

**SYNTHESIS OF MESOPOROUS ALUMINA NANOPARTICLE USING
AGAROSE TEMPLATE FOR LEWIS ACID CATALYST**

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*This report writing is dedicated to my beloved parent
Abdul Halim Abdullah & Jemilah Hashim and my family members,
to my adorable supervisor, Assoc Prof Dr Zainab Ramli, and also
to my special one, Jaya Junaidi and my friends.*

Thanks for everything...

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In the spirit of knowledge, I hope to provide useful inputs and remarkable insights for the readers in my research area.

ABSTRACT

Porous alumina with high surface areas and narrow pore size distribution has wide applications in catalysis, catalyst support, molecular separation and adsorbents. In this study, agarose gel having porous structure was used as template in the preparation of mesoporous alumina. This method was introduced in order to provide an alternative method to design the pore structure of metal oxide having nanosized grains. Four different amount of agarose gel template were used to synthesize this material, i.e. 0.5 wt%, 1.0 wt%, 2.0 wt% and 4.0 wt%. The agarose gel was coated with aluminium isopropoxide precursor. The XRD and FTIR results showed that the alumina has γ -phase structure. The alumina obtained from 2 wt% and 4 wt% of agarose gel template exhibits uniform mesopores alumina and the surface properties analyzed using nitrogen adsorption-desorption showed narrowest pore size distribution centered at 7.2 nm with the highest surface area obtained was 308 m²/g. The SEM images of agarose showed sponge-like pore structure while FESEM revealed that the size of granule-like nanoparticles mesoporous alumina decreased by increasing amount of agarose template. TEM proved that the mesoporous alumina particle was successfully obtained with rod-like morphology with average length of 5-7 nm. Lewis Acid site present in mesoporous alumina was confirmed by pyridine-FTIR and catalytic activity of alumina was evaluated in Knoevenagel condensation reaction of benzaldehyde with methyl cyanoacetate and dimethyl malonate separately. The percentage conversion of each reaction was 54% and 47%, respectively compared to uncatalyzed reaction which was 4.0% and 18%, respectively. The low conversion of dimethyl malonate was due to the bulky molecule product entrapped in the pore of alumina surface. The results obtained showed that synthesized mesoporous alumina is capable to catalyze Knoevenagel condensation reaction.

ABSTRAK

Alumina berliang meso dengan luas permukaan yang tinggi dan mempunyai taburan liang yang sempit digunakan secara meluas sebagai mangkin, penyokong mangkin, pemisahan molekul dan aplikasi penjerapan. Dalam kajian ini, gel agarose yang berstruktur liang digunakan sebagai templat untuk mensintesis alumina berliang meso. Kaedah ini diperkenalkan sebagai alternatif untuk merekebentuk struktur logam oksida berliang yang mempunyai butiran bersaiz nano. Empat kuantiti agarose yang berbeza digunakan untuk mensintesis alumina, i.e. 0.5wt%, 1.0 wt%, 2.0 wt% and 4.0 wt%. Gel agarose disaluti dengan precursor aluminium isopropoksida. Data XRD dan FTIR menunjukkan alumina bersaiz meso terhasil dalam fasa- γ . Kajian menunjukkan kuantiti agarose, 2 wt% and 4.0 wt% sebagai templat, menunjukkan keseragaman alumina berliang meso dimana liang permukaan dianalisis menggunakan penjerapan-nyahjerapan nitrogen mempunyai taburan puncak yang sempit berpusat pada 7.2 nm dengan luas permukaan tertinggi iaitu 308 m²/g. Imej SEM agarose menunjukkan liang merupai span manakala imej dari FESEM menunjukkan saiz alumina berbentuk butiran dan mengecil apabila bertambahnya kuantiti agarose. TEM Berjaya membuktikan partikel alumina berliang meso berbentuk rod dengan aggaran saiz diantara 5-7 nm. Kehadiran permukaan asid Lewis pada alumina berliang meso disahkan dengan pyridine-FTIR dan diuji dalam tindakbalas kondensasi Knoevenagel diantara benzaldehid dengan dimetil malonat dan metil cyanoacetat secara berasingan. Peratusan pertukaran bagi setiap produk dengan kehadiran mangkin adalah masing-masing sebanyak 54% dan 47% manakala tanpa kehadiran mangkin adalah sebanyak 4% dan 18%. Peratusan pertukaran dimetil malonate adalah rendah jika dibandingkan dengan metal cyanoacetat kerana kehadiran molekul berstruktur besar dimana sebahagian daripadanya akan terperangkap di permukaan liang mangkin. Keputusan yang diperolehi menunjukkan alumina berliang meso yang disintesis berpotensi untuk memangkinkan tindakbalas kondensasi Knoevenagel.

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LIST OF ABBREVIATIONS

FTIR	-	Fourierr transform infrared
FESEM	-	Field emission scanning electron microscopy
TEM	-	Transmission electron microscopy
GC	-	Gas chromatoghraphy
XRD	-	X-ray diffraction
Wt%	-	Weight percent
R _T	-	Retention time
FID	-	Flame ionization detector
IUPAC	-	International Union of Pure and Applied Chemistry
BET	-	Brunauer, Emmett and Teller
P/P _O	-	Relative presssure; obtained by forming the ratio of the equilibrium Pressure and the vapor pressure P _O of the adsorbate at the Temperature where the isotherm is measured

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CHAPTER 1

INTRODUCTION

1.1 Aluminium Oxide, Al_2O_3

Aluminium is the most common metallic element in the earth's crust and occurs in rocks such as feldspars and micas. Aluminium oxide is the amphoteric oxide of aluminium with the chemical formula Al_2O_3 as shown in Figure 1.1 [1]. It is also commonly referred to as alumina or aloxite in the mining, ceramic and materials science communities. There are two forms of anhydrous Al_2O_3 , namely, α - Al_2O_3 and γ - Al_2O_3 . α - Al_2O_3 is stable at high temperatures and also indefinitely metastable at low temperature. It occurs in nature as the mineral corundum and prepared by heating γ - Al_2O_3 or any hydrous oxide above 1000°C . α - Al_2O_3 is hard and is resistant to hydration and to attack by acids [2]. The density of α - Al_2O_3 is only about 0.595 g/cm^3 with a hexagonal close packed, HCP array of anions. Although the anions are topologically arrayed as if they are in closest packing, they are really not contacting with one another.

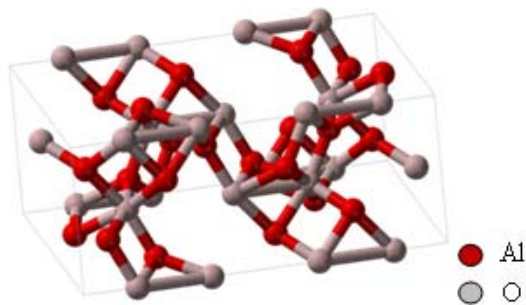


Figure 1.1: Molecular structure of alumina

γ - Al_2O_3 is obtained by dehydration of hydrous oxides at low temperatures $\sim 450^\circ\text{C}$ giving medium surface area lamellar powders, $\sim 100 \text{ m}^2\text{g}^{-1}$. γ - Al_2O_3 readily absorbs water and dissolves in acids. Metastable γ -form aluminas have a cation deficient cubic spinel structure [3]. Calcination at increasing temperatures gives rise to the sequence $\gamma\text{-Al}_2\text{O}_3 \rightarrow \delta\text{-Al}_2\text{O}_3 \rightarrow \theta\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$ [3].

Alumina is a low cost material most widely used as a catalyst and catalyst support. In addition, it is also used as the starting material for the preparation of Al_2O_3 based ceramics [4]. Aluminas are extensively used as catalyst supports due to their favorable textural properties and intrinsic acid–base characteristics as shown in Figure 1.2. In particular, γ -alumina which has a crystalline structure with large surface area is widely used as catalysts, catalysts support and adsorbents such as in automotive and petroleum industries. Alumina supports with large surface areas, large pore volumes, narrow pore size distributions within the mesoporous range, as well as suitable surface acidic–basic properties can often result in favorable enhancements in the catalytic performances [5]. Porosity is necessary for high surface area within the pellet, but pore shape and size distribution are critical secondary factors when diffusion resistance is present. The best supports are those that are easily manipulated to produce optimum texture properties.

According to IUPAC (Union of Pure and Applied Chemistry), the pores are classified in different classes depending on their width, W such as micropore ($W < 20 \text{ \AA}$), mesopore ($20 \text{ \AA} < W < 500 \text{ \AA}$) and macropore ($W > 500 \text{ \AA}$) [6]. For most applications, it is preferable to have a designed crystal structure and morphology, and nanosized grains. Therefore, synthesis of mesoporous aluminas (MA) with high surface areas and uniform mesopores has attracted much attention [7]. Many synthesis routes have been developed for the preparation of MA. Among them, organic–inorganic assemblies involving complicated sol–gel processes by using surfactants as structure-directing agents are regarded as one of the most promising approaches [8]. Various neutral and ionic surfactants have been used as templates for the preparation of MA.

The catalytic properties of transition aluminas largely depend on their crystalline structures and textural characteristics [8]. Controlling the morphological properties of materials during synthesis is of great importance, as these structural characteristics strongly influence the performance and purpose of the materials.

Templating is an approach which affords the ability to tailor the inner structural arrangements, such as pore size and overall porosity, along with the outer shape and size of the sample [9]. Many templates have been employed to prepare porous metal oxide structures, an example of these processes have recently been reviewed. Recently, researchers use the organic template such as cellulose, glucose starch and agarose in order to synthesize the porous metal oxide due to the ease removal of organic substance by calcination [7, 10, and 19].

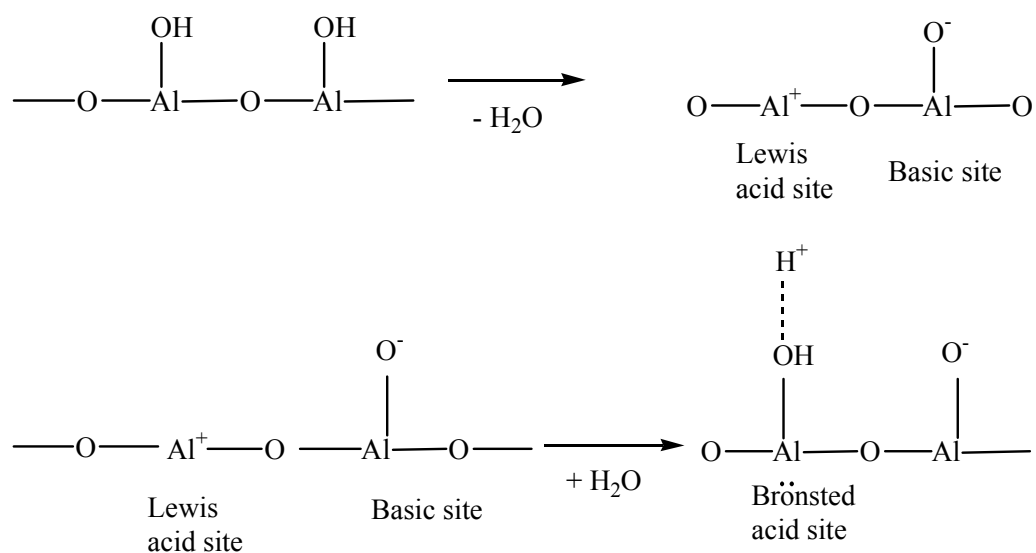


Figure 1.2: Acidic and basic site in alumina surface

Knoevenagel condensation reaction is commonly catalyzed by base as well as Lewis acid. The presence of Lewis acidity in aluminas is expected to have successful application as a catalytic material in Knoevenagel reaction with the combination of mesoporosity, nanosized particles, higher surface area and acid-base characteristic of alumina.

1.2 Research Background and Problem Statement

Alumina is a very interesting material with broad applicability as a support for various catalytically active phases. There are several methods that have been used to synthesize the alumina particles in different classes of preparation alumina such as by precipitation, sol gel technique without the presence of outside template, non-surfactant and surfactant templating techniques. Usually, conventional aluminas with surface areas of 50-300 m²/g are manufactured by precipitation technique [7].

One of the major problems related to the use of alumina catalysts is the deactivation by coke formation and pore plugging which limits the diffusion of substrates and products in and out the catalyst particles. It is known that the larger the contribution of micropore to the specific surface area and the wider the pore size distribution, the greater the enhancement in the deactivation rate.

Thus, synthesis of aluminas with mesoporous properties using templating techniques have been used to control the structural properties of materials including outer shape, inner porosity, and surface area. The type of template used can range from surfactant assemblies to latex spheres, inorganic crystals, and biomaterials. Recently, biopolymer templates have received attention due to the fact that they are readily available and inexpensive, making the structure-controlling process low cost and amenable to scale-up [10]. The templates used for examples are cellulose, collagen, β -chitin, starch and others.

Nowadays, catalyst is very important for the reaction of bulky molecule such as organic molecule or bioinorganic molecule. For example in pharmaceutical and commercial polymer products which consist of big molecule. Since alumina is known to possess Lewis acidity, Knoevenagel condensation reaction was chosen to evaluate the catalytic ability of the prepared alumina catalyst. The Knoevenagel reaction is a condensation reaction of an aldehyde or a ketone with an active methylene compound to give the corresponding alkene product together with H₂O.

In this study, attempt to prepare porous alumina by sol gel synthesis by using biomaterial agarose gel template is being carried out. Agarose gel is chosen over other biomaterials due to its availability and lowest. These porous alumina materials can be formed by treating an aluminum source that is derived from an aluminium alkoxide in an organic-aqueous solution with an organic structured directing agent to form meso-sized micelles followed by calcinations of the resulting composition. The potential of mesoporous alumina as Lewis acid catalyst for transformation of bulky organic molecule was investigated also.

1.3 Significance of Research

This research demonstrated the templating technique using aluminium isopropoxide as precursor and agarose gel biomaterial as the template in order to prepare an ordered mesoporous alumina. In addition, the research also investigated the effect of various amount of agarose used towards the formation of nanoparticle and narrow pore size distribution of alumina. The catalytic activity of the alumina was tested in the Knoevenagel condensation reaction.

1.4 Research Objectives

The main objective of this research is to synthesis an ordered mesoporous alumina by templating technique using a biomaterial (i.e agarose) to form a good catalytic material. Details of the objectives are: -

- 1) To synthesize an ordered porous alumina, by sol- gel synthesis within agarose gel template.
- 2) To characterize the synthesized alumina by FTIR, XRD, FESEM/TEM and N₂ adsorption.

- 3) To study the physicochemical properties of the synthesized alumina as Lewis acid catalyst.
- 4) To evaluate the catalytic ability of the catalyst in the Knoevenagel condensation reaction.

1.5 Scope of Study

This study involved an easy and simple sol gel method within templating technique by using agarose gel coated with aluminium isopropoxide as a precursor. Calcinations process was carried out to remove the agarose template in order to get mesoporous alumina with morphological characteristics inherited from the initial template, allowing designed pore structure and pore size.

The synthesized alumina obtained was characterized by using FTIR, XRD, FESEM/TEM and N₂ adsorption and is expected to exhibit nanosized grains with morphology design, having large surface areas, large pore volumes, and narrow pore size distributions within the mesoporous range. Lewis acidity of the sample was characterized using pyridine- adsorption and measured by FTIR spectroscopy.

Finally, the mesoporous catalysts obtained was tested as potential catalysts in Knoevenagel condensation reaction between methyl cyanoacetate, dimethyl malonate with main reactant which is benzaldehyde. The research design is schematically illustrated in Figure 1.3.

1.6 Outline of the Dissertation

This dissertation illustrates the information concerning the synthesis, characterization and the potential catalytic application of mesoporous alumina. Chapter 1 elucidates the research background and the importance strategies to

respond the current issue. Chapter 2 presents the literature search regarding this project whereas contains some information about the whole research done. Chapter 3 describes the experimental methodology with the characterization techniques used in this research. Chapter 4 explains the results and discussion of the synthesized mesoporous alumina and its catalytic activity. Finally, chapter 5 summarizes the results obtained with recommendation for future work.

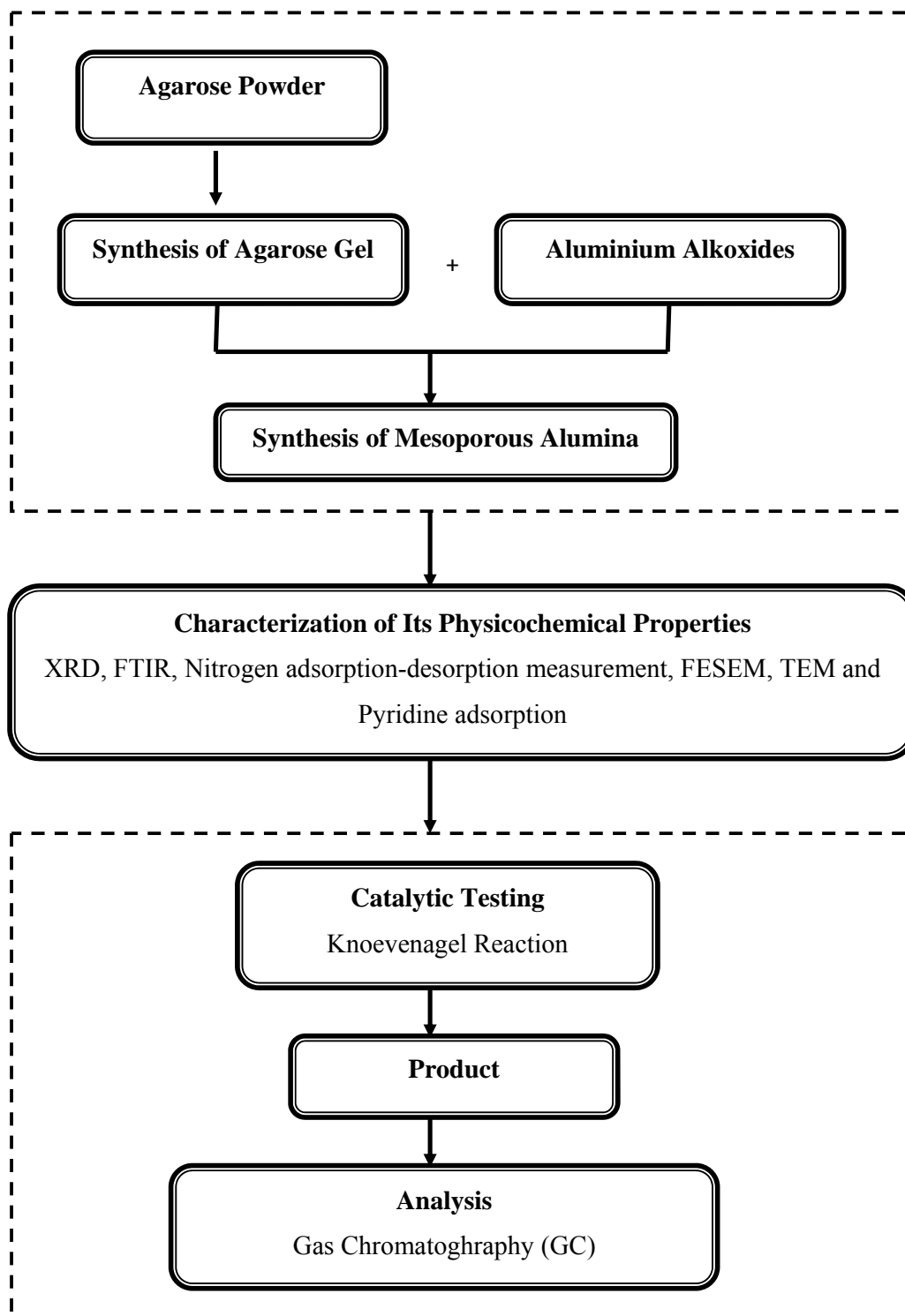


Figure 1.3: Flowchart of the research design

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