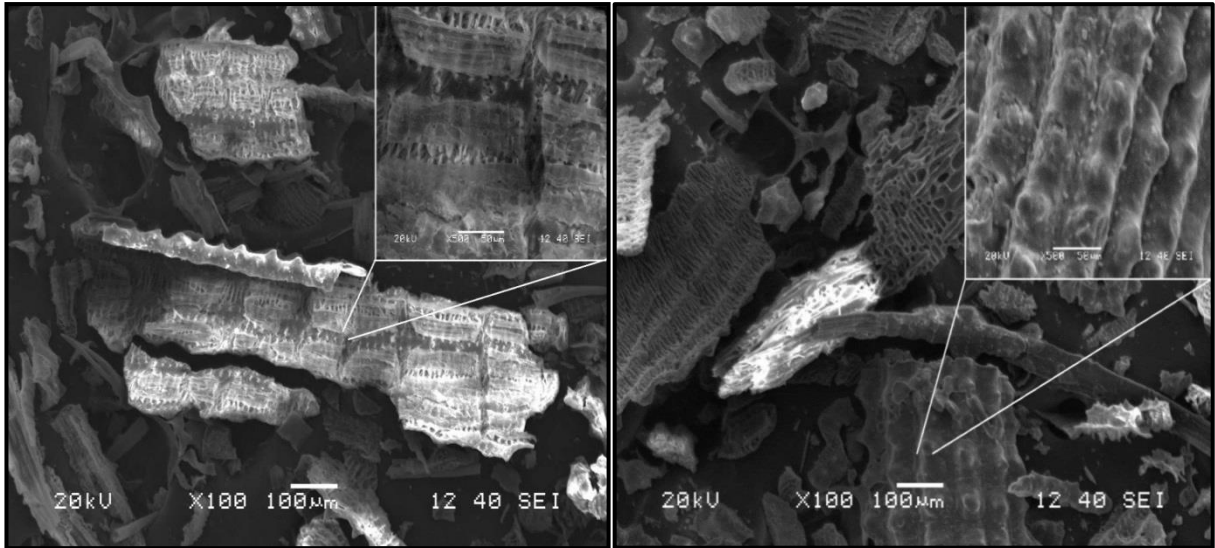


Fig 4.18: FESEM image of RHA (inner surface) **Fig 4.19:** FESEM image of RHA outer surface

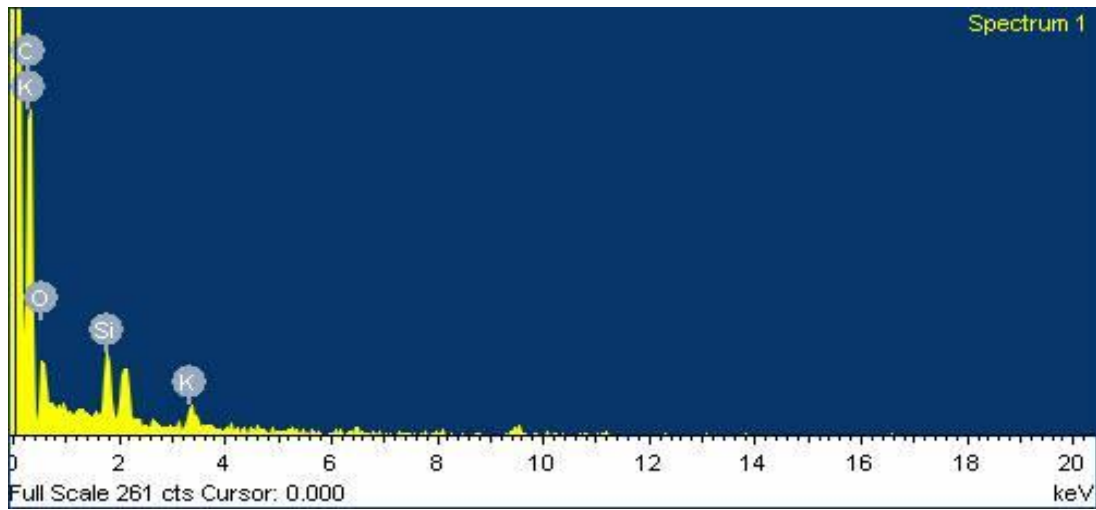


Figure 4.20: EDX pattern of rice husk ash at 650°C and leached with oxalic acid

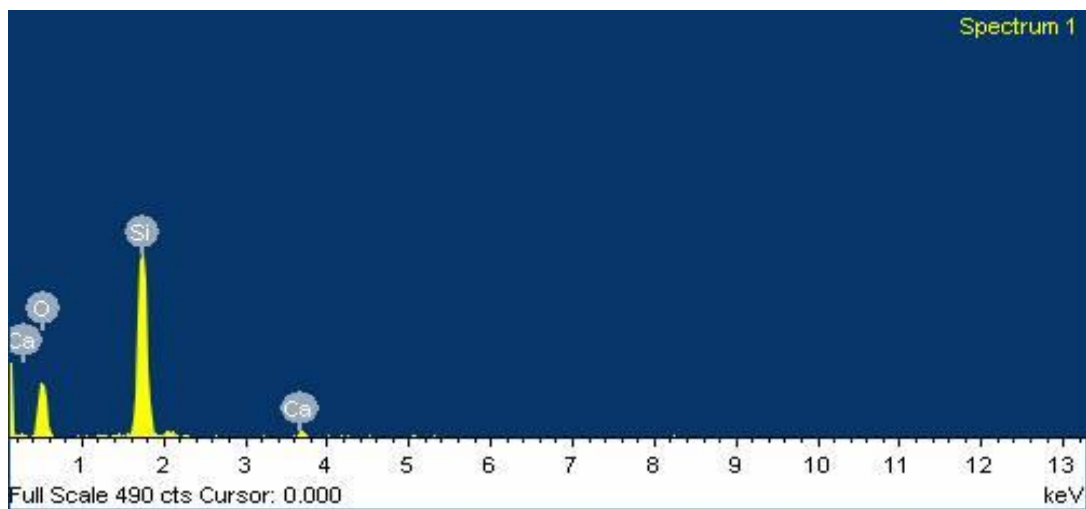


Figure 4.21: EDX pattern of RHA at 650°C without acid washed

This *Fig 4.22* shows the structure of rice husk ash which was pyrolysed at 650°C and acid washed with oxalic acid at 500X magnification. It shows the porous structure of surface and corn cob structure. The SEM structure of RHA 750 is shown in *Fig 4.23*. Cell walls around pores are fractured and elongated on heating and somewhat ordered reticulated backbones is exposed due to burning off less dense materials. RHA 750 shows less fractured internal structure and thicker cell walls reveals that it is having less pores than RHA 650°C. EDX analysis of RHA leached with oxalic acid at 650°C has shown 45.47% silica and the analysis at 750°C has shown 43% of silica. The presence of silica in SiO₂ form and oxygen are confirmed by EDX analysis shown in *fig 4.21*.

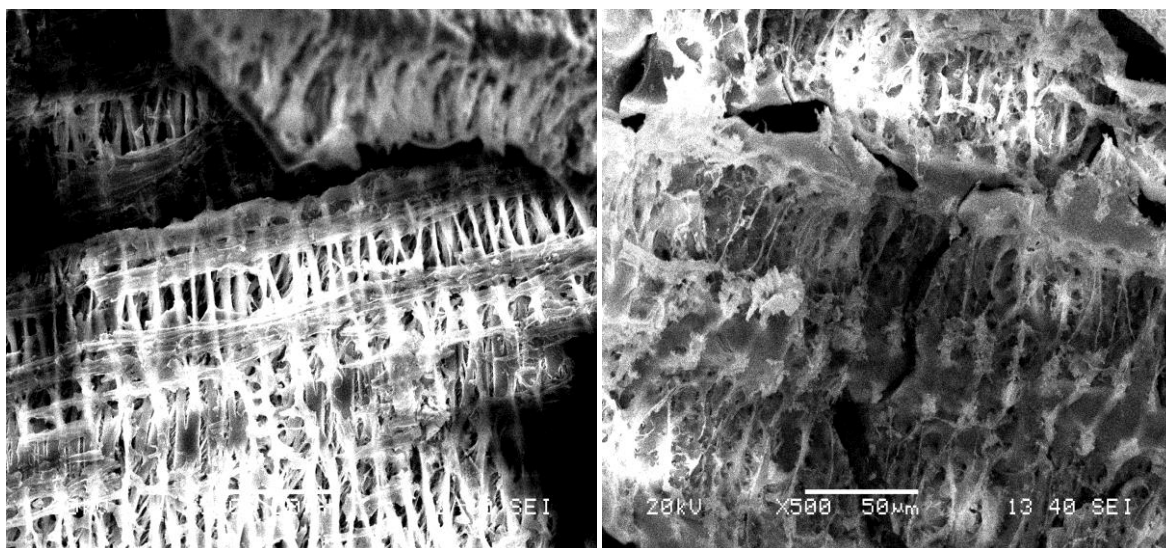


Fig 4.22: FESEM image of RHA 650° C **Fig 4.23:** FESEM image of RHA at750° C

4.2.2 FESEM and EDX Analysis of Silica Derived from Pyrolysed RHA

The silica extracted from water washed rice husk, before pyrolysis were scanned under SEM and EDX spectra analysis were performed. Silica obtained from pyrolysis of water washed RHA at temperatures of 650° C and 750° C were performed. The SEM image of silica, pyrolysed at 650° C, at 200x magnification and 500 x magnifications in the inset are shown in *Fig 4.24*. The EDX study of the silica sample indicates the presence of silicon and oxygen in form of silica 94.28% and Sodium and chlorine from the acid titration. *Fig 4.25* shows the SEM image of silica obtained from water washed rice husk pyrolysed at 750°C. EDX confirms the presence of silicon, 93.27%, in form of silica, sodium and chlorine formed during titration of the silica from the sodium silicate solution. The percentage of silicon is

seen to be little less than that in silica obtained from RHA pyrolysed at 650° C, this might be attributed to the higher presence of Na which can be removed by washing the silica filtrate before drying.

Similar to silica from RHA water washed prior to pyrolysis, silica obtained from RHA with prior acid wash with 1N HNO₃ and oxalic acid was also tested under FESEM and corresponding EDX performed. FESEM images of silica obtained at 650° C is shown in Fig 4.26. EDX analysis showed in Fig. 4.30 indicates the presence of 96.99% silicon in form of SiO₂ and 1.56% and 0.75 % of Cl and Na respectively. FESEM analysis of silica extracted from RHA after pyrolysis at 750° C with prior acid washing was also performed is also shown in Fig 4.27. EDX showed presence of 95.48% of silica in form of SiO₂ and remaining Na and Cl obtained during titration.

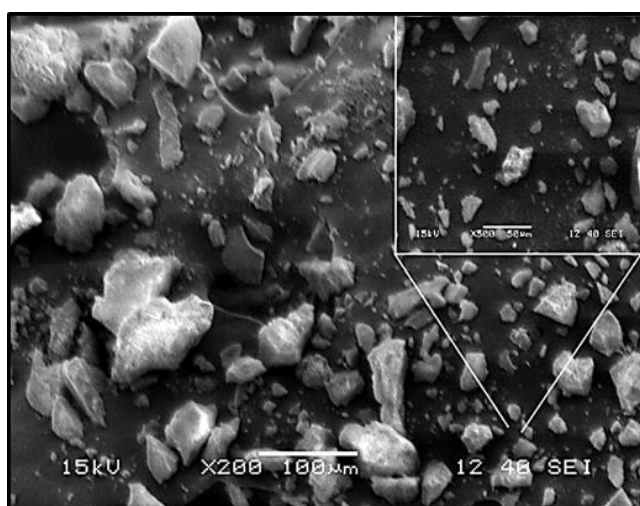


Fig 4.24: FESEM image of silica from RHA
Without acid washed at 650°C

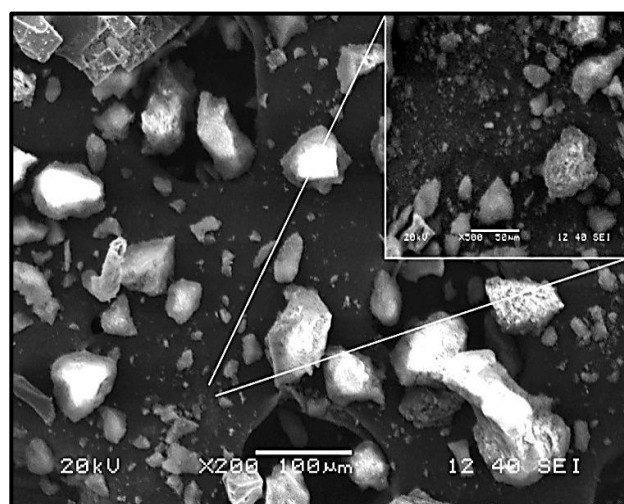


Fig 4.25: Silica from RHA without
acid washed at 750°C

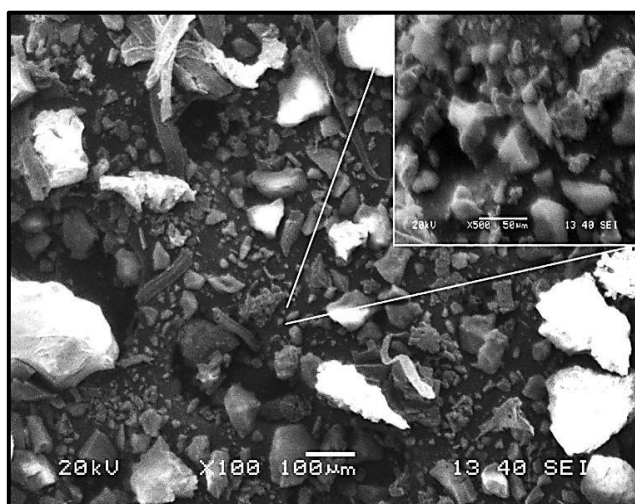


Fig 4.26: FESEM image of silica from RHA
washed with HNO₃ at 650°C

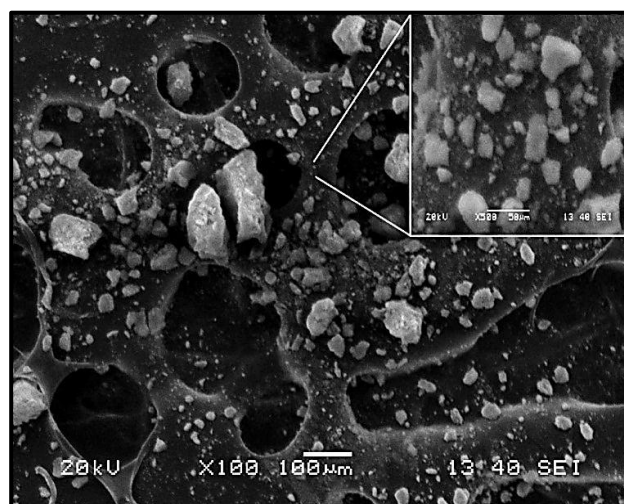


Fig 4.27: Silica from RHA Washed
with HNO₃ at 750°C

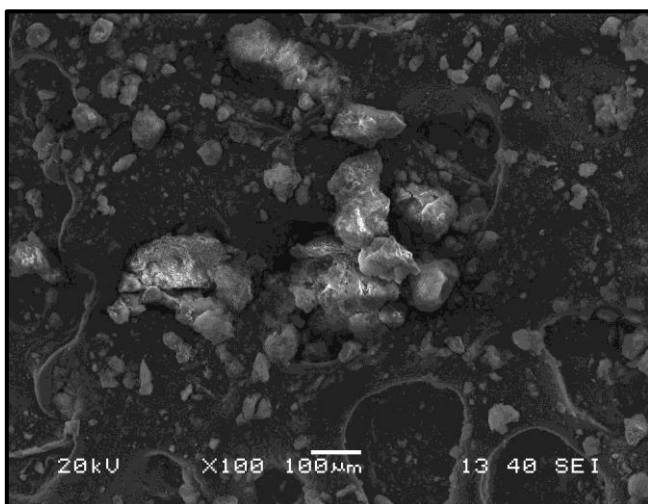


Fig 4.28: FESEM image of silica from RHA with oxalic acid (650° C)

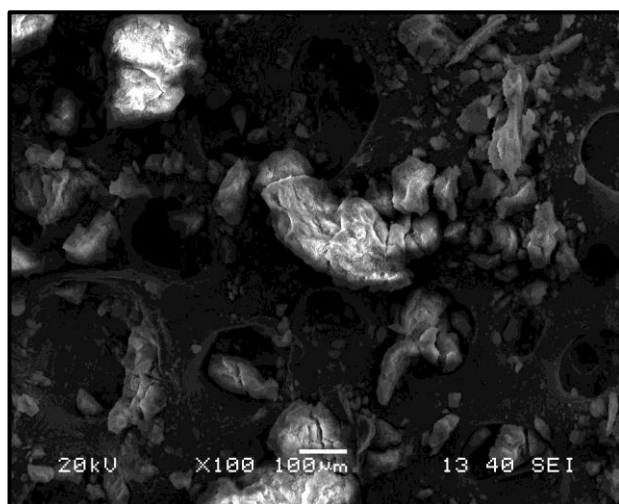


Fig 4.29: Silica from RHA acid washed with Oxalic acid at 750°C.

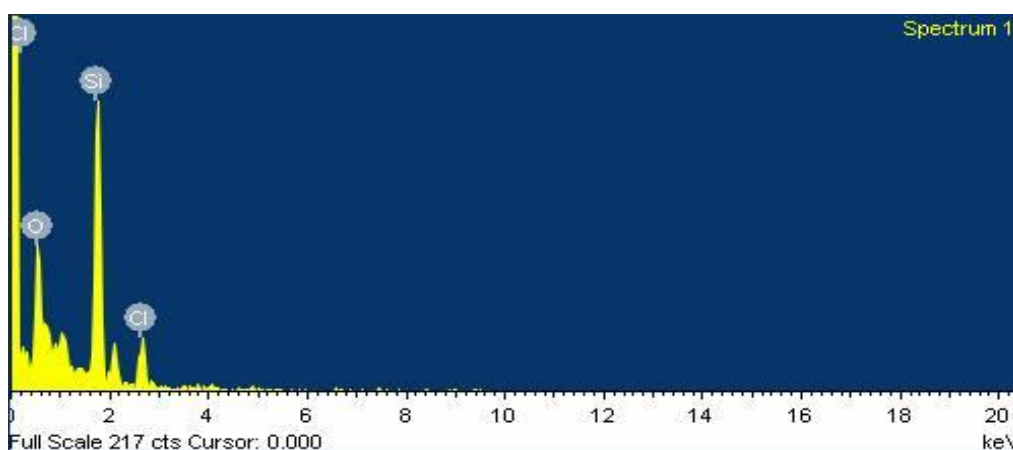


Fig4.30: EDX pattern of silica at 650°C obtained from rice husk leached with HNO₃

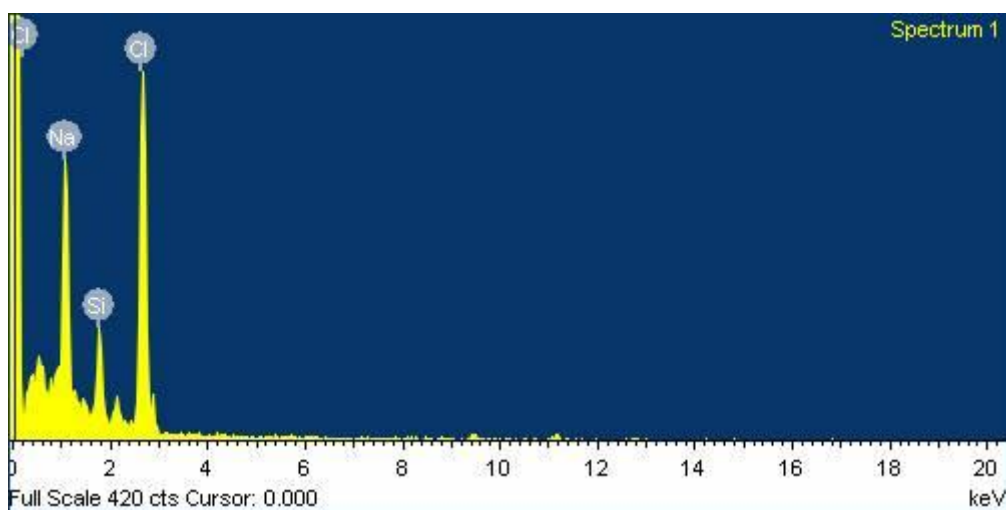


Fig4.31: EDX pattern of silica at 650°C obtained from rice husk leached with oxalic acid

Similarly, the silica obtained from oxalic acid washed rice husk ash pyrolysed at temperature of 650°C and 750°C was also analysed using FESEM and EDX. FESEM was analysed at 100X magnification is shown in *Fig. 4.28 and 4.29*. The EDX analysis of silica at 650°C showed 95.2 % of silica in the form of SiO₂ showed in *Fig.4.31* and 94.5% of silica at 750°C.

Both the *Figs. 4.32 and 4.33* are showing the FESEM image of metal modified silica. The structure of silica on which agglomerated masses are attached which are chromium and copper incorporated during synthesis at pH 10. The presence of silica in SiO₂ form is very less in percentage i.e. 31% at 650°C and 29.2% at 750°C due to the presence of chromium and copper loading which is showed in *Fig 4.34*.

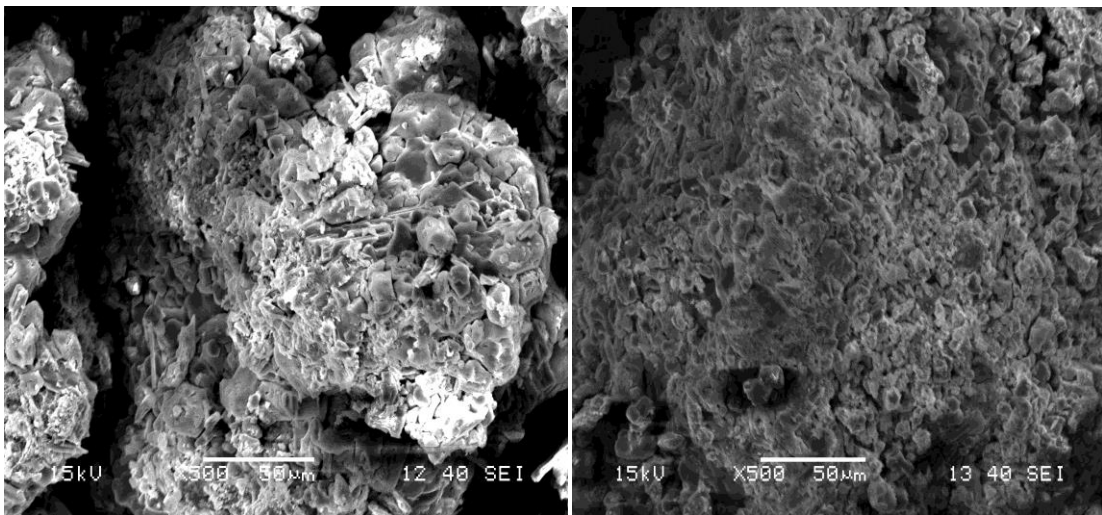


Fig 4.32: FESEM image of metal modified silica at 650°C **Fig 4.33:** Metal modified silica at 750°C

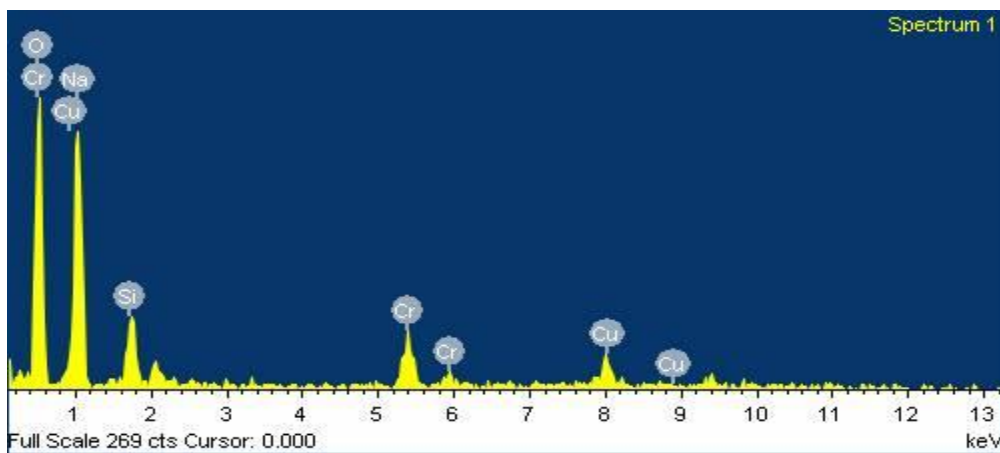


Fig4.34: EDX Pattern of metal modified silica obtained from RHA (650°C) with oxalic acid

4.3. Nitrogen Sorption Analysis

4.3.1. N₂ Adsorption-Desorption of silica derived from RH

Silica was obtained from Acid washed Rice husk pyrolysed at temperatures of 650, 750, 850°C were subjected to nitrogen adsorption and desorption tests. The multipoint BET curves indicating the isotherms are shown in *Fig. 4.35 and 4.36*. The isotherms were identified as type III indicating formation of multilayer and capillary condensation taking place in mesopores. A relative steep trend is shown for silica obtained at 750°C due to formation of multilayer. Type III isotherm curves usually result from agglomerate particles or aggregates containing non-uniform pores. The surface area, total pore volume and pore diameter were calculated using BET model and the results for the silica obtained from RHA pyrolysed at different temperatures is tabulated in *Table 4.17 and 4.18*. It is observed that the surface area decreases with the increase of the pyrolysis temperature. The increase of temperature decreases the amorphous nature of the silica obtained the microporous nature slowly diminishes due to more formation of crystalline silica at elevated temperatures. A maximum surface area was obtained for silica derived from RhSi pyrolysed at 650°C.

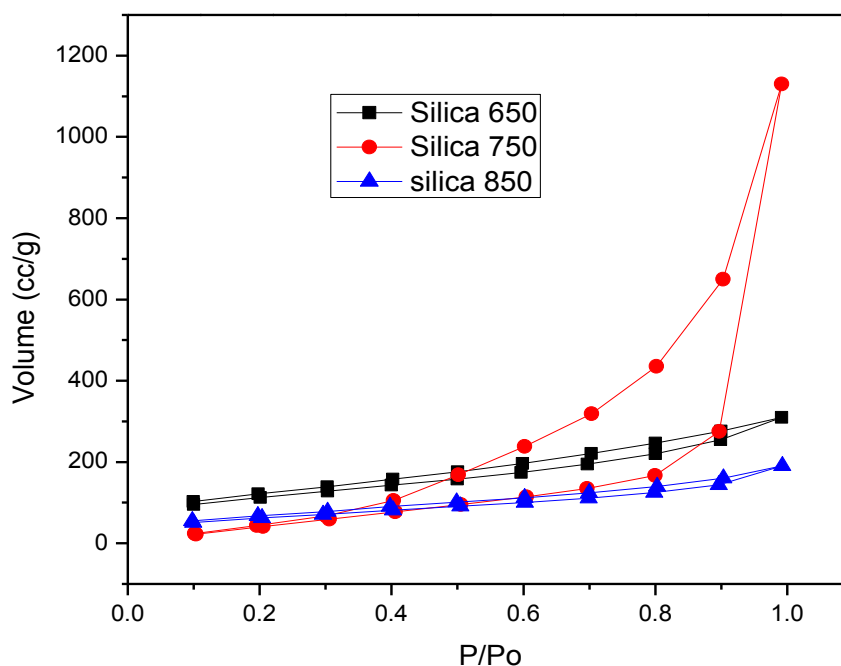


Figure 4.35: The N₂ Adsorption-Desorption analysis of Silica from RH leached with HNO₃ at different temperatures

Table 4.17: The N₂ Adsorption-Desorption Analysis Parameters of Silica Based on BET Calculations

Type of Silica	BET surface area (m ² /g)	Pore volume (cc/g)
Silica (RhSi650°C)	343.36	0.4796 for pores smaller than 225.9 nm
Silica (RhSi750°C)	243.25	0.2943 for pores smaller than 256.4 nm
Silica (RhSi 850°C)	119.56	0.1748 for pores smaller than 229.36 nm

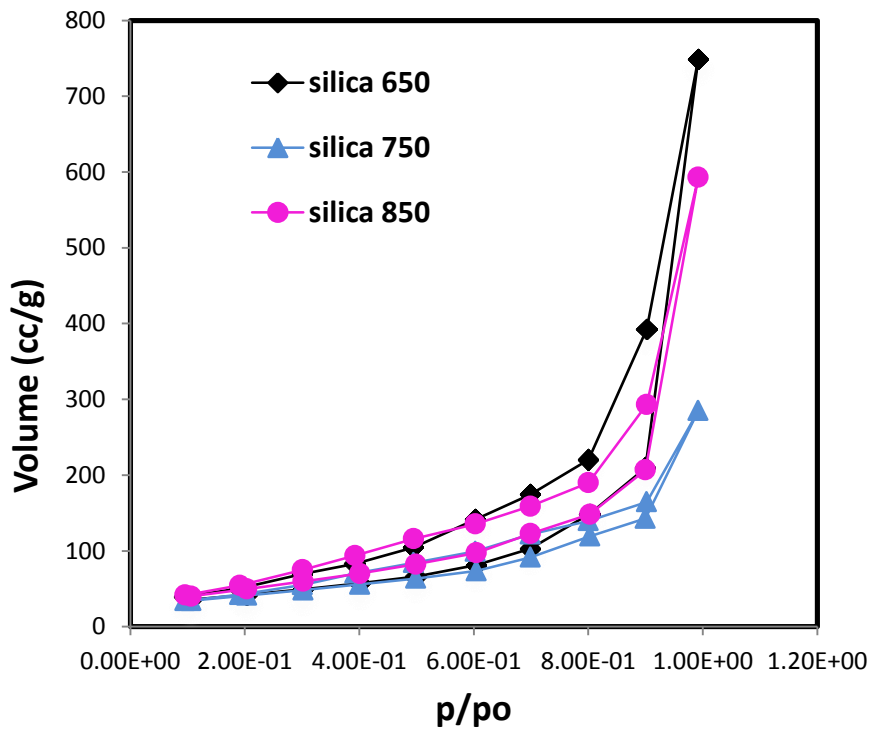


Figure 4.36: The N₂ Adsorption-Desorption analysis of Silica from RH leached with Oxalic acid at different temperatures

Table 4.18: The N₂ Adsorption-Desorption Analysis Parameters of Silica(treated with oxalic acid) Based on BET Calculations

Type of Silica	BET surface area (m ² /g)	Pore volume (cc/g)
Silica (650°C)	362	1.158 for pores smaller than 241.9 nm
Silica (750°C)	359	0.54 for pores smaller than 256.4 nm
Silica (850°C)	234	0.175 for pores smaller than 237.36 nm

A comparison on the BET surface area obtained after BET analysis of silica obtained from rice husk leached with HNO₃ and rice husk treated with Oxalic acid pyrolysed at different temperatures showed that the surface area is high for oxalic acid treated rice husk silica.

4.3.2. N₂ Adsorption-Desorption of metal Modified Silica Catalyst derived from rice husk ash

Fig. 4.37 shows the BET isotherms of Metal Modified Silica Catalyst extracted at pH of 10, 7 and 3. All the three catalysts exhibit type III adsorption isotherm curves. The volume of N₂ adsorbed for the catalyst extracted at lower pH is lower than that extracted at higher pH. The low specific surface area and low pore diameter in case of higher metal loading in comparison to the catalyst with lower metal loading, i.e higher pH causes the above. The isotherms of the catalysts extracted at the pH of 10, 7 and 3 have hysteresis loop. Presence of hysteresis loops indicates that a network of pores exist on the surface of silica. They are supposed to have narrow openings and a larger pore with the matrix, typically looking like ink-bottle shaped pores. Nitrogen accumulates and gets adsorbed in the small pores and its narrow openings. During desorption the rate of desorption does not match the adsorption rate and volume and some residual gases remain blocked in the pores leading to the fact that the adsorption and desorption lines don't meet. Type H3 hysteresis loop was observed for all the samples indicating that the catalyst has a wide pore size distribution consisting of various sized pores and having aggregated or agglomerated particles with non-uniform size and shape. The N₂ sorption surface

analysis parameters are presented in *Table 4.19*. A trend of decreasing surface area with increasing metal loading, i.e. decreasing pH, is observed. This is due to more metal uptake by the silica during preparation using the sol-gel techniques. The same trend has shown in *Fig 4.38 and Table 4.20*.

RhSi-Cr/Cu-10 was found to have a pore size in the range of 105 – 198 Å, RhSi-Cr/Cu-7 has a pore size range of 89 – 180 Å and RhSi-Cr/Cu-3 in the range of 62 – 155 Å. The incorporation of chromium and copper was found to close the smaller pores that existed in the RhSi-10 and RhSi-7. The specific surface area of RhSi extracted at pH 7 for samples pyrolysed at 750°C was 243.25 m²/g which decreased, on incorporation of chromium and copper, to 111.1 m²/g. The amount of chromium and copper loaded had a direct influence for decreasing the surface area of the catalysts.

On comparison of HNO₃ acid washed rice husk metal modified silica with oxalic acid washed rice husk metal modified silica showed the less specific surface area for oxalic acid washed rice husk metal modified silica at pH 10.

Table 4.19: The N₂ Adsorption-Desorption Analysis Parameters of Metal modified Silica Catalyst based on BET Calculations

Type of Silica Catalyst	BET surface area (m ² /g)	Pore volume (cc/g)
RhSi-Cr/Cu-10	182.7	0.2798 for pores smaller than 197.35 nm
RhSi-Cr/Cu-7	111.1	0.2402 for pores smaller than 217.15 nm
RhSi-Cr/Cu-3	79.94	0.1943 for pores smaller than 235.23 nm

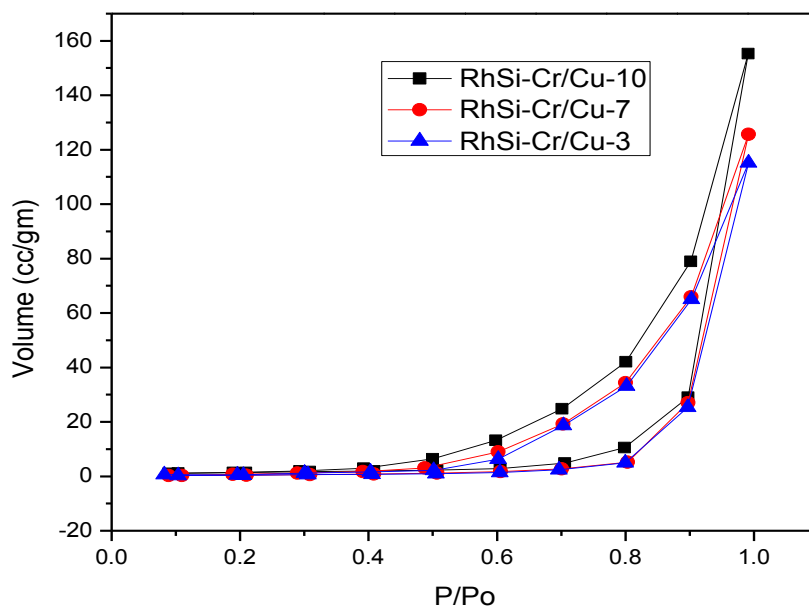


Figure 4.37: The N_2 Adsorption-Desorption analysis of Metal Modified Silica Catalyst from RH extracted at different pH

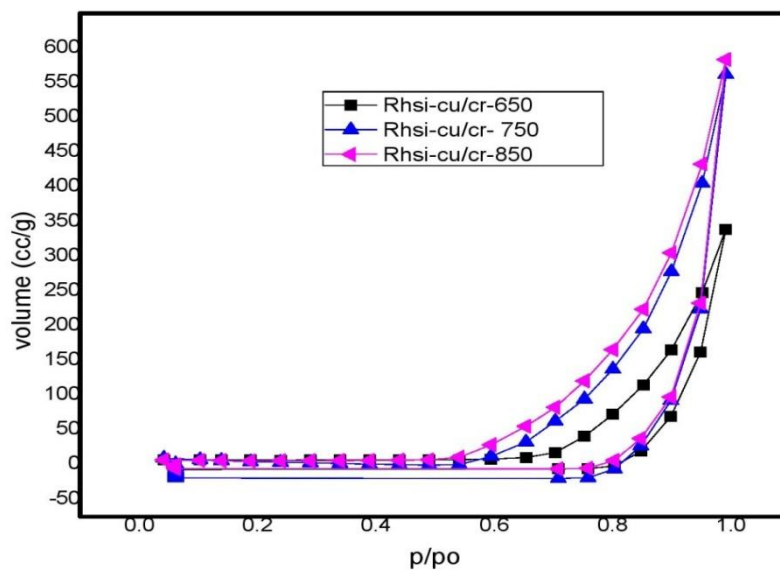


Figure 4.38: The N_2 Adsorption-Desorption analysis of Metal Modified Silica Catalyst from RH extracted at different pH

Table 4.20: The N₂ Adsorption-Desorption Analysis Parameters of Silica (RH treated with oxalic acid) Catalyst based on BET Calculations

Type of Silica Catalyst	BET surface area (m ² /g)	Pore volume (cc/g)
RhSi-Cr/Cu-10 (650°C)	161	0.902 for pores smaller than 225.6 nm
RhSi-Cr/Cu-10 (750°C)	104	0.869 for pores smaller than 224.1 nm
RhSi-Cr/Cu-10 (850°C)	72	0.524 for pores smaller than 228.4 nm

4.6. Oxidation of Styrene in the Liquid Phase.

The samples were removed at intervals of one hour from the reaction vessel to which 1 µl of m-xylene was added and the samples immediately injected into the GC-MS chamber. Benzaldehyde (Bhd) was the main product detected from GC and GC-MS. The byproducts produced were phenylacetaldehyde (PhAhd), benzoic acid (BzA) acetophenone (AcPh) and phenylglyoxal (PhGal). A maximum conversion of 76.65% of styrene was observed for RhSi-Cr/Cu-3 while only 12.56% conversion of styrene is observed for RhSi-Cr/Cu-10 has shown in *Table 4.21*. RhSi-Cr/Cu-7 has a medium conversion of 43.41%. RhSi-Cr/Cu-10 and RhSi-Cr/Cu-7 have higher surface area. Thus the diffusion of reactants and the products in and out from the pores are hindered due to unavailability of surface pores. The amount of chromium and copper loaded rather than the pore size distribution or surface area of the catalysts causes its catalytic activity. This observation corresponds to other literature where chromium-silica or copper-silica catalysts have been used for other types of oxidation reactions using H₂O₂ as oxidant. Bhd was only found when RhSi-Cr/Cu-10 was used as the catalyst with selectivity of PhAhd and AcPh are slightly higher when RhSi-Cr/Cu-7 was used compared to RhSi-Cr/Cu-3. BzA selectivity was 3 times higher when RhSi-Cr/Cu-3 was used compared to RhSi-Cr/Cu-7. A greater amount of BzA is found when greater amount of chromium and copper active sites causes oxidation of Bhd to BzA. Due to the higher catalytic activity of RhSi-Cr/Cu-3 it was further used to evaluate other reaction parameters.

Table 4.21: The effect of preparation pH of catalyst on the product selectivity during oxidation of styrene

Catalyst	Conversion (%)	Bhd (%)	PhAhd (%)	AcPh (%)	BzA (%)
RhSi-Cr/Cu-10	12.56	99.84	0	0.16	0
RhSi-Cr/Cu-7	43.41	82.14	5.6	6.3	5.96
RhSi-Cr/Cu-3	76.65	79.42	4.4	4.09	12.09

Effect of metal loading, i.e increasing the amount of Copper ion the catalyst was also analysed. RhSi-Cr/Cu-3 having 10%Cr and 5% Cu and RhSi-Cr/Cu-3 having 10%Cr and 10%Cu were compared keeping all other parameters like H₂O₂ to styrene ratio, temperature of reaction and mass of catalyst used same is depicted in *Table 4.22*. Conversion percent is seen to further increase on increasing copper loading content with increase in Bza selectivity too. Acetophenone and benzoic acid selectivity is also found to decrease. Overall More copper loading has given better conversion and also better selectivity to benzaldehyde and also reduced undesired products.

Table 4.22: The effect of copper loading in the catalyst on the product selectivity and conversion.

Catalyst	Conversion (%)	Bhd (%)	PhAhd (%)	AcPh (%)	BzA (%)
RhSi-Cr/Cu-3, 5% Cu	76.65	79.42	4.4	4.09	12.09
RhSi-Cr/Cu-3, 10% Cu	89.41	82.13	3.6	3.26	11.01

CHAPTER 5

EPILOUGE

5.1 Conclusions:

This work was carried out to extract silica from rice husk based on alkaline treatment of pyrolysed rice husk ash followed by acid precipitation. It is observed that the removal of mineral contaminants from the rice husk increased the yield of silica. The removal of contaminants by acid washing was carried out by using organic (Oxalic acid) as well as mineral (HNO_3) acid and pyrolysis was carried out in the temperature range of 650°C to 850°C . On comparison of acid washings between mineral acid and organic acid, it is found that the mineral acid is not environment friendly and it needs high amounts of water for the removal of acid. But it removes mineral contaminants efficiently than the organic acid. All the commercial techniques used to produce silica are operated at around 1400°C but the process used in this work has been operated in the temperature range of 650°C - 850°C . This proves that the present process is highly useful and energy efficient for waste utilization. The obtained silica was further treated for catalytic effect. To increase its catalytic activity, transition metals were incorporated on the surface of silica by sol-gel technique where acid precipitation was found to occur. It is observed that metal modified silica is obtained at three different values of pH of final solution (i.e. at pH of 3,7 and 10).

A comparison was made among all samples which were treated at various temperatures and leached with different acids during acid washings. The amorphous nature of silica obtained was proved by XRD analysis. BET studies revealed that the surface area decreases on increasing pyrolysis temperature and also by increasing metal loading. It is observed that high surface area is obtained with pyrolysis temperature of 650°C and at pH of 10. This study proved that the obtained silica contained high surface area in microporous range which can be used as catalyst framework and adsorbents. EDX analysis further confirmed the presence of silica in white ash and presence of metals and silica in metal modified silica.

Liquid phase oxidation of styrene was carried out by using the developed catalysts. The main product obtained was benzaldehyde (BZA). This product was characterized with GC and GC-MS analysis. The comparison was made for different catalysts developed at different pH values (i.e. 3, 7 and 10) and with different loading

concentrations of copper (i.e. 5% and 10%). This study revealed that the conversion of styrene is more for pH of 3 and for catalyst prepared with 10% copper loading. It is further observed that although the conversion is high for catalyst prepared at pH of 3, its surface area is less compared to catalysts prepared at pH of 7 and 10. This study proves that the catalytic activity not only depends on surface area but also on other factors like metal loading. This catalyst is useful in many catalytic activities in industries.

5.2 Future Work

Effect of pyrolysis temperature and effect of concentration of metal ions, effect of aging the precipitate, effect of calcining the dried catalyst, SDA concentration can be checked to obtain best possible method to prepare the catalyst. The reusability of the catalyst can also be checked. Styrene can be a common substance which can be chosen to be oxidized in presence of an oxidizing agent like H_2O_2 . The effect of varying the reaction temperature and time, use of different weight of catalyst, styrene to H_2O_2 ratio in the conversion percentage to benzaldehyde and conversion to product can be analyzed.

REFERENCES:

- [1] K.Y. Foo, B.H. Hameed *Advances in Colloid and Interface Science* 152 (2009) 39–47
- [2] K. Kordatosa, S. Gavelaa, A. Ntziounia, K.N. Pistiolasb, A. Kyritsib, V. Kasselouri-Rigopoulou, *Microporous and Mesoporous Materials* 115 (2008) 189–196
- [3] N. Yalcin, V. Sevinc, *Ceramics International* 27 (2001) 219–224
- [4] M.-T. Tsay, F.-W. Chang, Characterization and Reactivity of RHA-Al₂O₃ Composite Oxides Supported Nickel Catalysts. *J. Catal. Commun.* 2 (2001) 233–239.
- [5] W.-S. Chen, F.-W. Chang, L.S. Roselin, T.-C. Ou, S.-C. Lai., Partial oxidation of methanol over copper catalysts supported on rice husk ash. *J. Mol. Catal. A: Chem.* 318 (2010) 36–43.
- [6] F.-W. Chang, H.-C. Yang, L.S. Roselin, W.-Y. Kuo., Ethanol dehydrogenation over copper catalysts on rice husk ash prepared by ion exchange. *Appl. Catal. A: Gen.* 304 (2006) 30–39.
- [7] N. Grisdanurak, S. Chiarakorn, J. Wittayakun, Utilization of Mesoporous Molecular Sieves Synthesized from Natural Source Rice Husk Silica to Chlorinated Volatile Organic Compounds (CVOCs) Adsorption. *Korean J. Chem. Eng.* 20 (5) (2003) 950–955.
- [8] D.J. Londeree, Silica–Titania composites for water treatment, M. Eng. Thesis, University of Florida, (2002).
- [9] T.W. Dijkstra, R. Duchateau, A. Rutger, van Santen, A. Meetsma, G.P.A. Yap, *J. Am. Chem. Soc.* 124 (2002) 9856–9864.
- [10] J.A.J. Conner, W.A. Mallow, R.S. Rieber, Patent Genius 6524543
- [11] M.S. Joel, Chemically Modified Surfaces in Catalysis and Electrocatalysis, *ACS Symposium Series* 192, (American Chemical Society, Washington D.C., (1982), p. 1
- [12] F. Adam, A. Iqbal, The liquid phase oxidation of styrene with tungsten modified silica as a catalyst, *Chem. Engg. Journal.* 171 (2011) 1379–1386.
- [13] F. Adam, A. Iqbal, The oxidation of styrene by chromium–silica heterogeneous catalyst prepared from rice husk, *Chem. Engg. Journal.* 160 (2010) 742–750.
- [14] Z. Xinhong, W. Xiaolai, Synthesis, characterization and catalytic application of Cr–SBA-1 mesoporous molecular sieves, *J. Mol. Catal. A: Chem.* 261 (2007) 225–231.
- [15] Protor, A., J. Shultz, and U. Kalapathy. 2000. A simple method for production of pure silica from rice hull ash. *Bioresource Technology* 73:257–264.
- [16] Hunt, L. P., J. P. Dismukes, and J. A. Amick. 1984. Rice hull as a raw material for producing silicon. *Journal of the Electrochemical Society* 131:1683–1686.
- [17] Sanhuezu et al, synthesis of mesoporous material from two sources *J. Chem. Technology. Biotechnology.* 81 (2006) 614–617.

- [18] U. Kalapathy, A. Proctor, J. Shultz, A simple method for production of pure silica from rice hull ash, *Bioresour. Technol.* 73 (2000) 257.
- [19] N. Yalcin, V. Sevinc, Studies on silica obtained from rice husk, *Ceramics Int.* 27 (2001) 219.
- [20] C.J. Lee, G.S. Kim, S.H. Hyun, Synthesis via Silica Aerogels from Waterglass via new modified ambient drying. *J. Mater. Sci.* 37 (2002) 2237.
- [21] S-W. Hwang, H.H. Jung, S.H. Hyun, Y.S. Ahn, Effective preparation of crack-free silica aerogels via ambient drying. *J. Sol-Gel Sci. Technol.* 41 (2007) 139.
- [22] P.B. Sarawade, J-K Kim, A. Hilonga, H.T. Kim, Production of low-density sodium silicate-based hydrophobic silica aerogel beads by a novel fast gelation process and ambient pressure drying process. *Solid State Sci.* 12 (2010) 911.
- [23] T.Wang, Q. Tang, Silica aerogels. CN Patent 1449997A(2003).
- [24] Q. Tang, T.Wang, Preparation of silica aerogel from rice hull ash by supercritical carbon dioxide drying. *J. Supercrit. Fluids* 35 (2005) 91.
- [25] Farook Adam, Jimmy Nelson Appaturi, Anwar Iqbal, *Catalysis Today* 190 (2012) 2– 14
- [26] F.W. Chang, H.C. Yang, L.S. Roselin, W.Y. Kuo, *Appl. Catal. A: Gen.* 304 (2006) 30– 39.