SULPHATED MESOPOROUS SILICA SYNTHESIZED FROM RICE HUSK ASH FOR CHALCONE PRODUCTION

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ABSTRACT

Chalcone is an aromatic ketone that have important biological properties. It can be prepared by an aldol condensation between a benzaldehyde and an acetophenone in the presence of catalyst. A series of S-MCM-48 (SO_4^{2-} / MCM-48) was synthesized in this study. Rice husk ash (RHA), an agriculture waste was used as a silica (SiO_2) source to synthesis the MCM-48 mesoporous molecular sieves by mean of hydrothermal method and sulphation medification using sulfuric acid (H_2SO_4) as the sulphate sources. The pore packing order of the SO_4^{2}-doped material dependend strongly on the synthesis conditions such as aging temperature, pH of reaction mixture and dopant concentration. The physicochemical properties of mesoporous material was characterized by X-Ray diffraction (XRD), surface area analysis (BET), Fourier- Transform Infrared Spectroscopy (FTIR) and Thermogravimetric Analyzer (TGA). A simple preparation method was used to generate strong acidity catalyst by introducing sulphate groups onto the surface of MCM-48. The prepared sulphated MCM-48 has been used to catalyzed benzaldehyde and acetophenone and was analyzed by using GC. The conversion of acetophenone was calculated and the best conversion was 85.5% by using S-MCM-48(60) catalysts.

Keyword: SO_4^{2}-doped MCM-48; Heterogeneous catalyst; chalcone; mesoporous materials.

ABSTRAK

Chalcone adalah keton aromatik yang mempunyai sifat-sifat biologikal yang penting. Ia boleh disediakan melalui kondensasi aldol di antara benzaldehid dan asetofenon dengan kehadiran pemangkin. Siri sulphated-doped MCM-48 (SO_4^{2-} / MCM-48) telah di sintesis di dalam kajian ini. Abu sekam padi (RHA), adalah sisa pertanian yang digunakan sebagai sumber silika (SiO_2) untuk mensintesis MCM-48 penapis molekul mesoliang dan pengubahsuaian sulfat telah menggunakan asid sulfurik (H_2SO_4) sebagai sumber sulfat. Sulfat-pengisitepuan MCM-48 penapis molekul mesoliang telah disintesis secara hidrotermal. Urutan pengumpulan liang dari bahan SO_4-pengisitepuan sangat bergantung kepada beberapa keadaan sintesis penuaan seperti suhu, tindak balas campuran pH dan kepekatan pengisitepuan. Struktur bahan-bahan mesoliang diperincikan dengan pelbagai jenis kaedah fizik-kimia, dan maklumat sifat-sifat bahan yang diperolehi di antaranya dari teknik pembelauan sinar-X (XRD), luas permukaan analisis (BET), Fourier-Transform Spektroskopi Inframerah (FTIR) teknik dan analisis Termogravimetri (TGA). Satu sintesis mudah untuk menghasilkan mangkin asid kuat dengan menambahkan kumpulan sulfat ke permukaan MCM-48. S-MCM-48 penapis molekul mesoliang telah di gunakan untuk pemangkinan benzaldehid dan asetofenon dan telah di analisis menggunakan kromatografi gas (GC). Pertukaran hasil telah dikira dan pertukaran yang terbaik adalah 85.5% oleh pemangkin S-MCM-48(60).

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λ	wavelength
μ	micron (10^{-6})
2Θ	Bragg angle
m^2/g	meter square per gram
mL	milliliter
N_2	nitrogen
R^2	linear regression
^oC	degree celcius
kJ/kg	kilo joule per kilo gram
Cd^{2+}	cadmium ion
Zn^{2+}	zinc ion
ZSM-5	Zeolite Socony Mobil – 5
K	Kelvin
S_{BET}	specific surface area BET
nm	nano meter
g	grams

LIST OF ABBREVIATIONS

CTABr	Cetyltrimethylammonium bromide
CS	Claisen-Schmidt
[APN]/ [MB]	Concentration of acetophenone per concentration methyl benzoate
FTIR	Fourier Transformed Infrared
GC	Gas Chromatography technique
GC-FID	Gas Chromatography-Flame Ionized Detector
SiO_2	Silica
H_2SO_4	Sulfuric acid
S-MCM-48	Sulfate-doped MCM-48
BET	Surface area analysis
TGA	Thermogravimetric Analyzer
XRD	X-ray Diffraction technique
S- MCM-48(30)	30μl sulfate-doped MCM-48
S- MCM-48(60)	60μl sulfate-doped MCM-48

CHAPTER 1

INTRODUCTION

1.1 Research Background

Chalcones are a privileged class of compounds reported to have important biologically active properties. It is an important class of compounds widely distributed in nature and considered as the precursors for flavonoid synthesis in plants. Chemically, they consist of an open chain in which the two aromatic rings are joined by a three carbon unsaturated carbonyl system. For a structurally simple group of compounds, chalcones have displayed an impressive array of pharmacological activities including antimalarial and antileishmanial as well as antimicrobial, anti-inflammatory and antiviral effects. Of particular interest, the effectiveness of chalcones as potential anti-inflammatory and cancer chemopreventive agents has been investigated and are in the origin of a renewed interest in this class of compounds [1]. Chalcone derivatives have received a great deal of attention due to their relatively simple structures, and wide variety of pharmacological activities reported for these compounds include anti-inflammatory, antifungal ,antibacterial antimalarial and antitumor activities [2].

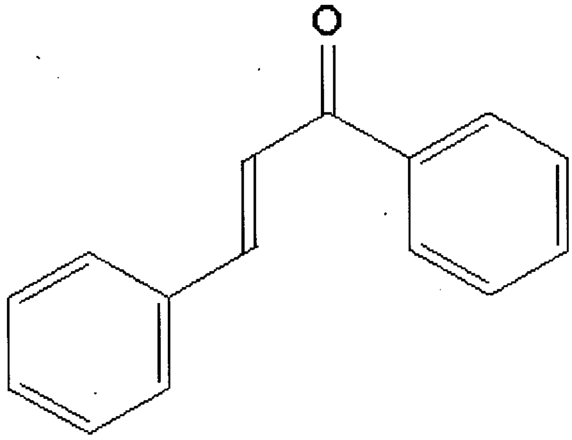


Figure 1.1 : Structure of Chalcone

Chalcones are valuable intermediates in the synthesis of many active pharmaceutical drugs like biosynthesis of flavonoids and Auwers synthesis of flavones [3]. Traditionally, chalcones could be obtained via Claisen-Schmidt condensation between acetophenone and benzaldehyde carried out in basic or acidic media under homogeneous conditions. However, homogeneous reactions present several hurdles, such as catalyst recovery and waste disposal problems. In this respect, heterogeneous catalysts combined with solvent-free reaction condition are considered as an eco-friendly alternative [4]. This reaction is catalyzed by acids and bases under homogeneous or heterogeneous conditions. Several researchers have reported the synthesis of chalcone by using different catalysts like zinc oxide, organolithium, KF–Al_2O_3 , modified phosphates, zeolites and hydrotalcites to get a better specification of chalcone products with low by-products and higher yield [5].

In view of the drawbacks, they are designing the specific deposition of acidic active sites on the large surface area and pores of mesoporous material for chalcone synthesis. In this study, purely siliceous MCM-48 will be synthesized using rice husk ash as catalyst support. The support will be functionalized with acid to promote formation of acid site on the support surface [6, 7].

In severe research, the synthesis of chalcone can be catalyzed by acids and bases under homogeneous or heterogeneous conditions. Researchers have published several reports on use of ultrasound as a process intensification tool for numerous catalytic reactions as well as in homogeneous and in heterogeneous reactions and it has proved to be a clean tool for improving yields and decreasing reaction time [5]. Despite the increase of research activities in the field of heterogeneous catalysis, synthesis of disubstituted compound using zeolite has not so far been successful. Although heterogeneously catalysed reactions using microporous molecular sieve did not show much potential, the large internal surface area and channel apertures of mesoporous molecular sieve MCM-41 is a promising alternative for reactions involving large molecules [6].

Our research strategy is to utilize the large surface area, pores and hydroxyl groups of mesoporous material i.e MCM-48 [8]. It is reported that MCM-48 synthesized from rice husk ash shows surface area >1300 m^2/g and pore volume >1.6 cm^3/g [8] which suggest that MCM-48 was among the best candidate to be use as support. Due to the high surface area and large number of hydroxyl groups of MCM-48, it is predicted to provide large amount of active site attachment. Besides, MCM-48 with its three dimensional pore system has been suggested to be a more advantageous system for catalytic applications, since it could allow faster diffusion through the channels and make this material more resistant to pore blocking [8].

MCM type materials are synthesised in the presence of a structure-directing agent surfactant in acidic/basic aqueous solution [9].Several studies have been conducted in the past to investigate the properties and the performance of the alumina mesoporous MCM-41 as catalyst supports. Mesoporous MCM-48 silica was synthesized using a cationic-neutral surfactant mixture as the structure-directing template and rice husk ash (RHA) as the silica source. The hydrothermally stable MCM-48 mesoporous molecular sieve was successfully prepared at extremely low cost using cetyltrimethylammonium bromide (CTABr) by carefully adjusting the synthesis conditions.In consideration of the excellent pore structure and to accelerate the application of MCM-48, many researchers have devoted their attentions on optimizing the synthesis conditions for MCM-48 by adjusting the crystallization temperature, crystallization time and adding assistants such as salts or cosurfactant [12]. MCM-48 can be synthesized by different ways with highly specific surface area, specific pore volume, and narrow pore size distribution. It shows high thermal stability up to 750 °C [13].

Since the utilization of base and organo-sulfonic acid led to low chalcone conversion [14-16, 17], we are targeting to enhance the activity using both the Brønsted and Lewis sites. Mesoporosity on the other hand will affect accessibility and dispersion of acid in MCM-48. In this research, Lewis acid will be selectively inserted into the mesopores resulting in either internal deposition or both internal and external deposition. The research will use the wet incipient technique in order to directively position the active sites [18, 19]. Sulfated-doped MCM-48 molecular sieve were synthesize hydrothermally. A range of acid loading will be prepared to investigate the optimum acid loading towards chalcone synthesis.

1.2 Problem Statement

There are many solid basic catalysts that have been applied in the synthesis of chalcone, such as MgO, hydrotalcites, natural phosphates, and aminopropylated mesoporous silica. Even though these reactions provide advantages due to their heterogenous nature. However, most of them require rather complicated preparation of the catalysts [16]. Recently, to improve the production in synthesis of chalcones, solid acid catalysis has been tried, but only few catalysts have been reported. Mesoporous molecular sieves with high surface area and large pore diameters overcome pore diameter constraint of zeolites and allow facile transformation of bulky molecules. Hence, it is among the suitable candidate to be used as support in chalcone synthesis in respect to its unique properties.

For chalcone synthesis using solid acid catalyst, both Brønsted and Lewis acid sites play a role in contributing excellent conversion and selectivity. In addition, funtionalization of mesoporous material with suitable functional groups could enhance catalysts performance. Several studies incorporating catalyst support with organo-sulfonic acid groups had been reported, however, Claisen-Schmidt condensation reactions showed limited catalytic avtivity in poor conversion and low chalcone yield.

1.3 Objectives

The objectives of this study are:

1. To synthesis the Silicious MCM-48 doped with sulphate.
2. To characterized the resulting catalyst using several physico-chemical method.
3. To test the catalytic activity of sulphated MCM-48 in chalcone production.

1.4 Scope of Study

The scope of this study is basically to synthesize and characterize the catalyst using several physico-chemical method and to determine the catalytic activity of sulphated-doped MCM-48 for chalcone production. There are some significant tasks to be carried out in order to achieve the objective of this study.

I. In this study, the Silicious MCM-48 doped with sulphate will be hydrothermally synthesized.

II. The characterization of the result catalyst using Powder X-ray diffraction (XRD), Fourier Transformation Infrared (FTIR), BET Surface Area Analysis, Thermogravimetric Analyzer (TGA).

III. Testing catalytic activity will be studied using a benzaldehyde and an acetophenone and analyze it by using Gas Chromatography-Flame Ionized Detector (GC-FID).

CHAPTER 2

LITERATURE REVIEW AND RESEARCH BACKGROUND

2.1 Catalyst

Catalysts are chemical compounds capable of directing and accelerating thermodynamically feasible reactions while remaining unaltered at the end of the reactions. Catalysts can be divided into two main types which are homogeneous and heterogeneous. Homogeneous catalysis is when the catalyst is soluble in the reaction medium. Most homogeneous catalysis processes take place in the liquid medium. Heterogeneous catalysis is when the catalysts exist in a different phase than the reaction medium. Reactions take place at the inter-phase of the two medium. Most heterogeneous catalysis involves the catalysts being in the solid medium while the reaction medium is gas or liquid medium. Enzyme accelerated reactions are also a form of catalysis. Heterogeneous catalyst provides high activity, high selectivity, high water tolerance properties and these properties depend on the amount and strengths of active acid or basic sites. Basic catalyst can be subdivided based on the type of metal oxides and their derivatives. Similarly, acidic catalyst can be subdivided depending upon their active acidic sites.

2.2 Rice Husk Ash (RHA)

Rice husk (Figure 2.1) is an agricultural waste material abundantly available in rice-producing countries. An increasing application of rice husk is as fuel in heat generation for drying rice, due to its high calorific power (approximately 16720 kJ/kg). In this combustion, rice husk ash (RHA) (Figure 2.2) is produced. The burning of rice husk in air always leads to the formation of silica ash, which varies from gray to black depending on inorganic impurities and unburned carbon amounts [20]. In recent years, RHA has been widely used as a construction material to produce concrete [21-23], or as a adsorbent to adsorb organic dye, such as indigo carmine dye [24], and inorganic metal such as lead, mercury [25], Cd^{2+} and Zn^{2+} metal ions [26]. However, the final disposal of the RHA after adsorption has not been reported. Due to its high silica content, RHA can be an economically viable raw material for the production of silicates and silica in recent years [27, 28]. And some researchers have synthesized ZSM-5 zeolite or MCM-48 from RHA [28], but the long time (generally about several days) and high temperature (generally at 150 °C) to synthesize these materials have limited this method to utilize RHA.

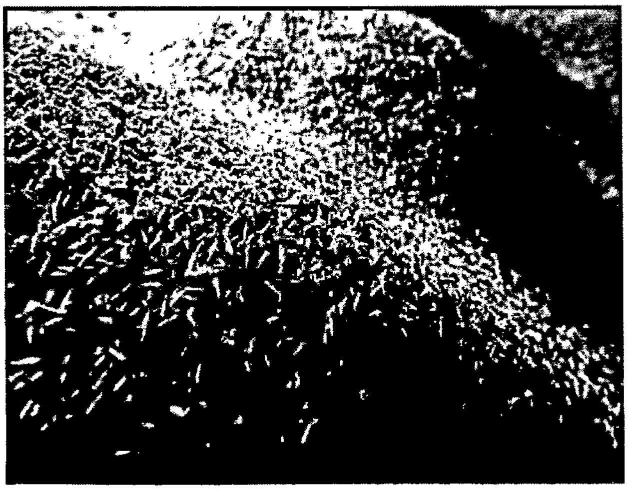


Figure 2.1: Rice Husk

Figure 2.2 : Rice Husk Ash

2.3 MCM-48

MCM-48 (Figure 2.3) attracted attentions mainly due to its attractive three-dimensional interwoven channel structure [13], ordered pore structure array, and narrow pore size distribution [30]. The MCM-48 materials with these unique properties have promising utility for incorporation of large organic molecules to improve the efficiency of photoelectricity conversion and study the photophysical and photochemical properties of organic molecules incorporated in host [30]. In consideration of the excellent pore structure and to accelerate the application of MCM-48,many researchers have devoted their attentions on optimizing the synthesis conditions for MCM-48 by adjusting the crystallization temperature, crystallization time and adding assistants such as salts or cosurfactant [12]. Similar phase transformations, i.e. MCM-41 to MCM-48 to lamellar, were observed for a number of studies during MCM-48 synthesis which were attributed to changes in the electrostatic interactions between condensing silica oligomers and surfactant assemblies [9].

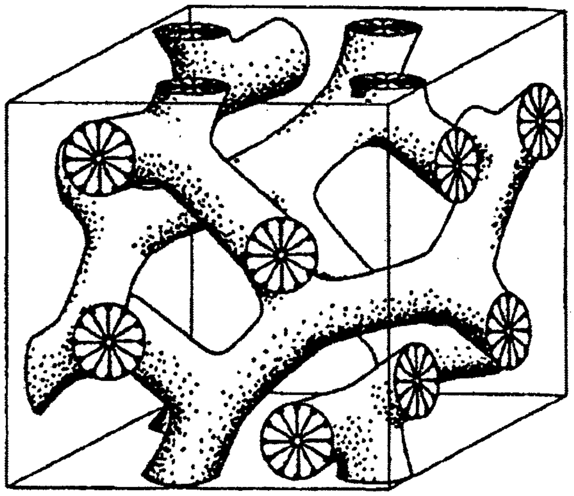


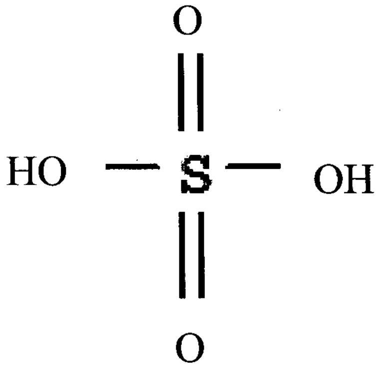
Figure 2.3 : Structure of MCM-48

Compared with parent MCM-48, Al-MCM-48 samples exhibited higher adsorption capacity and stronger adsorption affinity towards aromatic compounds. The incorporation of alumina into MCM-48 materials generated acid centers and more hydroxyl groups on the support surface, which can provide enhanced adsorption for the sorbate molecules and dispersion of active phases[10]. In addition, the tetrahedral Si (IV) in the Si-MCM- 48 framework can be replaced by other metal ions such as Al (III), Ti (IV), Mn (II), and other transition metal ions. This makes it possible to modify the Si-MCM-48 framework to enhance the electron transfer efficiency of incorporated molecules such as rhodamine B (RhB), which is one of the most readily available and useful reagents for use as an organic laser dye with a higher absorption coefficient and fluorescence yield for collecting and utilizing photoenergy [30].

2.4 Sulfuric Acid

Sulfuric acid is a strong mineral acid with the molecular formula H_2SO_4 (Figure 2.4). It is a clear, colourless, odourless, viscous liquid that is very corrosive. It is created from inorganic materials through a process that utilizes a special type of chemical reaction. Sixty-five percent of all fertilizers available on the market today are created from a combination of sulfuric acid and other chemicals. A variety of substances can be mixed with sulfuric acid in order to create new products. In this research, sulphation modification will use H_2SO_4 as the sulphate sources to synthesis the MCM-48.

Modification of MCM-41 with H_2SO_4 in the Mesoporous solid Brønsted acid catalyst for dibenzoylation of biphenyl by introducing sulphate groups onto the surface of AlMCM-41. From the previous work, a number of studies on sulphation of AlMCM-41, in order to increase the acidity, have been reported. However, they demonstrated that the sulphated AlMCM-41 only exhibits Lewis acidity [6]. The catalytic activity of the sulphated AlMCM-41 was studied in the dibenzoylation of biphenyl with benzoyl chloride reaction. The results obtained over sulphated AlMCM-41 were compared with those obtained using sulphuric acid, H-AlMCM-41 and sulphated amorphous silica [6].



$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$$

Figure 2.4 : Sulfuric Acid (H_2SO_4) Structure

2.5 Claisen-Schmidt Condensation

The fact that Claisen-Schmidt (CS) condensations stand out to be important in carbon–carbon bond formation as well as in the preparation of fine chemicals and intermediates, led them to be used as model reactions for the purpose of evaluating the catalytic performance [31]. Chalcones are important intermediates in the synthesis of many pharmaceuticals. They are commonly synthesized via the CS condensation between acetophenone and benzaldehyde and was reported that the CS reaction remains one of the most widely used for obtaining chalcones [32]. This reaction is catalyzed by acids and bases under heterogeneous condition [33]. The heterogeneous catalysts have also been used for the CS condensation, including Lewis acid, Brønsted acid, solid acid, solid base, and other catalysts with more or less success [31].

2.6 Chalcone Synthesis

Several other chalcones are being intensively studied, modified and synthesised in order to develop more potent biological activities [1]. Chalcones are valuable intermediates in the synthesis of many active pharmaceutical drugs like biosynthesis of flavonoids and Auwers synthesis of flavones. Figure 2.5 show the Claisen–Schmidt condensation between acetophenone and benzaldehyde gives chalcone. This reaction is catalyzed by acids and bases under homogeneous or heterogeneous conditions [5].

Chalcones and its derivatives are attracting increasing attention due to numerous pharmacological applications. They are main precursors for the biosynthesis of flavonoids and exhibit various biological activities such as anti-cancer, anti-inflammatory, nitric oxide regulation and anti-hyperglycemic agents [31]. Chalcone derivatives on estradiol framework have been synthesized. Some of the derivatives showed potent anticancer activity against some human cancer cell lines. Active anticancer derivatives were also evaluated for osmotic hemolysis using the erythrocyte as a model system. It was observed that chalcone derivatives showing cytotoxicity against cancer cell lines did not affect the fragility of erythrocytes and hence may be considered as non-toxic to normal cells [32].

In this study, a series of sulfonamide chalcone derivatives were synthesized and investigated for their abilities to inhibit β-hematin formation in vitro and their activity against cultured *Plasmodium falciparum* parasites. Results with these assays suggest that chalcones exert their antimalarial activity via multiple mechanisms [21].

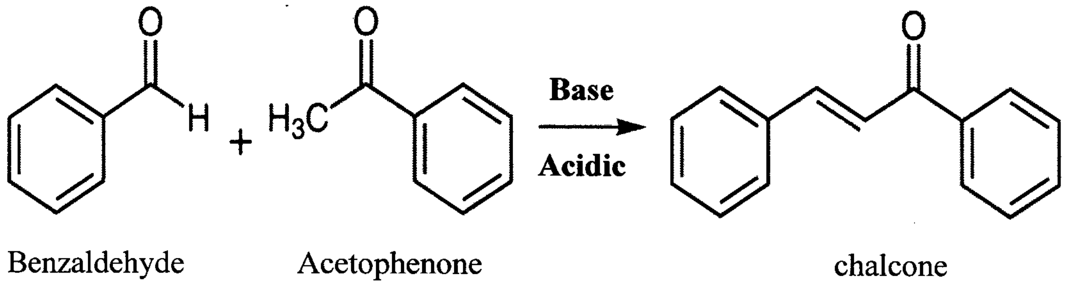


Figure 2.5 : Chalcone Synthesis by Claisen–Schmidt Condensation

CHAPTER 3

METHODOLOGY

3.1 Chemicals and Reagents

MCM-48 was synthesized from Rice Husk Ash (RHA) as a raw material combining with Sodium Hydroxide pellets Grade A supplied by QRëC to produced sodium silicate. CTABr and TritonX-100 were used as a surfactant mixture was supplied by Merk. Impregnation process was carried out using Sulfuric Acid (99%) and using toluene (99.5 v/v) as a solvent. Chalcone synthesis using acetophenone (98%), benzaldehyde (98+ %) and the internal standard methyl benzoate supplied by ACROS Organic. Ethanol supplied by Sigma-Aldrich was used as a solvent to test the catalysts. Figure 3.1 show the flow chart of research activities.