



**SYNTHESIS AND CHARACTERIZATION OF ZSM-5 ZEOLITE AS  
CATALYST IN CLAISEN-SCHMIDT CONDNSATION REACTION**

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## ABSTRACT

ZSM-5 zeolite is one type of heterogeneous catalyst which obtained in the solid form. There are several advantages of heterogeneous catalyst in the chemical reaction compared to homogeneous such cost reduction, environmental friendly and easy to separate. In this study, ZSM-5 zeolite was synthesized using hydrothermal method utilising rice husk ash (RHA) which is agriculture waste of silica source. Then, the prepared ZSM-5 zeolite with different ratios of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  was characterized by means of Fourier Transformed-Infrared Spectroscopy (FT-IR), Surface Area Analyzer (BET), X-Ray Diffraction (XRD) and Thermogravimetric Analysis (TGA). The catalytic activity of ZSM-5 zeolite was tested by the reaction of acetophenone and benzaldehyde to chalcone at 150 °C and 6 hours. The conversion of the reaction was evaluated using Gas Chromatography-Flame Ion Detector (GC-FID). The conversion to chalcone by H-ZSM-5(30) give yield up to 82.44 %, Na-ZSM-5(60) give 82.72 %, H-ZSM-5(60) give 82.86 % and Na-ZSM-5(30) give the highest yield of 91.95 %.

**Keywords:** heterogeneous catalyst, ZSM-5, zeolite, chalcone, acidic properties

## ABSTRAK

Zeolit ZSM-5 adalah salah satu jenis mangkin heterogen dalam keadaan pepejal. Terdapat pelbagai kelebihan mangkin heterogen dalam tindak balas kimia berbanding dengan mangkin homogen seperti pengurangan kos, mesra alam sekitar dan mudah untuk diasingkan. Dalam kajian ini, zeolit ZSM-5 akan disintesis dengan menggunakan kaedah hidrotermal abu sekam padi iaitu sumber silika sisa pertanian. Kemudian, zeolit ZSM-5 yang telah disediakan dengan pelbagai nisbah  $\text{SiO}_2/\text{Al}_2\text{O}_3$  akan ditentukan melalui spektrokopi transformasi Fourier-inframerah (FT-IR), analisis luas permukaan (BET), kaedah pembelauan sinar-X (XRD), dan analisis haba gravimetrik (TGA). Mangkin ZSM-5 diuji oleh tindak balas asetofenon dan benzaldehid kepada chalcone pada suhu  $150\text{ }^\circ\text{C}$  selama 6 jam. Pertukaran tindak balas dinilai dengan menggunakan gas kromatografi-pengesan nyalaan ion (GC-FID). Hasil produk chalcone menggunakan H-ZSM-5(30) dengan produk sehingga 82.44%, Na-ZSM-5(60) menghasilkan produk 82.72 %, H-ZSM-5(60) menghasilkan produk 82.86 % dan Na-ZSM-5(30) mencatatkan hasil produk tertinggi iaitu 91.95 %.

**Kata kunci:** mangkin heterogen, ZSM-5, zeolit, chalcone, ciri-ciri keasidan

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## LIST OF ABBREVIATIONS/ TERMS/ SYMBOLS

%	percentage
% C	conversion percentage
% wt	weight percentage
°C	degree celcius
AlCl <sub>3</sub>	aluminium chloride
APN	acetophenone
BET	Brunauer, Emmett, Teller
BF <sub>3</sub>	boron trifluoride
CuZSM-5	copper zeolite sieve mesoporous-5
DMSO	dimethyl sulfoxide
eq. KOH	equivalence potassium hydroxide
FCC	fluid catalytic cracking
FT-IR	Fourier Transformed-Infrared technique
g	gram
GC-FID	Gas Chromatography-Flame Ion Detector technique
h	hour
H <sup>+</sup>	hydrogen ion
H <sub>2</sub> O	water
H <sub>2</sub> SO <sub>4</sub>	sulphuric acid
HCl	hydrochloric acid
H-ZSM-5	hydrogen zeolite sieve mesoporous-5
H-ZSM-5(30)	H-ZSM-5 zeolite with ratio SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> = 30
H-ZSM-5(60)	H-ZSM-5 zeolite with ratio SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> = 60
KBr	potassium bromide
KF-Al <sub>2</sub> O <sub>3</sub>	potassium chloride on alumina
KOH	potassium hydroxide

mL	milliliter
Na <sup>+</sup>	sodium ion
NaOH	sodium hydroxide
NaZSM-5	sodium zeolite sieve mesoporous-5
NH <sub>4</sub> <sup>+</sup>	ammonium ion
NH <sub>4</sub> Cl	ammonium chloride
NiZSM-5	nickel zeolite sieve mesoporous-5
rt	room temperature
RHA	rice husk ash
SEM	scanning electron microscopy
SiOH	silanol group
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	silica or alumina
SO <sub>4</sub> <sup>2-</sup>	sulfate ion
TGA	thermogravimetric analyzer technique
XRD	x-ray diffraction technique
ZSM-5	zeolite sieve mesoporous-5

## CHAPTER I

### INTRODUCTION

#### 1.1 Background of study

Rice husk ash (RHA) is rich in silica content and can be produced from rice husk using correct combustion method. RHA can be used in concrete as an additional cementitious material [1]. Rice husk can be burnt into ash that accomplishes the physical characteristics and chemical composition of mineral admixtures. Pozzolanic activity of rice husk ash (RHA) depends on silica content, silica crystallization phase, and size and surface area of ash particles. Other than that, ash must contain only a small amount of carbon. Combustion of rice husk at controlled temperature can produce RHA that has amorphous silica content and large surface area [1].

Catalyst is a substance that speeds up the rate of chemical reaction [2]. Broadly, catalysis can be separated into homogeneous or heterogeneous forms [3]. Homogeneous catalysis involves the catalyst being in the same phase (solid, liquid or gas) as the reactants [3]. While heterogeneous catalysis involves catalyst in different phase (i.e. solid, liquid and gas, also oil and water) to the reactants [3]. Unlike homogeneous catalysts, heterogeneous catalysts offer a platform or surface for the chemical reaction to take place on [3]. Heterogeneous catalyst can be divided into two kinds of catalyst being acids catalyst and base catalyst [2]. As the previous research, acids catalyst which sulphated zirconia had been used in the esterification of octanoic acid and ethanol. Even though sulphated zirconia is good in its catalytic activity, can be recycled and thermal

resistant properties [2], it is not preferred in the research due to the properties of sulfated zirconia which has potential loss of  $\text{SO}_4^{2-}$  in its liquid phase application [4].

One of the important values of green chemistry is the removal of hazardous solvents in fine chemical synthesis using heterogeneous catalysts. This process also ensures low waste production. Solvent free reactions under heterogeneous system play crucial role in the greening of fine and specialty chemical production and offer a clean method to a broad range of organic products [5, 6, 7]. In a heterogeneous reaction, the catalyst is in a different phase (i.e. solid, liquid and gas, also oil and water) from the reactants [3]. The reaction rate for heterogeneous catalysis is moderate and it can be recovered after used. The processing methodology of heterogeneous catalysis is a continuous fixed bed operation possible. The heterogeneous catalyst is not sensitive to water or free fatty acids. Besides, the heterogeneous catalysis can be reused and the cost is potentially cheaper [8]. Operating parameters such as extent of catalyst loading, temperature, mode of mixing, alcohol or oil molar ratio [9], presence or absence of impurities in the feed stock and the time of reaction are essential in the heterogeneously catalyzed transesterification reaction. While in the homogeneous system, most of the waste was produced during the separation stage of the process [10, 11]. The environmental and societal cost increases due to rising waste disposal cost [12, 13]. The use of heterogeneous catalyst to replace homogeneous catalyst was expected to give easier separation, recycling of the catalyst and reduce the waste generation [13].

Zeolite is one type of the heterogeneous catalyst which obtained in the solid form [8]. Zeolites are largely used as catalysts, especially as acidic catalysts in petrochemical industry. Zeolite X was first used in fluidized catalytic cracking (FCC) in 1962, and other examples include zeolite Y for FCC (fluid catalytic cracking) [14] and hydrocracking [15], ZSM-5 for xylene isomerization [14], hydrodewaxing [16], alkylation [14], FCC [17], and catalytic cracking of low-value  $\text{C}_4$  olefins to propylene [18]. In 1972 Mobil Co. reported the synthesis of high silica zeolite ZSM-5 [19]. There is a difference between ZSM-5 and H-ZSM-5 where ZSM-5 is more general in any ions can occupy the ion exchange sites. For example, both H-ZSM-5 and Na-ZSM-5 are ZSM-5,

but it doesn't work the other way around. Unlike ZSM-5, H-ZSM-5, the zeolite ion exchange sites are occupied by  $H^+$  ions. This is normally done by ion exchange the zeolite with  $NH_4Cl$  to produce  $NH_4^+$  exchanged zeolite. Then, zeolite is heated to decompose the  $NH_4^+$  to  $H^+$  and ammonia. ZSM-5 is general term for Na-ZSM-5, and  $Na^+$  was exchanged to other cations when ZSM-5 was used in any application like H-ZSM-5, Ni-ZSM-5, and Cu-ZSM-5 etc.

H-ZSM-5 is an acidic Brønsted material and has high surface area, which makes it a great catalyst to produce high yield reaction result. Due to acidic properties and unique pore structure (microporous structure) which has excellent shape ability, H-ZSM-5 can catalyze a wide variety of organic reaction [18]. H-ZSM-5 has Brønsted acid center due to balance the negative charge with protons and form SiOH groups (Silanol groups) [19]. High surface area of H-ZSM-5 gives opportunity to increase the chemical reaction of acetophenone and benzaldehyde.

## 1.2 Problem statements

Nowadays, much of the research is focused on primary catalyst surface. This is regarding to the catalytic activity of the catalyst. Solid acid catalysis is very effective from the part of activity and reusability compared with homogeneous catalysts [2]. Previous research of synthesis of chalcone by using the SBA-15 materials functionalized with both propylsulfonic acid groups and aluminum species (AISBA-15-SO<sub>3</sub>H) as catalyst, only produced 4.4 wt% of yield [27]. So, to overcome this problem, the catalyst with higher surface area and having acid and base catalysts were explored.

### 1.3 Objective of study

The objectives of this study are:

- i. To synthesize ZSM-5 zeolite with the different ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$ .
- ii. To characterize the resulting catalysts using several characterization methods.
- iii. To test the catalytic activity of ZSM-5 zeolite in the chemical reaction of acetophenone to produce chalcone.

### 1.4 Scope of study

The scope of this study is to synthesize and determine the effect of different ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  on the catalytic activity of ZSM-5 zeolite. There are some significant tasks to be carried out in order to achieve the objective of this study. Firstly, the ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  in ZSM-5 zeolite of 30 and 60 were prepared. The ZSM-5 zeolite was synthesized from rice husk ash (RHA). The H-ZSM-5 zeolite was characterized by means of FT-IR, BET, XRD, and TGA. The conversion of the reaction was evaluated using GC-FID.

## CHAPTER II

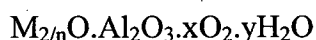
### LITERATURE REVIEW

#### 2.1 Zeolites

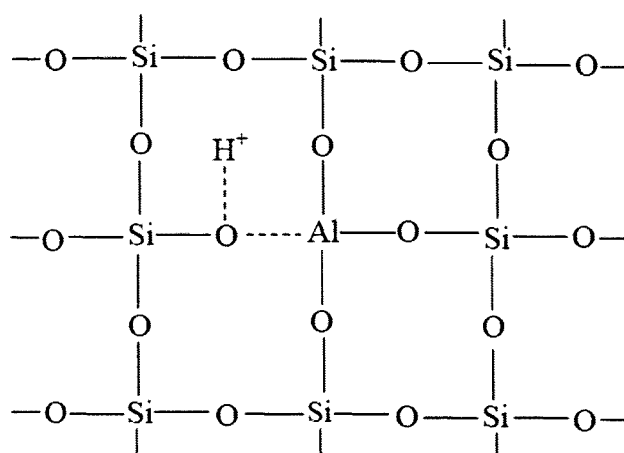
Zeolites are popular catalysts in inorganic solid catalysts for organic synthesis [20]. Common advantages for using zeolites in the transesterification are that they can be synthesized with different crystal structures, framework Si/Al ratios, and proton exchange levels [21].

According to Mukundan Devadas, the name “zeolites” originated from the Greek words zeo: (to boil) and lithos: (stone) [19, 22]. Zeolites were developed naturally as drop in sedimentary rocks where they formed under hydrothermal conditions. This is due to the effect of hot alkaline salt solutions which come from volcanic ash and pumice stones. In the 60's, the production of zeolites gave its industrial application and forced research on heterogeneous catalysis [23].

The structures of zeolites are crystalline, hydrated aluminosilicates and framework aluminosilicates. Framework aluminosilicates are based on an infinitely extending three-dimensional network of  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra linked to each other by sharing all of the oxygen. The empirical structure of zeolites can be presented as below:



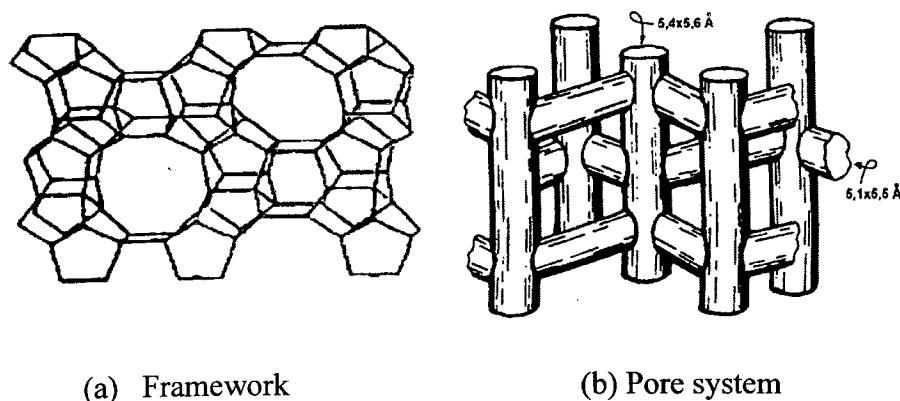
The acidity of zeolites has a strong affect on the catalytic activity [24, 27] due to the presence of both Brønsted and Lewis acid centers. Zeolites have Brønsted acid centers due to balance negative charge with protons and formed SiOH groups (Silanol group). The catalyst activity is found to be improved with increasing the Si/Al ratio [19, 21]. Numerous zeolites such as modified H-Y, H-Beta, H-ZSM-5, aluminophosphate and silicoaluminophosphate molecular sieves have been engaged as esterification catalysts [24-26]. Figure 2.1 shows the lattice structure of zeolite.



**Figure 2.1:** Zeolite with Brønsted acid center in the lattice structure.

Zeolite ZSM-5 is a highly siliceous zeolite where broadly used as catalyst in organic synthesis, petroleum refining and petrochemical due to its high solid acidity, hydrophilicity and its resilience in strong acidic environments [20]. The framework of ZSM-5 is formed by 5-1 secondary units which categorized in mordenite framework inverted (MFI) structure type [20]. In addition, ZMS-5 type is a highly porous material and has an interesting two-dimensional pore structure. The framework topology and pore system of ZSM-5 were illustrated as Figure 2.2.





**Figure 2.2:** Framework topology and pore structure of ZSM5 zeolite

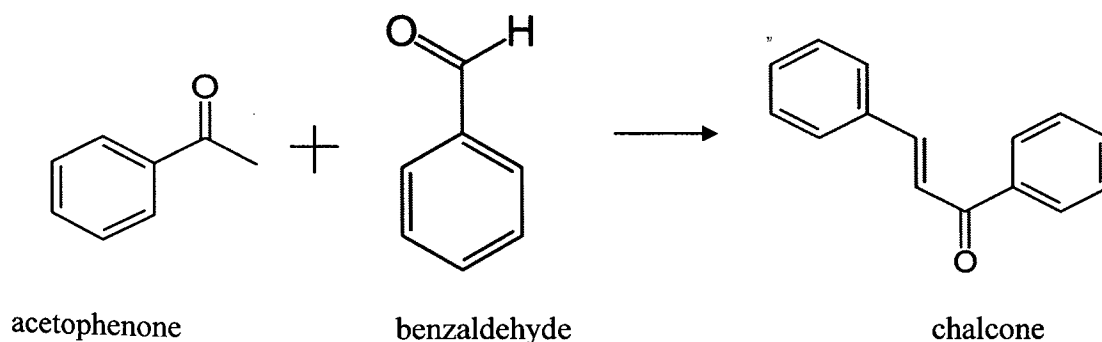
A lot of researches have been carried out to improve the synthetic methods and the quality of product at the same time to reduce the cost of production of zeolite ZSM-5 due to its highly siliceous and its potential in many applications. ZSM-5 crystallizes basically at temperature more than  $100\text{ }^{\circ}\text{C}$  with the presence of organic base template, mostly tetrapropylammonium cations [20]. From the previous research, there were many types of zeolites and zeolite ZSM-5 was chosen due to some reasons [20]. Firstly, it is known as flexibility in strong acid environments and usually synthesized as a high silica zeolite [20]. Next, ZSM-5 can help to retain more water by hydrogen bonding with its silanol as it is a hydrophilic zeolite [20].

In general industrial processes, heterogeneous catalysts are more desirable because it is non-corrosive, separable, and recyclable. The use of solid catalysts would also reduce the number of reaction and separation steps required in the conversion of chemical reaction, allowing for more economical processing and yielding higher quality product.

## 2.2 Chalcone synthesis

Chalcones forms the central precursor for a variety of important biological compounds of an aromatic ketone and can be used as synthetic intermediates in the preparation of several compounds [27]. Chalcones are valuable intermediates in the synthesis of many active pharmaceutical drugs like biosynthesis of flavonoids [31] and Auwers synthesis of flavones [28]. Its derivatives are materials high of interest because of their antioxidant, antibacterial, antifungal, antitumor and anti-inflammatory properties [27].

Synthesis of chalcone was done by the reaction of acetophenone and benzaldehyde with the presence of catalyst to produce trans-chalcone [30]. The reaction mechanism involves the formation of carbonium with the attack of a proton on the carbonyl group of the benzaldehyde followed by its attack to enolic form of the acetophenone as an acid catalyst was used in the synthesis of chalcone [30]. Figure 2.3 shows the chemical reaction to produce chalcone.



**Figure 2.3:** Reaction of acetophenone and benzaldehyde

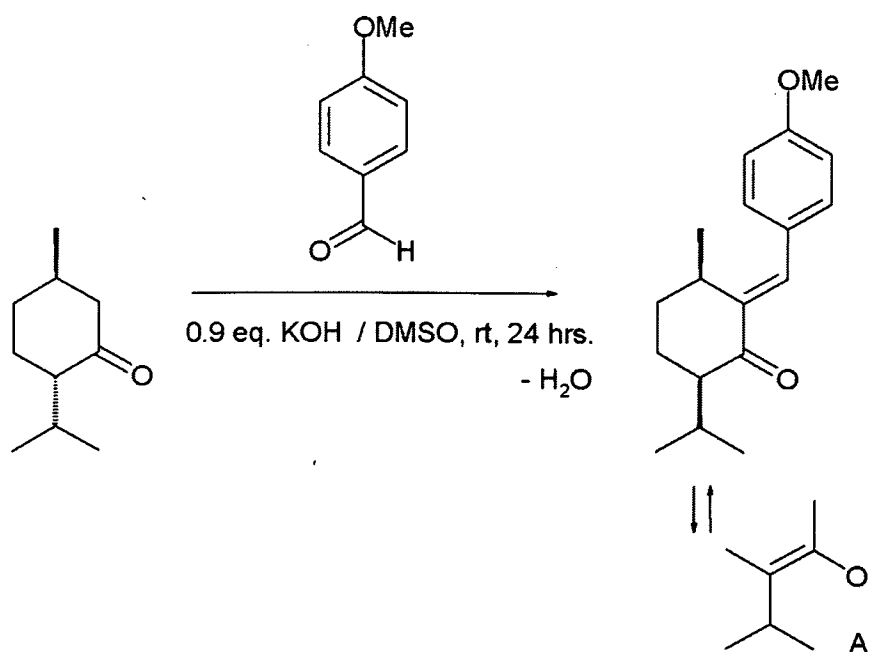
Green synthesis of chalcones was developed and related hybrids by using  $\text{Cu}_3(\text{BTC})_2$  as heterogeneous catalyst, under suitable temperature conditions for Aldol condensation. Generally, mild reaction conditions, enhanced rates, improved efficiency

of reaction with maximum atom economy, recyclable and inexpensive catalyst, use of green solvent system and reduced reaction time are the remarkable features exhibited by the process [30, 31]. Brønsted acidic ionic liquids as dual catalyst showed good catalytic activities and recycle capabilities for conventional homogenous or heterogeneous catalysts between acetophenone and benzaldehyde to produce chalcones [30].

### 2.3 Claisen-Schmidt condensation

Claisen-Schmidt condensation between acetophenone and benzaldehyde derivation is a priceless C-C bond formation reaction which can obtain  $\alpha$ - $\beta$ -unsaturated ketones called chalcones [27] with the presence of catalyst. Basically, the catalyst that had been used in Claisen Schmidt is heterogeneous catalysis which carried out in the presence of alumina [32], barium hydroxide [27, 32] and recently hydrotalcite [27, 32] and zeolite [32].

The past reports describe that base catalyzed synthesis of chalcones by the Claisen Schmidt condensation were burdened with several limitations, such as sub-optimal purity and inadequacy of the methods for purification and evaluation of synthesized compounds. Besides, undesirable side products, long reaction times and low yields also had been the limitation of base catalysis [32]. There is much kind of bases like NaOH, KOH and solid base KF-Al<sub>2</sub>O<sub>3</sub> under ultrasound irradiation had been used in the Claisen-Schmidt chalcone synthesis [32]. However, acid catalyzed reactions involves the use of AlCl<sub>3</sub>, BF<sub>3</sub> and dry HCl, extended reaction times, difficulty in the catalyst preparation, high temperatures, use of special apparatus, costly reagents and formation of side products in the Claisen-Schmidt chalcone synthesis [32]. The reaction of Claisen-Schmidt was shown in Figure 2.4.



**Figure 2.4:** Claisen-Schmidt reaction

Traditionally, the condition of Claisen-Schmidt condensation was at 50 °C using 10– 60% of alkaline hydroxides or sodium ethoxide catalysts over a period of 12–15 hours [28].

## **CHAPTER III**

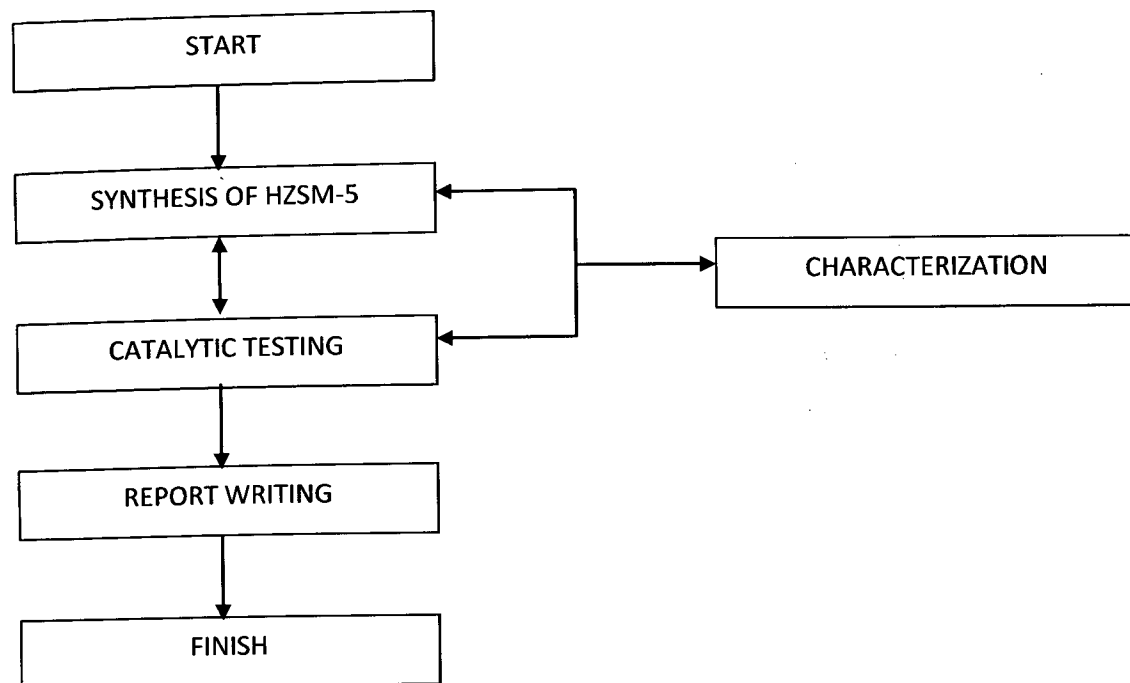
### **METHODOLOGY**

#### **3.1 Chemical and reagents**

Rice husk ash (RHA, 98%) is an agriculture waste silica source. Sodium aluminate ( $\text{NaAlO}_2$ , 53 %) supplied by Fisher Scientific was used as alumina source and react with sodium hydroxide (NaOH) supplied by QReC, Brightchem Sdn Bhd (99%) and then dissolved in distilled water. Later, the solution was mixed with sulphuric acid ( $\text{H}_2\text{SO}_4$ ) supplied by Acros Organic (96%) and tetrapropyl ammonium bromide (TPABr) supplied by Merk (>99%). For protonation, ammonium chloride ( $\text{NH}_4\text{Cl}$ ) supplied by Acros Organic (99%) was added.

#### **3.2 Description of methodology**

The research program was designed according to the methodology outlined in the scheme, consisting three stages, as shown in Figure 3.1.



**Figure 3.1:** Flow chart of research activities

### 3.2.1 Synthesis of ZSM-5 zeolite

In this project, there are two different ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  in H-ZSM-5 zeolite prepared being 60 and 30. Ratio 60 means the weight of Si was same while the weight of Al was reduced for half compared to ratio 30.

#### 3.2.1.1 ZSM-5 zeolite with $\text{SiO}_2/\text{Al}_2\text{O}_3(60)$

Solution I (the aluminium source) was prepared by adding 0.482 g  $\text{NaAlO}_3$  with 0.11 g NaOH and 10 mL of distilled water. The mixture was stirred until all the components were dissolved completely. Then, 2.95 g NaOH and 15mL distilled water was added into the mixture and stirred until clear solution was obtained. Solution II was prepared by adding 50mL distilled water with 3.1 g of 96 %  $\text{H}_2\text{SO}_4$  and 4.0 g TPABr. The mixture was stirred until all TPABr was dissolved. After that, Solution I and Solution II were mixed with 9.0 g RHA and 21.0 g distilled water and shaken for 5

minutes. Next, the mixture was stirred for 30 minutes before crystallization at 170 °C for two days in a stainless steel autoclave. The zeolites formed was then filtered and washed with distilled water. Then, pH of zeolite washed was checked and confirmed in the range of pH 6-7 before drying at 100 °C overnight and calcined in air at 550 °C at rate of 3 °C min<sup>-1</sup> for 5 hours.

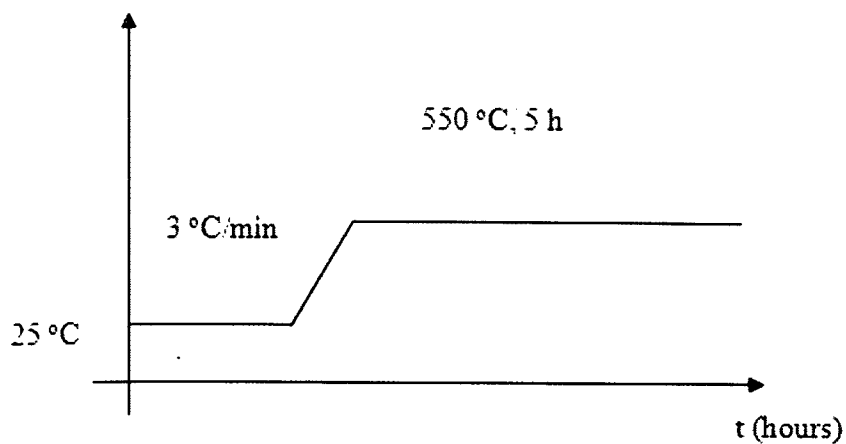
Protonation of 5.0 g calcined ZSM-5 in Na<sup>+</sup> formed was done with a 250 mL of 1.0 M NH<sub>4</sub>Cl solution. The mixture was stirred at 60 °C for 16 hours. Then, the solid was filtered, washed with distilled water, checked and confirmed the pH range was 6-7, and dried at 100 °C overnight. The solid powder was then calcined at 550 °C at the rate of 2 °C min<sup>-1</sup> for two hours.

### **3.2.1.2 ZSM-5 zeolite with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>(30)**

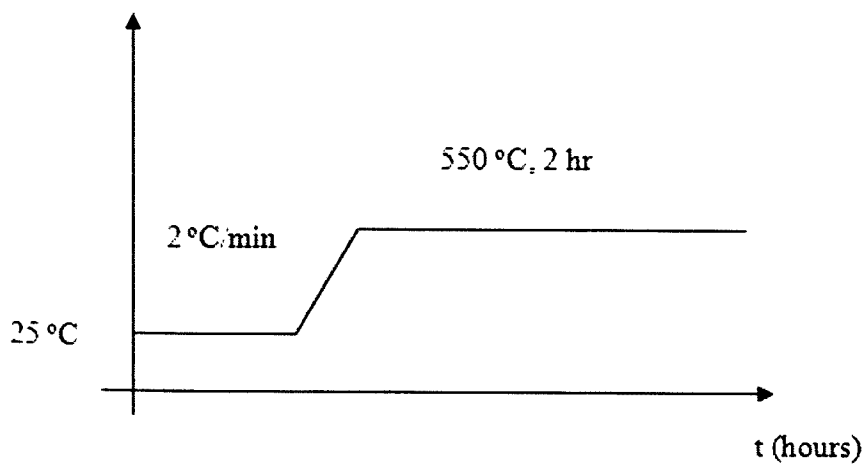
Solution I (the aluminium source) was prepared by adding 0.964 g NaAlO<sub>3</sub> with 0.11 g NaOH and 10 mL of distilled water. The mixture was stirred until all the components were dissolved completely. Then, 2.95 g NaOH and 15mL distilled water was added into the mixture and stirred until clear solution was obtained. Solution II was prepared by adding 50mL distilled water with 3.1 g of 96 % H<sub>2</sub>SO<sub>4</sub> and 4.0 g TPABr. The mixture was stirred until all TPABr was dissolved. After that, Solution I and Solution II were mixed with 9.0 g RHA and 21.0 g distilled water and shaken for 5 minutes. Next, the mixture was stirred for 30 minutes before crystallization at 170 °C for two days in a stainless steel autoclave. The zeolites formed was then filtered and washed with distilled water. Then, pH of zeolite washed was checked and confirmed in the range of pH 6-7 before drying at 100 °C overnight and calcined in air at 550 °C at rate of 3 °C min<sup>-1</sup> for 5 hours.

Protonation of 5.0 g calcined ZSM-5 in Na<sup>+</sup> formed was done with a 250 mL of 1.0 M NH<sub>4</sub>Cl solution. The mixture was stirred at 60 °C for 16 hours. Then, the solid was filtered, washed with distilled water checked and confirmed the pH range was 6-7, and dried at 100 °C overnight. The solid powder was then calcined at 550 °C at the rate

of  $2\text{ }^{\circ}\text{C min}^{-1}$  for two hours. Figure 3.2 shows the calcinations method to prepare Na-ZSM-5 and Figure 3.3 shows the calcinations method to prepare H-ZSM-5.



**Figure 3.2:** Calcination method to prepare Na-ZSM-5



**Figure 3.3:** Calcination method to prepare H-ZSM-5