

PERPUSTAKAAN UMP



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**SYNTHESIS OF NIOBIUM-DOPED MCM-48 MOLECULAR SIEVES AND ITS  
CATALYTIC PERFORMANCE FOR PRODUCTION OF CHALCONE**

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## ABSTRACT

Mesoporous silica known as M41S family was discovered as the first ordered mesoporous materials. Among them, MCM-48 a mesoporous cubic system with a highly interwoven and branched pore structure is a potential material in catalyst applications. MCM-48 mesoporous molecular sieves can be conveniently prepared by using rice-husk ash (RHA), an agriculture waste of silica ( $\text{SiO}_2$ ) sources. In this research, niobium-doped silica molecular sieves were hydrothermally synthesized utilizing niobium ethoxide as the sources of niobium. This niobium species has been introduced into a pure silica MCM-48 without destroying or disturbing its framework structure. The microstructure of mesoporous materials was characterized by a variety of physico-chemical methods such as X-Ray diffraction (XRD), UV-Vis diffuse reflectance, BET Surface Area Analysis, Thermogravimetry Analysis (TGA), Fourier-Transformed Infrared Spectroscopy (FTIR) and Gas Chromatography-Flame Ionized Detector (GC-FID) techniques. Chalcone has been prepared by an aldol condensation between a benzaldehyde and an acetophenone. The percentage of conversion of acetophenone was calculated by using area of peak obtained from GC analysis. The percentage of conversion of the uncalcined MCM-48, calcined MCM-48, 1% Nb-doped MCM-48 and 2% Nb-doped MCM-48 were 21.13%, 27.60%, 34.26% and 39.13% respectively. The niobium-doped MCM-48 has catalyzed the selective chalcone compound and the catalytic activities were ascribed to the strong acidity generated by the presences of the niobium species in MCM-48. It has been proven that the increase in amount of niobium loading in the samples has increased the performance of the catalysts.

*Keyword:* Niobium ethoxide; MCM-48; Lewis acidity; anti-cancer; Chalcone;

## ABSTRAK

Silika mesoliant yang dikenali sebagai keluarga M41S dijumpai sebagai bahan mesoliant teratur yang pertama. MCM-48 dengan sistem mesoliant yang sangat terjalin dan struktur liang yang bercabang merupakan bahan yang berpotensi dalam aplikasi pemangkin. MCM-48 penapis molekul mesoliant boleh dihasilkan dengan menggunakan abu sekam padi (RHA), didapati dari sumber sisa pertanian silika ( $\text{SiO}_2$ ). Dalam kajian ini, silika terdop mengandungi niobium penapis molekul yang telah disintesis menggunakan kaedah hidrotermal dan menggunakan niobium etoksida sebagai sumber niobium. Spesies niobium telah berjaya diperkenalkan ke dalam silika tulen MCM-48 tanpa merosakkan atau mengganggu struktur rangka molekul. Mikrostruktur bahan-bahan mesoliant dipercirikan dengan pelbagai kaedah fizik-kimia seperti X-Ray difraksi (XRD), UV-Vis berdifusi reflektansi, BET Permukaan Kawasan Analisis, Termogravimetri Analisis (TGA), Fourier-Transformasi Spektroskopi Inframerah (FTIR) dan Kromatografi pengesan Gas terion (GC-FID). Chalcone telah disintesis melalui proses kondensasi aldol diantara benzaldehida dan asetofenon. Peratusan penukaran asetofenon dikira dengan menggunakan keluasan puncak yang diperolehi dari analisis GC dan peratusan penukaran MCM-48 yang tidak terkapurkan, MCM-48 yang terkapurkan, MCM-48 yang didopkan dengan 1% niobium dan MCM-48 yg didopkan dengan 2% niobium masing masing adalah 21.13 %, 27.60%, 34.26 % dan 39.13%. Pemangkin niobium-terdop-MCM-48 dapat memangkinkan sebatian chalcone dan aktiviti pemangkinan berlaku disebabkan oleh asid kuat dan kehadiran spesies niobium di MCM-48. Ia telah terbukti bahawa peningkatan dalam jumlah muatan niobium di dalam sampel telah meningkatkan prestasi pemangkin.

*Kata Kunci:* niobium etoksida; MCM-48, keasidan lewis; anti kanser; chalcone;

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**LIST OF ABBREVIATIONS**

FTIR	Fourier transforms infrared spectroscopy
GC	Gas chromatography
Nb	Niobium
RHA	Rice Husk Ash
XRD	X-Ray Diffractogram
UV-Vis DR	Ultra Violet - Visible Diffuse Reflectance
Wt %	Weight %
SiO <sub>2</sub>	silica
nm	nanometer
MCM	Mobil Composition of Matter
TGA	Thermogravimetry Analysis
APN	acetophenone
BZD	benzaldehyde
MB	methyl benzoate
S	standard
IS	internal standard
Å	Angstrom
$\alpha$	alpha
$\beta$	beta
$\lambda$	wavelength
$\theta$	theta



## CHAPTER 1

### INTRODUCTION

#### 1.1 INTRODUCTION & RESEARCH BACKGROUND

Development of efficient catalyst is a challenge in catalysis research. One of the important principles of green chemistry is the elimination of hazardous solvents in fine chemical synthesis employing heterogeneous catalysts [1]. Chalcone and its derivatives have attracted increasing attention due to numerous applications especially in pharmacological applications. Traditionally, chalcone 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 obstacles, 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 [2].

Chalcone have numerous applications in pharmaceutical industries. Pharmacological actions of chalcone and its derivatives have been reported to possess many useful properties as they are main precursor for the biosynthesis of flavonoids and exhibit various biological activities including anti-inflammatory [3], anticancer [4], antimicrobial [5], antioxidant, cytotoxic, antitumor activities.

From the previous research many solid catalysts that have been used and applied in the synthesis of chalcone such as magnesium oxide, hydrotalcites, natural phosphates, and aminopropylated mesoporous silica. The major drawback is their poor selectivity to chalcone in strong basic conditions [2]. However, it is very difficult to separate the catalyst from the homogeneous reaction mixture. Moreover,

the traditional processes involving large amount of environmentally unacceptable wastes [2]. Increasing waste disposal cost is adding to the environmental costs and societal costs of an increasingly hostile public towards chemical waste. The use of heterogeneous catalyst in place of homogeneous catalyst is expected to offer easier separation, recycling of the catalyst and reduce the waste generation [1].

From the previous research on synthesis of anti-cancer compound, it has been proven that the most effective and widely used metal-containing chemotherapy anticancer drugs are cisplatin ( $[\text{cis-PtCl}_2(\text{NH}_3)_2]$ ) and many platinum complexes, however, these compounds have significant disadvantages including poor water solubility and serious side effects [6]. Thus many researches were done to overcome these shortcomings. Many non-platinum complexes have been synthesized and tested, in which some palladium complexes show significant antitumor activity in normal tumor cells and lower resistance of tumor cells to clinical treatments as well as lower side effects [7]. Palladium is a transition metal as well as niobium. In this case, metal catalyst are been studied to improve the synthesis of anti-tumor or anti-cancer and give higher significant advantages.

Previous research had shown that the rice husk ash containing 96-99%  $\text{SiO}_2$  can exist either in amorphous phase or in crystalline phases [8], [9]. The large amount of silica freely obtained from this source provides abundant and cheap alternatives of silica for many industrial uses. However, a few reports has been found on the synthesis of MCM-48 directly from RHA, since the synthesis of MCM-48 mesoporous materials seems to be more challenging than the synthesis of MCM-41. By using rice husk ash as the silica source in the synthesis of MCM-48, the production costs can be reduced subsequently besides helping to overcome environmental pollution. Indeed, it should be noticed that RHA is considered slightly impure silica. The content of silica and all impurities in RHA vary depending on the variety, climate and geographic location [10]. Therefore, in order to transform RHA to valuable mesoporous materials, modification and optimization of the synthesis condition should be carried out [11].

The MCM-48 is large-pore molecular sieves attracting much recent attention in catalysis and nanoscience. The structures of MCM-48 consist of two independent and intricately interwoven networks of mesoporous channels. It also has a uniform pore structure of cubic  $Ia3d$  symmetry, large internal surface area and present narrow pore size distributions that can be tunable from 2 nm to 10 nm. The three dimensional channel network of MCM-48 is much more desirable as compared to the one-dimensional channel of MCM-41 from a diffusional and catalytic point of view [12]. In spite of these advantages, very little attention has been paid to exploration of the applicability of MCM-48 material to catalytic reaction of anti-cancer productions [13].

However, surprisingly little research has been reported on MCM-48. It is maybe due to the difficulty of the MCM-48 synthesis since cubic MCM-48 mesophases are obtained as an intermediate between the transformations from a hexagonal or disordered mesophases to a more stable lamellar mesophase. Hence, instead of pure phase, the mixtures of different phases are frequently obtained during the synthesis [11]. There have been a large number of other studies of synthesis, modification, characterization, adsorption and catalytic applications of MCM-48. The MCM-48 silica attracts much attention as a prospective new material for template synthesis, adsorption and catalysis [14].

In this research, purely siliceous MCM-48 will be synthesizing using rice husk ash as a catalyst support. The usage the transition metal in the catalysts is mainly promoter in the mesoporous materials. Mesoporous oxide of niobium has also been reported. The production of chalcone has been carried out with niobium-doped MCM-48 transition metal catalyst under solvent free condition. The support will be functionalized with acid to promote formation of acid site on the surfaces of the MCM-48 [15, 16].

Since the utilization of base and organo-sulfonic acid led to low chalcone conversion and selectivity, we are targeting to enhance the activity using both the bronsted 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 depositions. The research will use wet incipient technique in order to directly position the active sites [17, 18]. Niobium-doped silica molecular sieves were hydrothermally synthesized utilizing niobium ethoxide as the sources of niobium. This niobium species will be introduced into a pure silica MCM-48 without destroying or disturb the framework structure of the molecular sieve. A range of acid loading will be prepared to investigate the optimum acid loading towards chalcone synthesis.

The nature of acid catalysts will be investigated and characterized using a several physico-chemical methods such as X-ray diffraction (XRD), UV-Vis diffuses reflectance, BET Surface Area Analysis and Fourier- Transformed Infrared Spectroscopy (FTIR), Thermogravimetry Analysis (TGA), and Gas Chromatography-Flame Ionized Detector (GC-FID) for product analysis [19]. A test of the Claisen-Schmidt reaction will be conducted to monitor the influence of the acid sites on the niobium-doped MCM-48 surface with the chalcone production.

Our research strategy is to utilize the large surface area, pores and hydroxyl groups of mesoporous material MCM-48. It's reported that MCM-48 synthesized from rice husk ash shows surface area  $>1300\text{m}^2/\text{g}$  and volume  $>1.6\text{ cm}^3/\text{g}$  which suggest that MCM-48 was among the best candidate to be used as support. Due to high surface area and large number of hydroxyl groups of MCM-48, it is predicted to provide large amount of active site attachment. Beside, MCM-48 with its three dimensional pores systems 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 [19].

## 1.2 PROBLEM STATEMENTS

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 heterogeneous nature, the major drawback is their poor selectivity of chalcone in strong basic conditions. To improve the selectivity in synthesis of chalcone, solid acid catalysis has been tried, but only few catalysts have been reported [20]. 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 Bronsted and Lewis acid sites play a role in contributing excellent conversion and selectivity [21]. In addition, functionalization of mesoporous material with suitable functional groups could enhance catalyst performance. Several study incorporating catalyst support with organo-sulfonic acid groups had been reported [21], however, catalyst showed limited catalytic activity in poor conversion and low chalcone yield [21].

## 1.3 OBJECTIVES

The objectives of this study are:

- To synthesize the Si-MCM-48 from rice husk ash doped with niobium oxide.
- To characterize the resulting catalyst using several physico chemical method.
- To test the catalytic activity of niobium-doped MCM-48 for chalcone production.

## 1.4 SCOPE OF STUDY

The scope of this study is basically to synthesis and determines the effect of niobium-doped MCM-48 in the production of chalcone. There are some significant tasks to be carried out in order to achieve the objective of this study.

- i. The MCM-48 has been synthesis from rice husk ash and in this study niobium ethoxide has been used as sources of niobium.
- ii. The characterization of the result catalyst using:
  - a. Powder X-ray diffraction (XRD)
  - b. Fourier Transformation Infrared (FTIR)
  - c. BET Surface Area Analysis
  - d. Thermogravimetry Analyzer (TGA)
  - e. UV-Vis diffuses reflectance (UV-Vis DR)
- iii. Testing the catalytic activity of the chalcone production (reaction between benzaldehyde and acetophenone) using Gas Chromatography-Flame Ionized Detector (GC-FID)

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 RICE HUSK ASH

Rice husk or straws, one of the agricultural waste in South-east Asia, have a large possibility to be employed as usefully renewable resources to produce energy and high purity silica ( $\text{SiO}_2$ ), because they consist of about 70% organics such as cellulose or hemi-cellulose, and 20% amorphous  $\text{SiO}_2$  [22]. Silica ash which is transformed from the husk by complete burning constitutes 15-20% of the total weight of the husk. Rice husk ash contains 90-99%  $\text{SiO}_2$  and 20% of the white ash residue left after the combustion causes air and water pollution [23].

Rice husk, an agricultural waste, is a fibrous material with high silica content, cellulose and lignin. Silica from rice husk finds it uses as a constituent of low cost cements and as a source for metallurgical as well as semiconductor-grade silicon. Silica is one of the basic raw materials in the glass and ceramic industries. Here, rice husk can be employed with advantage. As the ash is obtained as a fine powder, it does not require further grinding. Also the firing temperature is expected to be lower than normal because of the reactive nature of silica in ash. Silica in rice husk has also been employed for preparing silicon carbide whiskers at temperature lower than normal [24].

## 2.2 CATALYST

Catalyst can be classified into two categories, homogenous and heterogeneous. Homogenous catalyst is the catalyst, which present in the same phase as the reagent. Sulfuric acid has been widely used as homogeneous catalyst [25]. Whereas, catalyst that were present in a different phase from the reactant is called heterogeneous catalyst. Heterogeneous catalyst is the backbone of the modern chemical industry, because of the necessity to achieve environmental benign processes in the industry. In addition, heterogeneous catalyst offer numerous potential advantages over homogenous catalyst, such as easier working up procedures, easy catalyst separation from the reaction mixture, reduction of environmental pollutant, avoidance of salt formation and less waste disposals [26].

The condensation reaction in basic medium is usually carried out in the presence of sodium hydroxide, potassium hydroxide or alkali alcohol, and the acid-catalyzed methodologies include the use of dry HCl, Lewis acid as  $\text{TiCl}_4$ , *p*-toluenesulfonic acid, and more recently  $\text{BF}_3\text{-Et}_2\text{O}$ . There are many drawbacks under homogeneous conditions such as catalysis recovery and waste-disposal problems. In this aspect, a heterogeneous catalyst is considered as an eco-friendly alternative. Industry favors catalytic processes in view of easy handling, simple work-up and regenerability. Also green chemistry provides a good and eco-friendly method for the organic synthesis under solvent-free conditions [27].

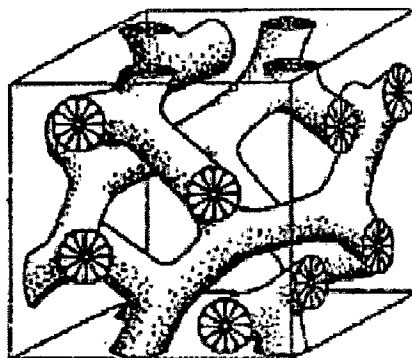
Previous research has reported that, the supported reagents on inorganic solids or the modification of the catalysts have been used to improve the selectivity and the yields in the heterogeneous process. Usually, metal salts can easily be impregnated on several solids supports. Usually, metal salts can easily be impregnated on several solids supports. Thus there have been many applications for these catalysts, leading to the synthesis of a wide variety of products. Thus there have been many applications for these catalysts, leading to the synthesis of a wide variety of products. The Claisen-Schmidt condensation of 2'-hydroxy acetophenone and benzaldehyde to chalcone and flavanones show that calcined Zn-Al (6)



hydrotalcites is active for this synthesis. Coating of ionic liquid '1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride' on Zn–Al hydrotalcites was accomplished employing incipient wetness process and on NaY, NaX, MK-5 and silica gel employing co-condensation methodology [28]. From the other catalysis studies, there are many solid basic catalysts that have been applied in the synthesis of chalcone, Novel solid sulfonic acid, bamboo char sulfonic acid has be applied in the Claisen–Schmidt condensation reaction of substituted benzaldehyde with acetophenone in a solvent-free condition [29].

### 2.3 MCM-48

Mesoporous materials from the M41S family possess several unique properties including; pores which are tunable form 15-100Å; uniform pore diameter in the mesoporous range; large surface areas above 700 m<sup>2</sup>/g, while the pore volume in the range of 0.7-1.2 cm<sup>3</sup> g<sup>-1</sup> [30].



MCM-48

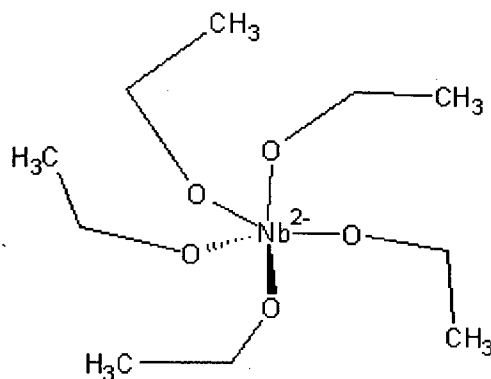
**Figure 2.1:** Cubic structure of MCM-48

The cubic structure of MCM-48 suggested being suitable for catalytic reactions, and three-dimensional interwoven structure would resist pore blockage. From the previous research, instead of synthesizing MCM-48 from RHA, they present a hydrothermal synthesis procedure to obtain MCM-48 readily using sodium silicate solution as the silica source, hexadecyltrimethylammonium bromide (HTABr) as the structure-directing agent, and various kind of alcohol such as methanol,

ethanol and 2-methylpropan-2-ol as an additive for the mesophase control. Other researchers have done the synthesis procedure of mesoporous powders and film by using TEOS (tetraethylorthosilicate) as a silica source. Ethanol, methanol, and MEK (methyl ethyl ketone) were used as a solvent. CTAB ( $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$ ) was used as surfactant-template [31]. Different methods or compound in the synthesis will be expected to enhance the catalytic reaction of the heterogeneous catalyst for liquid phase oxidation. Study of (Cr) MCM-48 molecular sieves, Tetraethyl orthosilicate (TEOS), chromium nitrate nanohydrate ( $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), sodium hydroxide (NaOH) were used as sources for silicon, chromium and alkali, respectively. Tetradecyltrimethylammonium (TDTMA) bromide and cetyltrimethylammonium bromide (CTABr) were used as a template for the synthesis. Chromium-containing MCM-48 was synthesized hydrothermally, as per the procedure reported, using Teflon-lined autoclave at 383K for 8 days with a gel composition [32].

## 2.4 NIOBIUM ETHOXIDE

Transition metal oxide materials with ordered pores in both the meso- and macro-size regime are predicted to be useful as catalytic support, adsorbent, chromatographic materials, light-weight structural materials, and in optical and electronic applications where the tuning of pore size, conductivity or insulating ability, and overall morphology are crucial [33]. From the research on the preparation and characterization of acidic catalysts  $\text{Nb}_2\text{O}_5/\text{TS-1}$  for synthesis of diols, niobium has been loaded on the surface of TS-1 (Titanium silicate) to introduce acidity. The surface acid strength of niobium oxide, namely niobic acid ( $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ) corresponds to the acid strength of 70% sulfuric acid and exhibit high catalytic activity, selectivity and stability for acid-catalyzed reactions. TS-1 loaded with niobium oxide to obtain Nb/TS-1 by impregnation technique using niobium ethoxide  $\text{Nb}(\text{OC}_2\text{H}_5)_5$  precursors.



**Figure 2.2:** Structure of niobium ethoxide

For comparison on the presence of Nb species, experiments were carried out to obtain niobium oxide and niobic acid. Niobic acid was prepared by hydrolysis of niobium ethoxide using neutral hydrolysis method [16]. Recent studies have called into question whether pure transition metals have any significant catalytic activity, however [34]. Based on studies of empirical hydrogen uptake kinetics, the catalytic effect of transition elements has been attributed to the presence of oxygen, which forms oxides with the transition metals [34]. It has also been demonstrated that among several transition metal oxides, the catalytic effect of  $\text{Nb}_2\text{O}_5$  is superior for both hydrogen absorption and desorption [34]. Although these empirical studies demonstrate the catalytic effect of oxides, the exact role of the additive and the corresponding mechanisms remain unclear [34].

## 2.5 ACETOPHENONE

Acetophenone is useful component of flavors and fragrances, it is found naturally as a component of honey, plums and strawberries [35]. Acetophenone are valuable derivatives, especially useful for the synthesis of heterocycles for medicinal chemistry purposes [36].

An improved process of preparation of acetophenone derivatives comprises the reaction of an aliphatic acid and an aromatic compound, having a substituent alkyl, cycloalkyl, or alkoxy group in the presence of  $\text{P}_2\text{O}_5$  in disperse phase and a

diatomaceous form of pure  $\text{SiO}_2$ . The acetylation proceeds by the attack of an electrophile ( $\text{CH}_3\text{CO}^+$ ) on the benzene ring resulting in the formation of acetophenone [37].

Previous study has reported that, a fast, general, environmentally friendly, and facile method for preparation of highly functionalized acetophenone derivatives under ultrasound irradiation in heterogeneous catalysis is presented. Synthesis of highly functionalized acetophenone derivatives is an important goal for organic synthesis, these derivatives being key intermediates in obtaining of fused heterocyclic, of both theoretical and practical interest such as biologically active compounds. The strategies adopted to obtain highly functionalized acetophenone involve  $\alpha$ -bromination of acetophenone derivatives, either with molecular bromine using heterogeneous catalyst [38].

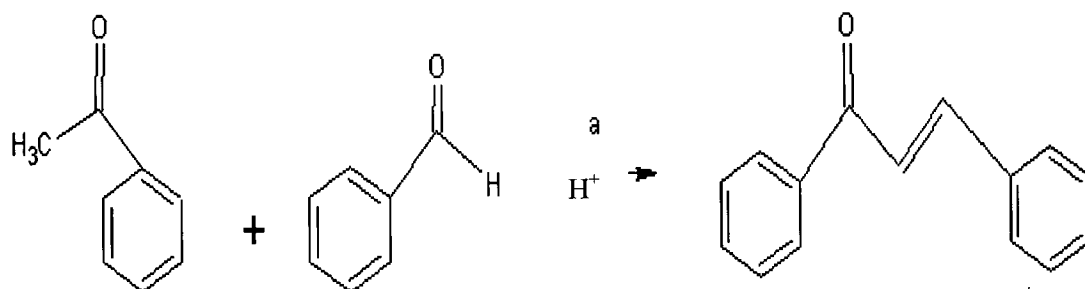
## 2.6 BENZALDEHYDE

Reaction of benzyl alcohols with Oxone and sodium bromide in aqueous acetonitrile gave the corresponding benzaldehydes in excellent yields. However, electron-rich benzyl alcohols afforded ring bromination products via bromodecarbonylation of the resulting benzaldehydes. The selective oxidation of benzylic alcohols to benzaldehydes is a transformation of considerable importance in organic synthesis. Whilst numerous reagents have been developed to effect this process, many of them use greater than stoichiometric quantities of toxic heavy metals or co-oxidants which severely handicap their applicability to large scale industrial processes [39].

Previous research have define that a series of benzaldehyde substituted phenyl carbonyl hydrazones has been synthesized and their formylation has been carried out by using Vilsmeier-Haack reaction. All the hydrazones and their formyl derivatives were screened for antibacterial activity [40].

## 2.7 CHALCONE SYNTHESIS

Chalcone are usually synthesized using the Claisen-Schmidt reaction in basic medium in polar solvent and purified by separation as the reaction led very often to a complex mixture [41]. Chalcone are key precursors in the synthesis of various flavanoid as they can be transformed easily in flavanones by cyclization in acid medium [42]. From the previous research on *the preparation of 1-(substitutedphenyl)-3-(substituted-phenyl)-2-propen-1-ones*, mixture of substituted acetophenone and aryl aldehydes was stirred in ethanol and then an aqueous solution of potassium hydroxide was added to it. The mixture was kept overnight at room temperature and then it was poured into crushed ice and acidified with dilute hydrochloric acid [43].



**Figure 2.3:** Synthesis of chalcone

The chalcone were synthesized by Claisen condensation between substituted acetophenone and different aromatic aldehydes. The selection of substituted acetophenone and substituted aromatic aldehydes was based on presence of electron withdrawing and electron releasing groups which would assist in later studies, on structure activity relationship [44].

Literature reveals that the present work deals with the reaction of 4-hydroxy acetophenone with different aromatic aldehydes to form chalcone, and the success of the various synthesized compound were assigned on for basis elemental analysis, IR and mass spectral data. The reaction behind that is the fact that the basic catalysts decrease the activity of the aldehydes component because of delocalization of the

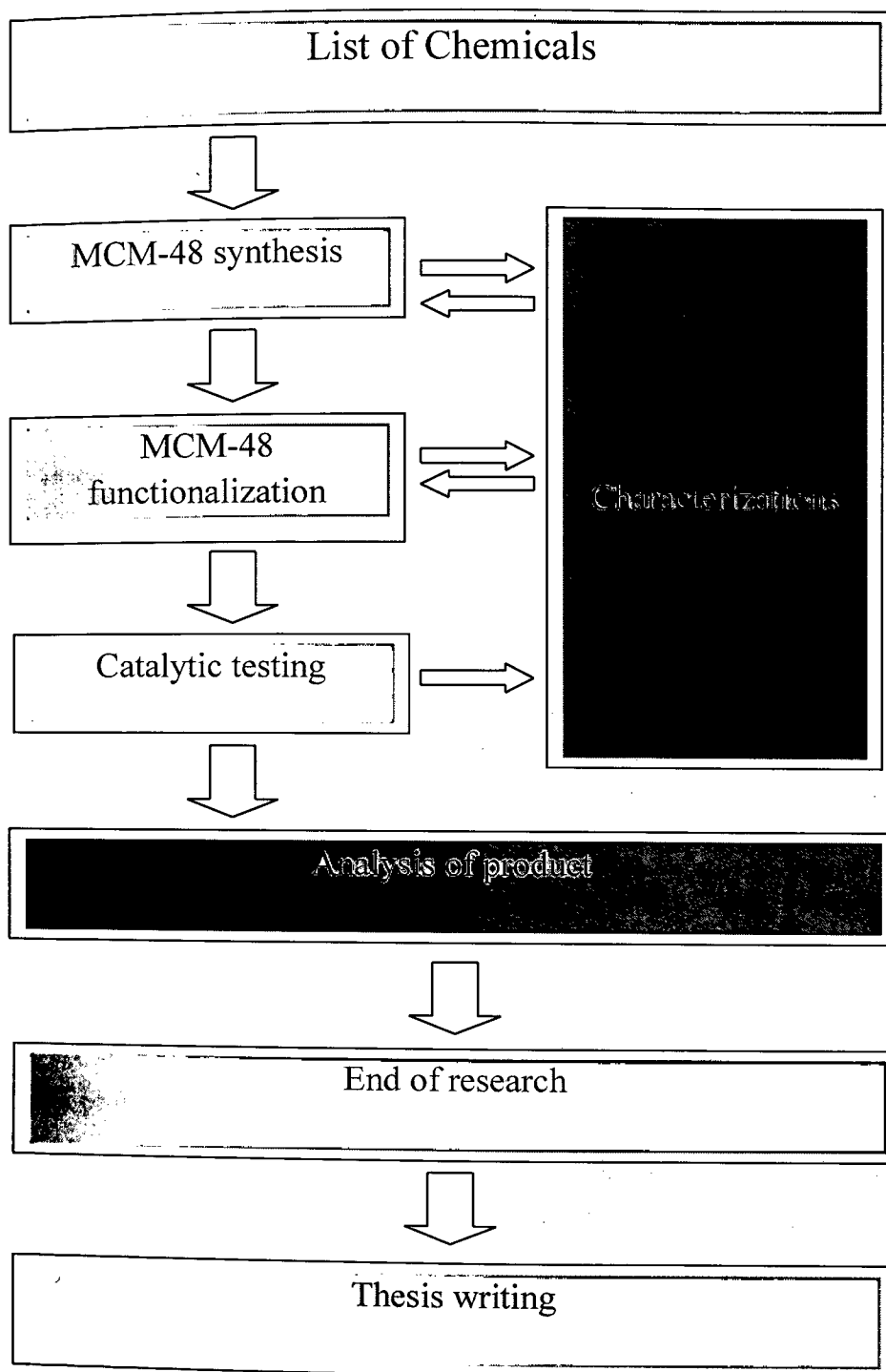
anion. It is necessary to use protective group for the preparation of the hydroxyl chalcone under basic condition [44].

## CHAPTER 3

### METHODOLOGY

#### 3.1 LIST OF CHEMICALS

Rice Husk Ash (98%), Benzaldehyde (98%, ACROS Organic), Acetophenone (98%, ACROS Organic), Niobium (v) Ethoxide (99.95%, ALDRICH), Methyl Benzoate (99%, ACROS Organic), Cethyltrimethylammoniumbromide (99%, Merck), Triton-100 X (97%, Merck), Sodium Hydroxide pellets (QRëC), ethanol (96%, Sigma-Aldrich), Nitric acid (~65%, Sigma-Aldrich), hexane (Sigma-Aldrich).

**Research Methodology****Figure 3.1:** Research methodology