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LIST OF ABBREVIATIONS

XRD	– X-Ray Diffraction
FESEM	– Field Emission Scanning Electron Micrograph
EDX	– Energy Dispersive X-Ray
FTIR	– Fourier Transform Infrared Spectroscopy
IR	– Infrared Spectroscopy
SOD	– Sodalite
Pt	– Platinum
Au	– Aurum
GC-FID	– Gas chromatography – Flame ionization detector
GC-MSD	– Gas chromatography – Mass selective detector
PTFE	– Polytetrafluoroethane

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CHAPTER 1

INTRODUCTION

1.0 Background of Study

Over the last 40 years, various solid acids and bases have been developed. Nowadays, solid acid-base catalysis is one of the economically and ecologically important fields in catalysis [1]. From the statistical survey, more than hundred types of industries processes are using acid as catalyst. On the other hand, base catalyst is far less behind. Thus, the emergence of novel solid base materials makes the new base-catalyzed reactions become commercially relevant. Based on this, fundamental studies on solid bases become necessary in order to achieve the success like those of solid acids catalysts.

Conventionally, the Knoevenagel reaction carried out in organic solvents is catalyzed by base homogenous catalysts such as ammonia, primary and secondary amines and their salts[2]as well as CuCl_2 , ZnCl_2 and SmCl_3 . However, in recent years, numerous acidic and basic heterogeneous catalysis have been applied in the Knoevenagel reaction. Zeolites have been reported as an efficient heterogeneous catalyst in Knoevenagel reaction for the carbon-carbon bond formation in organic syntheses[3].

Solid base catalysts exhibit higher activities and selectivities for many kinds of reactions, including condensation, alkylations, cyclizations, and isomerizations.

However, in industrial field, many of these processes were carried out by using liquid bases as catalysts. In addition, the versatile Knoevenagel condensation is classically catalyzed by bases in the liquid phase systems or Lewis acid under homogeneous conditions. The main problems with the usage of bases and acids in the reactions are huge organic waste generation due to formation of unwanted products resulting from polymerization, bis-addition and self condensation as well as the total dissolved salt resulting from the neutralization of the soluble bases or acids. The replacement of liquid basic catalysts by solid bases in the organic synthesis of fine and intermediate chemicals offers an opportunity to avoid salt formation, corrosion, and other environmental problems [4]. On the other hand, solid base catalysts are inexpensive and are more easily separable and recyclable than the homogeneous catalysts. Hence, the use of solid base catalysts is desirable from the viewpoints of economy and green chemistry and is currently gaining much attention.

However, little effort has been given to the study of solid base catalysts. Basic solids such as Cs-ZSM-5, MgO [5], NaX and CsNaX [6] have been used as catalysts in industrial processes due to their activity, thermal stability, and reusability. While metal ion-exchanged zeolites possess basic sites of relatively low strength, they can be easily regenerated from poisoning by air, as compared with strong solid bases, such as alkaline earth oxides. Nevertheless, applications of basic zeolites are limited by slow diffusion of substrates into their micropores for bulky molecular reactions and rapid deactivation due to coke formation [5].

It is therefore of interest to develop a high aluminum-containing zeolite with a basicity comparable to the basic homogeneous catalyst. Sodalite with high aluminum content ($\text{Si}/\text{Al} = 1$) and is expected possess high strength of basicity. Sodalite has very small pore. In this study, the porosity is not being taking into account, only the number of alkali metal exchanged on the sodalite like any other NaOH or base. Sodalite does not dissolve in reaction medium and hence can be recycled and reused.

In this study, nanosodalite with high aluminium content synthesized by hydrothermal method was reported. The catalytic activity was compared with that

microsodalite for Knoevenagel condensation reaction. The methods used to characterize basic sites were spectroscopic method using CO₂ as probe molecules, and catalytic test reactions. An advantage of an adequate choice of a test reaction is that it can give useful information about the catalyst under reaction conditions [4].

1.1 Statement of Problem

In general, most of the organic synthesis is based on the homogeneous catalysis. However, these homogeneous reactions are suffered from separation and regeneration. The solid base catalysts have many advantages over liquid base catalysts because they are non-corrosive, eco-environmentally, and present fewer disposal problems.

From the point of view of solid base, the properties of zeolites are adjustable to specific applications, and the solid may therefore seen in a sense as a new material. In spite of this, not much effort was done in preparing base zeolite. Only several exploration have been done to introduce base sites in faujasites type zeolite X and zeolite Y compared to other solid base materials [7]. However, some other zeolites that have not been investigated with regards to their basicity may show interesting base character. Based on this, fundamental studies on solid bases become necessary in order to achieve the success like those of solid acids catalysts.

Sodalite is a zeolite with high aluminum content (Si/Al = 1) and high stability in basic solution. However, it thus far has not found any significant catalytic applications due to its inaccessible cages with small pore openings (2.8 Å). Sodalite with nanosized particle with increased in external surface area offers great attractive possibilities to explore their potential utilization. In this study, sodalite with high aluminum content (Si/ Al = 1) have basicity and be able to catalyze the Knoevenagel condensation reaction.

1.2 Significant of Research

The substitution of the homogeneous catalysts with the heterogeneous ones is becoming more significant in chemical and life science industries due to their advantages. For instance, they are non-corrosive, fewer disposal problems, easy separation and reusable. Furthermore they can be designed to give high activity, selectivity, and longer catalyst life.

Knoevenagel condensation is a widely used method for the synthesis of fine chemical in industry. The reaction takes place generally based on homogeneous base as catalyst but is suffer from separation of products. In addition, this process generates huge amount of inorganic waste and many by-products. The use of solid base catalyst introduces advantages for industrial for a simplistic work-up, reduction of waste. Furthermore, separation and regeneration of the solid base catalyst can save cost.

1.3 Objectives

The objectives of this study are:

- 1) To synthesize nanosodalite with base properties.
- 2) To characterize the physical and chemical properties nano size sodalite.
- 3) To study the base properties of nanosodalite.
- 4) To compare the catalytic properties of nanosodalite in Knoevenagel base-catalyzed reaction.

1.4 Scope of Research

The scope of study included hydrothermal synthesis of sodalite nanocrystals without using any organic additives during the crystallization process. Sodium aluminate was used as Al source, fumed silica as silica source, and NaOH pellets as alkali and counter ion source. Effects of temperature and aging period were also studied in order to determine an optimum condition to obtain the nanosodalite.

The samples were characterized by X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy, Field Emission Scanning Electron Microscopy (FESEM). Basicity study was carried out by using CO₂ as probe molecules and monitored by FTIR spectroscopy. The basic catalysts were tested for the Knoevenagel condensation of benzaldehyde and malononitrile. The liquid products that were obtained were analyzed and identified by using Gas Chromatography (GC-FID) and the identification of the component was determined by Gas Chromatography-Mass Spectroscopy Detector (GC-MSD).

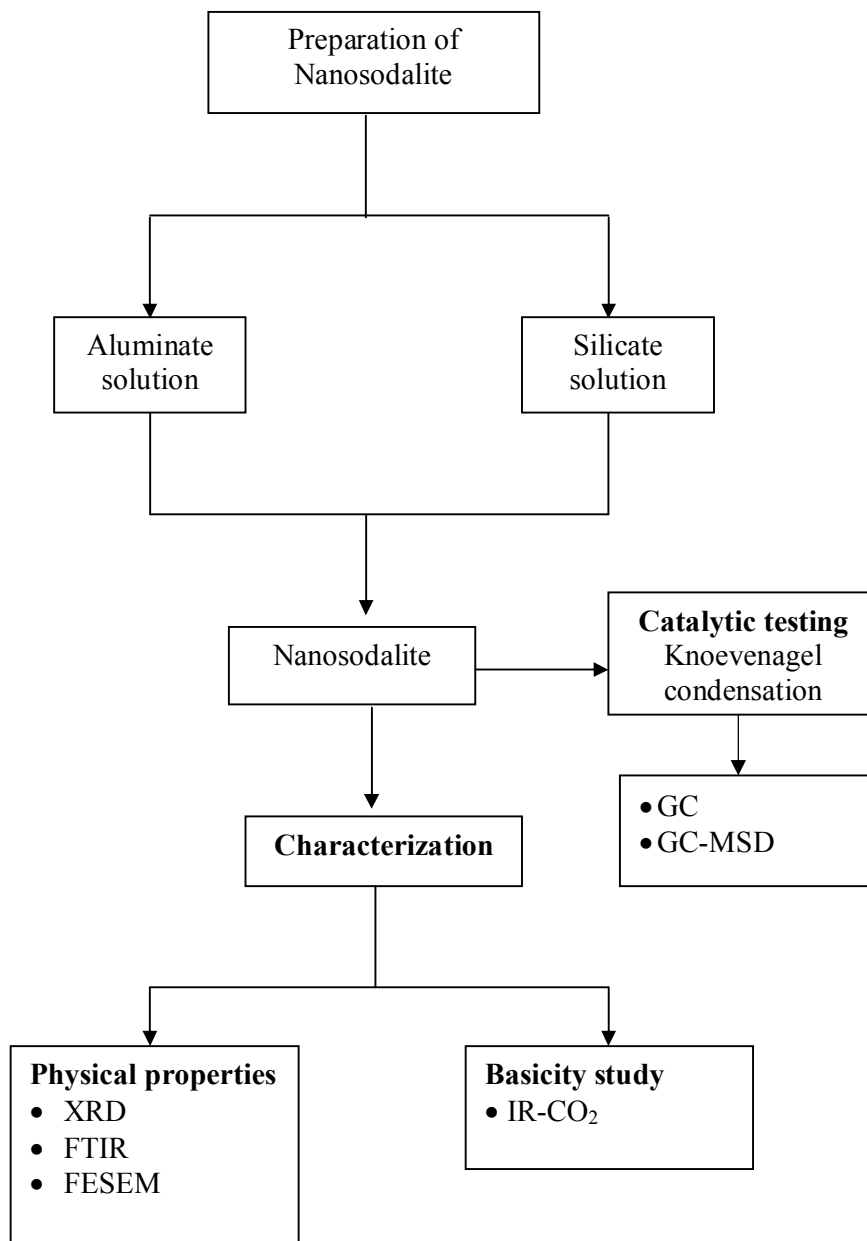


Figure 1.1: Flow chart of the experimental research.

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