

## ABSTRACT

It was found that the basic catalytic property of the metal oxide was increase with high surface area and nanosized particles. In this study, surface modified Barium oxide (BaO) was synthesized by hydration-dehydration method. Barium hydroxide (Ba(OH)<sub>2</sub>) has prepared from Barium Peroxide (BaO<sub>2</sub>) which acted as precursor. The Ba(OH)<sub>2</sub> was calcined at a temperature of 50°C to 300°C under vacuum atmosphere of 10<sup>-3</sup> mbar. Prepared samples were characterized using thermogravimetric-derivative thermogravimetry (TG-DTG), fourier-transform infrared (FTIR), X-ray powder diffraction (XRD), single point Brunauer-Emmet Teller (BET) surface area analysis and field emission scanning electron microscope (FESEM). The TG-DTG result shows that the major weight lost occurs at a temperature 110°C to 150°C which was 0.7%. This indicated the decomposition of barium hydroxide to barium oxide. The XRD diffractogram of BaO proved that Ba(OH)<sub>2</sub> has been transformed to BaO in tetragonal formed as the temperature increases. The particle size for the surface modified barium oxide was calculated using Scherer's equation and the resulting particle size was approximately 34 nm. Thus, the prepared surface modified BaO with nano size particles have been produced in this study. The amount of basic sites was investigated using the most fundamental chemical techniques of back titration and as the temperature increases from 150°C to 300°C, the basic sites increases from 0.67 to 1.67 mmol g<sup>-1</sup> respectively. This is most probably due to the formation of more BaO with basic sites that occur during the activation process at temperature 300°C. The chemical properties of the prepared surface modified BaO were measured using electron spin resonance (ESR) method. Based on ESR study, a single peak g-value at 1.9830 was observed throughout the 30 minutes UV radiation and shown that only one site which active in electron trapping sites.

## ABSTRAK

Ia telah terbukti bahawa sifat berbes mangkin oksida alkali bumi meningkat apabila luas permukaannya tinggi dan bersaiz nano. Dalam kajian ini, barium oksida (BaO) disintesis melalui kaedah penghidratan-penyahhidratan. Barium hidroksida (Ba(OH)<sub>2</sub>) telah disediakan daripada barium peroksida (BaO<sub>2</sub>) sebagai bahan permula. Ba(OH)<sub>2</sub> telah dipanaskan pada suhu 50°C hingga 300°C dalam keadaan vakum atmosfera pada tekanan 10<sup>-3</sup> mbar. Pencirian semua sampel telah dilakukan dengan menggunakan termogravimetri-pembezaan termogravimetri analisis (TG-DTG), spektroskopi inframerah (FTIR), pembelauan sinar-X (XRD), penjerapan gas nitrogen (NA) dan mikroskop imbasan elektron (FESEM). Keputusan TG-DTG menunjukkan purata kehilangan berat berlaku pada suhu 110°C hingga 150°C sebanyak 0.7%. Ini menunjukkan perubahan Ba(OH)<sub>2</sub> kepada BaO. Keputusan XRD menunjukkan apabila suhu meningkat, Ba(OH)<sub>2</sub> telah berubah kepada BaO dalam bentuk tetragonal. Saiz BaO yang dihasilkan telah dikira dengan menggunakan persamaan Scherer's dan saiznya menghampiri 34 nm. Ini jelas membuktikan bahawa BaO yang dihasilkan dalam penyelidikan ini adalah dalam saiz nano. Jumlah permukaan aktif dan kekuatan alkali telah dikenalpasti dengan menggunakan teknik asas kimia iaitu penitratan semula. Kebesan meningkat apabila suhu meningkat daripada 150°C kepada 300°C iaitu meningkat 0.67 dan 1.67 mmol g<sup>-1</sup>. Ini disebabkan oleh pembentukan lebih banyak permukaan aktif pada BaO pada suhu 300°C. Ciri-ciri kimia BaO yang dihasilkan diukur dengan menggunakan kaedah resonan putaran elektron (ESR). Berdasarkan kaedah ESR, dengan radiasi UV selama 30 minit, didapati puncak tunggal terhasil dengan nilai g adalah 1.9830 dan jelas membuktikan bahawa hanya satu sahaja permukaan di BaO yang aktif menangkap elektron.

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Background of Research

Chemical reactions which are promoted by catalyst have two types of reactions which are either acid-catalyzed or base-catalyzed reactions. In acid-catalyzed reactions, reactants act as base toward the acid catalysts, while in base-catalyzed reactions, reactants act as acids toward the base catalysts. In contrast to extensive studies of solid acid catalysts, fewer efforts have been given to the study of solid base catalysts. Certain metal oxides with a single component were found to act as solid base catalysts in the absence of such alkali metals as Na and K. In recent years, non oxide type catalysts have been recognized as solid base catalysts or heterogeneous basic catalysts (Hattori, 2001).

Alkaline earth metal oxides were used for the catalysts and starting materials for basic heterogeneous reaction. Barium oxide (BaO) is one of the compounds in alkaline earth metal oxide series. The chemical characteristic of BaO is the same as MgO and CaO since they were in the same group in the periodic table. Physico-chemical properties of BaO such as surface area, particle size and basicity on the other hand lies on their method of preparation, since different method of preparation would yield different product with different characteristics and properties. Alkaline earth metal oxide can be prepared by various preparation methods. This project was focused on the preparation of BaO from hydration-dehydration process at various temperatures.

## 1.2 Problem Statement

The knowledge about the actual catalytic sites or surface defect responsible for the reactivity remains unanswered. For most of the materials called solid base, the catalytic activities are on the removal of water and carbon dioxide from the surfaces. The nature of the surface basic sites varies with the severity of the pre-treatment conditions. Besides removing of water and carbon dioxide, rearrangement of surface and bulk atoms occurs during pre-treatment, which changes the number and nature of the basic sites with increasing pre-treatment temperature. Therefore, the optimum pre-treatment temperature varies with the type of reaction (Yacob *et al.*, 2009).

In local industry, conventional biodiesel was manufactured using homogeneous base catalyst such as potassium hydroxide and sodium hydroxide via a process called transesterification. The homogeneous base catalyst has the advantage of a fast reaction rate under mild condition, but requires a large amount of water to wash the catalyst off the product. Furthermore, the washing operation produces saponification and stable emulsion. This will lower the yields and is environmentally harmful.

In the other hand, although sulfuric acid can catalyze the transesterification, the acid catalyzed give slower reaction. Many researchers have studied to develop other methods that can solve these problems. They found that heterogenous base catalyst will make more economic advantage, easy separation from the reaction mixture and reduce environmental pollution (Hattori *et al.*, 1998).

## 1.3 Significance of Research

Solid-base catalysts have many advantages over liquid bases or organometallics. They present fewer disposal problems, while allowing easier separation and recovery of the products, catalysts, and solvent. They are noncorrosive. Thus, solid-base catalysts offer environmentally benign and more

economical pathways for the synthesis of fine chemicals. Because of these advantages, study on the synthesis of fine chemicals using solid bases as catalyst has increased over the past decade.

Barium oxide was prepared under vacuum atmosphere at various temperatures. Generation of basic sites at surface was dependence to the pre-treatment at high temperature. Basically, surface of these materials were covered with adsorbent molecule such as carbon dioxide, water and in some cases, oxygen as they handed in air.

The way to remove molecule covering the surfaces depends on the severity of pre-treatment. As the temperature increase, the molecule covering the surface was successively desorbed according to the strength of the interaction with the surface sites. The sites that appear on the surfaces by pre-treatment at low temperature were suggested to be different from those appearing at high temperatures. If simple desorption of molecules occurs during pre-treatment, the basic sites that appear at high temperatures should be strong (Hyun *et al.*, 2001).

#### **1.4 Objectives of Research**

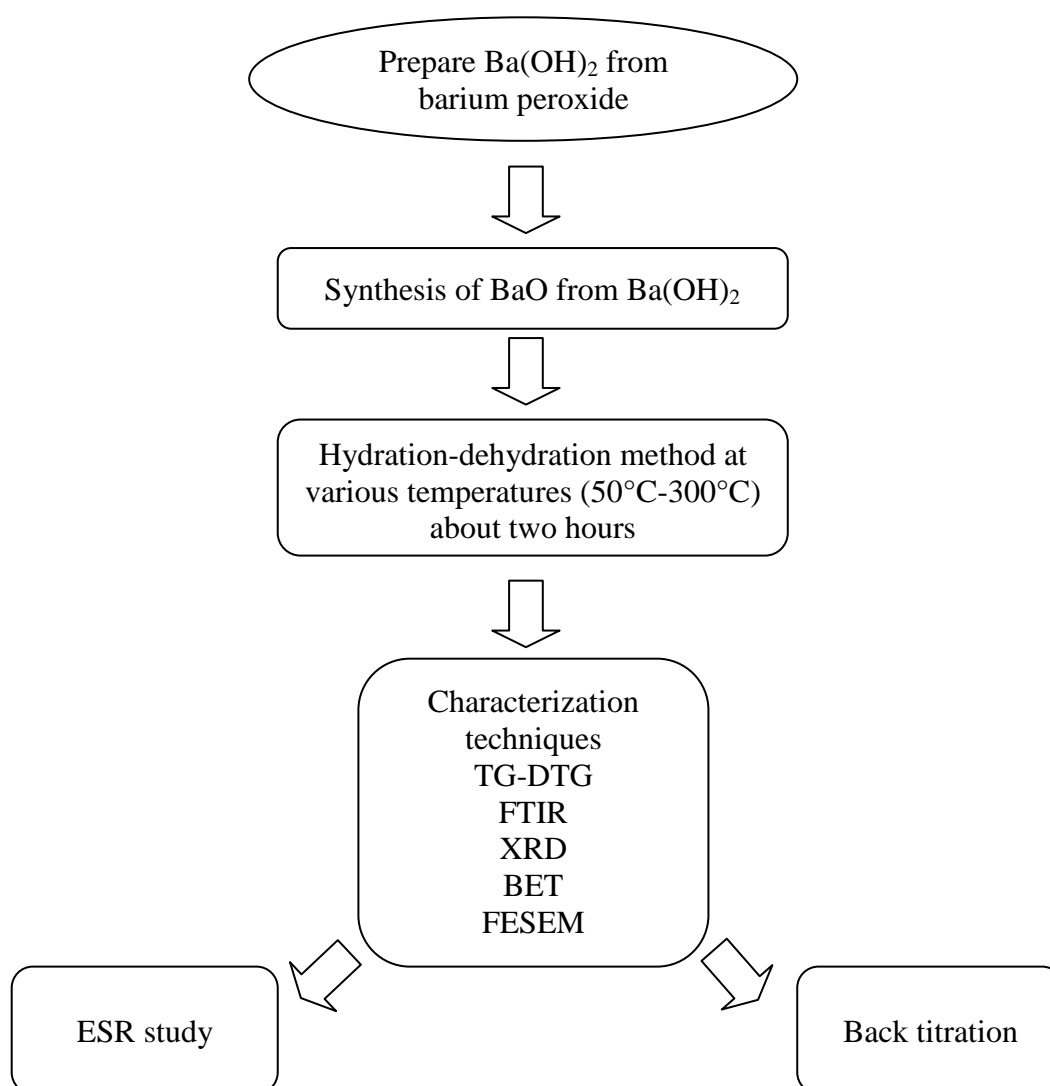
This study has the following objectives:

1. To prepare BaO via hydration-dehydration method from 50°C to 300°C respectively under vacuum atmosphere.
2. To identify and characterize the prepared BaO by various methods such as TG-DTG, FT-IR, XRD, BET and FESEM that explains the surface of BaO.
3. Back titration to determine the basicity of the prepared BaO effect by temperature of hydration-dehydration.
4. To investigate the ability of the surface defect to trap electron using Electron Spin Resonance (ESR) spectroscopy and determine the amount of basic sites.



## 1.5 Scope of Research

This study focus on the preparation of surface modified BaO using hydration-dehydration method. Figure 1.1 shows overview the schematic layout of research scope where barium peroxide was used as the starting material. The prepared Ba(OH)<sub>2</sub> was calcined at various temperatures: 50°C, 100°C, 150°C, 200°C, 250°C and 300°C for two hours respectively. The sample was characterized using thermogravimetric-derivative thermogravimetry (TG-DTG), fourier-transform infrared (FTIR), X-ray powder diffraction (XRD), nitrogen adsorption (single point BET analysis) and field emission scanning electron microscope (FESEM).



**Figure 1.1** Layout of research scope