DEVELOPMENT OF ZEOLITES AND ZEOLITE MEMBRANES FROM AHOKO NIGERIAN KAOLIN

A THESIS SUBMITTED TO THE UNIVERSITY OF MANCHESTER FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF ENGINEERING AND PHYSICAL SCIENCES

2011

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ABSTRACT

Zeolites and zeolite membranes are two important advanced chemical materials which are widely used in chemical processes. The manufacture of these materials usually involves the use of expensive chemicals.

This study involves the use of Ahoko Nigerian kaolin (ANK) as precursor material for the development of zeolites and zeolite membranes. The synthesis of zeolite A, Y and ZSM-5 was successfully obtained following a sequence, collection of the raw clay from Nigeria, metakaolinization, dealumination and actual hydrothermal synthesis of the zeolites. Raw ANK was refined using sedimentation technique and about 97% kaolin was recovered from the raw sample.

A novel metakaolinization technique was developed to convert kaolin into a reactive metastable phase. Amorphous metakaolin was obtained at a temperature of 600°C and exposure time of 10 min. This is a significant result because previous studies use higher temperatures and longer exposure times for the metakaolinization step. The metakaolin was used to prepare a number of different zeolites under various conditions. Highly crystalline zeolite A was obtained at an ageing time of 12 h, crystallization time of 6 h and crystallization temperature of 100°C. Zeolite Y was obtained at an ageing time of 3 h, crystallization time of 9 h and crystallization temperature of 100°C. Zeolite Y was also synthesised by using a dealuminated kaolin and highly crystallized zeolite Y with Si/Al ratio of 1.56 and BET surface area was obtained of 630 m²/g. ZSM-5 was synthesised using an ageing period of 36 h, crystallization time of 48 h and temperature of 140°C.

The results obtained from zeolite powder synthesis from ANK were then used as guide to prepare supported zeolite films and membranes by a hydrothermal method. The effect of the support surface (stainless steel) was investigated using two synthesis methods namely modified in-situ and secondary (seeded) growth. Zeolite A, Y and ZSM-5 films were successfully prepared from ANK for the first time and on two modified supports, etched and oxidised. The zeolite films and membranes developed showed complete coverage on the two supports with the oxidised showing better adhesion and intergrowth. The separation performance of the three developed zeolite membrane was tested by pervaporation of water/ethanol mixture. The results of pervaporation of ethanol/water mixture showed that zeolite A membrane is highly selective towards water mainly because
of hydrophilic properties occasioned by the high aluminium content. Zeolite Y membrane show a similar response when their separation performance was evaluated but with less selectivity because of reduced aluminium content. ZSM-5 showed selectivity towards ethanol because of its hydrophobicity allowing only ethanol to permeate. In all the zeolite membranes, the flux is lower in comparison to commercial zeolite membranes due mainly to the thickness of the zeolite layer. Oxidised support membranes showed better performance because of their better interaction between the oxide surface and the aluminosilicate gel. The results show that ANK can successfully be used to prepare zeolites and zeolite membrane.
DECLARATION

No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning. The work is original except where acknowledged by reference.

Date …03/11/2010……

Signed……A.S.Kovo……
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ACKNOWLEDGEMENTS

I am most grateful to Petroleum Technology Development Fund, Nigeria who fully sponsored my PhD program at the University of Manchester.

I would like to express my sincere appreciation and thanks to Dr Stuart Holmes for his efficient supervision of this work. His tireless encouragement and generation of novel ideas contributed most to the completion of this project.

The support of my wonderful wife and my lovely children, Nabilah and Najihah contributed in no small measure in the completion of this work. Their patience and continue encouragement in the face of several adversities was second to none. The whole PhD is dedicated to them, my wife and children.

I will also like to appreciate Dr. Patrick Hill who not only help with all SEM and TEM analysis, he also made out time out of his busy schedule to proof read part of the  thesis. Thank you Paddy. Other technicians in the school of chemical engineering are equally acknowledged.

To my mum, I say thank you for being a wonderful mother, your contribution toward my modest achievement in life remain indelible.

Finally, All thanks is due to the most Merciful, the Most Beneficent, Almighty Allah for guiding me and my family in the UK. We will forever remain your obedient servant.
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANK</td>
<td>Ahoko Nigerian kaolin</td>
</tr>
<tr>
<td>FCC</td>
<td>Fluid cracking catalyst</td>
</tr>
<tr>
<td>RHO</td>
<td>Roggianite</td>
</tr>
<tr>
<td>TON</td>
<td>Theta-1</td>
</tr>
<tr>
<td>BEA</td>
<td>Zeolite Beta</td>
</tr>
<tr>
<td>LTA</td>
<td>Linde Type A</td>
</tr>
<tr>
<td>LTL</td>
<td>Linde Type L</td>
</tr>
<tr>
<td>MWW</td>
<td>MCM-22 (Mobil composite of matter)</td>
</tr>
<tr>
<td>CHA</td>
<td>Chabazite</td>
</tr>
<tr>
<td>FAU</td>
<td>Faujasite</td>
</tr>
<tr>
<td>MON</td>
<td>Mordenite</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>Zeolite Socony Mobil</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmett and Teller</td>
</tr>
<tr>
<td>TEOS</td>
<td>Tetraethylorthosilicate</td>
</tr>
<tr>
<td>PBU</td>
<td>Primary building unit</td>
</tr>
<tr>
<td>SBU</td>
<td>Secondary building unit</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatograph</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>EDAX</td>
<td>Energy Dispersive X-ray Analysis</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray Fluorescence</td>
</tr>
<tr>
<td>MBTE</td>
<td>Methyl Tert-Butyl Ether</td>
</tr>
<tr>
<td>ETBE</td>
<td>Ethyl Tert Butyl Ether</td>
</tr>
<tr>
<td>MIM</td>
<td>Modified In-situ Method</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>SGM</td>
<td>Secondary Growth Method</td>
</tr>
<tr>
<td>TIPB</td>
<td>Tri-isopropylbenzene</td>
</tr>
<tr>
<td>PCS</td>
<td>Photon correlation spectroscopy</td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionization Detector</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal Conductivity Detector</td>
</tr>
<tr>
<td>WCOT</td>
<td>Wall Coated Open Tubular Column</td>
</tr>
<tr>
<td>PLOT</td>
<td>Porous Layer Open Tubular Column</td>
</tr>
<tr>
<td>SCOT</td>
<td>Support Coated Open Tubular Column</td>
</tr>
</tbody>
</table>
ABOUT THE AUTHOR

Kovo Abdulsalami Sanni was born in Okene, Kogi state, Nigeria on the 21st November, 1974. He had his early education in Okene and left secondary school in 1993. He got admitted in 1994/95 to study Bachelor of Engineering in Chemical Engineering at the Federal University of Technology, Minna, Nigeria. Upon graduating in 2000, he served his fatherland for one year before going back to his department to start working as assistant lecturer in 2001. He thereafter enrolled for a master degree programme in Chemical Engineering in the same university in 2002 and graduated in 2005. In 2007, he was awarded Petroleum Technology Development Fund (PTDF) scholarship to do a PhD under the supervision of Dr Stuart Holmes at the University of Manchester, UK with research focusing on the development of zeolites and zeolite membranes from local raw material (Ahoko kaolin) sourced from Nigeria.
CHAPTER ONE: GENERAL INTRODUCTION
Rarely in our technological society does the discovery of a new class of inorganic materials result in such a wide scientific interest and kaleidoscopic development of applications as has happened with zeolite molecular sieves’ Breck, 1974 [1]

Chapter 1 : General Introduction

1.1 Introduction

Zeolites are crystalline, microporous, aluminosilicate materials which have huge academic, scientific and industrial interest in the areas of ion exchange (detergent industry, radioactive waste storage, and treatment of liquid waste), separation (purification, drying, environmental treatment) and petroleum refining along with petrochemical, coal and fine chemical industries [1-3]. The ability of zeolites to act as multi-functional materials in many industrial applications is due to their inherent properties such as uniform pore size/shape, catalytic activity, mobile cation and hydrophilicity/hydrophobicity [4].

Zeolites were first discovered in 1756 by Cronstedt A.F as natural minerals in cavities and vugs of volcanic basalt rock [3]. They are mainly used in the treatment of sewage, hard water and as a drying agent. Natural zeolites have problems of inadequate supply, impurities, non uniform pore size and low ion exchange capacities. As a result synthetic zeolites have been developed. This produces a material with better qualities and wider applications. As will be discussed in chapter two the synthesis of zeolite involves mimicking the conditions of it natural formation but at lower temperature and much shorter time frame from a few minutes to a few days.

Zeolite synthesis is conventionally performed by a hydrothermal crystallization process using commercial chemicals serving as sources of silica and alumina [5]. Examples of such chemicals include sodium metasilicate, sodium aluminate, silica gel, tetraethylorthosilicate (TEOS), and aluminium hydroxide. These chemicals are generally expensive and their process of production is complicated leading to high costs for zeolite production which limits their commercialization [6] and uses in many industrial applications.
The use of a low cost and abundant material such as clay (kaolin) as a combined source of silica and alumina is highly desirable. The preparation of kaolin into zeolite via a metakaolinization process has been reported [7-9]. However, this study is important because kaolin composition varies with location [10]. The use of Ahoko Nigerian kaolin (ANK) for the first time to prepare zeolites is of value to the industrial aspirations of Nigeria.

A cost comparison of obtaining a silica and alumina source from a chemical feedstock and kaolin/metakaolin has been carried out [11]. It was shown that clay as a precursor to zeolite A synthesis has a comparative cost advantage of 15% over a commercial chemical such as sodium silicate. This was further justified by a simple cost comparison carried out (appendix A) which indicate a current cost advantage for kaolin as source of zeolite synthesis over commercial chemicals such as sodium metasilicate and aluminium hydroxide.

The experimental work was initially directed toward understanding the fundamentals of zeolitization of kaolin. Further investigations have been conducted to understand the influence of lower metakaolinization temperature on the synthesis of zeolites from kaolin.

The second area of research in this study is to investigate the synthesis of zeolite films and membranes from kaolin. Traditionally, zeolites are synthesized as powder, and are used in several chemical industries and their usage has its own problems such as pressure drop, mass and heat transfer related problems when used in applications such as catalysis and adsorption. This has necessitated recent preparation of zeolite as films, coatings or membranes, thereby promoting their application in new areas such as selective membranes [12, 13], sensors [14], corrosion control [15], and structured catalysts [16].

There are some other well developed industrial applications of membrane processes such as microfiltration, dialysis, and reverse osmosis. Other emerging areas are being developed and many are yet to be fully commercialised. Zeolite membranes are more expensive than polymer membranes, the high cost of zeolite membrane can be attributed to the cost of the material used in the preparation of the membrane as well as the cost of the supports and difficulty in synthesis. There is therefore the need to start finding alternative starting materials for zeolite membrane synthesis that are low cost and readily available.
1.2 Aims and Objectives

1. To investigate the refinement and metakaolinitization of the raw ANK to prepare zeolite powder and zeolite membranes

2. To investigate the synthesis and characterization of zeolitic materials from ANK.

3. To study the development of zeolite films and membranes of high quality using ANK.

4. To investigate the synthesis strategy best suited for zeolite films and membranes synthesis from ANK.

1.3 Outline of Thesis

This thesis consists of two main pieces of research. Chapter one presents a general overview of the research to be undertaken while chapter two presents the literature work on zeolite science. Chapter three contains information on all the characterization techniques used in the work. The first major part of the study is contained in chapter four. Chapter four presents the studies carried out on the synthesis and characterization of three different zeolitic materials using Ahoko Nigerian kaolin (ANK) for the first time. The processes including the sourcing of the raw kaolin from Nigeria, the refinement processes, metakaolinitization techniques used and the actual production processes are all described in this chapter. The results which showed that zeolite A, zeolite Y and ZSM-5 zeolite can be synthesised from ANK using metakaolin produced at lower temperatures and shorter exposure times than previously reported, and using two techniques (addition of external silica and dealumination) are also presented in this chapter. The second part of this research on the development of zeolite membrane from the source (ANK) is presented in chapter five. This chapter presents all the methods used in the preparation of zeolite membranes using ANK as a source of the precursor as well as the results obtained. The testing of the performance of zeolite membranes developed in terms of coherence, defects and separation performance is also presented in this chapter. The outcome showed a successful synthesis of coherent and good quality zeolite A, ZSM-5 and Y films and membranes in pre-treated stainless steel using ANK as source of precursor.
CHAPTER TWO

INTRODUCTION TO ZEOLITES
This chapter introduces zeolites as a science and discusses the structure and properties as well as the application of zeolite materials as an important industrial chemical. The hydrothermal synthesis of zeolites which is central to this work is also discussed in this chapter.

Chapter 2: Introduction to Zeolites

2.1 Introduction to Zeolites

Zeolites belong to an important class of hydrated aluminosilicate minerals of group I and group II elements [1]. They were discovered as a natural mineral in 1756 by a Swedish mineralogist named Cronstedt A. F. who noticed an unusual behaviour when the silicate mineral was heated. It shows visible loss of water, a phenomena he called ‘intumescence’ and from which the name zeolite, a Greek word meaning ‘boiling stone’[17] was derived.

Zeolites are highly crystalline and are based on fundamental building blocks of tetrahedral SiO\(_4\) and AlO\(_4\) giving rise to a three dimensional network. The structural formula is given as

\[
M_{a/n} [(AlO_2)_a(SiO_2)_b] cH_2O
\]

where \(M\) is the cation of valence \(n\), \(c\) is the number of water molecules, \(b/a\) is the silica to alumina ratio, \((a+b)\) is the number of tetrahedra present in the unit cell. The zeolite framework atoms are coordinated to four oxygen atoms bridging two framework atoms. Hence the aluminosilicate zeolite obtained from SiO\(_4\) tetrahedra and AlO\(_4\) tetrahedra possess residual negative charge and are compensated by extra-framework cation.

The framework composition is represented by the square bracket [1]. The zeolite frameworks are generally open. Water and cations are located within the channel and cavities. The cation presence is needed in the zeolite framework to neutralise the negative charge created as a result of isomorphous substitution of Si\(^{4+}\) by Al\(^{3+}\) in the framework as explained earlier. The mobility of this cation among other behaviour is responsible for the unique properties of zeolite and other zeolite-like materials [3].

Zeolites were originally discovered as naturally occurring minerals about 250 years ago, but are now mostly prepared in the laboratory as will be explained in section 2.7 [3].
Natural zeolites were initially found in cavities and vugs of basalt rock and it was later that they were found in sedimentary rock much closer to the earth crust. They were thought to have been formed as a result of several natural activities listed below:

- Crystal formation as a result of hydrothermal activity between solution and basaltic lava flows
- Volcanic sediment deposition in closed alkaline and saline lake-system
- Formation due to activity of groundwater system on volcanic minerals
- Volcanic deposition on alkaline soil
- Deposition resulting from low temperature alteration of marine sediment
- Formation resulting from low grade burial metamorphism

The first natural zeolite discovered was stilbite in 1756 and today, there are 40 known natural zeolites (table 2.1) with well defined structure and applications. They occur with low to medium silica to alumina ratio, hence their applications in industry are highly restricted when compared with their synthetic counterparts. Their best application is found in ion exchange mainly in radioactive treatment (clinoptilolite). They are also use in agricultural activities and as a sorbent and are both usually performed by mordenite (MOR) [18]. Natural zeolite production is expected to top 50,000 metric ton/yr with sales reaching 40,000 metric ton/yr in the next few years [19].
Table 2.1: Some natural zeolite and date of discovery [20]

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Date of discovery</th>
<th>Three-letter code used by IZA</th>
<th>Zeolite</th>
<th>Date of discovery</th>
<th>Three-letter code used by IZA</th>
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<tbody>
<tr>
<td>Stilbite</td>
<td>1756</td>
<td>STI</td>
<td>Mordenite</td>
<td>1864</td>
<td>MOR</td>
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<tr>
<td>Natrolite</td>
<td>1758</td>
<td>NAT</td>
<td>Clinoptilolite</td>
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<td>1772</td>
<td>CHA</td>
<td>Offretite</td>
<td>1890</td>
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<tr>
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<td>1775</td>
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<td>Kehoeite</td>
<td>1893</td>
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<td>Gonnardite</td>
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<td>1801</td>
<td>THO</td>
<td>Dachiardite</td>
<td>1905</td>
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<td>Scolecite</td>
<td>1801</td>
<td>-</td>
<td>Stellerite</td>
<td>1909</td>
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<td>1801</td>
<td>HEU</td>
<td>Ferrierite</td>
<td>1918</td>
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<td>1807</td>
<td>GME</td>
<td>Viseite</td>
<td>1942</td>
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<td>1813</td>
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<td>Yugawaralite</td>
<td>1952</td>
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<td>1816</td>
<td>GIS</td>
<td>Wairakite</td>
<td>1955</td>
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<td>1822</td>
<td>BRE</td>
<td>Bikitaite</td>
<td>1957</td>
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<td>Faujasite</td>
<td>1842</td>
<td>FAU</td>
<td></td>
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</tbody>
</table>

Dashes are not assigned code
2.2 Structure and Nomenclature of Zeolites

Zeolites are an important industrial chemical primarily due to their unique structures. The area of applications of zeolites such as ion exchange, catalysis and sorption are all attributed to the framework configuration and pore structure, hence understanding the structural characteristics is an important part of zeolite research.

The structure of a zeolite is generally described as a three dimensional material with a framework atom connecting tetrathedrally with four oxygen atoms [21]. The framework atom is usually Silicon (Si) and Aluminium (Al), however other metals such as Gallium, Germanium, Boron and Titanium can take the place of Si and Al [3].

The representation of a typical zeolite by its primary building unit is TO$_4$ where T is the framework atom as shown in figure 2.1.

![Figure 2.1](image)

Figure 2.1 The primary building unit TO$_4$ is shown on the left. On the right, two TO$_4$ units have been joined to demonstrate how they link together to form larger structures [22].

The primary building block of zeolite is represented by [TO$_4$] tetrahedra. The primary building unit (PBU) creates an infinite lattice of identical building blocks of repeating unit called secondary building unit (SBU). The SBU is the main unit that describes the zeolite structure with the exception of the water and cation in the framework. There are nine known SBUs that describe all the known zeolite frameworks as shown in figure 2.2. Cations are located within the zeolite pores to compensate for the residual negative charge generated by the isomorphous substitution of Si$^{4+}$ by Al$^{3+}$ during the zeolite framework formation.
Zeolite frameworks are generated from the listed SBUs and in some cases combinations of SBUs are used to form zeolites. For example zeolite A is generated using 4 ring or 6 ring and at the same time zeolite A can be formed from double 4 ring building unit. FAU can be obtained from sodalite framework which is made of single 6 member ring or 4-member ring, it can also be generated from double 6 ring building unit. A description of the structure of zeolites synthesised in this work is given in section 2.4.

The location of cations and water within the cavities and holes in the framework cannot be explained by the SBU [21]. The water molecules and cations present in zeolite framework are highly mobile with the water molecule capable of being removed reversibly at a temperature between 100-500°C when dehydrated. The zeolite structure is generally stable up to temperatures between 700 to 800°C.

![Secondary Building Units (SBUs) existing in the zeolite Framework](image)

Figure 2.2 Secondary Building Units (SBUs) existing in the zeolite Framework [23]

The nomenclature of zeolite framework has also evolved over the years with the early zeolites synthesized by Breck and co-workers named using Arabic letter such as zeolite A,B, X, Y and K. This later evolved into the use of Greek letters to represent the zeolites produced by Mobil company researchers, examples include zeolite Alpha, Beta, and Omega. The naming of synthetic zeolite was later taken further by assigning the name of
the parent zeolite mineral when the synthesized zeolite has the same topology as the parent mineral. Examples include synthetic mordenite, chabasite and erionite.

The structural committee of International Zeolite Association (IZA) finally produced an atlas of zeolite structure in which each zeolite framework type is assigned a three-letter code to describe and define the network of corner sharing tetrahedrally coordinated atoms irrespective of its composition [3, 24]. The three letter codes are usually derived from the source material’s name. There are about 194 different zeolite frameworks as at July 2010 and each with its individual code [25]. Example of the some of the most important zeolite framework with their codes include zeolite A with a code of LTA meaning Linde type A, while zeolite X and Y are assigned the code FAU meaning zeolite with faujasite topology and finally ZSM-5 and silicalite with illustrative code as MFI. Today the name of zeolites follows the three major conventions and they are all accepted.

2.3 Pore Structure

The structure of zeolite material cannot be completely explained without the understanding of the pore structure.

The adsorption properties of a zeolite in terms of its molecular sieving capacity and the selectivity are firmly rooted or dependent on the size and shape of the pores present in the zeolite framework. Zeolites can be classified based on the pore size which is defined by the number of T atoms present in the framework where T = Si or Al. The pore opening systems are known in zeolites especially for catalytic and adsorptive processes. These are:

- 8 member rings also called small pore opening. Examples include zeolite A and erionite.
- 10 member rings also called medium pore zeolite, the prominent member of this group is ZSM-5 zeolite.
- 12 member ring opening also called large zeolite and zeolite X and Y are typical example.

Examples of the three main pore systems in zeolite are shown in figure 2.3.
To determine the nature of pore size in zeolites, a selection of molecular probes is used for adsorption process through the zeolite. For example cyclohexane with size 6.5 to 7.4Å cannot adsorbed into 8-member ring pore system but can be readily adsorbed into 12 member ring hence cyclohexane can be used as a probe for only large pore zeolite and not small pore zeolite. The classification of pore structure has also been based on the dimensionality of the pore system and the shape of the pore mouth.

### 2.4 Description of Zeolites Studied

#### 2.4.1 Zeolite A

The framework system of zeolite A is described as a combination of sodalite cages joined together via double 4-ring showing an α- cage at the centre of the unit cell shown in figure 2.4.

---

Figure 2.3: Pore structure of zeolites studied in this research (A) 8-ring, zeolite A (B) 10- ring, ZSM-5 (C) 12- ring, zeolite Y [25]
The zeolite framework consists of alternative silica and alumina tetrahedral yielding Si/Al ratio of 1 following the Lowenstein’s rule which forbid Al-O-Al linkage in aluminosilicates [3]. The framework of the zeolite has the largest exchangeable cation making it a good material as an ion exchange agent. The aluminium in the framework of zeolite A is unstable as it is susceptible to attack by acid and water vapour at high temperature, the reason zeolite A is not widely used in catalysis.

2.4.2 Faujasite (Zeolite X and Y)

The faujasite structure is similar to the LTA structure described earlier however, the sodalite cage is linked with double 6-ring resulting in a super cage with 12 ring pore opening (figure 2.5). It has 3-dimensional channel system and can be imagined as stacking layers of sodalite cages similar to the arrangement of carbon atoms in diamond [21]. The X and Y- type zeolite are known to have the same framework structure but only differ in their framework Si/Al ratio. Zeolite X has Si/Al ratio of 1 to 1.5 while zeolite Y has Si/Al greater than 1.5 [3, 27]. The large pore size and three dimensional channel systems in zeolite Y enable it to be thermally stable and it has become an important material in catalytic cracking operation. The thermal stability can be further increased by dealumination thereby increasing the Si/Al ratio and producing ultra-stable zeolite (USY), a material currently used in the cracking of crude oil.
2.4.3 MFI

The MFI family is composed of two members namely, ZSM-5 and silicalite. The framework of MFI is composed of its characteristic 5-1 unit with D2d symmetry [3]. The symmetry link via edge sharing to form pentasil chain. The pentasil chains are connected with an oxygen bridge to form an MFI structure with 10 ring pores which is also three dimensional. There is an intersecting channel with straight 10 ring channel and sinusoidal 10-ring channel shown in figure 2.6, the aluminium content varies from ~10 to infinity and therefore, the Si/Al ratio lies over a wide margin [29]. The 10-ring channel system gives ZSM-5 a unique shape selectivity properties which allow it to be widely used in catalysis and sorption, it is an important source of catalyst in petroleum refining and petrochemical industry and they are even better utilized than zeolite Y [24]. Because of aluminium content of ZSM-5, no matter the amount, there is small level of hydrophilicity while its analogue silicalite-1 is completely free of aluminium making it hydrophobic.
2.5 Properties of Zeolites

In this section, the properties of zeolites are discussed.

2.5.1 Ion-Exchange

Ion exchange is an intrinsic characteristic of most zeolites and has become one of the most commercially important properties of zeolite. It is the property that allows the replacement of cation held in the zeolite framework by an external ion present in a bulk solution or in a melt [21]. The ion exchange property is due to the isomorphous substitution of Si$^{4+}$ by Al$^{3+}$ in the framework creating a net negative charge as explained in section 2.1. Different types of cations can be used to compensate for the ionic imbalance in the zeolite framework and to maintain ionic neutrality. Zeolites are generally synthesised using Na$^+$ ion as the compensating cation in the framework and in an exchanging reaction, other cations such as Mg$^{2+}$, Ca$^{2+}$, NH$_4^+$ and H$^+$ can replace Na$^+$.

An example of exchanging of sodium ion in zeolite framework by Ca$^{2+}$ is shown below

$$2\text{NaZ} + \text{CaCl}_2 \leftrightarrow \text{CaZ}_2 + 2\text{NaCl}$$

where Z is the zeolite.

Similar reactions are used in the generation of the acid catalyst when the cations in the zeolite framework are exchanged with proton from mineral acid or ammonium hydroxide thereby producing a protonated zeolite used as catalyst. The properties of zeolites as ion
exchange material is widely used and applied in detergents, waste water treatment and radionuclide separation[24].

## 2.5.2 Catalysis

The catalytic property of zeolites is another important application for which zeolites have been used. About 99% of the world petrol from crude oil depends on zeolite as catalyst for its production. The catalytic characteristics of zeolites are due to the combination of intrinsic properties of zeolite. These properties are responsible for the overall behaviour of zeolite as a catalyst however the generation of active sites otherwise called Bronsted sites (figure 2.7) by ion exchanging of ammonium hydroxide followed by calcination is the most important step in the production of zeolites as catalysts. Bronsted site is known as bridging hydroxyls and are generated at oxygen bridge site near the Si-O-Al cluster where the compensated cation are represented by protons. They are the main reason why zeolite is used as an industrial catalyst. This is because of the production of hydroxyl within the zeolite pore structure where there are high electrostatic field attracting organic reactant molecules and bond rearrangement can take place especially for cracking reactions.

![Figure 2.7: Bronsted acid site in zeolites [30]](image)

The reaction taking place during the production of the Bronsted site are shown below

$$\text{Na}_2\text{Z}_\text{(s)} + \text{NH}_4\text{aq}^+ \rightleftharpoons \text{NH}_4\text{Z}_\text{(s)} + \text{Na}^+$$

$$\text{NH}_4\text{Z}_\text{(s)} \xrightarrow{\text{Calcine}} \text{NH}_3 + \text{HZ}_\text{(s)}$$

This reaction is more associated with low silica zeolite such as zeolite X and Y, however for high silica zeolite such as ZSM-5, mineral acid such as HCl or H$_2$SO$_4$ can be used to produced the protonated zeolite by direct ion exchange thereby creating the Bronsted site. Some of the important applications of zeolites as an industrial catalyst include catalytic cracking, hydrocracking, hydroisomerization, NO$_x$ reduction and xylene isomerisation.
2.5.3 Adsorption

Adsorption can be described as a process whereby molecules of a gas or liquid material adhered to the surface of solid. These processes can be used to separate two mixtures of species depending on the affinity of the mixtures toward the solid surface. The solid surface is known as adsorbent while the adhering molecule is called adsorbate. The process of removing the adhered molecules is called desorption and this is achieved by changing the pressure and temperature of the system. These allow the reuse of the adsorbent.

The adsorption mechanism in zeolite depends on several factors such as the pore size of the zeolite, the ion exchange, the physical and chemical composition of adsorbate. These mechanisms include:

- Equilibrium selective adsorption
- Rate selective adsorption
- Shape selective adsorption
- Ion exchange
- Reactive adsorption

The adsorption properties of zeolites whichever mechanism controlled the process is broadly influenced by some specific properties of zeolites. Adsorption is an important characteristic of all zeolites as it directly influences the use of the material as a catalyst and separator. Adsorption in zeolite has both economic and environmental benefit because of their uses in oil refining and petrochemical over several years as catalysts just like it application in pollution abatement.

Some of the important uses of the adsorption and molecular sieving properties of zeolite include drying agent (zeolite 4A are used as general purpose drying agent such as gas drying column in GC), gas separation (pollution control) and separation of bulk mixture such as i-paraffin/n-paraffin system. Other specific utilization of adsorption properties of zeolites include:

- Aromatic removal from linear paraffin in the C\textsubscript{10}-C\textsubscript{15} range used in linear alkyl benzene production
• Nitrogenate removal
• Oxygenate removal
• Sulphur removal

2.6 Application of Zeolites

Both natural zeolites and synthetic zeolites have become an important and integral part of many process industries. The global market for zeolite production has continue to blossom to the extent that the world market for synthetic zeolite has been estimated to be around 1.8 million metric ton (Mt) while that of natural zeolite was projected to hit 5.5 Mt in 2010 [31].

Both types of zeolite have important uses while 90% of natural zeolites are mainly applied in the construction industry with the remaining used in such processes as animal feeding, horticulture, waste water treatment, odour control and other miscellaneous applications. Synthetic zeolites are mainly applied in process industries. According to the data obtained in 2001, 81% of synthetic zeolite is used in the detergent industry while the rest are used in catalysis, adsorption and other applications (Figure 2.8). Zeolites utilize the ion exchanging characteristic to function as an additive in detergents. In detergency zeolites, typically zeolite A (LTA), act as a water softener preventing carbonate precipitation through the exchange of calcium and magnesium ions with the highly mobile sodium ion present in the zeolite framework [32]. The increased application of zeolites in the detergent industry can be attributed to environmental concern. The use of phosphate builder has been banned in most countries because it causes eutrophication and is difficult to degrade when placed in water bodies, hence zeolites ie zeolite A and zeolite X offer a good replacement because of their high ion exchanging capacities.

The application of zeolites has its largest economic impact in the FCC processes. Zeolites give an increased yield over amorphous catalyst to the tune of around 1 billion US dollar a year [33]. Zeolite Y and ZSM-5 are two of the most important zeolite used in FCC catalysis. In fact ZSM-5 zeolite is regarded as good octane booster. Other octane booster zeolites in FCC operation include mordenite, silicalites, MCM-20 and zeolite beta.
Another example of the use of zeolites in catalysis is in hydrocracking. Hydrocracking involves the conversion of higher paraffins over noble metal containing zeolite catalysts to yield distillate products. The description of the hydrocracking processes including all the mechanism is well documented [34] but the main point is the crucial role played by zeolite catalyst in the process replacing the old catalyst such as alumina. Example of application of zeolites in different catalytic processes are shown table 2.2.
Table 2.2: Zeolite structure type used in commercial and emerging catalytic processes [21, 33]

<table>
<thead>
<tr>
<th>Zeolite type</th>
<th>Catalytic processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>FAU (Y)</td>
<td>Catalytic cracking, hydrocracking, aromatic alkylation, NOX reduction, acetylation</td>
</tr>
<tr>
<td>MON (mordenite)</td>
<td>Light alkane hydroisomerization, hydrocracking, dewaxing, NOX reduction, Aromatic alkylation and product, FCC additive, hydrocracking, olefin</td>
</tr>
<tr>
<td>MFI (ZSM-5, TS-1 and silicalite)</td>
<td>Dewaxing, methanol to gasoline, methanol to olefin</td>
</tr>
<tr>
<td>BEA (Beta)</td>
<td>Benzene alkylation, aliphatic alkylation, Acetylation</td>
</tr>
<tr>
<td>LTL (KL)</td>
<td>Baeyer Villiger reaction, FCC additive, etherification</td>
</tr>
<tr>
<td>MWW(MCM-22)</td>
<td>Alkane aromatization</td>
</tr>
<tr>
<td>CHA(SAPO-34)</td>
<td>Methanol to olefin</td>
</tr>
<tr>
<td>AEL (SAPO-11)</td>
<td>Long chain Alkane hydroisomerization, Beckmann re-arrangement</td>
</tr>
<tr>
<td>RHO (Rho)</td>
<td>Amination</td>
</tr>
<tr>
<td>TON(ZSM-22)</td>
<td>Long chain alkene hydroisomerization</td>
</tr>
</tbody>
</table>

The physiochemical characteristics of zeolites have now been explored in novel and non-traditional applications. Some of the most recent applications of zeolites in modern processes include:

- Optic and electronics [35, 36]
- Bio-catalysis [37]
- Synthesis of nanostructure catalyst [38, 39]
- Drug release [40, 41]
2.7 Synthesis of Zeolites

Natural zeolite formation is a result of natural reactions taking place between water present in several environments (saline, alkaline lake, saline soil, marine sediment, open hydrological system) with other solid materials present in such environment. The key materials which supply chemical species used in zeolite formation such as Si and Al include volcanic glass, crystalline clay, biogenic silica and quartz. The formation processes depend on several factors such as high temperature and high pressure. The reaction can take several thousands or more years to complete. Early developed zeolites such as clinoptilite and philipsite are metastable and are soon transformed to more stable zeolite such as analcime and heulandlite. As earlier explained million of tonnes of natural zeolites are produced annually but laboratory synthesis has also developed [42]. Further interest in the synthesis of zeolite can be attributed to its advantage over natural zeolite including high purity, uniform pore size, and good and tuneable ion exchange capabilities [3].

Synthetic zeolite was first reported by Ste克莱 Olt Deville in 1862 when he prepared Levynite by hydrothermal treatment of potassium silicate and sodium aluminate in a sealed glass tube. Even though there were no definitive characterization techniques, mineralogical and chemical analysis was used to identify the products [1]. Barrer and co-workers [5] made the breakthrough in the 1940s when they successfully synthesised analcime, however the real success was achieved by Breck and his colleagues working at Union Carbide Corporation (UCC) utilizing mild hydrothermal conditions and temperatures at 100°C and self generated pressure to synthesis the first non–natural zeolites A, X and Y. One remarkable discovery from the work of Breck and co-workers was the revelation that zeolites can actually be prepared at low temperature rather than the high temperature and thousand of years used for the preparation of natural zeolites. Continuous research in zeolite synthesis led to another significant development when in 1961 Barrer and Denny reported the synthesis of high silica zeolite using organic quaternary ammonium salt cation. This achievement led to the use of organic molecules as structural directing agent in zeolite synthesis by G. Kerr of Mobil oil Company producing high Si/Al ratio zeolite such as ZSM-5 and silicalite-1[3].

Several other developments continued to take place on zeolite synthesis including the synthesis of aluminophosphate material by E. M. Flanigen and S.T. Wilson in 1986 and the
introduction of elements other than Si and Al into the zeolite framework such as the synthesis of tita
nosilicate (TS-1) [3].

The synthesis of zeolite as a subject has been reviewed in several books and the literature [1, 3, 43-49] but in general hydrothermal, solvothermal and recently ionothermal are the basis of most of the work on the preparation of synthetic zeolites [3, 50]. Solvothermal is one of the new techniques used in the preparation of microporous compounds such as aluminophosphate. The technique utilizes organic solvents such as alcohol and amine to act as reaction medium rather than water during the zeolite synthesis. It primarily plays the role of dissolution of the reactants forming the solvent-reactant complex and this influences the reaction product based on other conditions of the interaction. The organic molecule can sometime act as a template directing the synthesis of a particular structure. This method was first used by D. M. Bibby to prepare sodalite in ethylene glycol medium. As in all synthesis process, solvothermal synthesis depends on the physical and chemical characteristics of the initial starting materials, the regularity of synthetic reactions and conditions and the relationship between the structure of the solvent and the desired products. The conditions of the reactions such as the initial starting gel compositions, crystallization temperature and time along with the polarity of the solvent significantly affect the types of zeolite formed. Example of solvent recently used to prepared zeolites include tetraethylene glycol and cyclopentylamine for the synthesis of aluminophosphates [3]. Ionothermal synthesis is another novel technique used to prepare zeolites and other porous materials such as metal organic framework (MOF). It uses ionic liquid or eutectic liquid to act as a solvent and template during zeolite crystallization. Ionic liquids are described as organic solvent with high polarity and pre-organised structure. The properties of ionic liquid include high solvating characteristic, near absence of vapour pressure and high thermal stability. Eutectic liquids are composed of two or more compounds with lower melting point than its constituent. It shares similar properties with ionic liquid but are less expensive. The reaction during ionothermal synthesis take place in ionic environment essentially different from hydrothermal synthesis and the mechanism is crystallization from solution. Because some ionic liquid used are hygroscopic in nature, water is not completely absent in the synthesis and are said to act as mineraliser aiding dissolution. Fluoride is also sometimes added to perform the same function. As an example, new structure such as SIZ-I and SIZ-6 have been synthesised using ionic liquid called 1-ethyl-3-methylimidazolium bromide [51].
The use of solvents other than water to synthesise zeolite has continued to gained interest, however the present work on the synthesis of zeolites and zeolite membranes from Ahoko Nigerian kaolin (ANK) will be restricted to hydrothermal synthesis.

Hydrothermal syntheses are broadly divided into sub-critical reactions in which the reaction temperature is mild within 100 to 240°C and super critical reactions whereby the reaction temperature can reach up to 1000°C, however most zeolite syntheses are performed at mild temperature and autogenous pressure [3]. The hydrothermal synthesis of zeolite can be divided into two broad steps [52].

- The initial formation of aluminosilicate gel
- The crystallization process of the gel

A schematic representation of formation process of zeolites is shown in figure 2.9.

Figure 2.9: Schematic of zeolite formation processes
A reaction scheme can also be presented for zeolite crystallization from the system of Na$_2$O-Al$_2$O$_3$-SiO$_2$-H$_2$O showing the gel preparation and crystallization:

\[
\text{NaOH (aq) + NaAl(OH)$_4$ (aq) + Na}_2\text{SiO}_3 (aq) \xrightarrow{T_1 \approx 25^\circ C} \left[ \text{Na}_a(\text{AlO}_2)_b(\text{SiO}_2)_c \cdot \text{NaOH} \cdot \text{H}_2\text{O} \right] \text{gel}
\]

\[
T_2 \approx 25 \text{ to } 175^\circ C
\]

\[
\text{Na}_x[(\text{AlO}_2)_x(\text{SiO}_2)_y].m\text{H}_2\text{O} + \text{solution}
\]

**Zeolite Crystals**

The gel is formed from copolymerization or condensation-polymerization mechanism. The crystallization process of zeolite formation usually takes place in an autoclave as shown in figure 2.10 for the type used in this work. Other types of autoclave and reactor system are also used to prepare zeolites. A typical procedure for hydrothermal synthesis of zeolites includes [53, 54], mixing of source materials usually in a strongly basic environment and stirring to form a homogenous gel. Ageing of the resulting gel under certain conditions is carried out before crystallization in a sealed autoclave at a specified temperature for a certain time. The recovery of the zeolite is usually done by washing and drying.

---

Figure 2.10: The Teflon-lined stainless steel autoclave used in this work
2.7.1 Zeolite Synthesis Starting Components

The basic reactants used in the synthesis include [1, 3, 18, 21, 29]:

- silicon source
- aluminium source
- metal ion
- base
- mineraliser
- water

The silica along with alumina function to provide the primary building unit(s) of the framework with the alumina further creating the framework residual charge. The alkali cation is the counter ion which neutralizes the residual charge in the framework and also acts as a guest molecule generating the ion exchanging characteristic. The OH is the mineraliser and provides the necessary environment or media suitable for nucleation and crystal growth and finally water acts as a solvent and also guest molecule.

Other material termed structural directing agent (SDA) or templates are used to enhance crystallization of specific or targeted zeolites. These are divided into two main groups namely:

- organic template
- inorganic template

Templating is defined as a process in zeolite synthesis during gelation or nucleation in which organic/inorganic molecules organises the oxide tetrahedra into a particular geometric topology around itself and provide the initial building bloc for a particular structure [55].

Template or SDA is important component of zeolite crystallization that influence the type of structure formed at the end of the synthesis. Inorganic templates (cation) have always been part of zeolite crystallization process, however the introduction of organic template
has widened the number of zeolite structures that have been prepared. Templates are generally selected based on some important criteria such as:

- the solubility of the solution,
- stability under synthesis conditions,
- steric compatibility
- possible framework stabilization
- ease of removal of the templates without destroying the zeolite framework

The template whether organic and inorganic basically perform four functions [52].

- Influence the gelation and/or nucleation process
- Lower the chemical potential of the lattice formed
- Improvement of the stability
- Control of the formation of a particular topology through its size and shape

Templates used in zeolite synthesis include cations such as Li\(^+\), Na\(^+\), K\(^+\), Ca\(^{2+}\) and Ba\(^{2+}\) and they are mainly used to template structures such as LTA, FAU, LTL, and CHA. Organic templates are also used to direct specific zeolite structure especially high silica zeolite. Examples include the use of tetrapropyl ammonium for the synthesis of ZSM-5, ZSM-8, ZSM-11 and neopentyltrimethylammonium to synthesize Losod.

The choice of specific crystallization conditions determine the exact nature of product formed [3, 45]. Different zeolite products are formed depending on the type of crystallization conditions utilized [56, 57]. The sequence of events leading to zeolite synthesis can be described as a crystallization of gel mixture comprising silica and alumina source combined with water in the presence of high pH [21]. The choice of parameters and other thermodynamic factors such as temperature, pressure; time etc have considerable influence on the nature of zeolitic product formed.

There are a number of materials which are used as silicon and aluminium sources including water glass (Na\(_2\)O.xSiO\(_2\)), sodium silicate, Ludox AS-40, colloidal sol, sodium aluminate, aluminium hydroxide, however clay usage as a combined source of silicon and aluminium
offers a more cost effective means of zeolite synthesis and this is the central point of the present research. Some of the basic materials used in the preparation of zeolite are presented below:

**Cation**

- Alkali metal hydroxide
- Alkaline earth hydroxide and oxides
- Other oxides and hydroxide
- Salts (fluorides, halide, carbonate, phosphates, sulphate etc)
- Organic bases and ammonium hydroxide especially quaternary bases
- Mixture of two or more of the above

**Aluminium**

- Metal aluminate
- Al(OH)$_3$, Al$_2$O$_3$, AlO.OH
- Al alkoxides
- Al salt
- Glasses
- Sediment
- Mineral especially clay mineral felspathoids, feldspar, and other zeolite

**Silicon**

- Silicates and silicate hydrate
- Water glass
- Silica sol
• Silica gels
• Silica and other synthetic glasses
• Minerals, including clay minerals, felspathoids, feldspars and other zeolite
• Basalts and mineral mixtures, sediments

2.7.2 Crystallization of Zeolites

The crystallization step is the most important process in zeolite synthesis and it involves a condensation reaction taking place between polysilicate and aluminate in a strongly basic solution. Furthermore crystallization of zeolites is a complicated processes but can be divided into two major steps. These are nucleation and crystal growth of zeolites.

Nucleation is the most important stage in zeolite crystallization. It involves the formation of aggregation of unstable nuclei from the supersaturated solution prepared from the initial precursor and with time become large enough to form stable nuclei from where crystal growth takes place. Nucleation can either be homogenous or heterogeneous in nature depending on the whether it occurs spontaneously or induced by the presence of impurities.

Nucleation and crystal growth are promoted by several parameters such the extent of time of incubation and the history of the system. Again the size of the crystal can be controlled based on the choice of conditions of the crystallization.

The understanding of the mechanism of zeolite formation will help in the rational design of zeolite of specific structure and properties. The actual mechanism of zeolite formation throughout the entire process of crystallization is still subject of much speculation with three routes currently accepted for zeolite formation. These are:

• Solid hydrogel transformation: This mechanism of zeolite formation suggests that zeolite synthesis take place as result of direct transformation of the solid gel phase used in zeolitization. In this mechanism it is understood that liquid component of the aluminosilicate gel take no part in the reaction toward zeolite formation. The mechanism originally proposed by Breck and Flanigen when they noticed that the resultant zeolite phase and the hydrogel always have the same composition during zeolite synthesis. It was later explained that zeolite crystallization take place via structural rearrangement of the framework of the solid aluminosilicate hydrogel
under hydrothermal conditions. The process has now been succinctly described. Following the mixing of the source materials, the aluminosilicate gel are formed by condensation reaction followed by depolymerization and then structural arrangement under the action OH$^-$(acting as catalysts). Example of the mechanism is the direct synthesis of ZSM-5 and ZSM-35 reported by Xu [3].

- **Solution mediated transport mechanism:** this mechanism is almost a direct opposite of the solid hydrogel system because the concept of the mechanism is that nucleation and crystal growth take place in solution. The solution mediated system take place via four major step:
  - Nucleation take place in solution or at the interface
  - Silicate and aluminate consumption also take place in solution
  - Actual crystal growth is facilitated by the solution
  - There is a continuous dissolution of the gel throughout the crystallization process leading to increase zeolite growth

An equilibrium is formed between the component of the aluminosilicates gel following mixing of the source material. Increase in the temperature of the mixture lead to shift in equilibrium between the solid gel and the liquid phase causing an increase in the concentration of polysilicate and aluminate. This thereby formed the required zeolite nuclei and followed by crystal growth. Continuous dissolution of the gel happens because of consumption of the polysilicate and aluminate ion in the liquid phase.

- **Dual-phase transition mechanism:** This mechanism was proposed as a compromised between the two mechanisms earlier discussed. It was later believed with more advanced detection technique that zeolite formation can proceed utilizing the two mechanisms. This strongly depends on the condition such as the source material. ZSM-5 is also a typical example of zeolite that followed both solid gel formation and liquid phase mechanism based on the nature of silicon sourced used.

The absence of in-situ tools that can be used to monitor the crystallization route of zeolite synthesis especially the state of the polysilicate and aluminate ions in solution, the structure of hydrogel, the nucleation process of zeolites and the role of SDAs is mainly
responsible for divergent opinions on the exact mechanism that control zeolite synthesis. The three mechanism discussed have all it merits but, it is more likely that solution mediated mechanism predominate during zeolite crystallization because nucleation is most likely to happen in solution than in solid phase, in addition, the composition of the liquid at the initiation of reaction usually changed at the end of the crystallization.

The conditions of reactions mixture during zeolite synthesis is a major factor that determine the type of zeolite formed eventually. There are already general conditions which have been highlighted as common to all synthesis. The composition of the starting is the most important and they are usually given or known from experience and the nature of starting material (reactive or not) such as freshly co-precipitated gels, or amorphous solid. Other conditions include the presence of relatively high pH introduced in the form of an alkali metal hydroxide or other strong base and high degree of super-saturation of the component of the gel leading to the nucleation of a large number of crystals [3, 21, 58]. There are several other factor influencing zeolite crystallization:

- Aging conditions/time
- Crystallization temperature
- Crystallization time
- Reaction container
- Seeding
- Structural directing agent (SDA)

The effect of each of these factors are covered in literature [5, 33, 49] however, for the purpose of the present research, the effect of temperature, time and ageing of synthesis gel are studied.

**Heating Temperature**

Temperature has a considerable effect on the synthesis of a particular zeolite. In addition temperature also acts as the generator of the autogenous pressure that can have an impact on the crystallization and structure of zeolite. The change in temperature can affect the polymeric state of silicate, the dissolution, and the transformation of the gel [3, 59]. Increase in the temperature of crystallization beyond the mild temperature of around 90-
110°C normally used to synthesis most commercial zeolites leads to co-crystallization of different zeolite phases. For example, study by Xu et al [3] showed that zeolite X and Y can be crystallized from synthetic system Na$_2$O-SiO$_2$-Al$_2$O$_3$-H$_2$O when the crystallization temperature is within 100 to 150°C, however increase in temperature to range of 200 to 300°C will cause the co-crystallization of zeolite sodalite and mordenite.

Temperature is an important control parameter in zeolite crystallization processes. Sources of heating in zeolite synthesis presently come from two areas. These are conventional oven and microwave heating [60-62]. While ovens have been used over a long time as a source of heating in zeolite preparation, the use of microwave heating was introduced to hasten or shorten the crystallization time. What is however important in the use of microwave as a source of heating is the quality of the starting aluminosilicate gel. The aluminosilicate gel are aged prior to microwave treatment thereby promoting strong nucleation, reduction of induction and short crystallization process when in the microwave. Several zeolites have been synthesised by microwave heating with the zeolite crystallization completed within minutes compared to conventional heating that can take several hours or days.

Increase in temperature influences basic properties of zeolites such as the phase, change in induction period and increase in the crystallization rate. The control of crystallization temperature during hydrothermal reaction is important because of the metastability of zeolite phase. Increase in temperature can generally lead to increased dissolution of both the silicates and aluminate species and this can cause a shift leading to the formation of the most stable phase of the targeted zeolite obeying the Ostwald’s rule of successive transformation [63].

**Ageing time**

Ageing is defined as the gap in time between the formation of aluminosilicate gel and crystallization [3, 43, 58]. Ageing increases the number of nuclei presents in the synthesis mixture and can lead to growth of more crystals. During the ageing process, the aluminosilicate gel is expected to be chemically and structurally reorganised increasing the supersaturation level necessary for zeolite nucleation [33]. The work of Julide et al [64] conclusively shows that ageing of zeolite synthesis gel causes an increase in the degree of crystallization when the right conditions of experiment are chosen. According to their paper, ageing of aluminosilicate gel at room temperature causes an increase in the silica to alumina ratio as it promotes the incorporation of more silica into the framework even at
low level of alkalinity. This assertion was also confirmed by Ginter and co-workers [43] who posited that prolonged ageing leads to insertion of additional silica into aluminosilicate solid and this increased the number of smaller nuclei reacting giving better and higher yield of zeolite NaY.

**Crystallization Time**

Crystallization time is also an important parameter that controls the type of final zeolite product obtained. The key objective during the synthesis of zeolite is to use the minimum time to prepare the desired zeolite material. Therefore optimization of crystallization time depends absolutely on the choice of other parameters such as crystallization temperature, concentration of mineraliser and seeding. In most cases, increase in such parameters will ultimately reduce the induction time and indeed the crystallization time.

Dyer [21], stated the two ways the effect of time play a part in the formation of zeolite from reacting species or gels

- An induction period during which the reaction mixture is held near ambient temperature prior to raising the crystallization temperature often optimizes zeolite yield (as in X and Y synthesis).
- Different zeolites crystallize from one reaction mixture at different times. This second time element is because all zeolite are metastable species whereby the initial zeolite formed is an open structure which with time are transformed into more dense or closed structure following Ostwald’s law of successive transformation. An example is the conversion of Philipsite (an open structure) to clinoptilolite (a less open structure) and finally to dense and most stable analcime. Similarly mordenite can also transform to analcime.

It is however difficult to isolate single factors to study, therefore to study the synergic effect of the factor, several experiments are required. The choice of factors used in this research is based on experience and economic production of the final material.
CHAPTER THREE: CHARACTERIZATION TECHNIQUES
This chapter describes all the method of analysis used in this study. These methods include X-ray diffraction (analysis of zeolite and kaolin structures), scanning electronic microscopy (Image analysis and Si/Al ratio determination), X-ray fluorescence (determination of chemical composition of kaolin), Transmission electronic microscope (image analysis). Other techniques used include nitrogen adsorption (surface area and pore size analysis), Mercury Porosimetry (porosity and particle size analysis), Gas chromatography (separation of chemical species and quantification), and Photon correlation spectroscopy (measurement of particle size of colloids). The basic theoretical principles and the working operation of each of the techniques are described. The descriptions of how each of the techniques was used in the experiments in this study are also mentioned.

Chapter 3: Characterization Techniques

3.1 X-Ray Diffraction

XRD is an important and definitive characterization tool widely utilized to elucidate the structure of synthesised zeolites and other crystalline samples. It is a test used to confirm the structural characteristics of a synthesised specimen because it gives a unique fingerprint of samples under investigation. XRD is based on the principle of scattering phenomena whereby crystals perform the function of diffraction grating toward an incident X-ray. The atoms in the crystals scatter the X-rays in all directions and in a way unique to specific material.

X-rays are normally produced by the sudden deceleration of fast moving particles. This usually takes place in an X-ray tube where electrons are emitted from the cathode (a glowing tungsten filament) and are accelerated through the vacuum where they strike a metal target anode. Several metallic elements are used as anode in X-ray generation. These include Chromium (Cr), Molybdenum (Mo), Cobalt (Co) and Copper (Cu), however Cu is generally used in powder diffraction. The energy of the produced X-ray by the listed metal target are within the range of 4-21KeV corresponding to wavelength of 3.1-0.59Å. A large amount of heat usually accompanies X-ray generation hence the metal must be durable and conductive so that any excess heat can be dissipated readily.

The diffraction of X-rays in crystals was discovered in 1912 at the University of Munich by Max Theodor Felix Von Laue. In his work, he showed that X-rays are an electromagnetic radiation of small wavelength similar in dimension to those of the bond
distance in crystals which can act as a diffraction grating for incoming X-rays. This work earned him a Nobel Prize for Physics in 1914.

The diffraction of X-ray was further simplified by W. L. Bragg in 1912 when his work on irradiation of cleaved mica crystals with X-ray beam revealed that crystals behave in a similar way as mirror whereby the angle of incidence is always equal to angle diffraction. He concluded that crystal obeys the same law of specular reflection as visible light.

Bragg used certain principles to derive an equation which is the basis of most structural analysis by XRD today. Atoms to be probed are taken to be lattice points on lattice planes and are modelled as a mirror and this allows the use of law of specular reflection. The interference criterion is that the travelling wave must be constructive and be in phase because destructive interference will result in no reflection.

Consider the interaction of X-ray with lattice plane as shown in figure 3.1.

![Figure 3.1: Reflection from a lattice plane](image)

The figure shows that ray 2 travels a longer distance than ray 1. The difference in path between the two rays is given as \(AB + BC\) and is dependent on the lattice spacing or \(d_{hkl}\), where hkl are the Miller indices for the plane under consideration. The path difference must also be equal to the order of the reflection of the wavelength to have a constructive interference.

\[
AB + BC = n\lambda \quad n = 1,2,3 \ldots \tag{3-1}
\]
Where \( n \) is the order of reflection. Analysis of the right angle triangle ABC show that

\[
\sin \theta = \frac{AB}{d}, \quad AB = d\sin \theta \tag{3-2}
\]

This is similar to BC and the above equation become

\[
d\sin \theta + d\sin \theta = n\lambda \tag{3-3}
\]

\[
2d\sin \theta = n\lambda \tag{3-4}
\]

This is called Bragg’s law. Where \( n \) is generally taken as unity, \( d \) is the interplanar spacing of the atoms, \( \lambda \) is the wavelength of the incident X-ray. Crystalline materials contain infinite number of lattice planes and of different Miller indices, and hence various d-spacing can be calculated from the modification of the Bragg equation for any crystal system. The various d-spacing values are used to generate diffraction maximum at any particular angle \( \theta \) and the position of the line are a function of the lattice parameters, the miller indices and the X-ray wavelength. Therefore studying the diffraction of X-ray is used to generate information about the structural properties of any crystalline material.

X-ray powder diffraction is used to analyse bulk samples and follows Bragg’s law. A powder or polycrystalline materials are samples that contain large number of small crystallites. An X-ray beam striking a powdered sample or specimen will be diffracted in all directions as governed by Bragg’s law, this diffraction results in each lattice gap producing a cone of diffraction as shown in figure 3.2.
It is important to state that each of the cones is made up of closed spaced dots, which is a diffraction point of a single crystallite within the polycrystalline materials. Powder x-ray diffraction therefore relies on the ideal of determining the diffraction angle $2\theta$ of the many diffraction cones present in powdered sample. The powder diffractometer utilize a scintillation detectors or Geiger Muller tube [65] to determine and measure the position of the diffracted beams. The beam is scanned over the sample in a circular path cutting the diffraction cone at the diffraction maxima, figure 3.3.
The sample behaves like a mirror and can be focussed on the detector based on the geometry of the instrumentation. Random distribution of all the possible hkl planes for powder sample entails that only crystallites having reflecting planes parallel to the specimen surface will contribute to the reflected intensities. The intensities of the reflection is a function of the distribution of the electron in the unit cell. The highest electron densities are obtained around the atoms. The intensity therefore depend on the nature of atoms and the location of the atoms in the unit cell. Planes going through areas with high electron density will reflect strongly while planes with low electron density will give weak intensities. Each set of lattice planes, hkl, will scatter incident radiation to satisfy the Bragg equation and a detector is employed to measure the intensity of the scattered X-ray as a function of angle and the intensity of the reflected rays. All peaks in the X-diffraction pattern must be assigned their hkl values. The d-spacing when known is used to estimate the unit cell size from the equation below.

\[
a = \sqrt{d^2(h^2 + k^2 + l^2)}
\]  
(3-5)

where \(a\) is called the lattice parameter, \(d\) is the spacing of the planes and hkl is the Miller indices.

The position of diffraction peaks and their intensities are used for the identification of unknown structure by comparing with standard of the same material. The various atoms present in a unit cell have specific scattering factors proportional to the atomic number of that atom. Since structure factor is a derivative of the total scattering of the entire electron present in the atom. The summation of the scattering factor is called the structure factor \(F_{hkl}\). When the structure factor is squared, it is proportional to the intensity of the hkl reflection. A detailed mathematical treatment of this process is in the literature[67].

Powder x-ray diffraction is the main characterization tool used in identifying zeolites during synthesis and modification stages. With powder XRD, the long range atomic structure of a zeolite can be resolved. This structure is usually the framework topology and pinpoints the position of the extra framework cation. Each zeolite type and other crystalline materials have a distinct XRD pattern and each pattern can provide important structural information such as crystal size, strain or stress in the sample or material, degree of crystallinity, extent of heteroatom substitution. Much of the zeolite identification involves comparing the XRD pattern of the synthesised sample with those of standard sample usually provided by International Zeolite Association (IZA).
As a summary, X-ray diffraction gives valuable information about identification of crystal structure, unit cell parameters, degree of crystallinity and the crystallite size.

Equipment and experimental conditions

All the analysis herein i.e. the zeolite powder, zeolite membrane, kaolin and metakaolin samples were carried out using the XRD machine model X’pert Pro by Philips. The beam was focused using a 1/8” and 1/4” divergence slit. Since most zeolites features are found within the diffraction angle of $2\theta = 50^\circ$, all the measurements were carried out within the range of 3 to $50^\circ$. The scan step used was 65.1352s while the scan step size was 0.0170° ($2\theta$) and the generator setting was fixed at 30 mA and 40 kV. Refined Ahoko Nigerian kaolin (ANK) sample was dehydroxylated using temperature programmed XRD. Heating furnace was added to the XRD apparatus and the temperature was programme from 30°C to 900°C before the refined kaolin sample was added using the standard sample holder. When analysing zeolite films and membranes, the zeolite films and membranes samples were mounted into the standard sample holder and were held in position using blue-tac to ensure that the discs are in a horizontal position and at the same level with the sample holder.

3.2 X-Ray Fluorescence (XRF)[68]

Since it was first commercialised, X-ray fluorescence (XRF) has continued to be used in the analysis of chemical composition of mainly solid samples. XRF is a non-destructive technique which is used for rapid multi-element analysis. It allows the simultaneous determination of several elements in solid or liquid state with high sensitivities. The accuracy of the technique compares favourably with other methods of chemical analysis. It is an efficient and effective method of analysis for both major and trace elements in many materials such as ceramics, metal and rock.

The fundamental approach of XRF is based on the fact that when electrons are ejected from inner shell of an atom, there is immediate replacement of the electron by a higher shell electron filling the hole in the lower shell. This result in the emission of X-ray photon which is equal to the difference in energy between the two shells.
The excitation radiation must have energy that is more than the binding energy of the particular shell or sub-shell from which the electron is to be removed. For example, the incident photon (hv) energy should be greater than the binding energy of the k-shell and is called k absorption edge for $k_\alpha$ and $k_\beta$ X-ray emission. Any vacancy created is filled by the outer shell electron thereby giving out photon or fluorescence radiation. This photon is a characteristic of a particular element according to Moseley’s law [68]. The law states that each element is associated with a characteristic X-ray spectrum and wavelength will changes in the same way from one element to another.

Generally XRF is composed of three main components namely the X-ray source, the crystal spectrometer and the detection system as shown in figure 3.5. The X-rays are obtained using either a radioactive source or X-ray tube as an exciter. Radioactive sources can either be of primary or secondary type. The primary source are made up of $^{55}$Fe, $^{100}$Cd while the secondary source include Cu, Se, Y, and Mo. The primary X-ray are usually directed at secondary exciter target which is Tin. An X-ray is generated and is focused or aimed at the unknown sample causing emission of characteristic X-ray of that unknown sample. The energy spectrum is used to identify the element while the intensity is used to quantify the concentration of the element in the sample.

The X-ray source produces a high energy (short wavelength) ray which causes a fluorescent ray to be emitted from the specimen as earlier explained. This fluorescence travels through a set of collimators and is focused on to a set of crystal plane which are oriented to reflect one X-ray wavelength at a given angle based on Bragg’s law: $n\lambda = 20\sin\theta$ where $n$ is a positive integer representing the order of reflection. The intensity of various wavelengths is recorded by the detector by rotating the analysing crystals. Synchrotron radiation has also been utilized to replace the primary X-ray tube.
The analysing crystal is made up of material of good quality that will give sharp and intensive XRF peaks with small d-spacing. Some of the materials used as analysing crystals include LIF, pyrolysed graphite and multilayer Ni/C.

The detector are usually a scintillation counter with a thin Be window and a gas flow proportional counter with short and long wavelength.

Specifically XRF can be operated in two different modes namely wavelength dispersive X-ray (WD) and energy dispersive X-ray (ED) mode.

The WDS utilize the reflection of X-rays off crystals at a characteristic angle to detect X-ray of specific wavelength while the EDS is based on the principle of specific energy separation which are displayed as histogram.

The excitation in WDXRF is performed using X-ray tube and the process of detection and measurement of the intensity is similar to that of XRD. The characteristic X-ray of each element has definitive wave length and adjustment of the crystal at a specific angle will diffract the wavelength of specific X-ray with diffraction obeying the Bragg’s equation.

The energy or intensity of the X-ray emerging is obtained using the formula

\[ E(\text{Kev}) = \frac{12.396}{\lambda} \, (\text{Å}) \]  \hspace{1cm} (3-6)

The WDXRF consist of an X-ray tube, an analysing crystal and a detector as shown in figure 3.5. The diffracted beam passes through a receiving slit and into a scintillator or gas flow proportion detector. The X-rays are absorbed by the gas molecule and photoelectrons are ejected. This signal is handled by the electronics and an output is generated giving intensity versus 2-theta. The collimation functions to limit angle that is allowed to strike the diffraction device.
The EDXRF is made up of an X-rays source, sample and the detector. Other device such as filter, secondary target and collimator are used to improve the intensity of the source spectrum, hence higher energy X-ray on transmitted in EDXRF than WDXRF. The secondary target is used in EDXRF to obtain monochromatic peak with lower background.

The detector used in EDXRF is called a single semi conductor and it helps to arrange directly the X-ray based on their energy. The WDXRF is believed to be more energy efficient than EDXRF because of less diffraction loss. The element are identified by the wavelength of the emitted X-ray while the concentration of such element us quantified by the intensity of such X-ray.

The X-ray emerging from the sample is usually detected with the aid of solid state detector which is cooled to liquid nitrogen temperature. Pulses (signal) are converted into pulse height using analog to digital converter.

**Equipment and experimental conditions**

The XRF was used to analyse the composition of the raw Ahoko Nigerian kaolin (ANK), refined ANK, and the dealuminated metakaolin. The equipment used was a WDXRF model AXIOS, manufactured by PANalytical. Samples were pelletized to 6 mm masks, using wax as a binder with a powder to wax ratio of 11 g to 3 g.
3.3 Scanning Electron Microscope (SEM)\(^{[69]}\)

Scanning electron microscopy (SEM) is a basic technique used to study the microstructural characteristics of solid materials including kaolin, zeolites and zeolite membranes. The use of SEM to image materials is primarily due to its high resolution, with values in the order of 25 to 50 Å. In addition, a three-dimensional image can be obtained using SEM, because of a greater depth of field provided by SEM than transmission electron microscope (TEM). This means that more information about the specimen can be deduced. The construction of SEM was said to have been started by Von Ardenne in 1938. He actually added scan coil to a TEM to produce what was then called scanning transmission microscope (STEM). STEM possess electrostatic condenser lenses (usually two) along with scan coil and CRT, however the CRT was not used to photograph the image.

The first real SEM was constructed in 1942 by Zworykin and it was used to examined a thick specimen of samples. They fundamentally recognised the use of secondary electron emission to control topography contrast. Zworykin and co-workers made several improvements in the working of SEM. The spot size, gun brightness and signal to noise ratio were all improved using different methods. For example they used a field emitter source to increase the gun brightness.

The next generation of improvement to the SEM was initiated by E.W. Oatley working at the University of Cambridge in 1948. He was able to design an SEM with high resolution reaching 50 nm. In 1956 K.C.A. Smith improved the SEM by using signal processing to increase resolution using non linear signal amplification. He was the one that replaced electrostatic lenses with electromagnetic lenses and also introduced double deflection scanning to improve the scanning system. The detector on the SEM system was also not left out in the transformation taking place. In 1960 Everhart and Thornley modified the detector originally used by Zworykin by attaching a scintillator to the face of the photomultiplier. The quality of signal was increased by this modification and better signal to noise ratio and voltage contrast was observed for the first time.

Other notable changes and modification occurred in 1963 when Pease used three magnetic lenses and a Everhart Thornley detector system to drive a new system called SEM V which was later produced in large quantities and was readily received in the market. There was also the development of a Lanthium hexaboride electron gun. This allows
more electron current to be concentrated into a smaller beam spot thereby improving the resolution. The 1970s saw the development of the energy dispersive x-ray detector as an addition to the SEM. This system allows the simultaneous analysis of compositional information along with the topographic and crystallographic information from the system.

The configuration of a typical SEM is shown in figure 3.6.

![Figure 3.6: A schematic diagram of a scanning electron microscope](image)

The SEM is made up of an electron gun situated on the top of the column which generates an electron with energy level in the region of 0.1-30 eV. Because of the large size of electron beam, electromagnetic lenses and apertures are used to focus and direct the electron beam to form a focused electron spot on the samples. The size of the electron sources is demagnified from 50 µm to a spot size of around 100 nm. A high vacuum is usually provided to aid electron transport without interference or scattering by air. An electron beam scanning coil and signal detection system are also needed for the image processing of the sample surface.

The operating principle of the components of SEM is rather complex, a description of the major component and their function is given. The electron gun is the platform that is used to provide a stable source of electrons which form the electron beam. Electrons used in the gun are obtained through a process called thermionic emission. The electron gun is
expected to provide a stable electron beam with good qualities such as high current, small spot size, and variable energy. There are different types of electron guns currently in use in SEM. These include tungsten “hairflux” or Lanthanum hexaboride cathode. However modern SEMs tend to use a field emission source because they provide higher current and lower energy dispersion.

Tungsten electron guns are made up of three main parts, namely a V-shaped hairpin tungsten filament (the cathode), a Wehnelt cylinder and an anode. The tungsten filament is heated to a temperature of 1527°C. Applying a current to the filament allows escape of electrons from the tip of the filament. A potential difference set up by the application of 0.1-30kV voltage causes acceleration of the electron toward the anode. An alternative to the tungsten filament is called lanthanum hexaboride which has lower work function and hence can provide a stronger electron emission at the same heating temperature as tungsten filament. The emitter is composed of a LaB$_6$ single crystal of 100-200 µm diameter and 0.55 in length. The crystal sits on graphite support and serves as a resistor heater to increase the temperature, causing emission of electrons. LaB$_6$ electron gun is known to provide higher SEM image resolution. Field emission gun (FEG) is gradually being used to replaced the high temperature dependent emission gun as earlier described. The FEG, a strong electric field is applied between the anode and cathode. The electron source in FEG is a single crystal tungsten wire with a sharp tip obtained by electrolyte etching. There are two types of FEG; namely thermal field emission and cold field.

Electron lenses are mainly used to demagnify the image of the emission sources in order to produce a narrow and focused beam of electrons on the surface of the sample under examination. The electron lenses are controlled by a magnetic field which consist of a series of electron-magnets. There are two types of electron lenses used in SEM. These are condenser which is used to converge the electron beam while objective lenses are used to focus the electron beam into the probe point on the specimen surface, also further offering demagnification. More detail about the operation of electron lenses can also be found in the relevant literature [70].

SEM works under the principle of interaction between the specimen and the electron beam producing a signal which can be used to produce images. The SEM uses a well focused beam of electrons to scan the surface of samples producing large numbers of signals in the process. The electron signals are processed into a visual signal and that is what is displayed
on a cathode ray tube (CRT). There are basically two types of interaction between the electron beam and the samples. These are called elastic and inelastic interaction as shown in fig.3.7. In elastic interaction, there is negligible amount of energy loss during collision between the incident electron and the atomic nucleus of the outer shell electron of the sample, hence elastic interaction is characterized by the wide direction angle change of the scattered electron, often resulting in a backscattered electron (BSE), where it is scattered through an angle greater than 90°. The scattered electron (BSE) is useful in imaging sample. Inelastic interaction results in a large quantum or substantial amount of energy being transferred to the atom of the samples resulting in significant loss of energy. This interaction leads to the generation of a secondary electron (SE) which possesses energy of around 50 eV. This is the most important signal used to form images. There are number of other signals formed during inelastic interaction which include emission of characteristic x-ray, Auger electron and cathodoluminescence.

![Figure 3.7: Interaction of incident with sample](image)

In this study, only the secondary electron and the characteristic x-ray are relevant and will be briefly described.

Secondary electrons are the most important and widely used signal from the interaction of the incident electron and the specimen. There are actually loosely held or bound electrons
which are emitted when an incident beam strike the surface of the sample. They have low energy, in the region of 3-5 eV and easily escape within a few nanometres of material surfaces hence secondary electron emission accurately shows the topographic information of observed material with high resolution.

The Everhart-Thorley detector is the standard collector of secondary electrons. A scintillator is used to convert the energy of the electron into a photon (visible light) which is collected in a photomultiplier tube (PMT). The quantum energy of the photon is converted back into electron by the PMT, the output voltage is amplified and output on the screen of the SEM is shown with brightness modulation. Secondary electrons are mainly used for the visualization of surface texture and roughness of samples.

The characteristic X-ray is mainly used to provide chemical composition of a specimen in the SEM. Characteristic X-ray are generated as a result of collision between the inner shell electron and the primary electron. The displacement of the inner shell electron will cause an outer shell electron to fall to fill the inner shell in order to maintain proper charge in the orbital. As a result of the reversion to the ground state, there is generation of X-ray photon, otherwise known as characteristic X-ray because each element has it own specific and unique X-ray peak which is used to estimate the composition of such material.

One of the limitations of the conventional SEM is the requirement for a high vacuum sample environment. In SEM, samples have to be conductive, dry and clean, however the environmental scanning electron microscopy (ESEM) was developed to solve this limitation of SEM. ESEM permits the examination of samples through range of variable conditions which include varying pressure, temperature and gas composition. Significantly ESEM removes the high vacuum limitation of a conventional SEM. The ESEM processes images using secondary electrons in a gaseous environment of known composition at a pressure and temperature of up to 50 Torr and 1500°C respectively. Like SEM, the Everhart-Thornley detector cannot function in a gaseous environment and a number of improvements have taken place on the type of detection system in ESEM. The most recent is the use of gaseous secondary electron (GSED) to collect the electron. This type of detector can discriminate against 'parasitic' electron signals emission.
**Equipment and Experimental Conditions**

The analysis of both the raw kaolin, refined kaolin, zeolite samples synthesized from ANK and zeolite membrane/films fabricated on stainless steel support were carried out using an FEI Quanta 200 environmental SEM. For kaolin and zeolites samples, coating was carried out with gold to make sure all the samples were conductive at low vacuum, while zeolite membrane/films were analysed without any gold coating at high vacuum. The chemical composition of most of the samples were also analysed by an EDAX attached to the ESEM. In some cases also, the particle size of both the zeolite powder sample and the depositing zeolite crystals on the support were measured along with the thickness of the films using the soft imaging software also attached with the ESEM system.

**3.4 Transmission Electron Microscope (TEM)**<sup>71, 72</sup>

TEM is ranked as the best tool used in the characterization of materials over a wide spatial range from atomic scale upwards. TEM is another type of microscopy technique which is capable of operating in image and diffraction modes<sup>[73]</sup>. The principle of operation is very similar to SEM and has been described in several literature sources<sup>[73, 74]</sup>. The major difference being that TEM involves the transmission of electrons through a thin specimen and images are subsequently formed by using appropriate lenses while SEM utilized the effect of reflection of electrons to produced secondary and backscattered electrons and are then use to image bulk samples.

Understanding the operation of TEM is fundamentally dependent on clear meaning of type of electron involved in the imaging process in TEM and indeed other microscope. Nothing can be seen in TEM except where there is interaction between the electron and the specimen. Electrons are generally known to interact with specimen in two basic ways namely elastic and inelastic interaction. When the electron is scattered with no loss of energy, it is called elastic scattering, this type of interactions are responsible for the creation of contrast in TEM image and create the intensity in diffraction pattern. The more practical interaction in TEM is called inelastic scattering. Such interactions generate important signals which are used for the secondary analysis of the sample. Some of the signal which has also been mentioned in our discussion of SEM (cf. section 3.3) includes characteristic X-ray, secondary electron and catholuminscense.
TEM involves the production of well focused electron beam which is focused to a very thin sample usually less than 20 nm. It consists of an electron gun and a series of electromagnetic lenses and are located within a column.

The column is usually evacuated during operation to create the required vacuum environment. The electron beams is produced from the gun and are accelerated by a high voltage and get focused onto the sample just like SEM.

In TEM, the focused beam is used as a probe and this probe is focused to a small spot often less than 1 µm in diameter. The electron gun serves as a probe source and can emit small wavelength allowing the penetration of the sample by the electron.

Electron penetration can also be enhanced by using high voltage TEM because high-energy electrons interact less strongly with matter than low energy electrons. TEM utilizes two modes for specimen observation namely diffraction and image mode. The diffraction mode is equivalent to the XRD pattern while image mode produces an image of the illuminated area.

TEM has a very high magnification power which is close to $10^6$ and this is because of very small wavelength in the incident electron. It produces a very high lateral resolution as a result of the well focused electron beam [73]. TEM can give the following information about materials: crystal structure, crystal quality, grain size and crystal orientation.

However TEM has its own drawbacks and these include depth of resolution which is low and image perfection usually two-dimension from three dimension object. Other problems of TEM is the difficulty in sample preparation which is critical and of course the cost which is high [73].

**Equipment and Experimental Conditions**

In this study, TEM images were taken first to help in the identification of the raw and refined Ahoko Nigerian kaolin (ANK). All the samples used for TEM analysis were initially ground with a pestle and mortar. Grinding to get thin sample was necessary in TEM because it gives a better resolution. Thereafter an acetone mixture of small quantity of the sample was added to a copper grid (SPI supplies, UK) leaving the acetone to evaporate before inserting in the TEM machine.
3.6 Nitrogen Adsorption \[^{75,76}\]

The total surface area of zeolite and other porous materials is an important parameter that determines its applicability because it helps to determine the accessibility of the active site to probing molecules. The pore architecture, i.e. the pore size, pore distribution and pore volume, is responsible for the control of transport phenomena and selectivity especially for catalysed reactions and membrane applications.

The determination of surface area and pore size distribution of zeolite and kaolin sample are now mainly carried out using $\text{N}_2$ adsorption, which is generally understood to refer to the enrichment of one or more of a component between two bulk phases (the interfacial layer). In this case one of the phases must be solid and the other phase fluid (either gas or liquid). The solid phase is generally referred to as the adsorbent while the fluid phase is called the adsorbate. Nitrogen is a preferred adsorbive material because of the presence of permanent quadrupole moment and this is responsible for formation of well defined monolayer on most surface in addition, liquid nitrogen is commercially and abundantly available. The relationship between the adsorbed and the equilibrium pressure or concentration at constant temperature is called the adsorption isotherm. There are basically two type of adsorption. These are physical adsorption (physisorption) and chemical adsorption (chemisorption). Physisorption is a type of adsorption which is physical in nature and mainly controlled by Van Der Waal forces. Chemisorption involves formation of an actual bond (ionic or covalent) between the adsorbent and sorbate. In ionic chemisorption, molecules are restricted to the reactive area of the material surface, limiting adsorption to a monolayer. Physisorption processes are more robust and can involve multilayer formation, which attain equilibrium rapidly.

Physisorption is used mainly to determine the surface area and pore architecture of zeolite, kaolin and other porous materials. The adsorption characteristics of all zeolites are an important parameter for the optimization of its application. The main isotherm resulting from physical adsorption are grouped into six classes according to IUPAC classification and are shown in Figure 3.8. The shape of the isotherm is agreed to be the characteristic of the micropore filling of the adsorption.
Figure 3.8: The six adsorption isotherm [75]

The type I isotherm is a concave to the relative pressure (p/p°) rising sharply from low pressure and reaching a plateau as the limiting value of the relative pressure tends toward 1. This is known to cause strong absorbent-adsorbate interaction in the micropore of molecular dimension. The level of micropore filling taking place results in an increased adsorption and decreased relative pressure when there is a reduction in the width of micropore. There is a short range of relative pressure required to attain a plateau and this is an indication of small external area.

The type II isotherm is another concave to the relative pressure axis just like the type I isotherm. It then takes the form of linear shape before forming convex in relation to the relative pressure. The isotherm demonstrates that the layer thickness reduces steadily with increase in the relative pressure. The condition necessary for the formation of type II isotherm has been clearly spelt out and it is expected to lead to completely covered monolayer and the starting of multilayer. These conditions happen when the equilibrium pressure is equal to the saturation vapour pressure resulting in a bulky liquid or solid. This type of isotherm usually occurs when non-porous or macroporous adsorbent is used. The absence of adsorption hysteresis resulting in a completely reversibility of the desorption-adsorption isotherm is an important condition in this type of isotherm.
Among the rare isotherm is the type III isotherm. It is usually convex over the entire range of the relative pressure axis. It is known to be an indicative of weak adsorbent-adsorbate interaction. The type IV isotherm can be likened to the type II isotherm and exhibit a hysteresis loop. The loop is made up of upper branch representation increasing addition of the adsorbent and progressive withdrawal. The hysteresis described the filling and removal of the mesopore by capillary condensation. Each system has different hysteresis loop shape and it is responsible for the filling of the micropores.

The type V isotherm just like IV initially convex to the relative pressure and level off with increase in pressure. This is a sign of weak adsorbate-adsorbent interaction. It exhibit hysteresis loop which was explained to be responsible for the processes of pore filling and removal. They are scarce and rarely take place in adsorption.

The type VI is a rare isotherm. It is stepped isotherm and is caused by layer by layer adsorption in a uniform surface.

Brunauer-Emmett-Teller (BET) has emerged as the main method used in determining surface area of most porous materials. The BET technique introduces assumptions that extend the Langmuir mechanism to multilayer adsorption. The BET model is based on the concept of the adsorbed molecule in one layer acting as adsorption site for other molecules in the upper layers at pressure below the saturation vapour pressure.

The evaluation of surface area using BET method basically involves two steps namely:

- Construction of BET plot used to derive the monolayer capacity
- The calculation of specific surface area

The BET equation has been described mathematically in a linear form as:

\[
\frac{p}{p_0} \frac{1}{n_m} \left( \frac{p}{p_0} \right) = \frac{1}{n_mC} + \frac{C-1}{n_mC} \left( \frac{p}{p_0} \right) \quad (3-5)
\]

When C is a BET constant

\( n_m \) is the monolayer capacity

\( p/p_0 \) is the relative pressure (pressure/ saturation pressure)
n is the specific surface excess amount

Hence the BET plot is a straight line plot of

\[
\frac{p}{p_0} \frac{n(1-\frac{p}{p_0})}{n_m C} \text{ vs } \frac{p}{p_0}
\]

and it gives a gradient of

\[
S = \frac{(C-1)}{n_mC}
\]

and intercept of

\[
\frac{1}{n_mC}
\]

The monolayer capacity \(n_m\) can be calculated from the following relation

\[
n_m = \frac{1}{\text{slope} + \text{intercept}}
\]

and \(C\) is obtained from

\[
C = \frac{\text{slope}}{\text{intercept}} + 1
\]

The specific surface area \(a_{(BET)}\) is then obtained from the BET monolayer capacity using the equation.

\[
a_{(BET)} = n_m La
\]

Where:

\(L\) is the Avogadro constant

\(a\) is the average area occupied by each molecule in the completed monolayer. The average area is usually calculated based on the density of liquid adsorptive in the bulk liquid state

\[
a = f(M/\rho L)^{2/3}
\]

Where \(f\) is a packing factor which has a definite value, \(\rho\) is the absolute density of the liquid adsorptive at the operating temperature, \(M\) is the molar mass of the adsorbate.

Some of the standard values \((f)\) of some adsorbate used include \(N_2 0.162(-196^\circ C), O_2 0.141(-196^\circ C), Ar 0.138(-196^\circ C), CO_2 0.163(-78^\circ C)\).


**Equipment and experimental conditions**

The BET surface area and pore diameter of the raw and refined ANK sample along with surface area of some of the synthesised zeolites samples were carried out using nitrogen adsorption. The nitrogen adsorption data were collected using Micromeritics ASAP2010 nitrogen gas analyser. The samples (about 0.05 g) in all cases were initially conditioned by outgassing overnight to remove any sign of moisture or other gases which can influence the isotherm. After the conditioning, the samples are weighed again to obtain accurate weight of the sample. The sample kept in a glass tube was then exposed to nitrogen at a temperature of 77 K at different incremental pressure. The quantity of gas adsorbed and the amount of adsorbed gas molecule is automatically recorded by the machine and are retrieved by the computing system.

**3.7 Mercury Porosimetry**

Mercury porosimetry is also important tool used in the investigation of the internal structure of many solid materials. It can basically serve as a complimentary technique to other methods such as N\textsubscript{2} adsorption and helium pycnometer used in porous material characterization. In addition to the use of nitrogen adsorption to obtain the surface area, and the pore size of the samples used in this work, mercury porosimetry was employed to give a clearer picture of the particle size and percent porosity during the refining process of the raw ANK. This is to elucidate the extent of the separation of the finer kaolin sample particle from the mainly coarse quartz impurities. The principle of mercury porosimetry will only be briefly described.

The mercury porosimetry technique is developed from the non-wetting characteristic of mercury when in contact with a host of solid materials. Therefore under the influence of adequate pressure mercury penetrates through the open pores of solid materials and the pore radius is inversely proportional to the forcing pressure following Washburn equation [76]

\[ P r = -2\gamma \cos \theta \]  

(3.12)

Where

\( r \) represent the radius of the pore site of mercury intrusion
γ is the surface tension of mercury

θ is called the angular contact between the mercury and the solid sample on a surface.

The technique uses mercury intrusion to obtain the pore size and particle size distribution in powder and solid materials. Other information that can be assessed includes apparent density, bulk density, and pore volume. By means of controlled pressure, mercury is forced into the pores of the sample while the volume of the entering mercury is obtained accurately by the system. The size of the pore corresponding to the given pressure is calculated from the Washburn equation given earlier.

**Equipment and experimental conditions**

In this work, the porosity, pore and particle size distribution of raw ANK and the refined component was determined from Thermo Pascal 140 mercury porosimetry under a pressure range of 0.1-200 MPa. Mercury surface tension of 480 Dyne/cm and contact angle of 141.3° were used. A blank was prepared using a normal dilatometer and the actual analysis were carried on the same dilatometer after outgassing and filling of the dilatometer with mercury.

**3.9 Photon Correlation Spectroscopy**

The small size of colloidal zeolite seeds produced for secondary growth synthesis of zeolite membrane make it difficult to measure by direct microscopic methods, hence the properties of interaction between light and particle present in a liquid media was used to measure the particle size of the colloidal zeolite seed produced. The method of measuring particle size of material present in a colloidal state with aid of their interaction between the particle and light is called Photon correlation spectroscopy (PCS) or dynamic light scattering (DLC). Faraday was the first to observe light scattering in solutions. When trying to produce ultra-thin films, Faraday prepared colloidal gold and reported that this solution would scatter a narrow beam of light passed through it [77].

The characterisation of colloidal phases with the aid of photon correlation spectroscopy is dependent on the measurement of Brownian motion and this is related to the particle size of the colloid. Brownian motion is a well known process and is described as a random movement of particles in a medium as a result of bombardment of the particle by solvent
surrounding the particle. Basic parameters which control Brownian motion such as the velocity of the solvent, diffusion coefficient, viscosity and temperature are used effectively to interpret the particle size of the matter.

The interaction of light with matter is used to characterize the property of the material. There are three different classes of light scattering and each is a function of parameters such as the intensity, particle diameter and the wavelength of the laser. The different scattering of light by matter include, Rayleigh, Debye and Mie scattering. Rayleigh scattering are applicable to particle involving small particle size acting on point source of scattered while both Debye and Mie scattering have particle that are large and has refractive index different from the dispersion medium.

The Rayleigh approximation show that for small particle the intensity of the scattered light is given as

\[ I \propto d^6 \]  
\[ (3-12) \]

and

\[ I = \frac{1}{\gamma^4} \]  
\[ (3-13) \]

Where:

I = intensity of light scattered  
\( d \) = particle diameter  
\( \gamma \) = Laser wavelength

The particle size as shown in the equation indicates that the intensity of light scattered is a direct function of the wavelength of the light source. The second relation show there is inverse relationship between the intensity of the light and the wavelength i.e. reduce wavelength will lead to higher scattering intensity.

Small particle indicate uniform scattering on light in all direction, hence there is no change in intensity. The particle size is obtained from a relation developed by Stoke-Einstein as:
\[ d(H) = \frac{kT}{3\pi \mu D} \] (3-14)

Where:
- \( d(H) \) = hydrodynamic diameter
- \( D \) = diffusion coefficient
- \( K \) = Boltzman’s constant
- \( T \) = absolute temperature
- \( \mu \) = viscosity of the fluid

It should be stressed that the diameter of the particle in the fluid is the value obtained for particle that undergo the same translation movement as the particle has diffusion coefficient.

Rayleigh determined that when the size of suspended particles is well under the induced wavelength, the intensity of the scattered light would be the same in all directions. As the particles grow, the intensity of the scattering would become more dependent on the angle of incidence, as stated later by Debye, Mie and Einstein, among others [78]. In practice, the diffusion coefficient is obtained from the calculation of the particles position at a given time. A value for the hydrodynamic radius can then be obtained by applying the Stoke-Einstein equation for diffusion coefficient [79].
Figure 3.9: Schematic diagram of PCS set up [80]

The set up of the PCS is shown in figure 3.9. The apparatus is made up of a light source which is monochromatic and coherent He-Ne laser with a fixed wavelength. The light emerging is converged on the sample with the aid of focusing lenses. The scattered light is detected with aid of photomultiplier. Any fluctuation in the intensity of the scattered light are converted into an electric pulse and are then compared with a correlate. The data obtained from the autocorrelation is passed onto the computer for data analysis. The correlator is the signal comparator and is designed to measure the degree of similarity between the two signal or one signal with itself at a varying time interval.

**Equipment and experimental conditions**

The apparatus by Malvern instruments (Zeta-sizer 1000 HS) was used for the analysis of the particle sizes of colloidal zeolite seed used for zeolite membrane preparation by secondary growth method (SGM) strategy. The samples were put into 3 mL polystyrene cuvettes with a light path of 10 mm for the analysis.
3.10 Gas Chromatography\textsuperscript{[81, 82]}

The history of gas chromatography (GC) has been traced to the pioneering work of Martin and James (1952) on partition chromatography. Gas chromatography is a separation process in which component of a sample are partition between two phases namely stationary and gas phases. The sample is introduced, heated, and carried by the gas phase through a column containing the stationary phase. The sample partition takes place based on the difference in the solubility of the analyte at the given temperature.

The general principle of GC is based on the affinity between the analyte and the stationary phase i.e the more the analyte is retained in the column, the longer it will take to be detected or eluted. GC operation is based on the introduction of the sample as a vapour onto the chromatography column. While in the column, the component solubility in the gas phase is dependent on it vapour pressure, column temperature and the affinity between the compound and the stationary phase. There is a partition of the molecules in between the gas phase and the stationary phase as a result of the different vapour pressure. The process of the partition continued until the molecules are pushed toward the detector by the gas phase. As a result of the difference in the vapour pressure, different compounds in the sample arrive at different times. A schematic diagram of GC is shown in figure 3.10.

![Schematic diagram of typical GC set up](image.png)
The GC is also made up of flow controller, injector, column and detector and of course a data system.

The mobile phase in GC is the phase that possesses the component molecule during the separation process. There is the constant interchange of the sample between the stationary phase as the molecule are always pushed toward the detector by the flow of the carrier gas, hence the flow rate of the carrier gas contribute to the determination of the retention time of any analyte. Carrier gas must be of high purity and most impurities such as oxygen are removed by passing the gas over an adsorbent.

The column is an important component of the GC. It is responsible for the separation of analyte before detection, identification and quantification. There are two type of column used in GC namely packed and capillary column. Capillary column is now preferred over packed column because of higher performance as result of better property such as the length. The stationary phase used in the column includes solid adsorbent, polymer compound and liquid phase. Nowadays, the stationary phase is bonded to the inner wall of the column giving a better performance. Example of capillary column include wall coated open tubular column (WCOT), porous layer open tubular column (PLOT), and support coated open tubular column (SCOT). The column oven is used to maintain the chromatography column at a preset temperature during the analysis. It is operated either isothermal or non isothermal mode.

The detector in GC is used to respond and give an output of the sample component as they elute from the chromatography column. The detector in a GC is expected to possess certain basic properties such as stability, linear dynamic range, selectivity, sensitivity, and response time.

There are several different types of detector used in GC. Examples include flame ionization detector (FID), electron capture detector (ECD) and thermal conductivity detector (TCD). The properties and basic operational requirement of the three main detector system in GC are well known, however it is important to stress that FID is the best and most common used detector because of it high sensitivity to most organic compound, insensitivity to impurities in the carrier gas, stability toward change in temperature or pressure and wide linear dynamic range.
In a typical GC analysis, the sample is injected into the separation column made up of the stationary phase and the flowing carrier gas usually via an auto sampler. The sample is vaporised in the injector and mixed with the carrier gas and flow through the column. At the end of the column, the mobile phase passes through the detector and is combusted and consequently an electric signal is generated and amplified. The voltage is recorded and is obtained as a chromatogram of the sample. The signals obtained are directly proportional to the concentration of the species in the carrier phase.

**Equipment and experimental conditions**

Agilent model GC machine was used for the offline analysis of sample obtained from pervaporation of water/ethanol mixture. The type of column used was Poraplot while the detector used was flame ionisation detector. The carrier gas was helium. The GC instrument is equipped with an autosampler which operate in cycle to automate the injection and as well enhance reproducibility. For both analysis carried out, standard solution were injected in to the column to obtain a calibration curve (Appendix E). The peak area of the sample analysed were then used to determine the concentration of ethanol.

Table 3.1: GC operating conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column type</td>
<td>Agilent-HP-5MS</td>
</tr>
<tr>
<td>Detector type</td>
<td>FID04</td>
</tr>
<tr>
<td>Column oven temperature initial</td>
<td>35°C</td>
</tr>
<tr>
<td>Column oven temperature final temperature</td>
<td>210°C</td>
</tr>
<tr>
<td>Injector temperature</td>
<td>275°C</td>
</tr>
<tr>
<td>Detector temperature</td>
<td>250°C</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Helium</td>
</tr>
<tr>
<td>Carrier gas flow rate</td>
<td>1ml/min</td>
</tr>
<tr>
<td>Column length</td>
<td>30m</td>
</tr>
<tr>
<td>Split ratio</td>
<td>25:1</td>
</tr>
<tr>
<td>Wash liquid</td>
<td>Water</td>
</tr>
<tr>
<td>Number of injection for each sample</td>
<td>3</td>
</tr>
</tbody>
</table>
CHAPTER FOUR

ZEOLITES SYNTHESIS FROM AHOKO NIGERIAN KAOLIN
Chapter 4: Zeolites Synthesis from Ahoko Nigerian Kaolin

4.1 Introduction

Zeolites are the most important member of the microporous material family because of their unique properties and applications in ion exchange, catalysis, adsorption and separation processes as earlier stated in chapter one. Hence studies on the preparation of this important materials from several raw materials have being reported[1, 84]. The use of natural materials for the production of zeolites has economic advantage over conventional commercial chemicals [85]. Synthetic zeolites are usually prepared from different sources of silica and alumina that are expensive leading to high cost of zeolites in the market. This problem therefore can be addressed by using less expensive raw material and minimizing the energy requirement of the entire zeolite production processes.

Kaolin clay has continued to be investigated as a potential precursor to zeolite synthesis [86-88] and has acted as good material for the synthesis of several types of zeolites and other microporous materials. Natural kaolin with Si/Al of ~1 can only yield sodalite and cancrinites (non zeolitic material) when reacted with aqueous bases, but requires temperature modification, which increases the kaolin reactivity through a process known as dehydroxylation or metakaolinization, to form low silica zeolites [1, 5, 89]. For the formation of high silica zeolite such as zeolite Y and ZSM-5, modification of the chemical composition of the parent kaolin must be performed through dealumination or addition of external silica to make up the required Si/Al of the starting zeolite aluminosilicate gel.

Kaolin is the parent group name of kaolinite mineral and it consists of dioctahedral 1:1 layer structures with composition of \( \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \). Other members of the group include Dickite and Nacrite. Kaolin minerals have varied structural make up from one deposit to another. These variations affect the ordering of the kaolinite structure and their subsequent chemical reactivity [10]. Kaolin chemical composition can vary from one deposit to another or from location to another location in term of molar Si/Al ratio and the
concentration of impurities making the studies on Ahoko Nigerian Kaolin (ANK) important.

The use of kaolin and other low cost materials to prepare zeolites especially zeolite A, FAU and ZSM-5 is primarily due to the desire to produce zeolites that are less expensive than currently. Kaolin is a well placed material and is regarded as the next generation material because it is more abundant and environmental friendly than precursors used in zeolite production, hence their application in the synthesis of zeolites has continued to receive tremendous research interest.

4.2 Kaolin

Kaolinite is the primary clay mineral material present in the kaolinite mineral group [90]. The name kaolin has its origin from Chinese word called ‘Kao-Ling’ meaning ‘High hill’[10]. More importantly kaolin is viewed industrially as a term that means clays which is composed mainly of minerals called kaolinite and are amenable to property variation making them useful in the production of series of industrial products [91].

Impurities such as quartz, feldspar, and iron are usually found with clay minerals but because they do not exhibit plasticity, they are called non clay or accessory minerals [10]. This associated mineral requires removal or reduction because it generally reduces the commercial value of the clay mineral hence purification is very important before usage. Kaolinite is a layered structure with a general chemical composition of \( \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \) [92]. It can be viewed as a continuous two dimensional structure containing a silica tetrahedral sheet with central cation usually octahedral alumina which is linked to four shared oxygen atoms as shown in figure 4.1.
Figure 4.1: The layered structure of kaolinite [93]

The position of Si, Al and O in the kaolinite structure is well documented but the location of the OH is in some doubt, however the bonding system of OH in the interlayer has been explained by Benco et al [94]. Four different OH groups were identified and two are part of weak bond formation and the remainder do not participate in H-bonding.

The surface of clay mineral generally can be thought to be hydrophobic however in kaolinite, the presence of hydroxyl group and defect sites at the surface introduce hydrophilicity. The defects present can easily be detected with the aid of an XRD. The patterns of ordered kaolin are sharp and narrow in their peaks while disordered show broad and asymmetries peaks [10]. However two tests are normally performed to identify the degree of order in a kaolin sample namely Hinckley index range and Weiss index [10].

Kaolin obtained naturally is usually fractionated to enrich the kaolinite content and reduce other unwanted clay mineral before application in manufacturing materials such as zeolites [95-97]. The most common and simplest method of enriching the kaolin content of raw kaolin sample is fractionation by sedimentation[10]. The refining process of kaolin is clearly divided into two groups namely removal of foreign material by chemical method and refinement by sedimentation to remove larger impurities especially quartz which is trapped within the mineral aggregates.

However addition of chemicals in the treatment process can impair the properties of the parent material, therefore, the use of chemical treatment should be a last resort [95].
Even though there are several other methods such as selective flocculation, flotation, delamination, ultrasonic treatment that can be used to process raw kaolin, fractionation by sedimentation is the most common procedure used for kaolin processing to obtain highly pure kaolin at laboratory level [67, 95]. Sedimentation is based on the principle that a particle with different mass and density will settle at different terminal velocity in a given viscous media [98].

Stokes’ law enables the separation based on the clay particle size which is assumed to have a spherical shape [10]. The law is based on the relationship between the Stokes’ frictional force $3\pi\eta vd$ acting on dispersed particles at constant velocity $v$, and the difference between the gravitational force $mg = \rho Vg$ and the buoyancy force $\rho_o Vg$ and given in equation below

$$\rho Vg - \rho_o Vg = 3\pi\eta vd$$

$$V(\rho - \rho_o)g = 3\pi\eta vd$$  \hspace{1cm} (4-1)

Here

$V$ is the particle volume $= \frac{\pi d^3}{6}$ \hspace{1cm} (4-2)

$\rho$ is the density of the particle

$\rho_o$ is the density of the solvent

$g$ is the gravitational acceleration $= 9.81 \text{ m/s}^2$

$\eta$ is the viscosity of solvent

$d$ is particle diameter

$v$ is settling velocity

The settling velocity can also be expressed as a function of distance travelled by particle and time i.e

$$v = \frac{h}{t}$$  \hspace{1cm} (4-3)
By substituting equation (2) and (3) in to (1), the time $t$ required by a particle to settle in a given distance $h$ can be obtained as

$$\frac{18\eta h}{(\rho - \rho_o)d^2g}$$

(4-4)

Atterberg software [99] is usually used to estimate time of settling of free falling particle given the necessary parameters. This was used in this study to calculate the estimated settling time of quartz as will be shown in the experimental section (cf.4.6).

The largest usage of kaolin is in the paper industry where it is utilized as a filler and coating agent. Other uses of kaolin include:

- Additive in the production of paint
- Processing into catalyst by activation
- Production of ceramics, sanitary ware, electrical porcelain etc

There is growing interest in the use of kaolin as a combined source of silica and alumina [3] for zeolite synthesis. The use of different kaolin deposits around the globe to synthesise zeolites has gained ground however there has not been any major work on the use of Nigerian kaolin deposits to synthesise zeolites.

Nigeria is blessed with 3 billion metric ton of good kaolin clays among which Ahoko clay are a part. Presently there are two kaolin processing plants in Nigeria. One in Kankara, Katsina state and the second one is called Crystal kaolin factory in Plateau state. Both plants were commissioned in 1998, however their uses are mainly in the paper industry. Ahoko kaolin which is being used for this study is located in Kogi state and was recently discovered. The location of Ahoko kaolin deposit is shown in figure 4.2.
Ahoko clay deposit is situated between Abuja federal capital and Lokoja, the state capital of Kogi state. The mine area covers over 39 hectares of land.

### 4.3 Metakaolinization of Kaolin

Kaolin in its natural state is less reactive and forms hydrosodalite when reacted with sodium hydroxide [60]. In the synthesis of zeolites, kaolin needs to be made reactive through a process called metakaolinization or dehydroxylation before zeolitization can take place. The process of metakaolinization involves the loss of hydrogen and framework oxygen [1]. This process is usually performed by a method of calcination of kaolin to form metakaolin between the temperatures of 550°C to 900°C. Metakaolinization directly
involves the loss of hydroxyl group and this is followed by rearrangement of the octahedral layer to tetrahedral orientation in the calcined clay [101, 102]. Kaolin is an aluminosilicate and the $\text{Al}^{3+}$ ion can be in the form of IV and VI coordination state and it is essential in zeolite formation that $\text{Al}^{3+}$ is in IV coordination, hence metakaolin with IV Al coordination and amorphous in nature is a necessary path toward zeolite synthesis from kaolin[7, 102, 103].

The transition of kaolin when heated in a furnace circulating with air has been well reported[1, 104, 105] and found to have a number of technological uses. This reaction series includes the formation of highly disordered metakaolin formed at around 550-900°C when kaolin is air calcined as shown below:

$$2\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \xrightarrow{550-900^\circ\text{C}} 2\text{Al}_2\text{Si}_2\text{O}_7 + 4\text{H}_2\text{O}$$

Metakaolin

On further heating, a new phase is obtained at around 925°C called spinel, a defected alumina-silica structure

$$2\text{Al}_2\text{Si}_2\text{O}_7 \xrightarrow{925-950^\circ\text{C}} \text{Si}_3\text{Al}_4\text{O}_{12} + \text{SiO}_2$$

Spinel

A more stable material called mullite and cristobalite are formed at a temperature of 1050°C

$$3\text{Si}_3\text{Al}_4\text{O}_{12} \xrightarrow{1050^\circ\text{C}} 2\text{Si}_2\text{Al}_6\text{O}_{13} + 5\text{SiO}_2$$

Mullite Cristobalite

The present research will be limited to the formation of metakaolin.

There is some disagreement as to the nature and the exact temperature of formation of metakaolin [102]. The present study does not intend to solve the many contradictions in the literature regarding the different metakaolinization temperature and time of exposure of kaolin to heating, rather this research intends to develop a new rapid but effective, and
energy saving technique of dehydroxylation of kaolin as will be presented in section 4.6.3 and 4.7.2.

Several workers [7, 9, 106-109], all seem to agree on the use of 900-950°C as the temperature to perform metakaolinization in the synthesis of different zeolite, however the time of exposure of kaolin at 900°C varies. This conflict of information requires further investigation to find the required time of exposure and temperature of metakaolinization. Chandrasekhar and co-workers [8] have studied the effect of calcination temperature on zeolite synthesis. They stated that increase in temperature of metakaolinization beyond 700°C can ultimately lead to higher yield of zeolite NaX, this was in contrast to other work on the effect of temperature of calcination on the zeolite products from kaolin by Murat et al [110]. They concluded in their paper that the temperature has effect on the chemical reactivity of metakaolin only if the natural kaolin is of low crystallinity and contains high percentage of iron.

A different school of thought has successfully synthesised zeolite using different temperature of metakaolinization and time of exposure. Most of these workers [85-87, 102] have all reported metakaolinization temperatures of 600-650°C for different exposure times between 30 min to 18 h.

The summary of different opinion on the temperature of metakaolinization and exposure time used to produced metakaolin is shown table 4.1. While it is absolutely necessary to resolve this seeming wide disparity in the metakaolinization temperature, it is also important to develop a process that can operate at reduced temperature and time thereby saving energy and cost. The ultimate aim is to get a material of maximum reactivity.
Table 4.1: Different metakaolinization temperature and exposure time of metakaolin used to synthesise zeolite as reported in the literature

<table>
<thead>
<tr>
<th>Metakaolinization Temperature</th>
<th>Exposure Time</th>
<th>Zeolite</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>900°C</td>
<td>30 minute</td>
<td>Zeolite X and A</td>
<td>[111]</td>
</tr>
<tr>
<td>1003K and 1273K</td>
<td>2 h</td>
<td>Zeolite in microsphere</td>
<td>[112]</td>
</tr>
<tr>
<td>900°C</td>
<td>1 h</td>
<td>Zeolite 4A</td>
<td>[113]</td>
</tr>
<tr>
<td>900°C and 1000°C</td>
<td>NA</td>
<td>Faujasite</td>
<td>[9]</td>
</tr>
<tr>
<td>700°C</td>
<td>5 h</td>
<td>Zeolite X</td>
<td>[114]</td>
</tr>
<tr>
<td>950°C</td>
<td>NA</td>
<td>Zeolite NAY</td>
<td>[115]</td>
</tr>
<tr>
<td>670°C</td>
<td>6 h</td>
<td>Faujasite</td>
<td>[116]</td>
</tr>
<tr>
<td>700°C</td>
<td>2 h</td>
<td>Zeolite A</td>
<td>[60]</td>
</tr>
<tr>
<td>900°C</td>
<td>30 min</td>
<td>Zeolite 13X</td>
<td>[109]</td>
</tr>
<tr>
<td>800°C</td>
<td>1 h</td>
<td>Zeolite N-A</td>
<td>[86]</td>
</tr>
<tr>
<td>800°C</td>
<td>3 h</td>
<td>Zeolite 4A</td>
<td>[117]</td>
</tr>
<tr>
<td>600°C</td>
<td>2 h</td>
<td>Zeolite N-A</td>
<td>[85]</td>
</tr>
<tr>
<td>800°C</td>
<td>3 h</td>
<td>Mordenite</td>
<td>[118]</td>
</tr>
<tr>
<td>950°C</td>
<td>45 min</td>
<td>Zeolite NA</td>
<td>[107]</td>
</tr>
<tr>
<td>900°C</td>
<td>2 h</td>
<td>Zeolite A and X</td>
<td>[119]</td>
</tr>
<tr>
<td>800°C</td>
<td>1 h</td>
<td>Zeolite X</td>
<td>[106]</td>
</tr>
<tr>
<td>900°C</td>
<td>1 h</td>
<td>Zeolite NaX</td>
<td>[8]</td>
</tr>
<tr>
<td>700°C</td>
<td>1 h</td>
<td>Zeolite Na-A</td>
<td>[120]</td>
</tr>
<tr>
<td>700°C</td>
<td>18 h</td>
<td>Zeolite A</td>
<td>[121]</td>
</tr>
<tr>
<td>850°C</td>
<td>1.5 h</td>
<td>Zeolite 4A</td>
<td>[122]</td>
</tr>
<tr>
<td>600°C</td>
<td>3 h</td>
<td>Zeolite A</td>
<td>[110]</td>
</tr>
</tbody>
</table>

NA: Not available

4.4 Dealumination of Metakaolin

Kaolin is an ideal candidate for the preparation of low silica zeolites especially zeolite A because it shared similar chemical composition. The Si/Al in zeolite A and kaolin are almost the same (~1).

Usually to prepare medium and high silica zeolite such as faujasite (Zeolite X and Y) and ZSM-5 or mordenite, additional silica is needed to augment the Si/Al ratio of kaolin in the starting gel of such high silica zeolite. Another process route that can be used is called dealumination. This process takes place when there is a reaction of kaolin or metakaolin with mineral acid such as HCl, H$_2$SO$_4$ and HNO$_3$. Such reaction cause a preferential
dissolution of the Al-containing octahedral site in relation to the silica tetrahedra releasing alumina in the kaolin [123] as shown in reaction sequence shown below [124].

\[6\text{HCl} + \text{Al}_2\text{O}_3 \rightarrow 2\text{AlCl}_3 + 3\text{H}_2\text{O}\]

\[6\text{HNO}_3 + \text{Al}_2\text{O}_3 \rightarrow 2\text{Al(NO}_3\text{)}_3 + 3\text{H}_2\text{O}\]

\[3\text{H}_2\text{SO}_4 + \text{Al}_2\text{O}_3 \rightarrow \text{Al}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O}\]

The process also promotes the formation of high BET surface area and pore volume material with some introduction of microporosity increasing their application in catalysis, adsorption, energy storage, drug delivery, gas sensing, biomedical applications and electrochemistry [125, 126] as distinct material or when converted into zeolitic form. Despite its obvious advantage over metakaolin mainly because of the improved properties, only the work of Colina et al [106, 127] on the synthesis of zeolite X from dealuminated kaolin are cited in the literature.

4.5 Kaolin as a Precursor to Zeolites

The synthesis of crystalline aluminosilicate zeolites can be carried out from clay minerals especially kaolinite, halloysite [128], illite-smectite [129], montmorillonite [130] and bentonite [131] and other low cost material as have been explained in section 4.1. In the use of kaolin as a precursor to zeolite production, previous work has shown that the improvement of the properties of the kaolin by chemical methods which is necessary for zeolite formation is difficult due to its low reactivity [5]. Kaolin cannot be significantly affected by acid or alkaline treatments, even under high concentration. Therefore, kaolin is usually processed into zeolite after calcination at temperatures between 550-950°C [132] to obtain a more reactive phase (metakaolin) with the loss of structural water and reorganization of the structure. Only a small part of octahedral is maintained, while the rest are transformed into much more reactive tetra- and penta-co-ordinated units [133]. The temperature regime of kaolin calcination strongly influences the reactivity of the obtained solids, however calcination of the kaolin at higher temperatures usually leads to the formation of mullite and cristobalite [132].

Several authors have reported the production of different zeolites from different kaolin deposit around the world using specific synthesis conditions.
Some of the reported work and the results obtained are presented in table 4.2.
Table 4.2: Some of the most important reported study on the synthesis of zeolites from kaolin

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Location of kaolin deposit</th>
<th>Method of synthesis</th>
<th>Highlight of studies</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A, X and Y</td>
<td>USA and Ventas Tecnicas from Mexico City</td>
<td>Hydrothermal synthesis</td>
<td>Metakaolinization temperature, Alkalinity, induction time</td>
<td>The major highlight of the study is that kaolin can be used to supply silica and alumina necessary for zeolite formation, however not all the silica and alumina component of kaolin are used during zeolite production. According to their explanation, crystallization of zeolites from kaolin is a series of rearrangements and transformations of the tetrahedral silica ($\text{Si}^{4+}$) and octahedral aluminium ($\text{Al}^{3+}$) from the original precursor. The balance in the electrical charge is provided by the substitution of the positive ion in the framework hole.</td>
</tr>
<tr>
<td>NaX</td>
<td>Kerala India</td>
<td>Hydrothermal synthesis</td>
<td>Metakaolinization influence of time and alkalinity</td>
<td>Kerala kaolin was found to be an excellent source for zeolite NaX and more importantly, they found that metakaolinization temperature played a very important role on the nature of zeolite formed from a particular kaolinite. Both uncalcined clay and clay calcined at 400$^\circ$C, 500$^\circ$C and 600$^\circ$C produced hydrosodalite when reacted with alkali but hydrothermal treatment above 700$^\circ$C to 900$^\circ$C produced zeolite NaX. The optimum temperature was found to be 900$^\circ$C and pure phase of zeolite NaX was obtained when the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio was 3 with the supplement for the ratio provided by sodium silicate.</td>
</tr>
<tr>
<td>4A</td>
<td>Handong kaolin deposit in Korea</td>
<td>Ultrasonic procedure as a basis for comparison with the conventional hydrothermal method.</td>
<td>Crystallization temperature</td>
<td>Their method involved preparation of the measured amount of metakaolin obtained by calcination of clay along with calculated quantity of sodium hydroxide and distilled water. The mixture which corresponds to the required ratio for zeolite 4A synthesis was put into an ultrasonic bath and was subjected to an irradiation frequency of 47 KHz over a period of time. No zeolite 4A crystallized at a temperature of 60$^\circ$C. When the conventional hydrothermal procedure was used but zeolite 4A with a 70% crystallinity was obtained at 60$^\circ$C using the ultrasonic method. They concluded that ultrasonic irradiation of aluminosilicate mixture lead to a faster rate of crystallization of zeolite 4A.</td>
</tr>
</tbody>
</table>
A. X and Y

Seven kaolin samples from different areas across the world namely Makh'tesh (Israel), Cornwall (England), Georgia (USA), Lave (France), Bogma (Sinai).

Hydrothermal synthesis

degree of crystallinity of the kaolinite and the activity of impurities on the final product

One of the key outcomes of their research is that zeolitization of metakaolin was influenced as a result of the presence of colloidal silica which supplied the excess silica requirement. They concluded that a massive improvement in the synthesis of zeolite X was achieved when the time of synthesis was increased to 72 hours.

4A

Indian clay

Hydrothermal synthesis

The group utilized three samples of kaolin and studied the percentage purity of the zeolite based on the properties of the starting material. Even though, they found that the ion exchange properties of the zeolite synthesised compared well with standard zeolites used in the industry, the presence of impurities especially Fe₂O₃ impeded the crystallinity and purity of the final product.

NaY

Russian kaolin

Hydrothermal synthesis

Crystallization time

Takhtamysheva and co-workers were able to synthesise zeolite Na-Y of 90 to 100% degree of crystallinity using a narrow range of precursor composition given as SiO₂/Al₂O₃ = 6-14:1, Na₂O:SiO₂=0.3-2:2, Na₂O:Al₂O₃ = 3-12:1 and H₂O:Na₂O = 8-140:1.

They also utilized high concentration of seeds which facilitate the formation of the pure phase of zeolite Na-Y, careful manipulation of other synthesis parameters, particularly temperature and time of reaction (which also affect the synthesis product) were employed. They found that time of crystallization was the dominant factor affecting the purity of zeolite Na-Y.
<p>| | | | |</p>
<table>
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</thead>
<tbody>
<tr>
<td>X</td>
<td>NA</td>
<td>Hydrothermal synthesis</td>
<td>Crystallization time</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>The outcome of their work showed that maximum reactivity of the calcined clay was obtained at a temperature between 600 and 950°C from which maximum concentration of 4- and 5-coordinated aluminium was obtained and a minimum concentration of 6-coordinated aluminium was also seen. Increase in temperature beyond this range leads to the formation of mullite and cristobalite. Interestingly XRD studies shows that zeolite X did not appear until around 48h of crystallization and the intensity peaks of the zeolite X grew linearly and stopped after a period of 200h. This gives a clear boundary conditions under which further research on the synthesis of zeolite X and possibly zeolite Y can be restricted.</td>
</tr>
<tr>
<td>Na-A</td>
<td>Chilean kaolin</td>
<td>Hydrothermal synthesis</td>
<td>The SiO$_2$/Al$_2$O$_3$, H$_2$O/Na$_2$O and Na$_2$O/SiO$_2$ ratios, temperature and time of crystallization.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>They found that zeolite Na-A was obtained from Chilean kaolin under the following experimental conditions: SiO$_2$/Al$_2$O$_3$ = 2.5, Na$_2$O/SiO$_2$ = 1.0, H$_2$O/Na$_2$O = 5, reaction time = 15h and temperature of crystallization = 100°C. A combination of XRD, IR, SEM and DTA was used to identify the zeolite phases.</td>
</tr>
<tr>
<td>Y</td>
<td>Indian kaolin</td>
<td>Hydrothermal synthesis</td>
<td>They used the following molar ratio to obtain zeolite Y: SiO$_2$/Al$_2$O$_3$ = 7.5-15, Na$_2$O/SiO$_2$ = 0.5-1, and</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ageing of the precursor played the most important part in the synthesis of zeolite Y according to the work. Reduced ageing time lead to a predominance of zeolite P, which is an impurity. However, as aging time increases, this zeolite phase begins to decrease and pure and a highly crystalline zeolite Y phase was obtained after 10 days. Other factors, such as time of reaction and seeding also affected the synthesis product, especially its crystallinity, although ageing time was the dominant factors that precipitate the formation of pure zeolite Y phase.</td>
</tr>
</tbody>
</table>
Development of zeolites and zeolite membranes from Ahoko Nigerian Kaolin

A.S. Kovo, 2010

<p>| | | | |</p>
<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Indian kaolin</td>
<td>Microwave synthesis</td>
<td>Ageing time</td>
</tr>
<tr>
<td>4A</td>
<td>English and French kaolin</td>
<td>Hydrothermal synthesis</td>
<td></td>
</tr>
<tr>
<td>Zeolite</td>
<td>Source</td>
<td>Synthesis Method</td>
<td>Parameters</td>
</tr>
<tr>
<td>---------</td>
<td>--------</td>
<td>-----------------</td>
<td>------------</td>
</tr>
<tr>
<td>A</td>
<td>Georgian USA kaolin</td>
<td>Hydrothermal and microwave synthesis</td>
<td>Time</td>
</tr>
<tr>
<td>NaX</td>
<td>NA</td>
<td>Hydrothermal synthesis</td>
<td>Crystallization time</td>
</tr>
<tr>
<td>MOR</td>
<td>Brazilian kaolin</td>
<td>Hydrothermal synthesis</td>
<td>Crystallization time</td>
</tr>
<tr>
<td>X</td>
<td>Spanish kaolin</td>
<td>Hydrothermal synthesis using dealumined kaolin</td>
<td>molar ratio, reaction times and temperature</td>
</tr>
</tbody>
</table>
synthesis of zeolite X from kaolin as dealuminated kaolin is more reactive.

A  Venezuelan kaolin  Hydrothermal synthesis  Molar ratio and synthesis time

Their results also showed that beyond 850°C, there was no zeolite formation from the metakaol in that can be explained as due to absence of tetrahedral Al which is responsible for the zeolite formation. There is a clear relationship between the calcination temperature and the metakaolin reactivity as depicted in their work by the Al(4)Al(6) interrelationship during the calcination process. This work, again, did not specify the exact temperature and time of formation of metakaolin rather only values are given. They however confirm the dependence of metakaolin reactivity on the nature of zeolite synthesised.

A  Argentina kaolin  Hydrothermal synthesis

The main focus of this study was to use the impact grinding of kaolin as alternative to the conventional method of kaolin calcinations, which has been reported before. Kaolin samples were subjected to impact grinding using Herzog HSM 100 oscillating mill and time was monitored to study the point of destruction of structure of the kaolin before they were utilised in the synthesis of the zeolite as performed conventionally. Their work shows that grinding result in the gradual loss of crystallinity of the kaolin as the time of grinding increases. However in the study of formation of zeolite, at low grinding time, the predominant product is the sodium hydro-sodalite while the proportion of zeolite A increased with increasing grinding time. They explained the presence of sodium hydro-sodalite at low grinding time on the low concentration of silicate and aluminate required for zeolite polymerization. However with increased grinding, a complete structural break down occurred, resulting in an amorphous and a more reactive material normally used for zeolite synthesis. This is a different approach of developing zeolites from kaolin.
<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Origin</th>
<th>Synthesis Method</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>13X</td>
<td>Spanish kaolin</td>
<td>Hydrothermal synthesis</td>
<td>The use of Spanish kaolin as a substitute in zeolite 13X synthesis as a builder in the production of detergent has also been carried out</td>
</tr>
<tr>
<td>X, LTA, Cornwall, NA-P, J</td>
<td>Cornwall</td>
<td>Hydrothermal synthesis</td>
<td>In the Na$_2$O-Al$_2$O$_3$-SiO$_2$-H$_2$O system, the main crystalline phases obtained at low NaOH concentrations and 100°C were sodalite, cancrinites and zeolite LTA. At high SiO$_2$/Al$_2$O$_3$ ratio solutions (adding precipitated silica), zeolites X and Na-P1 also crystallized. Other authors [109, 140] have also reported the formation of zeolite X from kaolinite usually with additional silica sources. On the other hand, at high NaOH concentrations and 200°C, several zeolites, including sodalite, cancrinites and a nearly pure JBW-type structure are obtained</td>
</tr>
</tbody>
</table>
Summary

The literature as shown in table 4.2 indicates that some low silica and medium silica (Zeolite A and FAU) have been synthesised from kaolin serving as silica and alumina sources. The zeolites were produced using different synthesis conditions and different metakaolinitization temperature and exposure time for the conversion of the kaolin into reactive metaphase. However the conditions of synthesis of zeolite have not being clearly defined unlike for example, synthesis from commercial chemicals which uses well defined synthesis conditions for zeolite production. Therefore it is important to define these conditions necessary for the synthesis of zeolites from Ahoko Nigerian kaolin (ANK) because the formation of zeolite depends on these conditions. There are several other unanswered questions such as exact temperature and exposure time used to produce metakaolin (section 4.3). Furthermore the chemical composition and reactivity is believed to vary from location to location based on the geology, hence ANK which is being used for the first time to produce zeolites will add to the research on zeolite synthesis from kaolin and potentially make it a viable source of zeolites for Nigerian market which hitherto depend on imported zeolites to service her process industries.

4.6 Experimental

The feasibility of Ahoko Nigerian kaolin (ANK) as an alumina and silica source for zeolite synthesis was investigated in this section. The original ANK was characterized using XRD, SEM, TEM, XRF, nitrogen adsorption, and mercury porosimetry. Refinement of the raw ANK was then carried out and followed by metakaolinitization (earlier explained in section 4.4) and finally dealumination was carried out. Zeolite A, Y, and ZSM-5 was synthesised based on the results of metakaolinitization. Zeolite Y and ZSM-5 was also prepared using dealuminated kaolin (no addition of external silica) using the best synthesis conditions obtained from synthesis involving metakaolin and external silica. Characterization of all the synthesised zeolites were carried out using XRD, SEM/EDAX, and some selected samples by nitrogen adsorption.
4.6.1 Collection and Pre-Treatment of Raw ANK

ANK representative samples were taken from Kogi State, Nigeria. Initial analyses of the raw sample were carried out with the aid of XRD, SEM, XRF, N\textsubscript{2} Adsorption. This was done to know the constituent mineral and determine the impurities present. The same tests were carried out on commercial kaolin obtained from WBB UK which served as our reference kaolin. The refinement process for ANK is as shown in figure 4.3.

![Figure 4.3: Flow chart of ANK refining process](image)

4.6.2 Refining of Raw ANK

The XRD and XRF analysis along with the other tests of the natural ANK showed that much of the non-clay fraction was quartz. This requires refining, as quartz and many other non-clay minerals can impede the application of zeolites in catalysis because of their abrasivity.

Size separation based on differences in particle size and density, as typified by Stokes law of settling particles in solution, is adopted for the purification process. Stokes law for free settling particles has already been discussed in the literature (see section 4.2). The solution to the model (also in section 4.2) has been simulated and software called Atterberg or Sedigraph enables the calculation of the settling time of quartz given the density of the quartz and the height of the settling tubes [99].
The procedure for the refining of the raw ANK is described in figure 4

![Tumbler for disaggregation of raw kaolin sample](image1)
![Settling tank](image2)
![Freeze dryer to obtain dried refined kaolin](image3)

Figure 4.4: Experimental step to purify ANK

The experiment involves the disaggregation of the solid rock in a tumbler and was used to obtain a good sample of kaolin slurry using deionised water. Size separation was achieved by allowing free settling of clay suspension in 24 measuring cylinders of 30 cm height used as settling tubes. A clay suspension was created from a mixture of clay (2 cm) and deionised water (28 ml) and the settling time of the heavier component (quartz) was determined from the Atterberg software based on expected particle sizes of 10, 4 and 2 µm as shown in table 4.3. This was based on the density of quartz, temperature of the surrounding environment and the height of the settling tube. At the end of the settling time, the heavier (coarse) component naturally settled and the kaolin sample (lighter fraction) remains as supernatant. The supernatant was decanted into a different measuring cylinder and was allowed to settle for 24 h. A settled clay sample, (the fine fraction, <2 µm) was obtained after decanting the suspended deionised water. This process was repeated in order to obtain enough samples for future experiments. The settled fine clay and the heavier portion were dried using an Edward freezer dryer for 24 h and then characterized by XRD, XRF, SEM, BET and mercury porosimetry. WBB kaolin was sourced from UK and served as standard kaolin for comparison with refined ANK.

1 The particle size of 2, 4 and 10µm, for the settling of quartz was chosen based on personal communication with Dr Paddy Hill, Chemical Engineering, University of Manchester, UK.
4.6.3 Metakaolinization of ANK

The production of metakaolin which will be used in the development of different zeolites was performed using two sequential steps:

- Temperature programme XRD metakaolinization of ANK to confirm the formation of an amorphous material.
- Development of a fast and rapid method of producing the metakaolin.

The second step was carried out as follows using the result of the first steps: A muffle furnace (Nabertherm, Germany) was initially heated to a temperature of 600°C using a heating rate of 10°C/min. Immediately after the furnace attained the temperature of 600°C, a crucible (shallow and depth of 20 mm) containing 5 g of ANK were loaded into the furnace and was removed after 3 min and cooled in air. The process was repeated at different times 4 min, 5 min, 6 min, 7 min, 8 min, 9 min, 10 min, 20 min, 40 min and 50 min. The products obtained were characterized using XRD.
4.6.4. Dealumination of ANK

Dealumination was carried out using the metakaolin produced at 600°C and exposure time of 10 min. 15 g of the metakaolin was mixed with 200 ml of 5M H₂SO₄ (Sigma-Aldrich) in a Pyrex glass beaker acting as a reactor with reflux condenser in a magnetic stirrer/hot plate. The mixture was heated to constant temperature of 80°C under continuous stirring condition. Samples were prepared at different heating time of 2, 3, 4, and 8 h. After the heating, the samples were cooled to room temperature and separation was carried out by centrifugation and washed with distilled water to remove the sulphate ions and confirmed by BaCl₂ test. The test was carried out by adding 0.1 M of BaCl₂ (obtained from Sigma-Aldrich) to the washed samples. Non formation of thick white precipitate indicate the absence of sulphate ion in the dealuminated metakaolin sample. The samples were dried and kept in tightly closed plastic bottle for analysis. The products obtained at each time was analysed by XRD, SEM and XRF.

4.6.5. Synthesis of Zeolitic Materials from ANK

4.6.5.1. Zeolite A

The synthesis was carried out using metakaolin produced at 600°C and at exposure time of 10 min. The effect of ageing, crystallization time and temperature were studied. The aluminosilicate gel used for the synthesis of zeolite A was prepared from reaction mixture with molar composition [137]:

\[
3.75\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 2.5\text{SiO}_2 : 243.7\text{H}_2\text{O}
\]

Sodium hydroxide pellets 99% w/w (Sigma –Aldrich) were used as a source of Na₂O and ANK metakaolin serve as a combined source of alumina and silica.

0.832 g of sodium hydroxide was measured and dissolved in 12 g of deionised water and stirred briefly for 5 min. 0.693 g of ANK metakaolin were then added to the mixture to obtain the synthesis mixture. The aluminosilicate gel was subsequently aged with continuous stirring at room temperature at varying ageing time. Hydrothermal treatment of the aged mixture was performed using a Teflon lined-autoclave in an oven maintained at varying crystallization temperature and time as shown in table 4.4. At the end of the
hydrothermal reaction, the mixture was filtered and washed using deionised water until the pH was below 8. Subsequently the sample was dried in oven at temperature of 60°C for 6 hours. The samples were characterized using XRD and SEM.

Table 4.4: Experimental conditions of zeolite A from ANK

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ageing (h)</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite A</td>
<td>0</td>
<td>100</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>100</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>100</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>100</td>
<td>6</td>
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<td></td>
<td>24</td>
<td>80</td>
<td>6</td>
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<td></td>
<td>24</td>
<td>90</td>
<td>6</td>
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<td>200</td>
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<td>24</td>
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<td>2</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>100</td>
<td>3</td>
</tr>
</tbody>
</table>

Synthesis of zeolite A was attempted using refined ANK without metakaolinization to test the influence of metakaolinization on the synthesis of zeolite from kaolin. The experiment was repeated using crystallization time of 12 h, crystallization temperature of 100°C and ageing time of 6 h following the same procedure as earlier reported.

4.6.5.2 Zeolite Y

In the synthesis of zeolite Y from ANK, three factors were also studied namely ageing time at room temperature, crystallization time and crystallization temperature.

The aluminosilicate gel used to Zeolite Y synthesis was produced based on following the molar ratio [136].

\[
15\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:15\text{SiO}_2:45\text{H}_2\text{O}
\]

Sodium hydroxide pellets (99%w/w) and anhydrous sodium metasilicate (Sigma-Aldrich) which serve as source of additional silica were both supplied by Sigma-Aldrich. ANK Metakaolin served as a combined source of alumina and silica.
36.406 g of deionised water were measured and divided into two equal parts. 0.3602 g of sodium hydroxide pellets were dissolved in the first halve of the precursor, this was followed by dissolving in 1 g of ANK metakaolin. 7.4814 g of anhydrous sodium metasilicate were measured and added to the second halve of the deionised water. Both sets of precursors were subsequently mixed together to form a homogenous aluminosilicate gel. The gel was then aged with continuous stirring at room temperature at varying ageing times. This was followed by crystallization using a Teflon autoclave at different synthesis conditions as shown in table 4.5. At the end of the hydrothermal treatment, the autoclave was removed from the oven and the sample taken out, filtered and washed with deionised water until the pH was between 7 and 8. The washed sample was subsequently dried overnight at 60°C.

The products obtained were characterized with XRD and SEM. Zeolite Y was finally synthesised using dealuminated metakaolin following the same procedure. Dealuminated kaolin with Si/Al of 6 was used and the composition of the aluminosilicate gel was chosen as 2.2Na2O:Al2O3:6SiO2:140H2O. The synthesis conditions used include crystallization temperature 100°C, crystallization time 9 h and ageing time at room temperature 24 h. Analysis of the product was carried out by SEM, XRD and the BET surface area and pore sizes of selected samples were analysed using an ASAP 2001 Micromeritics machine.

Table 4.5: Experimental conditions of zeolite synthesised from ANK based on the additional of external silica

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ageing (h)</th>
<th>Temperature ( ºC)</th>
<th>Time ( h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite Y</td>
<td>12</td>
<td>100</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>100</td>
<td>9</td>
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<td>12</td>
<td>70</td>
<td>9</td>
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</tbody>
</table>

4.6.5.3 ZSM-5 Zeolite

A complete overview of the synthesis procedure is presented in a schematic diagram shown in figure 4.5.
The composition of the synthesis gel was taken based on the work of Abdmeziem et al[142, 143] as

\[23.4\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:83.4\text{SiO}_2:4.2(\text{TPA})_2\text{O}:3750\text{H}_2\text{O} .\]

ANK metakaolin with silica to alumina ratio of 1 produced at a temperature of 600°C and exposure time of 10 minute was used as combined source of alumina and silica. Additional silica was supplied using Ludox AS 40 colloidal silica 40wt % suspension in H₂O.

A solution of NaOH was prepared by adding 6.59 g of NaOH pellet to 11.05 g of water. 42.99 g of additional silica (Ludox AS 40) was added to the above solution and the mixture was stirred continuously for 5 min. This was followed by the addition of 15 g of (TPA)₂O which serves as a template with the resulting solution stirred to ensure complete homogenisation. 1 g of metakaolin was then added to the solution and the resulting gel was vigorously stirred for 2 h. The gel obtained was left to age for a period between 12-48 h at room temperature and was then hydrothermally treated at a temperature between 100-170°C using Teflon-line autoclave at different crystallization times of 24-72 h (detail of synthesis conditions are shown in table 4.6). At the end of each run, the reaction was stopped and was allowed to cool in cold water before finally washing to reduce the pH to below 8 using a vacuum filtration system. The filtered samples were then dried in oven at
100°C overnight. Calcination was carried out 550°C for 3h using heating rate of 1°C/min to remove the structural directing agent (SDA).

Table 4.6: Experimental conditions of ZSM-5 synthesised from ANK based on the addition of external silica

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ageing (h)</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5</td>
<td>48</td>
<td>170</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>170</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>170</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>170</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>100</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>140</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>200</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>170</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>170</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>170</td>
<td>72</td>
</tr>
</tbody>
</table>

Finally dealuminated kaolin was used to prepare ZSM-5 zeolite following the same procedure as the one described for ZSM-5 synthesis using external silica. Dealuminated with Si/Al ratio of 16 was used in aluminosilicate gel with composition 4.5Na₂O: Al₂O₃: 20SiO₂: 4(TPA)₂O: 1500H₂O. The conditions chosen for ZSM-5 synthesis from dealuminated include crystallization temperature 140°C, crystallization time 48 h and ageing time at room temperature 36 h. The products was analysed by XRD, SEM and the products from dealuminated ANK metakaolin was further analysed by BET surface area.
4.7 Results and Discussion

4.7.1. Refinement of Ahoko Nigerian Kaolin

The uses of kaolin in any industrial processes require proper and deliberate identification and purification procedures. Kaolin is usually characterized by a combination of several techniques because of their high crystallinity and unique structure.

Pre-treatment of the raw Ahoko Nigerian kaolin (ANK) was carried out for the first time before it was used in the synthesis of zeolite A, Y, and ZSM-5. In order to identify the ANK (figure 4.6) and verify the existence of impurities, the XRD pattern obtained was compared with WBB kaolin UK which served as reference kaolin for this work.

The XRD pattern of the as-shipped ANK sample (figure 4.7) shows several peaks due to the mineral present in the material. An analysis of the peaks indicate a sharp peak with low intensity at $2\theta = 12.335^\circ$ (d = 7.15 Å). This is the main peak used in the identification of kaolin[144, 145]. Further analysis of the sample by XRD indicates the presence of large quantities of quartz existing at peak position corresponding to $2\theta = 26.37^\circ$.

Natural kaolin deposit are predominantly an association of kaolinite and quartz [146] and as such the high concentration of quartz in ANK is not unexpected. Other impurities found with kaolin include hydrated mica, and non-crystalline hydroxide of iron. The level of each impurity in individual kaolinite deposit depends on location and geology of the deposit.

However the industrial application of kaolin especially for the synthesis of zeolites and zeolite membrane requires that the quartz content be reduce to minimum level.
The XRF shows the chemical composition of the sample (Table 4.7) and it indicates a high percentage of SiO$_2$ (with 1-2% margin of error). The high silica content as reflected in the XRF analysis is a clear evidence of the high content of quartz present in the sample. This analysis corroborates the XRD result.

Table 4.7: XRF analysis of the as-shipped ANK sample

<table>
<thead>
<tr>
<th>Chemical constituent</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>72.455</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>18.963</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.021</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.431</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>1.0471</td>
</tr>
<tr>
<td>MgO</td>
<td>0.132</td>
</tr>
<tr>
<td>LOI$^a$</td>
<td>6.170</td>
</tr>
</tbody>
</table>

$^a$Loss on Ignition
The SEM and TEM were also used to further elucidate the morphology of the raw ANK sample and identify it as well. The results are shown in figure 4.8 and 4.9. The SEM and TEM images of the sample revealed the existence of kaolinite minerals in association with quartz.

Figure 4.7: SEM image of the raw ANK sample

Figure 4.8: TEM image of raw Ahoko Nigerian kaolin
The SEM and TEM images show a well crystallized kaolinite particle with a typical pseudo-hexagonal platelet shape as reported for other kaolinite in the literature[147-149], however the angular orientation of the SEM images depicts the consolidation of quartz with the clay mineral [147]. Therefore just like most other naturally occurring minerals, ANK requires purification or enrichment before it can be used in the synthesis of zeolites and zeolite membranes.

The presence of quartz is not desirable in kaolin [150] because it is difficult to dissolve hence it is necessary to eliminate or reduce the amount of quartz before the kaolin is used in the synthesis of zeolites. A further look at table 4.7 indicates a low concentration of alumina (18 wt %) in the raw sample, which is in contrast with the theoretical concentration of alumina in kaolin. Generally zeolite synthesis requires a substantial amount of alumina in the kaolin which is within limit provided for kaolin used for zeolite synthesis [118]. The combination of a high concentration of quartz and low amount of alumina present in the as-shipped kaolin make enrichment necessary.

There are several techniques used in the purification of crude kaolin and each of the method has its advantages and weak points. The most important factor considered in the choice of purification is the effect of the processing on the microstructure of the kaolinite mineral.

Some of the well known techniques usually used to refine kaolin are selective flocculation [151], high gradient magnetic separation [152-154], flotation purification [155] and particle size separation by sedimentation [156-159].

The first three methods mentioned have major advantage over the particle size separation by sedimentation mainly because the processes are faster but the techniques are more expensive and influence the chemical and microstructure of the kaolin sample. The choice of sedimentation technique as a purification procedure is clear. It is cheaper and offers little modification of the microstructure of the parent material especially when dispersant or deflocculant are not used. Particle size of kaolin is major parameter which determine the clay mineral from all the associated non-clay mineral [10] hence the particle size of the kaolin sample was deliberately chosen to obtained the purest form of the clay from combining with impurities. Usually there is standard upper or lower limit, but generally particle sizes are set between 1 to 10 micron. The separation by particle size by sedimentation have unique advantage of not altering the properties and structure of kaolin.
even though the method is slow and require carefully control of the concentration of kaolin in the settling cylinder to avoid flocculation.

The settling time for >2 micron fraction (quartz) was determined using the Stokes’ model to be 23 h 15 mins. The choice of particle size of quartz was explained as been based on personal communication with Dr. Paddy Hill of Chemical Engineering. The time of settling was determined using Atterberg software and was based on the density, height of settling tubes, and temperature of the medium. This means that the <2 µm kaolinite phase remained in suspension during settling and the quartz settled out [67].

The analysis of the purified and coarse kaolin was performed using the same technique as the raw sample. The XRD pattern of the refined sample reveals a sharp and narrow peak with a basal reflection at $2\theta = 12.37^\circ$ (d= 7.15 Å). This is similar to the peak position in the raw sample. It is important to note that the peak positions in refined ANK compared well with those of WBB kaolin sourced from UK (figure 4.12) which was used as standard in this work. This is significant because ANK has never been characterized in this way before.

![Figure 4.9: XRD pattern of refined ANK](image)

**Figure 4.9:** XRD pattern of refined ANK

- K = kaolinite
- Q = Quartz
- M = Mica
Figure 4.10: XRD pattern of ANK residue

Figure 4.11: XRD pattern of WBB kaolin UK used as a standard
Quantitative analysis of the XRD pattern of the raw, refined and coarse ANK samples was also performed using Siroquant software\textsuperscript{2}, to determine the level of quartz reduction during the refinement process (Table 4.8). The percentage of kaolin and quartz in the raw sample was determined to be 22.7 and 77.3\% respectively, however the refining process resulted in the production of fine product with kaolinite concentration of 97.4\% and 2.5 \% quartz (with an error margin of 0.46\%). Analyses of the coarse fraction revealed that 72.7\% of quartz is present with 27.4\% of kaolinite still existing in association with it.

Table 4.8: Analysis of the kaolin samples by Siroquant software

<table>
<thead>
<tr>
<th>Sample</th>
<th>Kaolin wt%</th>
<th>Quartz wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Ahoko kaolin</td>
<td>22.7</td>
<td>77.3</td>
</tr>
<tr>
<td>Refined Ahoko kaolin</td>
<td>97.4</td>
<td>2.5</td>
</tr>
<tr>
<td>Standard WBB kaolin</td>
<td>95.4</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Further chemical analysis by XRF (table 4.9) corroborates the results obtained with the XRD analysis.

Table 4.9: XRF result of Refined ANK

<table>
<thead>
<tr>
<th>Chemical constituent</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2}</td>
<td>54.039</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>40.827</td>
</tr>
<tr>
<td>Na\textsubscript{2}O</td>
<td>0.109</td>
</tr>
<tr>
<td>K\textsubscript{2}O</td>
<td>0.537</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>2.009</td>
</tr>
<tr>
<td>MgO</td>
<td>0.177</td>
</tr>
<tr>
<td>LOI\textsuperscript{a}</td>
<td>2.07</td>
</tr>
</tbody>
</table>

The result in table 4.9 shows a significant reduction in the percentage composition of SiO\textsubscript{2} and corresponding increase in the percentage composition of Al\textsubscript{2}O\textsubscript{3} for the refined ANK.

\textsuperscript{2} Siroquant is quantitative XRD analytical software used for the identification of minerals and other crystalline materials. It does not require specialist crystallographic knowledge to obtain a reliable analysis. It contains over 1800 common minerals in its database.
A high percentage of $\text{Al}_2\text{O}_3 (> 30\%)$ in the purified sample also indicates that Ahoko kaolin clay can be classified as kaolinite rich clay.

The surface morphology of both the refined and coarse sample was studied by SEM and TEM to further confirm the refinement that has taken place. The SEM and TEM images of the refined kaolin (figure 4.13 and appendix B) clearly reveal kaolinite particles with varying sizes. These come with a low aspect (crystal-width to thickness) ratio. Apart from the usual pseudo-hexagonal platelet which is still visible, rough edge are also observed in most of the particles, however the observed platelets show thinness of kaolinite flakes indicating finesse of the kaolin surface. The SEM and TEM also reveal highly ordered and crystalline particles.

![Figure 4.12: SEM image of refined ANK](image.png)

The coarser size fraction as shown in SEM and TEM (Appendix B) shows an increased amount of quartz existing in the form of irregular but angular shaped crystals. It is also evident that 100% separation is not achieved, as particle of kaolinite minerals are still visible along with the quartz crystals.

It must also be stated again that other processes for kaolin separation methods would have given a higher percentage recovery, but the advantage of the chosen procedure ensure that no chemical is added as a dispersant [95] and all the outcome of the analysis can only be
attributed to kaolin as the chemical make-up of the parent material is not altered and the process is cost effective.

Other parameters such as porosity, surface area, etc of kaolin which is germane to the synthesis of zeolite from kaolin was also investigated using (ASAP 2001 micromeritic nitrogen adsorption and Pascal 140/240 system. mercury porosimetry. The result are shown in table 4.10.

<table>
<thead>
<tr>
<th>Raw Ahoko kaolin</th>
<th>Refined Ahoko kaolin</th>
<th>Residual Ahoko kaolin</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BET surface area m²/g</strong></td>
<td>7.424</td>
<td>15.227</td>
</tr>
<tr>
<td><strong>Porosity %</strong></td>
<td>3.144</td>
<td>28.818</td>
</tr>
<tr>
<td><strong>Total pore volume cm³/g</strong></td>
<td>0.028</td>
<td>0.052</td>
</tr>
</tbody>
</table>

*the porosity values were obtained using the Pascal 140 mercury porosimetry system

The result obtained from both nitrogen adsorption and mercury porosimetry shows changes that took place in the BET surface area and porosity from the as-shipped kaolin and the refined Ahoko kaolin during the refining process. The value obtained for most of the parameters e.g. surface area, and porosity compared well with similar kaolin reported in the literature [160].

### 4.7.2 Metakaolinization of ANK

The drive to reduce the energy consumption during metakaolinization was the motivating factor in the development of new strategy to produce quality metakaolin that can be transformed into zeolites. However the transformation sequence to metakaolin as used in zeolite synthesis has been confusing and inconsistent in the literature. Several works on the preparation of zeolites from kaolin have reported using different metakaolinization temperature and varying exposure time (cf.4.4). The process of bringing the kaolin sample to the required temperature and it effect on how metakaolinization is achieved has not also been explored.
In this study, a fast and rapid method of metakaolinization which has potential to be developed into a continuous process and has not been reported before was used. Since ANK has not been characterized before, it is important to know the thermal properties of the material. This will show the temperature of metakaolinization. In-situ high temperature (temperature programmed) XRD was used to monitor the phase change taking place during the metakaolinization of ANK.

The temperature programmed XRD of the refined kaolin, obtained at increasing temperatures are presented in figures 4.14. The outcome of the analysis allows the monitoring of the process taking place during dehydroxylation from room temperature to a temperature above 700°C.

As shown in figure 4.14, the heating of kaolin sample from room temperature to 500°C caused an increased intensity of the main reflections. According to Franco et al [161], this is probably due to the loss of the hydration water which results in a better ordering in the structure of the kaolinite molecule, however there was complete loss of the main reflection (12.3°) at 600°C leaving only a small halos which indicate the formation of a non crystalline phase. Therefore metakaolin based on the temperature programme XRD result
can be described as an amorphous material containing free silica, free alumina as reported by Brindley et al [162].

The result of the temperature programme XRD acted as a guide to develop a new route for the production of metakaolin with the main aim of reducing the time of exposure taken to obtained the amorphous material. The furnace was pre-heated at 600°C and 5g of the refined ANK was loaded separately and taken out at different time of exposure. Samples were obtained at 1, 2, 3, 4, 5, 6, 9, 10, 20, 40 and 50 min. The percent crystallinity of the product at each exposure time was estimated by comparing with the parent material which was assumed to be 100% crystalline. The graph of percent crystallinity as shown in figure 4.15 show that x-ray amorphous material was obtained by the 6min of exposure which is completely different from the time reported for metakaolin used in the synthesis of zeolites. Similar experiment was performed on the standard kaolin obtained from WBB kaolin (UK) to again act a reference kaolin. It is obvious that ANK and the reference shared the same characteristic. Samples obtained at10min was taken for XRF analysis in order to check for possible variation in the chemical composition from the parent material. The results as shown in table 4.11 reveal that the chemical of the metakaolin is practically the same as the starting refined kaolin.

![Figure 4.14: Loss of crystallinity with time of metakaolinization (△ ANK, ■ WBB Kaolin)](image)

*Figure 4.14: Loss of crystallinity with time of metakaolinization (△ ANK, ■ WBB Kaolin)*
Table 4.11: XRF of metakaolin produced at 600°C and at 10 min exposure time

<table>
<thead>
<tr>
<th>Chemical constituent</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>54.195</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>41.477</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.066</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.537</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.887</td>
</tr>
<tr>
<td>MgO</td>
<td>0.54</td>
</tr>
</tbody>
</table>

The XRF result excludes other trace oxides

4.7.3 Dealumination of Metakaolin obtained from ANK

Kaolin is known to be an unreactive material [163] and it was not contemplated to dealuminate the material directly although there are some reports of the dealumination of kaolin mineral at high temperature [164-166]. It is much easier to dealuminate metakaolin which is a more reactive phase allowing preferential dissolution of the Al component.

The purpose of the dealumination of ANK is to create a material that have a similar SiO₂/Al₂O₃ ratio as the ratio required for the key materials in the starting gel of high silica zeolites synthesis. As explained in section 4.5, the acid treatment of kaolin causes selective leaching of alumina, magnesium, and iron content from the octahedral sheet or layer lowering the alumina content in the end.

Four different samples of dealuminated ANK metakaolin were produced at 80°C and different heating times of 1, 2, 4, and 8 h. The XRD pattern of the produced dealuminated kaolin at 8 h is presented in figure 4.16. Only the XRD pattern of the 8h dealumination is presented because there is basically no structural change as expected. The XRD pattern is essentially X-ray amorphous similar to the XRD pattern of the starting metakaolin material, however it is noticed that initial impurities in the parent kaolin was not affected as a result of the dealumination. While the quartz peak at 26°(2-theta) was reduced very little compared to the metakaolin starting material, the mica peak at 8° remained unmodified. This is mainly because of the high resistance of the impurities to the acid
treatment [163]. There is a peak between 20-25° (2 theta) which has been assigned to sulphate ions still present in the sample.

There is increased background between 25-30° (2-theta). This has been attributed to the presence of amorphous silica as result of the selective dissolution of Al$^{3+}$ cation.

The XRF analysis of the samples at the four different times is shown in table 4.12. The leaching of the alumina content of the kaolin ultimately alters the chemical composition and minimally changes the structure of the parent starting material. The results show that increase in time of dealumination at a constant temperature of 80°C lead to corresponding decreases in the aluminium content. The small iron content of the resulting metakaolin was also substantially reduced from 2.117% to 0.188% (not shown). This is in agreement with the observation made by Lenarda et al and Okada et al [167, 168] on their work on mesoporous catalyst and microporous silica production from metakaolin.

This reaction has been used in the production of solid acid catalyst by several researchers because not only is the chemical composition of the metakaolin altered, several properties of the dealuminated kaolin such as surface area, pore size as well as active site are enhanced depending on the severity of the leaching process.

The results obtained showed that acid leaching of ANK metakaolin results in a 76.9% loss of alumina within 8 h of dealumination. The result is similar to the work of Belver et al [163] and show that the ANK has been made reactive as a result of the metakaolinization and dealumination reaction. Further increase in the dealumination time will lead to the complete removal of the alumina content of the kaolin and the production of silica. Hence ANK is also a good candidate for the preparation of different type of silica. In this work, the prepared dealuminated kaolin was used to synthesise high silica zeolite (zeolite Y and ZSM-5) without the addition of external silica.

The SEM image as shown in figure 4.17 for the sample obtained at 8 h of dealumination also reveal that structural modification indeed took place. The morphology of the sample dealuminated show flaky particles that is stacked together. This is different from the platelet feature of the parent material. The surfaces are generally rough as a result of the destruction of the bond that held the tetrahedral and octahedral layer together.
Table 4.12: Silica and alumina composition of dealuminated ANK metakaolin measured by XRF

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>SiO₂/Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21.145</td>
<td>75.03</td>
<td>6.0</td>
</tr>
<tr>
<td>2</td>
<td>18.19</td>
<td>78.84</td>
<td>7.4</td>
</tr>
<tr>
<td>4</td>
<td>11.37</td>
<td>85.82</td>
<td>12.8</td>
</tr>
<tr>
<td>8</td>
<td>9.33</td>
<td>87.79</td>
<td>16.0</td>
</tr>
</tbody>
</table>

Figure 4.15: XRD pattern of dealuminated ANK metakaolin at heating time of 8h

Q = quartz  
M = mica
4.7.4 Synthesis of Zeolite A, Y, and ZSM-5 from ANK

Three different types of zeolites were synthesised. These are zeolite A, zeolite Y, and ZSM-5. While zeolite A is a low silica and can be prepared directly from the kaolin using conventional hydrothermal technique, both zeolite Y and ZSM-5 were prepared using two methods namely conventional hydrothermal synthesis from kaolin plus external silica and conventional hydrothermal synthesis using dealuminated kaolin. The outcome of the study on the preparation of zeolites from ANK is presented in the next section.

4.7.4.1 Synthesis and Characterization of Zeolite A

Effect of Ageing Time

The XRD pattern of the reaction products at different ageing time and constant crystallization time and temperature of 6h and 100°C is shown in figure 4.18. The pattern obtained compared well with commercial zeolite A sample from Aldrich UK with all the diffraction peaks matching with those of the reference sample. The XRD pattern shows that zeolite A was formed after all the ageing times studied. Traces of quartz and mica are found in all the samples at 2 theta = 26° indicating the unreactive behaviour of quartz.

The results show that zeolite crystallinity increases with increased ageing time of the synthesis mixture. This is seen from the increase in the intensity of the reflection of the main peak corresponding to the formation of zeolite A. It is important to notice from the results that unlike similar work on the synthesis of zeolite A [8] from kaolin which require
ageing to initiate the nucleation of the zeolite synthesis, Zeolite A formation was obtained even when there was no ageing of the synthesis mixture. This may be attributed to the reactivity of the ANK metakaolin which might be higher than kaolin used in other work. Enhanced zeolite formation was observed because, according to Akoleker [114], the conversion of metakaolin to zeolites takes place in two main phases. First, there is initial conversion of metakaolin to aluminosilicate gel and this is followed by the fixing of aluminium inside the lattices of the silicate ring to form zeolite framework. Ageing of the synthesis mixture causes silica to dissolve and release silicate ions into the surrounding solution thereby increasing higher crystallization and yield.

The SEM images of the final zeolite products obtained at different ageing period are shown in figure 4.19. The images show that a well crystallized cubic morphology typical of zeolite A [109] was achieved even at zero ageing of the mixture. This corroborates the XRD result confirming the formation of zeolite A. Ageing is therefore not necessary based on the work carried out and this can have an effect on the eventual cost of synthesising zeolite from ANK. The results generally shows that crystalline zeolite A phase was clearly obtained at most condition of synthesis chosen for this reaction, however, ageing time of 6 h, crystallization temperature of 100°C and crystallization time of 6 h seem to produced the best zeolite A crystal that compared with commercial zeolite A.

The potential of making commercial zeolite A from ANK using lower metakaolinization temperature and exposure time look promising and further work will need to performed to synthesis zeolite A on large scale using the parameters generated.
Figure 4.17: XRD pattern of Zeolite A from ANK (Effect of ageing time at room temperature at constant crystallization time and temperature)
Effect of Crystallization Time

The XRD pattern of products obtained at the different times is shown in figure 4.20. No zeolite formation was noticed or observed by the first two hour of crystallization. This can be attributed to the fact that in the initial period of crystallization or heating, after mixing of the metakaolin and alkali solution, some time is taken before dissolution of the metakaolin is completed. It is not clear how long it will take to complete the dissolution process, however the process does not have to complete before zeolitization process starts. The ageing process was expected to promote some degree of dissolution and possibly influence quick formation of zeolite A during crystallization. The gel formed remained amorphous during the first two (2) hour of crystallization. The peak due to the impurities in the original refined ANK which are mica and quartz at 2-theta = 9° and 26° remain detected. It is known that the impurities does not impair or interfere with the formation of zeolite A. However by the third hour of synthesis, the XRD pattern shows that zeolite A with moderate crystallinity compared with the reference zeolite was formed.
All the peaks of zeolite A such as 2 theta = 7.20°, 10°, 12° completely match those of commercial zeolite A sample. Increase in the synthesis time show further crystal growth taking place with XRD analysis indicating crystallinity better than that of the commercial sample. This time of crystallization (6 h) was taken to be enough for the zeolite formation from ANK.

The morphology of the samples obtained at different crystallization time was obtained as shown in figure 4.21. The SEM image of the samples obtained in the first two hour reveals morphology with distorted pseudo-hexagonal platelet of kaolin which in this case can be ascribed to the metakaolin used in the preparation of the sample. 3h of crystallization show a zeolite A crystal with poorly defined cubic shape and with no identifiable edges. However complete cubic crystal with sharp and defined edge can be clearly seen when the crystallization time was taken to 6 h.

Higher reflectivity as shown by an increase in the intensity of the XRD pattern are also noticed when the time of crystallization was increased further to 6 h. This can be attributed to improved opportunity for the alkalinity content of the synthesis gel to cause increased solubilization of the silicate and aluminate ions leading to more enhanced poly-condensation reaction between the polysilicate and aluminate [3].

Further analysis of the outcome of the synthesis of zeolite A by varying time of crystallization was performed by SEM. Figures 4.21 clearly show the continuous changes taking place when the time of crystallization was increasing from 0 to 6 h. Figure 4.21c and 4.21d shows a well resolved micrograph of zeolite A with cubic shape [139] after 3 and 6h of crystallization which again further corroborates the analysis by XRD. This is in contrast with similar report on the synthesis of zeolite A from kaolin in which longer times are used to synthesis zeolite A [8, 108]. These results therefore have potential of lowering the production cost of zeolite A from kaolin.

The Si/Al ratio of the zeolite A material obtained was analysed using EDAX similar to measurement carried out by Imbert et al [138] in their work. The Si/Al ratio of zeolite A produced at crystallization time of 6h with the ageing time held at 12 h and crystallization temperature fixed at 100°C was calculated to be 1.0. The Si/Al ratio agree well with reported ratio for the commercial zeolite A and value quoted in the literature [169]. The average particle size of zeolite A synthesis based on the best condition with respect to this study at ageing time of 12 h, crystallization time of 6 h and crystallization temperature of
100°C was calculated as 2.3 µm. The particle size obtained for zeolite A compared well with similar synthesis of zeolite A from Indian clay used for detergent processes. Zeolite A crystal with less than 10 micron is renowned to be good as detergent builder because the performance depend on the size and morphology of the zeolite crystal [87].

Figure 4.19: XRD pattern of Zeolite A from ANK (Effect of time of crystallization at constant ageing time and crystallization temperature)
Effect of Crystallization Temperature

Hydrothermal reaction of the metakaolin/alkali mixture to form zeolite A from ANK was also studied by varying the crystallization temperature between 80 to 200°C. The reaction and ageing time were both fixed at constant value of 6h and 12h respectively during the synthesis.

Figure 4.22 shows the XRD pattern of samples synthesised when the temperature of crystallization was varied from 80°C to 200°C. It is observed that after crystallization at 80°C for 6h, zeolite A of low crystallinity was formed. The characteristic peaks at 2-theta = 7.20°, 10.17°, 12.45°, 23.99°, 27.11° matched those of the commercial zeolite A sample. Further increase to 100°C still at a fixed heating and ageing time promote the formation of pure phase of zeolite A. A low background intensity indicate low level of impurities in the zeolite formed again, an indication of good refinement that was carried on ANK which was meant to eliminate the quartz content of the raw kaolin. The intensity of the major zeolite A peak increase, however at 150°C there is a noticeable decrease in the formation of zeolite A with reduction in the intensity of main zeolite diffraction peaks. This started the process of transformation of the zeolite into different phase. At 200°C, there is a complete
phase change with the characteristic zeolite A peak at 2 theta = 7.20 and 10° completely disappear and there is appearance of new peak at 12-14° and 26°. These peaks have been assigned to zeolite P. Hence zeolite P can be seen as the next stable zeolite phases of zeolite A synthesis from ANK following Ostwald’s law of successive transformation of zeolite which state that in the formation of polymorph from liquid, vapour or solution, the first polymorph to appear is the least stable thermodynamically and is successively replaced by more stable zeolite [137].

The morphology/chemical composition of the synthesis products at different crystallization time temperature was also examined using SEM/EDAX. Crystalline phase was obtained at 80°C even without clearly defined cubic shape. This is in agreement with the XRD results which indicate formation of zeolite A with low crystallinity. Figure 4.23 shows a product obtained at 100°C clearly revealing typical zeolite A crystals with sharp and well defined crystals. These results also show a product of pure phase with minor impurities. These clearly show that 100°C is the ideal crystallization temperature for zeolite A formation from ANK. The Si/Al was determined from chemical composition of Si and Al in the zeolite A sample as analysed by EDAX and values obtained showed that Si/Al increase with increasing crystallization temperature. 0.90 was obtained at a crystallization temperature of 80°C while an ideal value of 1.0 was obtained when the crystallization temperature was raised to 100°C. This value compared well with the value of Si/Al reported for standard zeolite A.

The influence of temperature on zeolite formation have been described by Rees et al [141]. The crystallization temperature direct the transformation by changing the distribution of silicates, aluminate and the aluminosilicate in the liquid phase increasing the concentration of silica and alumina and thereby promoting supersaturation, a necessity for nucleus formation.

Crystallization temperature of 100°C was confirmed as the ideal temperature for zeolite A formation from ANK. This is the generally used temperature for zeolite A formation from kaolin using conventional hydrothermal synthesis method. Temperature along with crystallization time can be said to be the key parameter that affect zeolite transformation from ANK.
Figure 4.21: XRD pattern of Zeolite A from ANK from ANK (Effect of Temperature at constant ageing time and crystallization time)
The summary of the synthesis of zeolite A from ANK can finally be described as follows:
The series of evolution that a synthesis mixture goes through during the process of zeolite crystallization was evident during the preparation of zeolite A from ANK. The addition of the metakaolin which supplied the silica and alumina to the water/alkali mixture formed the aluminosilicate gel which is strongly inhomogeneous and provide the site for the zeolite nucleation. Either with or without ageing, zeolite A formation takes place as a result of dissolution and depolymerization of the silica and alumina content of the metakaolin linking together to form needed nucleus which serves as growth centre for the crystallization.

### 4.7.4.2 Synthesis and Characterization of Zeolite Y

Zeolite Y is a typical medium pore zeolite that has continued to receive attention because of its industrial importance [170]. Studying the conditions under which such zeolite is formed from kaolin is therefore imperative. The importance of using kaolin as a raw material for zeolite Y synthesis cannot be over emphasised. Apart from the cost benefit due
to zeolite Y from kaolin, most zeolite synthesis using commercial chemicals such as aluminium sulphate required that sodium sulphate is removed from the effluent after crystallization but with kaolin, no purification is required.

The synthesis of zeolite Y using kaolin as precursor has been studied before, using different conditions such as the source of kaolin deposit, metakaolining temperature, exposure time and other parameters [136]. In this study the synthesis of zeolite Y was carried out under different ageing conditions, reaction time and temperature to systematically monitor the nature of crystalline material, and other physiochemical properties of the product. Two synthesis procedures were used in the study to prepare zeolite Y from ANK. The synthesis involves the use of external silica and synthesis directly from dealuminated ANK metakaolin. In the first synthesis method, the sodium aluminosilicate gel was obtained by initially preparing two equal part of alkali solution. 1g of metakaolin was added to one of the alkali solution and 7.4814 g of the external silica sodium metasilicate was added to the second part. The two mixtures were separately and thoroughly mixed by stirring for 10 min before it was combined together. The synthesis mixture obtained was then aged for certain period and was thereafter hydrothermally reacted in an autoclave. The initial condition was also carefully chosen and each parameter of ageing time, synthesis time and crystallization temperature was varied while holding the other constant. In the synthesis of zeolite Y from dealuminated kaolin, an alkali solution was prepared along with dealuminated kaolin and was then followed by ageing for 24 h and thereafter by hydrothermal synthesis using crystallization temperature of 100°C and crystallization time of 9 h.

**Effect of Ageing Time**

The X-ray diffraction patterns of zeolite Y obtained at different ageing times at room temperature are shown in figure 4.24. The pattern was compared with pattern of commercial zeolite Y (PQ Corporation, Netherlands) acting as a reference zeolite Y. The results obtained show a near perfect match between the zeolite Y synthesised from Ahoko kaolin and the reference zeolite Y even when the synthesis mixture was only aged for 3h. However the crystallinity of the zeolite Y increases with increasing ageing time showing that ageing of zeolite mixture have a considerable influence on zeolite synthesis from metakaolin even if it does not initiate the reaction [135]. Increase in the ageing time was beneficial to the quality of the synthesis Y sample as there was a high quality XRD pattern.
Ginter et al [43] has also demonstrate that prolonged ageing of aluminosilicate gel during zeolite Y synthesis from kaolin lead to insertion of more silica into the gel and this give rise to increase in the nucleus. In the synthesis, no seeding was necessary to induce zeolite formation, the induction phase must have been by-passed probably as a result of the reactivity of the metakaolin which reacted positively and quickly to form the necessary nuclei required for crystal growth. But ageing is recommended for inclusion in zeolite Y synthesis because it helps in promoting and increasing nucleation and crystallization.

The outcome of this work shows that diffraction peaks of synthesised zeolite Y was maximum at ageing time of 12 h showing almost the same intensity of the characteristic peak at 2 theta = 6.18° C as the reference zeolite Y. Previous studies on the influence of ageing on zeolite Y synthesis from natural sources have only been done on the use of fly ash as a precursor [171]. This is first time ageing of aluminosilicate gel prepared from metakaolin is investigated for the synthesis of zeolite Y. Ageing beyond the required time if unknown can cause incorporation of additional Si which can cause a transformation into other zeolitic phase following Ostwald’s law of successive transformation.

The SEM image of zeolite Y was taken to support the outcome of the XRD analysis. Figure 4.25 shows the SEM of the zeolite Y sample synthesised at different ageing times. The formation of zeolite Y crystallites were obvious from the SEM image obtained and this compared well with similar images of zeolite Y in the literature[172]. Well defined crystal shape with average particle size distribution of 2 µm was obtained. The Si/Al ratio was calculated from the EDAX analysis. The Si/Al increases with increase in the ageing time with the following value obtained at different ageing time 1.77 (3 h), 1.81(12 h) and 1.94(24 h). The Si/Al ratio generally agrees with value reported for commercial zeolite Y which is quoted to be > 1.5.

The outcome of the present study so far validate the earlier assertion that conversion of kaolin to zeolite Y is a function of initial reactivity and crystallinity [136] of the parent kaolin material. While other kaolin deposit used to synthesis zeolite Y require ageing [173] to form zeolite, ANK seem very reactive and did not require ageing to form the initial nucleus for zeolite Y formation, however ageing plays a part by increasing the intensity of reflection/crystallinity of the final product. Previous research effort on the synthesis of faujasite from kaolin has not achieved tangible results. Only zeolite X is commonly cited being produced from kaolin, zeolite Y has not being widely reported. The choice of
composition, the amount of alkali, the selection of synthesis parameter as well as the nature of the parent kaolin material might be responsible for lack of much information of zeolite Y synthesis from kaolin.

Figure 4.23: XRD pattern of Zeolite Y prepared from ANK on the effect of ageing at fixed crystallization time and temperature of 9 h and 100°C respectively.
Figure 4.24: SEM image of zeolite Y prepared from ANK on the effect of ageing at A = 3h, B = 12 h and C = 24 h with fixed crystallization time and temperature at 9 h and 100°C respectively. Scale bars = 5 μm

**Effect of Crystallization Time**

As previously stated, crystallization time is one of the basic parameters in zeolite synthesis that demand careful selection in order to prepare the targeted zeolite mainly because of unstable nature of zeolites. This parameter was also studied in the synthesis of zeolite Y from ANK.

Figure 4.26 depict the XRD pattern of the samples obtained at various crystallization time with the ageing time at room temperature and heating temperature fixed at 24 h and 100°C respectively. When the aluminosilicate gel prepared from ANK was aged at the fixed 24 h and heating temperature of 100°C, no zeolite formation was noticed during the first 3 h of crystallization time indicating that the conversion of the polysilicate and aluminate was not possible. Increase in time of reaction to 6 h causes the crystallization of zeolite Y which compared well with commercial zeolite Y. It is clear that the crystallinity increases when the time of synthesis increase from 3 h to 6 h and 9 h.
Crystallization time of 9 h obtained for the synthesis of zeolite Y from ANK is in contrast to the work of Lapide et al [134] who reported the synthesis of zeolite Y after 72 h and Sathy et al [136] who reported about 16 h for the synthesis of pure zeolite Y phase from an Indian kaolin. The crystallinity of the synthesised zeolite Y from Ahoko kaolin appears more than the standard zeolite Y used for comparison. The formation of zeolite Y from ANK metakaolin within 9 h of crystallization might be ascribed to the high reactivity of the ANK metakaolin compared with other kaolin used. The high reactivity of the metakaolin facilitates faster dissolution in the base. The Si/Al ratio of the aluminosilicate gel also increase and in the process more reaction take place which favour faujasite crystallization [8].

The approach used in metakaolinization rapidly causes the destruction of the silica and alumina layer in the kaolin structure thereby rendering free silica and alumina and making them more reactive. A further test by NMR might be required to show the coordination state of alumina in the metakaolin. It has been postulated that 4-coordinated aluminium is the requirement for metakaolin used for zeolites synthesis [174].

The SEM images of the sample obtained at different reaction times are shown in figure 4.27. The SEM shows a well defined octahedral crystals shape similar to the type reported by Chandrasekhar and co-workers [136]. The SEM also reveals gradual growth of crystal with increasing time of reaction. The Si/Al ratio of the sample prepared at crystallization time of 9 h, ageing time of 12 h and crystallization temperature of 100°C was calculated to be 1.83 from the EDAX analysis and fall within the standard range of Si/Al ratio for zeolite Y.
Figure 4.25: XRD pattern of Zeolite Y prepared from ANK on the effect of crystallization time with fixed crystallization temperature and ageing time at 100°C and 24 h respectively.

Figure 4.26: SEM image of zeolite Y from ANK (Effect of constant crystallization A= 3 h, B= 6 h and C = 9 h at fixed ageing time and crystallization temperature ). Scale bars = 2µm.
Effect of Crystallization Temperature

The effect of temperature of crystallization was also monitored while fixing the ageing time at 24 h and crystallization time at 9 h. The temperature of crystallization was varied between 70 to 100°C and did not go beyond that value. The aim is to check the behaviour of low temperature synthesis of zeolite Y from ANK. Zeolites Y are usually prepared using crystallization temperature of 100°C.

Figure 4.28 shows XRD pattern of the zeolite Y. Low temperature was then chosen to observe their zeolite Y zeolitization processes. Crystallization at 70°C did not support the formation of any zeolite with only amorphous aluminosilicate gel and the associated mica at 2 theta =9° and quartz at 26.6° observed. However increase in the temperature to 80°C yields zeolite Y with characteristic peak at 2 theta = 6.22°. Crystallization temperature is regarded as the most important parameter that influences zeolite crystallization because a small change in the heating temperature can cause instant transformation in the zeolite phase. Increase in the crystallization temperature to 80°C immediately cause the evolution of zeolite Y phase and it compare well with the standard zeolite Y. Even though the intensity is low compared to the reference sample, the peak are sharp and show low background indicating near absence of amorphous phase at the temperature. Further increase to 100°C reveal peak of zeolite Y that compete strongly with the reference zeolite.

This work shows the possibility of synthesising zeolite Y at 80°C or 90°C instead of 100°C reported in the literature [135, 136] Crystallization at constant temperature produced zeolitic products that depend on the concentration of the hydroxide present which is also fixed based on original molar composition of the starting aluminosilicate gel. However increase in temperature causes an increase in the crystallization of more zeolitic material as result of increase in the nucleation and crystal growth of the aluminosilicate gel [109].

Previously Caballero et al [108] has previously obtained similar result on the effect of temperature on zeolite X synthesis.

SEM was also performed (figure 4.29) to corroborate the outcome of XRD analysis. The images obtained show a fully grown zeolite at 80°C and 90°C similar to the image by Samia et al [175] in which commercial chemical was used as silica and alumina source. The Si/Al ratio of the sample obtained at 80°C was obtained from EDAX as 1.57 and the average particle size was measured using the soft imaging software in the SEM as 2.3 μm.
Figure 4.27: XRD pattern of Zeolite Y prepared from ANK on the effect of temperature at fixed crystallization time of 9 h and ageing time of 12 h

Figure 4.28: SEM image of zeolite Y from ANK (A = 70°C, B = 80°C and C = 100°C) Scale bars = 5 µm
The summary of zeolite Y formation from ANK can be described thus:

These results generally show that zeolite Y was successfully prepared from ANK. The evolution of zeolite Y phase follows the digestion of the ANK metakaolin into the mixture of the external silica (sodium metasilicate) and the alkaline solution. It is clear that the commercial chemical is more soluble and the concentration of the base which in this case is provided by NaOH and the external silica help facilitate the crystallization leading to the rapid formation of zeolite Y phase 3 h after crystallization.

The formation of zeolite nuclei is due to the interaction between the silicate and aluminate ion in the mixture containing the metakaolin and external silica along with the alkali solution which is known to facilitate supersaturation by aiding dissolution of the individual precursor. Barrer et al [5] has already argued that zeolitization is strongly affected by the pre-treatment and reactivity of the parent material. ANK can be said to be highly reactive compared to several other kaolin used to prepare zeolites.

4.7.4.3 Synthesis of Zeolite Y from Dealuminated ANK

Zeolite Y was prepared from dealuminated ANK using the outcome of the synthesis in section 4.7.4.2. The use of additional or external silica to synthesise high silica zeolite from kaolin such as zeolite Y has its own disadvantages. Apart from additional extra cost, the different dissolution rate of the soluble silica source such as sodium silicate and metakaolin can affect the quality of zeolite obtained eventually.

In this study, zeolite Y was synthesized using dealuminated kaolin obtained at 2h of dealumination (cf 4.6) with Si/Al ratio of ~ 6. The chemical composition of the starting gel was chosen as

$$2.2\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:6\text{SiO}_2:140\text{H}_2\text{O}[176]$$

with no additional silica and the conditions of the reaction was chosen from the best conditions obtained in the earlier work on the zeolite Y synthesis with external silica. The XRD of the synthesised zeolite Y from dealuminated kaolin is shown in figure 4.30. The pattern compared well with the reference zeolite Y and shows a high degree of purity as a result of low background. The only similar work reported before was on the synthesis of zeolite X from dealuminated kaolin [108]. It was confirmed that dealuminated kaolin is
more reactive than calcined clay because of increased activity and high surface area which is more susceptible to alkali attack thereby promoting the zeolitization reaction. Dissolution rate is therefore high and leading to fast formation of supersaturated solution which constantly produces the nuclei to grow the zeolite.

The SEM image (Figure 4.31) reveals clear zeolite Y morphology with the octagonal shape which is similar to the shape earlier obtained. The SEM image also shows low concentration of impurities in the sample which confirm the XRD finding that few impurities are present in the dealuminated kaolin which transform to zeolite. The Si/Al ratio was obtained as 1.69 using the EDAX while the average particle size distribution was measured again by the SEM using the soft imaging software and this give a value of 2.5µm. The BET surface area and pore volume of the synthesis sample was analysed by nitrogen adsorption. The values obtained are 616.13 m²/g and 0.29 cm³/g respectively. The BET surface area compared well with the standard zeolite Y sample with BET surface area of 630m²/g.

Figure 4.29: XRD pattern of zeolite Y synthesised from dealuminated ANK
Figure 4.30: SEM image of zeolite Y synthesised from dealuminated at ageing time of 12 h, reaction time of 9 h and crystallization temperature of 100°C. Scale bar = 5 µm

4.7.4.4 Synthesis and Characterization of ZSM-5

Hundreds of thousands of ton of ZSM-5 are used yearly worldwide [170] for different industrial applications mainly in refining, petrochemical and fine chemical production. The preparation of such an important product using a low cost material such as kaolin for the first time is a welcome development especially from a Nigeria’s perspective. Nigeria has four refineries and a petrochemical plant which depend on imported zeolite such as ZSM-5. Developing the technology for the utilization of an abundant raw material such as the Ahoko kaolin deposit for ZSM-5 production, even though a long term objective is important to the industrialization aspiration of Nigeria. In this section, the discussions of results obtained from the synthesis of ZSM-5 from ANK are presented. Two synthesis methods were used in this study to prepare ZSM-5 from ANK in a similar way to the synthesis of zeolite Y.

Effect of Ageing Time

The process of making zeolite via crystallization is well established as previously discussed. It is comprised of initial induction stage, formation of supersaturation, nucleation and crystal growth. The promotion of each is dependent on the dissolution rate
of the precursor; hence it is a necessity in zeolite synthesis for dissolution to be effectively controlled. Ageing of synthesis mixture prior to the hydrothermal reaction influences the dissolution of the different source material ie metakaolin, colloidal silica and SDA and can approach equilibrium.

The XRD pattern (figure 4.32) shows that ZSM-5 phase was crystallized as confirmed by the diffraction peaks present at 2-theta = 7-9 and 23-25° matched with the reference ZSM-5 zeolite. The peaks are sharp and well resolved and this is evidence of good crystallization between the ANK metakaolin and external colloidal silica. There was an appearance of mordenite at 2 theta = 6.52° usually associated with ZSM-5 synthesis. In addition, the region between 25-30° (2-theta) shows presence of quartz and other amorphous materials. There is an appreciable increase in the reflection of main ZSM-5 peaks when the ageing is increased from 0 to 48 h indicating increased purity and higher crystallinity. The mordenite peak which appears in the XRD also begins to decrease as the ageing time increase, evidence of the high level of purity of the zeolite phase.

Hence in this work, ageing time of 48 h can be chosen as ideal ageing time for the formation of ZSM-5 from ANK. The SEM images (figure 4.33) of the ZSM-5 samples synthesised at different ageing time also corroborate the results of XRD. The SEM reveals a well crystallized ZSM-5 sample with large, high quality hexagonal morphology. The effect of ageing time can be visualized from the SEM images of sample obtained at 0 to 48 h. The images reveal gradual transformation of the ZSM-5 sample with poor quality and irregular shape crystals at ageing time of 0 h to perfect hexagonal crystals of the zeolite with minor impurities at 48 h of ageing. The chemical composition of the sample obtained at ageing time of 48 h was analysed using EDAX and the Si/Al ratio was calculated as 11.71.
Figure 4.31: XRD patterns of ZSM-5 synthesised from ANK showing the effect of ageing time at a fixed crystallization time of 72 h and reaction temperature of 170°C respectively.

Figure 4.32: SEM image of ZSM-5 sample synthesised from ANK. Ageing time A = 0h, B = 12, C = 36, D = 48 h while holding crystallization time and temperature at 72 and 170°C respectively. Scale bar = 20µm.
**Influence of Crystallization Time**

ZSM-5 with composition stated below:

\[
23.4\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:83.4\text{SiO}_2:4.2(\text{TPA})_2\text{O}:3750\text{H}_2\text{O}
\]

was synthesised at different crystallization times of 24, 36, 48 and 72 h while holding crystallization temperature and ageing time at 170°C and 48 h respectively. The XRD pattern of the ZSM-5 samples synthesised from ANK with varying time is given in figure 4.34. The peaks are compared with commercial ZSM-5 sample obtained from EKA Sweden used as reference sample and was assumed to be 100% crystalline.

Peak of ZSM-5 can be seen appearing after 24 h of crystallization but with low intensity. Further increase in the synthesis time leads to substantial increase in the crystallinity of ZSM-5, However, mordenite phase was seen to be co-crystallizing with the main ZSM-5 phase with peak located at 6.52° (2-theta). There was increase in the main peaks of ZSM-5 when the crystallization time was increase to 48h, however the peak of mordenite was always present. The positions of the peaks correspond to the commercial ZSM-5 sample. There is appearance of small peak of mordenite, this can attributed to the precipitation of competing phase which is often the case during zeolite synthesis. The appearance of mordenite alongside the main ZSM-5 peaks have been attributed to the similarities between the synthesis conditions of both ZSM-5 and mordenite zeolite [177].

The SEM images of the calcined samples were also obtained and presented in figure 4.35. The SEM images for sample obtained at 24, 36, 48 and 72 h shows separated and hexagonal single crystals of ZSM-5 zeolite. There is trace of amorphous phases or impurities. This can be attributed to the presence of unreacted metakaolin. The SEM image is similar to ZSM-5 reported in the literature from other source such as smectite clay[142],serpentine [178]. The Si/Al ratio and the average particle size of the calcined ZSM-5 samples at crystallization time of 48h were also measured as 11.05 and 3.43µm. The Si/Al ratio is within the range of the ratio expected of ZSM-5. The particle size obtained from ZSM-5 is small and meets industrial requirement. The industry is interested in zeolite with the smallest crystal in order to minimise rate limiting step of intracrystalline diffusion affecting the total chemical process.
Figure 4.33: XRD pattern of ZSM-5 synthesised from ANK (effect of time of crystallization). Ageing time and crystallization temperature was fixed at 48 h and 170°C respectively.
Figure 4.34: SEM image of ZSM-5 sample synthesised from ANK. Crystallization time was A =24h, B=36, C=48, and D=72 h while holding crystallization temperature and ageing time at 170°C and 48 h respectively. Scale bars is 20 µm for image A,C, and D and 10µm for image B.

**Influence of Crystallization Temperature**

Increase in crystallization temperature is well known to reduce the induction period and accelerate the rate of nucleation and crystallization [177]. Therefore variation in the crystallization temperature was also studied in the work to understand the extent of it influence on the synthesis of ZSM-5 from ANK.

The crystallization of ZSM-5 zeolite from ANK was studied at a varying temperature between 100 to 200°C while holding the reaction time and ageing time at 72 h and 48 h respectively. The XRD result of the synthesis are shown in figure 4.36 and the SEM image of the product obtained at 100, 140, 170°C and 200°C are shown in figure 4.37.

At the temperature of 100°C, an amorphous solid with irregular shape as supported by both XRD and SEM (figure 4.37A) was formed. Therefore ZSM-5 zeolite cannot be synthesised as this temperature. Chareonpanich et al [179] obtained a similar result in their work on the synthesis of ZSM-5- from lignite fly ash and rice husk. At 140°C, the XRD pattern of crystallizing ZSM-5 zeolite was noticed with sharp diffraction peaks which matched up with the commercial sample at the ZSM-5 characteristic peak at 7-9° and 23-25° as shown...
in figure 4.36. There was decrease in the degree of crystallinity of the ZSM-5 zeolite when the temperature of crystallization was increased to 170°C as reflected in the reduction in the intensity of the key diffraction peaks. This again signals the process of transformation series which can lead to change of zeolite phase based on Ostwald’s law of successive transformation already mentioned. When compared with commercial ZSM-5 sample, the sample prepared from ANK compared favourable well if not better. The SEM image of the ZSM-5 at 140°C reveals a well crystallized sample. The quality of the crystal is better than that obtained at 170°C and is supported by XRD analysis. The Si/Al of the sample was measured with the aid of EDAX and was found to be 16.70. This is compared well with reported Si/Al ratio of ZSM-5 synthesised from commercial chemicals. The crystallization temperature of 140°C was taken as the optimum temperature for synthesising ZSM-5 from ANK because further increase in temperature lead to co-crystallization of the more stable phase which in this case is quartz at 2theta = 20.9° and 26°. A similar result on the phase transformation of ZSM-5 to quartz phase has also been reported by Kulkarni et al [180]. The XRD pattern shows almost complete conversion of the zeolitic content into the quartz, hence the synthesis behaviour of ZSM-5 from kaolin can be said to be similar to those from commercial chemical. In this synthesis, crystallization temperature of 140°C gives a good phase of ZSM-5 with some small quantity of mordenite zeolite.
Figure 4.35: XRD pattern of ZSM-5 synthesised from ANK (effect of crystallization temperature. Ageing time and crystallization time was fixed at 48h and 72 h respectively).

Figure 4.46: SEM image of ZSM-5 sample synthesised from ANK. Crystallization temperature was at A =100°C, B=140°C, C= 170°C and D=200°C while holding crystallization time and ageing time at 72 h and 48 h respectively. Scale bars = 20 µm.
The synthesis of ZSM-5 with composition shown below

\[4.5\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 20\text{SiO}_2 : 4\text{(TPA)}_2\text{O} : 1500\text{H}_2\text{O}\]

was synthesised from dealuminated ANK. The dealuminated ANK metakaolin produced at Si /Al ratio of 16 was used in the synthesis of ZSM-5. The sample was prepared as reported in section 4.6 except that external silica was not added and the synthesis conditions was chosen from the best sample obtained from the synthesis using external silica. The as-synthesised ZSM-5 was also detemplated by calcination at 550\(^\circ\)C for 8h. The XRD and SEM of the calcined sample obtained are shown in figure 4.37 and figure 4.38 respectively.

The XRD pattern (figure 4.37) result shows the major peaks of ZSM-5 at 7-9\(^\circ\) and 23-25\(^\circ\) and matched the pattern of commercial ZSM-5 zeolite. The mordenite peaks that appear in the sample prepared with external silica did not show up in the dealuminated prepared ZSM-5. The reason for this behaviour is not clear but it can be ascribed to complete utilization of the polysilicate and aluminate during polymerization/condensation reaction leaving little for crystallization of other zeolitic phase, mordenite. Dealuminated kaolin is known to be more reactive because of increase in surface area and active sites in the kaolin framework.

The SEM image (figure 4.38) of the ZSM-5 zeolite prepared from dealuminated ANK show a uniform distribution of the zeolite particle with clear structural hexagonal shape and sizes. The image indicates that the calcined ZSM-5 zeolite consists of well resolved crystallite with uniform particle size distribution of size of ~3 \(\mu\)m. The Si/Al ratio of the sample was measured by EDAX and was found to be 20.0. High Si/Al ratio comes from the earlier dealumination process carried out which remove most of the aluminium in the crystal structure allowing more silica to go into solution during the polymerization and condensation reaction and leading to the formation of the necessary nuclei. A high silica content in the zeolite framework means that the zeolite synthesised will likely possess high thermal and chemical stability making a good material for many industrial process. The BET surface area of the ZSM-5 sample prepared from dealuminated ANK metakaolin was
determined as 262 m$^2$/g. This value compared well with the BET surface area of commercial ZSM-5 sample obtained from EKA Sweden which is 300 m$^2$/g.

Finally ZSM-5 synthesis using natural source such as fly ash, rice husk have being carried out before, only one literature reported the synthesis of the ZSM-5 from metakaolin but not the dealuminated phase. This study has therefore shown that ZSM-5 can be successfully developed from ANK using addition of external silica to the metakaolin and dealumination of the metakaolin.

![XRD pattern of ZSM-5 prepared from dealuminated ANK using ageing time of 36h, crystallization time of 48h, and crystallization temperature of 140°C](image)

**Figure 4.36**: XRD pattern of ZSM-5 prepared from dealuminated ANK using ageing time of 36h, crystallization time of 48h, and crystallization temperature of 140°C.
Figure 4.37: SEM image of calcined ZSM-5 sample prepared from dealuminated ANK using ageing time of 36 h, crystallization time of 48 h, and crystallization temperature of 140°C. Scale bar = 20 µm

4.8 Summary

The Ahoko Nigerian Kaolin (ANK) has been used as a source of raw material for the preparation of zeolites. ANK was successfully refined from a quartz rich raw kaolin sample using sedimentation processes and about 97% kaolin was obtained. A novel metakaolinization technique was thereafter developed and used in this study to successfully synthesised well-crystallized zeolite A, Y, and ZSM-5.

A combination of SEM and XRD provide a good picture of the metakaolin produced using the new method. The technique involve preheating of oven at 600°C and subsequent loading of kaolin samples into it before removing it over a period time to monitor their change in crystallinity. Metakaolinization temperature of 600°C and exposure time of 10 min was found to be enough to obtain an amorphous material characteristic of metakaolin. The use of metakaolinization temperature of 600°C and short exposure time of 10 min to synthesis zeolites can potentially reduce the cost of energy and time required to obtain metakaolin before it can be used for zeolite synthesis.
The metakaolin produced was used to prepare zeolites and was found to be reactive enough to promote nucleation and crystal growth of all the zeolites produced (Zeolite A, Zeolite Y and ZSM-5 Zeolite).

The outcome of zeolites synthesis from ANK is this study can be summarised as shown in table 4.13.

Table 4.13: Summary of results of synthesis of zeolites from ANK

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Molar Composition</th>
<th>Ageing time h</th>
<th>Crystallization time h</th>
<th>Crystallization temperature °C</th>
<th>Si/Al ratio</th>
<th>Average particle size µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite A</td>
<td>3.75Na2O:Al2O3:2.5SiO2:243.7H2O</td>
<td>12</td>
<td>6</td>
<td>100</td>
<td>1.00</td>
<td>2.30</td>
</tr>
<tr>
<td>Zeolite Y</td>
<td>15Na2O: Al2O3:15SiO2:45H2O</td>
<td>12</td>
<td>9</td>
<td>100</td>
<td>1.82</td>
<td>2.00</td>
</tr>
<tr>
<td>Zeolite Ya</td>
<td>2.2Na2O:Al2O3:6SiO2:140H2O</td>
<td>12</td>
<td>9</td>
<td>100</td>
<td>2.14</td>
<td>2.50</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>23.4Na2O:Al2O3:83.4SiO2:4.2(TPA)2O:3750H2O</td>
<td>36</td>
<td>48</td>
<td>140</td>
<td>16.70</td>
<td>3.43</td>
</tr>
<tr>
<td>ZSM-5b</td>
<td>4.5Na2O:Al2O3:20SiO2:4(TPA)2O:1500H2O</td>
<td>36</td>
<td>48</td>
<td>140</td>
<td>20.00</td>
<td>3.00</td>
</tr>
</tbody>
</table>

*a,b* zelite Y and ZSM-5 synthesised by dealumination of ANK metakaolin

Zeolite A was successfully synthesised from the ANK metakaolin over a range of conditions. Highly crystalline zeolite A was obtained using crystallization time of 6h, ageing time for 12h and crystallization temperature of 100°C. The outcome of the synthesis of zeolite A from ANK indicates that ageing is not an important synthesis parameter because zeolite formed regardless of whether ageing was carried out or not. This is an indication of high reactivity of ANK compared to other kaolin deposits which require ageing of their metakaolin before they can be used to synthesise zeolites. Ageing does not initiate the reaction in zeolite A synthesis from ANK metakaolin.

Zeolite Y was successfully obtained between 6 and 9 h of crystallization and temperature of between 80 to 100°C crystallization temperature. Ageing played a significant role by increasing the crystallinity of the final product even though zeolite Y was still obtained using minimum ageing time. Two methods was used to prepare the zeolite Y i.e.
metakaolin with external silica and dealuminated kaolin. The outcome of zeolite Y synthesised from ANK was also different from most report on the synthesis of zeolite Y from kaolin where longer crystallization times are reported.

ZSM-5 zeolite was also successfully synthesized from ANK by conventional hydrothermal method using two routes similar to zeolite Y synthesis. The results obtained from the synthesis of ZSM-5 from the ANK metakaolin shows that ZSM-5 formation depends on some basic synthesis conditions mostly crystallization temperature, crystallization time and ageing of the synthesis gel. Maximum crystallinity of ZSM-5 phase was obtained when synthesis was carried out at crystallization time of 48 h, crystallization temperature of 140°C and ageing time at 36 h (room temperature).
CHAPTER FIVE

ZEOLITE MEMBRANES FROM AHOKO NIGERIAN KAOLIN
This section of the thesis deals with the preparation of supported zeolite membranes using ANK as the main precursor of the zeolitic component. The outcome of the work carried out on the preparation of zeolites from kaolin as shown in the previous chapter (chapter 4) shows that kaolin is a good, cheap, viable and environmental benign source of zeolite production. Therefore a more useful product such as zeolite membrane, if produced from kaolin, will certainly go a long way in reducing cost of production. The outcome of the study on the production of zeolites (Zeolite A, Zeolite Y and ZSM-5) from ANK forms the basis for the study on zeolite membrane development.

Chapter 5 : Zeolite Membranes from Ahoko Nigerian Kaolin

5.1 Background on Membranes

A membrane is a material which acts as a semi-permeable barrier separating two phases and restricts fluid movement or transport in a unique or specific way [181]. The material that moves faster through the membrane is called a permeate while the component that is slow is called the retentate. The unique function of a membrane is to obtain an enriched material in the permeate and a residue in the retentate. This separation process is shown in figure 5.1.

A membrane has also been defined in term of its morphology as a material which is discrete but might be thin or thick and functions to moderate the permeation of chemical species in contact with it [183].
Membranes are important in several chemical industries. Some of the early applications of membranes are in the areas of microfiltration, ultrafiltration, osmosis, and dialysis. Greater attention is now being paid to the technology of membrane development in their use in gas separation, pervaporation, and membrane reactors [181].

Membranes are generally divided into three main categories:

- Organic membranes: These basically include all polymeric membrane materials.
- Inorganic membranes: These include all ceramic and metallic membranes.
- Composite membranes: These are also known as hybrid membranes because it is a combination of organic and inorganic membranes.

Membranes are also further divided into two groups.

- Self-supported membranes: In this type of membrane, the materials are deposited onto a temporary support and it is removed after the completion of the synthesis. The major disadvantage of this type of membrane is lack of basic strength required for major chemical or process operation.
- Supported membranes: This is the most common type of membranes. A defect free and continuous membrane layer is grown on top of a stable support material. The support or substrate offers significant mechanical strength to the membrane.

### 5.2 Terminologies used in this Chapter

Before continuing with the work on zeolite membrane development from kaolin, it is necessary to define the basic terms used throughout this chapter of the thesis.

- Zeolite coatings: This refers generally to the deposition of zeolite on support surfaces.
- Zeolite films: This refers to coherent coating of zeolite crystals on support surface i.e when the support is completely covered by the zeolite crystallites.
- Zeolite membrane: This refers to deposition of zeolite crystals on the surface of a porous support usually employed for separation of mixture based on size, adsorption, or diffusion.
• Coherent zeolite membrane: This refers to deposition of zeolite films onto a porous support.

5.3 Organic Membranes

Most polymeric materials can be utilized to synthesise membranes. However, because the chemical and mechanical property of polymers differs, the choice of polymer is dependent on their application. Typical examples of polymers used in membranes and their specific applications are listed in table 5.1. The use of different polymers depends on whether they are used as porous or dense membranes. Porous membranes are applicable in such applications as microfiltration and ultrafiltration while dense membranes are mainly used in gas separation and pervaporation.

Table 5.1: Some of the polymer used in different membrane application [182]

<table>
<thead>
<tr>
<th>Applications</th>
<th>Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microfiltration</td>
<td>Polycarbonate</td>
</tr>
<tr>
<td></td>
<td>Poly (Vinylidene-fluoride)</td>
</tr>
<tr>
<td></td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>Dialysis</td>
<td>Cellulose</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>Aromatic polyamide</td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td>Polysulfone</td>
</tr>
<tr>
<td></td>
<td>Cellulose ester</td>
</tr>
<tr>
<td></td>
<td>Polycrylonitrile</td>
</tr>
<tr>
<td>Gas separation</td>
<td>Polyoxadiaziles</td>
</tr>
<tr>
<td></td>
<td>Polytriazoles</td>
</tr>
</tbody>
</table>

Organic membranes represent over 50% of the entire membrane market [184]. However there are some fundamental problems when compared with inorganic membranes. Some of the important problems of organic membranes include low thermal stability, lack of chemical resistance and lack of mechanical stability. This has led to the development of inorganic membranes. Although inorganic membranes are more expensive, they have certain properties lacking in organic membranes as will be mentioned in the next section.
5.4 Inorganic Membranes

The development of inorganic membranes in the 1940’s onwards was driven by two major industrial advances, namely nuclear power and ultrafiltration/microfiltration processes. Uranium enrichment was based on the fact that inorganic membranes which are mainly ceramic-based can be produced in a very large quantities and are robust compared to polymeric membranes [185]. Furthermore, inorganic membranes were found to be reliable and posses long life even under harsh chemical environments. The advantages and disadvantages of inorganic membranes are shown in table 5.2.

Table 5.2: Comparison of inorganic membranes over organic membranes [184, 185]

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long term stability at high temperatures</td>
<td>High capital cost</td>
</tr>
<tr>
<td>Resistance to harsh environments</td>
<td>Brittle</td>
</tr>
<tr>
<td>Resistance to high pressure drops</td>
<td>Low membrane surface per module volume</td>
</tr>
<tr>
<td>Inertness to microbiological degradation</td>
<td>Difficulty in achieving high selectivities in large scale microporous membrane</td>
</tr>
<tr>
<td>Easy cleanibility after fouling</td>
<td>Low permeability of the highly selective membrane</td>
</tr>
<tr>
<td>Easy catalytic activation</td>
<td>Difficult membrane to module sealing at high temperature</td>
</tr>
<tr>
<td>Greater control of pore dimension and pore size distribution</td>
<td></td>
</tr>
<tr>
<td>High throughput volume</td>
<td></td>
</tr>
</tbody>
</table>

Some examples of popular inorganic membranes are listed below:

- Silica and other oxide ceramic membranes
- Zeolite membranes
- Metal membranes
• Carbon and other non-oxide ceramic membranes
• Proton and oxygen ion conducting ceramic membranes
• Inorganic-organic hybrid membranes

In recent years the increasing usage of inorganic membrane in the field of fuel cells and catalytic reactors has further encourage researchers to think of developing enhanced synthesis strategies for its production.

5.4.1 Division of Inorganic Membranes

Different inorganic membranes are in existence and they are distinguished by the nature of the material used in their preparation and the function performed by them. Inorganic membranes can either be self-supported or supported membranes.

The inorganic membranes can be further divided into two main categories namely:

- Dense membranes
- Porous membranes

Dense Inorganic membrane: These membranes are composed of polycrystalline ceramic or metals which permit the permeation of certain chemical species through their crystal lattice. A typical example is a palladium membrane known to be highly selective toward hydrogen.

Porous inorganic membranes: This type of membrane is composed of a porous metal or ceramic base acting as a support and a porous top layer [185]. The support system contains pore diameter of sufficient size to allow low flow resistance. It also provides the necessary mechanical strength to the small pore top layer. Based on the IUPAC definition, the ranges of pore classification include microporous with pore size less than 2 nm, mesoporous with pore size in the range of 2-50 nm and macroporous with pore size greater than 50 nm. Compared to dense membranes, porous inorganic membranes provide improved permeability as the mechanism of transport is a combination of adsorption-diffusion and permeation based on pore size difference (molecular sieving). In the last century, another type of porous inorganic membrane called microporous inorganic membranes has gained significant interest because of its potential industrial applications.
Microporous inorganic membranes can be further classified as either amorphous or crystalline based on their structure and chemical nature.

Crystalline inorganic membranes are essentially prepared from zeolites. Zeolite membranes have received special attention in the past ten years because of their unique properties. The uniform micropore structure of zeolites gives it an important molecular sieving capability in addition to other properties such as adsorption, catalysis, and ion exchanging [186-188]. Zeolite membranes also offer higher thermal and chemical resistance compared to all other inorganic membranes.

5.5 Background to Zeolite Membranes

Zeolite membranes have remained one of the most studied inorganic membranes because of their wide application. These are not only restricted to separation processes and catalytic membrane reactors but several other emerging processes such as applications in microreactors, sensors, and electrodes [18]. The first reported synthesis of a zeolite membrane was the synthesis of a composite membrane which is a zeolite embedded polymer membrane [189]. This type of membrane has the poor mechanical and chemical stability inherent in the polymer material. The initial effort towards the preparation of polycrystalline zeolite membrane started in the 80s by Suzuki [190], however significant step were taken in the early 90s with the successful synthesis of MFI type zeolite membranes with high quality in terms of separation efficiency [191-197]. Some milestones in the development of zeolite membranes are shown in table 5.3 [198].
Table 5.3: Milestone in the development of zeolite membrane [199]

<table>
<thead>
<tr>
<th><strong>Milestone</strong></th>
<th><strong>Year</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed matrix membrane</td>
<td>1986</td>
</tr>
<tr>
<td>Suzuki patent</td>
<td>1987</td>
</tr>
<tr>
<td>Zeolite A membrane</td>
<td>1991</td>
</tr>
<tr>
<td>Silicalite membrane</td>
<td>1991</td>
</tr>
<tr>
<td>Vapour phase transport method</td>
<td>1994</td>
</tr>
<tr>
<td>Zeolite membrane reactor</td>
<td>1995</td>
</tr>
<tr>
<td>Secondary growth method</td>
<td>1999</td>
</tr>
<tr>
<td>Microelectronic fabrication</td>
<td>2001</td>
</tr>
<tr>
<td>Mitsui plant</td>
<td>2001</td>
</tr>
<tr>
<td>Silicalite b-oriented membrane</td>
<td>2003</td>
</tr>
<tr>
<td>Silicalite coated crystals particles</td>
<td>2004</td>
</tr>
<tr>
<td>Core shell micro-composite</td>
<td>2006</td>
</tr>
</tbody>
</table>

5.6 Type of Zeolite Membranes

Even though there are well over 194 zeolite structure that have been developed [3], only a few zeolites have so far been fabricated into a films and membranes [189, 200].

Zeolites that have been fabricated into a membrane configuration are zeolite A [201, 202] faujasite (zeolite X and Y) [203-205], MFI(ZSM-5 and silicalites) [206, 207], mordenite [208], zeolite P [209], zeolite L [210], and others from the aluminophosphate series such as SAPO-34, and SAPO-5 [211, 212].

The properties of these zeolites are well documented [3]. From all the zeolites fabricated into membranes, ZSM-5 and silicalite are the most widely studied [189]. This is attributed to two factors: firstly, the close proximity between the pore size of MFI zeolites and the kinetic diameter of most hydrocarbons enabling it to function as a molecular sieve and more importantly, the ease of preparation of ZSM-5 and silicalite compared to other zeolite membranes.
5.7 Zeolite Membrane Applications

Zeolites have properties which can be modified to suit specific applications. An example is the tunable hydrophilic/hydrophobic properties of zeolites by modification of the aluminium content of the zeolitic material to change the interaction with water-organic mixture. The application of zeolite membrane in the key areas of separation and membrane reactor is the focus of this section and the zeolites studied in this work (zeolite A, zeolite Y and ZSM-5) form the basis of the discussion.

5.7.1 Applications of Zeolite Membranes in Gas Separation

The separation of gas mixtures is an important industrial application of zeolite membranes. The development of supported zeolite membranes with both high flux and selectivity is good requirement for gas separation. Zeolite membranes can be used in the separation of range of gaseous mixtures including those found during refinery operation and environmental abatement. Table 5.4 shows some of the gas mixture recently studied using zeolite membrane.

<table>
<thead>
<tr>
<th>Zeolites</th>
<th>Chemical species</th>
<th>Support</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5</td>
<td>Butane isomer</td>
<td>α-alumina</td>
<td>[213]</td>
</tr>
<tr>
<td>MFI (ZSM-5)</td>
<td>n-butane/i-butane</td>
<td>α-alumina</td>
<td>[214]</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>CO₂/N₂</td>
<td>α-alumina</td>
<td>[215]</td>
</tr>
<tr>
<td>LTA</td>
<td>N₂/O₂</td>
<td>Carbon</td>
<td>[216]</td>
</tr>
<tr>
<td>Al-ZSM-5</td>
<td>H₂/SF₆</td>
<td>Stainless steel</td>
<td>[217]</td>
</tr>
<tr>
<td>MFI-type</td>
<td>n-butane/i-butane</td>
<td>α-alumina</td>
<td>[191]</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>H₂/N₂</td>
<td>α-alumina</td>
<td>[218]</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>H₂/n-butane</td>
<td>γ-alumina</td>
<td>[219]</td>
</tr>
<tr>
<td>Ce-ZSM-5</td>
<td>H₂/CO₂</td>
<td>α-alumina</td>
<td>[220]</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>n-C₄H₁₀/i-C₄H₁₀</td>
<td>α-alumina</td>
<td>[221]</td>
</tr>
</tbody>
</table>
The mechanisms of gas separation by zeolite membranes is illustrated in figure 5.2. When the pore size of the membrane exceeds an average of 0.1 µm, gases permeates the zeolite membrane by convective flow resulting in no separation. When the pore sizes are smaller than 0.1µm, i.e making the pore size almost the same or smaller than the mean free paths of gas molecules, the permeation through the membrane is governed by Knudsen diffusion. When the pore size is extremely small (≤20 Å), permeation occur via molecular sieving. This process unique to zeolite membranes is complex and includes both diffusion in the gas phase and diffusion of adsorbed phases on the surface of the pores [214].

![Figure 5.2: The mechanism for permeation of gases through porous membrane typical of zeolite membrane](image)

The literature contains substantial information on the applications of different zeolite membrane in gas separation. A-type zeolite membrane have being studied in detail in separating small sized gas mixture such as O₂/N₂, C₂H₄/N₂ [222].

Zeolite membrane with MFI structure have also being extensively studied in the separation of gas mixture such as H₂/hydrocarbon [223] and hydrocarbon mixtures [213].
5.7.2 Applications of Zeolite Membranes in Membrane Reactors

Zeolite membranes have found important applications in the operation of reactors because of their unique properties. A membrane reactor is used to simultaneously carry out reactions and separation in one unit [224]. Higher conversion is usually achieved because of continual removal of one of the products facilitated by the zeolite membrane. Other uses of the zeolite membrane in a reactor include:

- Removal of by-products likely to poison the desired end product and the catalyst.
- Controlling the addition of reagents by limiting their concentration
- Allowing two reactions to take place in a reactor by permeating one product to act as reagent to the other [186]. This takes place when a zeolite membrane is used to selectively allow permeate to act as a reactant for another reaction.

Examples of application of zeolite membrane in reactor to carry out specific reaction are presented in table 5.5.

Table 5.5: Typical examples of zeolite membranes used in membrane reactor

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Type of membrane reactor</th>
<th>Application</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicalite-1</td>
<td>Fixed bed reactor</td>
<td>Ethylbenzene conversion to styrene</td>
<td>[225]</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>Fixed bed reactor</td>
<td>Methyl-Tert-Butyl-ether (MBTE) synthesis</td>
<td>[226]</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>Zeolite membrane reactor</td>
<td>Methanol from CO₂ and H₂</td>
<td>[227]</td>
</tr>
<tr>
<td>Silicalites-1</td>
<td>Fixed bed reactor</td>
<td>Hydro-isomerisation reactions</td>
<td>[228]</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>Fixed bed reactor</td>
<td>Xylene isomerisation</td>
<td>[229]</td>
</tr>
</tbody>
</table>
5.7.3 Application of Zeolite Membrane in Pervaporation

This is one of the foremost applications of zeolite membranes and was the first that was successfully commercialised for the dehydration of alcohol [230]. Pervaporation is defined as permselective vaporization of a liquid mixture (the feed) which is subjected to permeation through a zeolite membrane and the product (permeate) is obtained as vapour at reduced pressure. It is depicted as shown in figure 5.3. It is an energy efficient and effective process and can easily replace more energy consuming processes such as distillation, and adsorption [231]. It can effectively be used to separate difficult liquid mixture such as azeotropies or close boiling mixtures [187].

![Figure 5.3: Schematic illustration of principle of pervaporation](image)

The applications of pervaporation are divided into three areas:

- Dehydration of organic solvents usually carried out by zeolite A and zeolite Y membrane.

- Removal of organic compounds from aqueous solutions usually carried out by ZSM-5 zeolite.

- Separation of anhydrous organic mixtures.

The operation of pervaporation is dependent on the physical nature of the membrane, the physicochemical characteristics of the feed mixture and the permeate-membrane interaction [232]. The usefulness of pervaporation over conventional distillation separation is due to the following factors:
• Reduction of energy demand since only the permeate fraction is vaporised.

• High selectivity especially when there is an absence of any defect, pinhole or non-zeolitic pores in the membrane.

• Simple equipment or instrumentation is required in comparison to distillation.

• It can be used to separate azetropes unlike distillation.

Pervaporation does not depend on vapour-liquid equilibrium as the transport resistance depends on the mobility of the permeate species in the membrane.

The driving force in pervaporation is the pressure difference between the permeate region kept at low pressure and the feed region usually kept at atmospheric or elevated pressure [187].

The mechanism of pervaporation has been explained in detail by Jia et al [233]. It is governed by molecular sieving, diffusion and adsorption. The impact of any of these mechanisms depends on the characteristic of the permeating mixture and also on the inherent properties of the membrane material. For example, the separation of two isomers of butane by pervaporation is governed by molecular sieving because of difference between the two isomers and the pore size of ZSM-5. Pervaporation is a novel separation process developing rapidly because of its effectiveness and energy efficiency during the separation of azeotropic and close-boiling liquid mixture, organic solvent dehydration, and the recovery of highly diluted added value organic species from water [234].

The sequence of steps involved in a typical pervaporation process is summarised below:

• Selective sorption onto the membrane on the feed side

• Selective diffusion through the membrane

• Desorption into the vapour phase on the permeate side

Example of areas of application of zeolite membrane in chemical industry and specific cases of pervaporation carried by zeolite membranes are shown in table 5.6 and 5.7.
Table 5.6: Typical examples of areas of application of zeolite membrane in pervaporation process [31, 232, 239, 241, 287]

<table>
<thead>
<tr>
<th>Application</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Separation of water from organic water/water mixture or dehydration or dewatering</td>
<td>Separation and/or dehydration of water/organic azetropes ((H_2O/\text{EtOH}, H_2O/IPA, H_2O/pyridine, \text{Isopropanol-water system})) Dehydration of organic solvents,</td>
</tr>
<tr>
<td>Extraction of volatile species from aqueous and gaseous stream</td>
<td>Extraction of chlorinated hydrocarbons Separation of aromatic species Dealcoholization of beer and wine Extraction of volatile organic species from air</td>
</tr>
<tr>
<td>Separation of organic/organic mixture</td>
<td>Separation of azetropes ((\text{EtOH/cyclohexane, MeOH/MTBE, EtOH/ETBE})) Separation of isomers (e.g xylenes)</td>
</tr>
<tr>
<td>Acid separation</td>
<td>Acetic acid-water system</td>
</tr>
</tbody>
</table>
Table 5.7: Examples of pervaporation processes performed by zeolite membranes

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Chemical species</th>
<th>Support</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite A</td>
<td>Water/ethanol</td>
<td>Sintered stainless steel</td>
<td>[201]</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>Water/organic mixture</td>
<td>α-alumina</td>
<td>[235]</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>Water/Isopropanol</td>
<td>α-alumina</td>
<td>[236]</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>Ethanol/water</td>
<td>α-alumina</td>
<td>[237]</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>Water/ethanol</td>
<td>Kaolin</td>
<td>[238]</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>Organic water</td>
<td>Alumina</td>
<td>[239]</td>
</tr>
<tr>
<td>Zeolite K-LTL</td>
<td>Aqueous organic mixture</td>
<td>Alumina</td>
<td>[240]</td>
</tr>
<tr>
<td>Silicalite-1</td>
<td>dichlorinated organic compounds</td>
<td>Sintered stainless steel</td>
<td>[241]</td>
</tr>
<tr>
<td>Zeolite T</td>
<td>Water/organic mixture</td>
<td>Mullite</td>
<td>[242]</td>
</tr>
<tr>
<td>B-ZSM-5</td>
<td>Organic/water</td>
<td>Al$_2$O$_3$-coated SiC multi-channel monolith</td>
<td>[243]</td>
</tr>
<tr>
<td>X-type zeolite membrane</td>
<td>1,3propanediol/glycerol</td>
<td>Alumina</td>
<td>[244]</td>
</tr>
</tbody>
</table>

5.7.4 Other Applications of Zeolite Membranes

In addition to the uses of zeolite membranes in the areas of separation of liquid or gas mixture, catalysis and as an ion exchange materials. They have recently been investigated
Development of zeolites and zeolite membranes from Ahoko Nigerian Kaolin

A.S.Kovo, 2010

for other applications to further exploit the uniqueness in their structure [189]. Some of the most recent applications of zeolite membranes are briefly described:

- **The use of zeolite membrane as ionic conductors:** The presence of aluminium atoms in the zeolite framework induces a negative overall charge. This unique property enables zeolites to have the capacity to occlude the charge balancing cation within the pore spaces of the zeolite framework. In addition, the concentration of the cation in the framework can be tuned by varying the Si/Al ratio in the framework. This enables the insertion of different types of cations into the framework by ion exchange, thereby altering its properties. This property allows zeolites to behave as an ion conductor and can be used as a solid electrolyte in fuel cells, chemical sensors and batteries. Ionic conduction in medium pore zeolites (X-ZSM-5 (X = Li, Na, K, Pb)) and large pore zeolites such as faujasite have been studied to ascertain the behaviour of cations and other occluded material such as water within their frameworks. According to the work of Nair et al. [189], ionic conduction increases with decreasing Si/Al ratio in all zeolites. In addition, sodium ion occluded zeolites are known to have the highest ionic conduction compared to other cations. This was speculated to be related to the strong interaction between Na$^+$ ion and water molecule present in the framework leading to enhanced cation mobility.

- **Zeolite membrane and films as nanostructured host and dielectrics:** The presence of uniform void spaces in the zeolite framework makes it an ideal candidate as a host material. They can conveniently play host to series of nanostructural material such as nanowires, nanotubes and nanoclusters. The development in the synthesis strategies available for preparing defect-free zeolite material has provided the opportunity to make array of nano-structured material inside the zeolite cages.

### 5.8 Zeolite Membrane Synthesis

Hydrothermal synthesis represents the most common method of preparation of zeolite membranes and films. Hydrothermal synthesis is a process whereby zeolite layers are deposited on the surface of supports through crystallization of an aluminosilicate mixture in the form of a gel or clear solution. This is formulated from deionised water, a silica
source, an alumina source, a structural directing agent (SDA) and a mineralizing agent (usually NaOH). The synthesis of the zeolite membrane is performed via hydrothermal crystallization similar to the synthesis of zeolite powder. The gel or clear solution formed from mixing the synthesis precursors are placed in contact with the support in a reactor, usually an autoclave, and the preferred zeolite is grown on the supports depending on the controlled thermodynamic conditions such as time and temperature of crystallization, and the composition. Several precursors have been used as source of silica and alumina to synthesis zeolite membrane. These are well known commercial chemicals (Table 5.8). To date, kaolin has not been utilized as a source of silica and alumina to fabricate zeolite membranes.
Table 5.8: Some precursors used in zeolite membranes/ films preparation

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Precursor used</th>
<th>Thickness</th>
<th>Supports used</th>
<th>Method of synthesis</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite A</td>
<td>Sodium silicate, sodium aluminate granular</td>
<td>0.6 µm</td>
<td>Stainless steel plate</td>
<td>In-situ method plus sonication control</td>
<td>[245]</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>Water glass $\text{SiO}_2$, Sodium aluminate</td>
<td>0.4-3.8 µm</td>
<td>Porous alumina</td>
<td>Secondary growth</td>
<td>[202]</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>Sodium aluminate, water glass</td>
<td>2.5 µm</td>
<td>Porous alumina</td>
<td>In-situ crystallization</td>
<td>[246]</td>
</tr>
<tr>
<td>Zeolite 4A</td>
<td>Sodium silicate, sodium aluminate</td>
<td>25-80 µm</td>
<td>Stainless steel</td>
<td>Secondary growth</td>
<td>[247]</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>Ludox AS-40, sodium aluminate</td>
<td>5 µm</td>
<td>Sintered stainless steel</td>
<td>Secondary growth</td>
<td>[201]</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>Aluminium sulphate, silica</td>
<td>25 µm</td>
<td>Alumina</td>
<td>Secondary growth</td>
<td>[218]</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>Tetraethylorthosilicate, aluminium foil</td>
<td>30 µm</td>
<td>Alumina</td>
<td>In-situ crystallization</td>
<td>[223]</td>
</tr>
<tr>
<td>Zeolite Y</td>
<td>Sodium aluminate, water glass</td>
<td>8.13 µm</td>
<td>Secondary growth</td>
<td>[248]</td>
<td></td>
</tr>
<tr>
<td>Zeolite Y</td>
<td>Water glass, sodium aluminate</td>
<td>3 µm</td>
<td>Alumina</td>
<td>Secondary growth</td>
<td>[249]</td>
</tr>
</tbody>
</table>

Nucleation and growth of zeolite crystals is expected to take place on the support. However, this is not always the case as nucleation can happen in the bulk solution leading to poor growth and coverage. Defect and pinholes are permanent feature in zeolite membranes and eliminating them is almost impossible [250] but several post synthesis methods have also been proposed [251]. Some of the post synthesis methods are coking, chemical vapour deposition and silane coupling [252]. Several preparative strategies are
reported for zeolite membrane synthesis [250, 253-257] as will be discussed in section 5.8.1.

5.8.1 Method of Zeolite Membrane Synthesis

Some of the well known methods of preparation of zeolite membrane are listed below:

- In-situ crystallization
- Secondary (seeded) growth process
- Vapour phase transport

5.8.1.1 In-situ Hydrothermal Method

In-situ hydrothermal synthesis is the most popular and commonly used method of preparing a supported zeolite membrane. The method basically involves bringing together the synthesis solution or gel and the support in a reactor (usually an autoclave) and allowing the zeolite film to grow on the surface of the support under hydrothermal conditions.

In-situ crystallization mostly takes place via a heterogeneous growth mechanism. The mechanism, which is still a subject of debate, requires the formation of zeolite nuclei on the surface of the support and this is followed by crystal growth forming coherent zeolite films covering the support. This method requires stringent control of certain conditions to allow supersaturation, nucleation and crystallization to take place on the surface or close to the support in order to obtain a continuous and an inter-grown zeolite film.

Some of these conditions include:

1. Composition of the synthesis solution or gel
2. The type of supports
3. Pre-treatment or modification of supports
4. The orientation of support when immersed in the synthesis solution or gel
5. Synthesis parameters such as time, temperature of crystallization, number of synthesis cycle.

Following crystallization, the supports are removed from the synthesis gel after cooling and then are calcined (where necessary) and dried in an oven.

The method is similar to the process of making zeolite powders. The physical and chemical nature of the support has a great influence on the interaction between the synthesis solution or gel and the support itself. For example, aluminium can diffuse into a zeolite framework when alumina supports are used and this can technically transform the zeolite into a different phase [231].

The position of a support in the reactor can also be a significant factor. Substrates are usually placed vertically in a synthesis mixture to avoid sedimentation of particles under gravity. This is to enable better synthesis mixture–support interaction and adhesion and to prevent forming extremely thick films.

Some of the advantages of the in-situ process are:

- Simplicity
- Practicability

Some of the problems of in-situ crystallization have also been highlighted. This includes:

- Lack of control of nucleation and crystal growth.
- In-situ crystallization usually requires longer time resulting in the formation of impure zeolitic phase [258].

5.8.1.2 Secondary (Seeded) Growth Method

The secondary growth method is considered to be an advancement over the in-situ method. The method involves the growth of zeolite seed crystals which is deposited well in advance onto the substrate. This is followed closely by the transformation of zeolite synthesis gel via hydrothermal treatment. This method allows the synthesis of orderly and well-aligned crystal in the substrate unlike the in-situ crystallization method. The major advantage of this method is the reproducibility which is almost absent in the in-situ process. Other advantages include:
1. Low crystallization temperature

2. Shorter crystallization time

3. Less stringent conditions to form coherent zeolite films

4. A preferred method for large scale production of zeolite membranes

The secondary growth method involved two basic steps:

1. Use of zeolite seeds to coat the support surface

2. Crystal growth of the seed layer into a continuous zeolite membrane using a zeolite synthesis mixture (gel or solution).

Several methods are used in the preparation of seeded supports. These are dip coating [259] spin coating [260], chemical vapour deposition [261], pulsed laser ablation [262], and vacuum seeding [263].

Zeolite seeds are usually prepared as a colloidal sol via hydrothermal synthesis just like powder synthesis or through ball milling of commercial zeolite powder as applied in this research.

The second step is basically the same as the in-situ crystallization method. This involves allowing the seeds to grow into a compact, coherent film by contacting the seeded substrate and performing hydrothermal crystallization or synthesis.

**5.8.1.3 Vapour Phase Transport Method (VPT)**

This method is based on high temperature steam treatment of a dry gel converting it into a thin film of zeolite by nucleation and crystallization on the surface of the support [264]

This method allows complete conversion of the reacting gel into a zeolite layer thereby allowing the possibility of obtaining a zeolite membrane with high Si/Al ratio [265]. This is a major advantage over the in-situ method.

The VPT method comprises of two steps, namely:

- Formation of a hydrogel of silica, alumina, and sodium on the support surface. Usually the support is placed in a holder inside the autoclave.
The second step is the actual crystallization of the dry gel in the reactor with steam generated from the liquid content of the reacting species.

The steam used can be generated in two different ways. First, it can be made from water and the SDA or template fed to the dry gel by saturated vapour pressure. This method can lead to low consumption of the SDA. The second but preferred method involves placing the SDA in the support along with other solid material and allowing only the water to generate the steam [266]. This allows the utilization of the SDA in the formation of the desired structure and also leads to the formation of a thin and oriented film.

### 5.9 Support Materials for Zeolite Films/ Membrane Synthesis

Supports are used in the synthesis of zeolite membrane basically to provide mechanical strength and durability to the membrane. In addition, the choice of the proper support is significant in zeolite membrane/film preparation as nucleation, crystallization and growth are expected to take place on the surface of the substrate. Adhesion of the zeolite layer is important in zeolite membrane synthesis and is known to depend on the type of support [264]. For example, ZSM-5 is known to adhere well to stainless steel and silver [186]. The supports used in zeolite synthesis come in different shapes such as disc, tubular, and multi-channel monoliths [3].

It has been reported that the structural properties and the chemical nature of the support plays a significant role on the type of zeolite formed and their growth characteristics. There are several types of support presently used in zeolite membrane preparation. These include α-alumina [267], λ-alumina [268], stainless steel[245], glass [269], and zirconia[270]. However, the common type used for zeolite membrane synthesis is alumina and stainless steel[217]. Alumina is used because of its compatibility with zeolite synthesis gel/solution. Metal oxides such as alumina and titanium are known to provide a better environment for zeolite deposition, adhesion and anchorage [264], hence they are widely used. Alumina’s biggest disadvantage is the brittleness which makes an alumina support poor in some applications. Hence the support of choice for most zeolite membranes synthesis is stainless steel. Stainless steel is important in zeolite membrane synthesis because of the following reasons [217]: It has high and superior heat conductivity and can be used in many membrane reactors where heat transfer is desirable.
• It can be applied in many high temperature applications and this is particularly desirable because most industrial processes take place at high temperature.

• It can easily be integrated into the membrane module.

• It is cheaper.

The pore size of the substrate is vital when used as a support for zeolite membrane synthesis. The pores of the support should be small compared to the zeolite crystal being deposited in order to form a continuous zeolite film. SEM image of the support used in this study is shown in figure 5.4.

Figure 5.4: SEM image of stainless steel support used in this research showing both (A) the surface morphology and (B) the edge view.

Deposition of zeolite synthesis mixture onto the support to obtain good adhesion is a vital aspect of support selection in zeolite membrane synthesis. All supports are usually modified to ensure better synthesis mixture-support interaction because the as-received support contain carbon deposits and surface contaminants which have detrimental effect on zeolite nucleation and their removal is necessary for good film coverage [271].
Chemical treatment and air calcination methods are the main pre-support treatment technique. These remove the contaminants and introduce some micro-surface roughness which is known to enhance adhesion of zeolite membranes. In addition surface oxides are known to promote zeolite nucleation because of interaction by the –OH group and the zeolite synthesis gel [247]. It also burns off all organic and other contaminants present. Chemical modifications are usually performed by acid treatment of the support surface. Mineral acid such as nitric acid, hydrochloric acid are often used as they cause etching of the supports surface. These introduce structural and chemical modification of the support and remove the surface contaminant.

There is no global rule on the type of modification process for supports used in the synthesis of zeolite membranes/films. Both treatment processes will be investigated in this study to synthesis zeolites membranes/films from kaolin.

### 5.10 Mechanism of Zeolite Membrane Formation

The exact mechanism of formation of supported zeolite membranes/films from reacting species and the influence of different supports material is a complex process that is yet to be fully understood [272]. Zeolite membrane synthesis is still a new subject and in its infancy state. The prediction of the most appropriate conditions of synthesis and mechanism of preparing defect free and high coverage films are evolving [273]. It is a process that involves several steps because the autoclaves or reactors used for zeolite membrane synthesis contain two or three different materials which are directly involved in the reactions leading up to the formation of the membrane/film. The different materials present in zeolite membrane formation include:

- Synthesis gel or solution
- Supports or substrates
- Seed crystals

The effect of the three listed materials are responsible for the classification of zeolite membrane formation into five classes according to Lin et al [198]. The first three classes (1-3) occur by a process called homogenous nucleation whereby zeolite layers are formed on the surface of the substrate by the physical deposition of zeolite nuclei followed by homogenous crystal growth in the synthesis gel or solution [198]. The deposition of the
nuclei on the surface of the support can be as a result of gravity or any other physical attractive force between the substrate and the synthesis solution or gel.

Class 2 describes the formation of zeolite membrane with minimum deposition of zeolite crystals, whereby the deposition of zeolite nuclei is restricted, this usually leads to synthesis of zeolite membrane with reduced thickness and is the preferred method for the in-situ crystallization method of zeolite membrane synthesis. The supports are usually in vertical or slanted position causing the zeolite nuclei to fall under gravity to the bottom of the reactor or autoclave. In this case the surface of the support has a significant influence on the formation of the zeolite membrane.

Class 3 is zeolite membrane formation process whereby the seeded zeolite crystals are used to promote nucleation and create viable growth sites on the substrate surfaces. Zeolite A membrane has been prepared following this mechanism [274]. In this particular synthesis, the membrane was prepared on the outer surface of tubular support. The seeded crystals goes through a process of dissolution and formation of amorphous gel on the support surface before the transformation of the gel into zeolite and subsequent formation of zeolite membrane via nucleation and growth sequence. This mechanism usually results in the formation of a polycrystalline membrane with random orientation.

The formation of zeolite membranes can also happen within the vicinity of heterogeneous nucleation and this is illustrated by class 4. This involves heterogeneous nucleation on or close to the support surface and subsequent growing of crystal of continuous zeolite layer usually with preferred orientation. Clear solutions with high concentration is preferred over gel solution for this process. Preferred orientation of the nuclei which cause a preferred growth direction can be responsible for the formation oriented zeolite membrane [198].

The secondary growth mechanism, which is use to prepare highly reproducible zeolite membranes is illustrated by class 5. Just like class 3, the zeolite seeds are deposited on the supported usually by physical means (e.g. dip coating or physical rubbing) and during the hydrothermal synthesis, the seeded crystals grow early limiting the induction phase and oriented zeolite layers are formed. Longer times of crystallization are discouraged. These processes allow the formation of the expected zeolite phase as opposed to other competing phases which are prevalent when in-situ hydrothermal mechanism is used.
5.11 Experimental

This section describes all the experiments performed in the preparation of supported zeolite films and membranes using ANK as a combined source of silica and alumina. The sequence of work from the support pre-treatments and the actual fabrication of zeolite films and membranes using modified in-situ method (MIM) and secondary growth method (SGM) on modified stainless steels are hereby presented.

5.11.1 Materials used in The Synthesis of Zeolite A, ZSM5 and Zeolite Y Films and Membranes

The materials used were obtained from range of sources. Non-porous stainless steel was sourced from Multi-Metal Service Ltd, Lancashire, UK. The non-porous stainless steel was cut into 20mm×20mm pieces with a thickness is 1.5mm. Porous stainless steel with diameter 20mm and pore size of 0.5µm was obtained from Aegis Advanced Material, UK. Metakaolin was obtained from ANK calcined at 600°C for 10min. Ludox AS 40 (Aldrich) was used as an additional source of silica, Tetra methyl ammonium hydroxide (TPAOH) 1M (Aldrich) serves as the structural directing agent (SDA) for ZSM-5 films and membrane synthesis. Sodium hydroxide (Aldrich) and deionised water are the other reagents used in the preparation of the zeolite films and membranes.

5.11.2 Support Modification

The nature of the support is vital in zeolite membrane/film preparation as it is important to have good synthesis gel/substrate interaction and/or adhesion. Therefore, it is important to investigate and understand the influence of the support surface on zeolite membrane formation from kaolin. Two types of modification techniques ie etching and surface oxidation were used. The surface coverage and in some cases the thickness of the growing zeolite film/membrane was studied in order to confirm the best modification method.

5.11.2.1 Pre-Treatment of Support Materials

Two types of the same material, non-porous and porous stainless steel were used. The non-porous and porous stainless steels were roughened using sand paper of grid size 800. The
supports were then washed by soaking in Dish-Bac detergent and followed by sonication for 2h to remove grease and other dirt. The stainless steel was subsequently rinsed with deionised water and left to dry at room temperature over night. SEM and XRD analysis of both the cleaned non-porous and porous stainless steels were performed.

The two modification methods used to study the adhesion of a zeolite crystallite on a metal surface were developed by Davies. P et al and Hang Chau et al [264, 275]. The cleaned substrates were divided into two sets. The first set (called etched) were treated with 2.2M KOH, washed with deionised water and then treated with 37% concentrated HCl. Thereafter, these set of supports was washed in 1M NaOH solution to remove all chloride ions before washing again in deionised water. The supports were then left to dry at 60°C over night.

The second set of supports (called oxidised) were kept in an air oven at a temperature of 650°C for 10 h. The two set of supports were then characterized by XRD and SEM to record the change in structure and morphology. The supports were then used in the synthesis of zeolite membrane/films.

5.11.3 Preparation of Zeolite Films/Membranes

Modified in-situ method (MIM) and secondary growth methods (SGM) were used to prepare the zeolite films and membranes from kaolin and the effect of supports treatment on the film/ membrane formed were studied.

The feasibility of making zeolite membrane from kaolin was investigated by firstly preparing zeolite films on non-porous stainless steel and the result used to synthesise the zeolite membranes.

All syntheses were carried out in a Teflon-lined stainless steel autoclave. In all cases, the autoclaves were cleaned between each synthesis using 10wt. % NaOH solution which was heated in an oven and maintained at a temperature of 170°C for at least 6 h.
5.11.3.1 Synthesis of Zeolite A Films from ANK using Modified In-situ and Secondary Growth Method on Non-porous Stainless Steel Supports

The preparation of zeolite A films was initially carried out on a non-porous support by MIM and SGM to investigate the interaction between non-porous support and synthesis solution prepared from metakaolin. Non-porous stainless was used because they are cheap and will enable the study of best synthesis conditions for film formation from kaolin before using the more expensive porous stainless steel.

Films of zeolite A with molar composition of $3.75\text{Na}_2\text{O}:2\text{Al}_2\text{O}_3:2.5\text{SiO}_2:243\text{H}_2\text{O}$ was grown hydrothermally on the non-porous supports at different crystallization time based on our earlier work on the synthesis of zeolites powder from Ahoko Nigerian kaolin in chapter 4. Metakaolin [276] served as a combined source of silica and alumina, NaOH was used as mineraliser.

5.11.3.1.1. Preparation of Zeolite A films using Modified in-situ Method

This method involves coating the supports with a film of metakaolin to serve as a growth centre. 0.2g of the 3g of metakaolin required to prepare zeolite A synthesis solution was added to 25ml of deionised water and the supports (etched and oxidised) were immersed into it. This was then heated until dehydration formed a film of metakaolin on the metal surface. In order to prepare the synthesis mixture or gel, 15.74 g of deionised water was mixed with 1.425 g of NaOH in a closed plastic bottle and was stirred for 5min to enhance dissolution of the NaOH. Thereafter the outstanding 2.8 g of metakaolin was added to the NaOH solution and was aged at room temperature for 24 h under continuous stirring. After the ageing, the support coated with metakaolin film was put vertically into an autoclave with the aid of our home-made Teflon holder (figure 5.5). Hydrothermal crystallization was performed in a preheated oven at a constant temperature of 100°C while the crystallization time was varied from 3-12h.
5.11.3.1.2. Preparation of Zeolite A films using Secondary Growth Method

Seed preparation

Commercial zeolite A (BDH England) were used in the preparation of the seeds similar to Li et al [244]. The zeolites powder was crushed gently in an agate mortar and then milled. Ball milling of the zeolite powder were ground based on the following parameters [277]:

- Vessel: A 500 mL plastic bottle was used (radius 1.375”).
- Speed: 160 rpm
- Grinding media: Ceramic (zircon oxide) beads, D=1mm.
- Amount of material: 250 mL
- Wetting agent: water, 250 mL
- Grinding time: 24 h

At the end of the ball milling operations, the grinding media was separated from the mixture.

Thereafter the slurry of the zeolite was formed with deionised water. The slurry was treated in an ultrasonic bath for 5 h and the suspension obtained was kept in the slurry bottle for 7 days allowing the heavier particles to completely settle while the smaller

Figure 5.5: Schematic representation of autoclave used in the hydrothermal synthesis with the home-made Teflon holder
fraction remained to form the colloidal suspension. The pH were determined as well as the particle size with the aid of Zetasizer 3000HS.

**Seeding of colloidal zeolites**

Seeding of the supports was performed using the dip coating method. The support was dipped into the colloidal suspension for 2 min and removed slowly and vertically. The supports were dried for 30 min at room temperature and then for 30 min at 100°C. This process of seeding was repeated twice to ensure complete coverage of the substrate surface.

**Preparation of Synthesis Gel**

The major difference between the SGM and the MIM is the decoupling of the nucleation and crystal growth component or phase. With the seeded support, crystal growth is mainly restricted to the surface of the support and this promotes quick formation of the zeolitic phases on the surface of the support.

The synthesis gel was prepared as follows:

The two sets of modified stainless steel supports were also used in this synthesis. For zeolite A membrane/film, NaOH solution was prepared by adding 1.40 g of NaOH to 15.74 g of deionised water. This was followed by adding 3g of kaolin. The gel obtained was stirred continuously. Ageing of the synthesis gel was carried out for 24 h. At the end of the ageing phase, the seeded supports (both etched and oxidised) were put into the autoclave vertically. This was followed by careful pouring of the synthesis gel into the autoclave making sure that the gel did not hit the supports. The hydrothermal reaction was performed at a temperature of 100°C in a preheated oven. Crystallization time was also varied between 3, 6, 9, and 12 h.

**5.11.3.1.3 Synthesis of Zeolite A Membrane on Porous Stainless Steel Supports from ANK using Modified In-situ and Secondary Growth Method**

Zeolite A membrane was then developed based on the best crystallization time obtained for the films. The method used to prepare the films was repeated to prepare A-membrane on
both etched and oxidised porous stainless steel following the same procedure and using crystallization time of 9 h and 6 h for MIM and SGM respectively.

5.11.3.2 Synthesis of ZSM-5 Films from ANK using Modified in-situ and Secondary Growth Method on Non-porous Stainless Steel Supports

ZSM-5 films were developed from ANK using the two synthesis method MIM and SGM. The molar composition of the starting aluminosilicate gel was chosen also based on the study in chapter four as $23.4\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot83.4\text{SiO}_2\cdot4.2\text{(TPA)}_2\text{O}\cdot375\text{H}_2\text{O}$. In addition to the metakaolin and NaOH, Ludox AS40 (Aldrich) served as an additional source of silica while TPAOH was used as a template.

5.11.3.2.1 Preparation of ZSM-5 films using Modified In-situ Method

The ZSM-5 films were prepared as follows. 0.1g of the 1g required to prepare ZSM-5 synthesis mixture was also added to 25ml of deionised water and the supports added to it. The supports/ metakaolin solution was evaporated to dryness and a film was formed on the substrates. The synthesis gel was then prepared as follows: A solution of NaOH was prepared by adding 6.59 g of NaOH pellets to 11.05 g of deionised water. 42.99 g of additional silica provided by Ludox AS 40 was added to the NaOH solution under vigorous stirring. This was immediately followed by the addition of 15 g of (TPA)$_2$O acting as structural directing agent. The remaining 0.9 g of metakaolin was finally added to the above gel and the vigorous stirring was continued for 2 h. The resulting gel was left to aged for 48 h. After ageing, the supports were put vertically into the autoclave. Hydrothermal crystallization was carried at a constant temperature of 170°C while the crystallization time was varied from 24-72 h.

After each synthesis, the autoclaves were removed from the oven and quenched in cold water. The support was then removed and washed with deionised water via vacuum filtration system until the pH was below 8.0. The excess zeolite powder obtained in each synthesis was also washed until the pH is below 8 and kept for analysis.

The ZSM-5 films and powder were then calcined by heating from room temperature to 500°C at a heating rate of 1°C/min to remove the structural directing agent (SDA) for all ZSM-5 samples. A low heating rate was used to prevent the film from cracking or creating...
defects on the surface of the film since stainless steel is known to have a high thermal expansion coefficient [255].

5.11.3.2 Preparation of ZSM-5 films using Secondary Growth Method

Commercial ZSM-5 zeolite (EKA Sweden) was obtained and preparation of the colloidal seed and the actual seeding was carried out similar to zeolite A earlier described.

The synthesis gel was prepared as follows: A solution of NaOH was prepared by adding 6.59g of NaOH pellets to 11.05 g of deionised water. 42.99 g of additional silica provided by Ludox AS 40 was added to the NaOH solution under vigorous stirring. This was followed by the addition of 15 g of TPAOH to act as a structural directing agent. 1.0 g of metakaolin was finally added to the above gel and vigorously stirred for 2h. The resulting gel was left to age for 48 h. After ageing, the supports were put vertically into the autoclave with the aid of the Teflon holder. Hydrothermal crystallization was done at a constant temperature of 170°C while the crystallization time was varied from 24, 36, 48 and 72 h. After each synthesis, the autoclaves were removed from the static oven, and cooled. The membrane/film was then removed and washed with deionised water via vacuum filtration system until the pH is below 8.0. The excess zeolite powder obtained in each synthesis was also washed until the pH was below 8 and retained for analysis. The SDA was also removed as previously described.

5.11.3.2.3: Synthesis of ZSM-5 Membrane on Porous Stainless Steel Supports using Modified In-situ and Secondary Growth Method from ANK

ZSM-5 membrane was then developed based on the best crystallization time obtained for the films. The method used to prepare the films was repeated to prepare ZSM-5 membrane on both etched and oxidised porous stainless steel following the same procedure and using crystallization time of 48 h and 36 h for MIM and SGM respectively.

5.11.3.3 Synthesis of Zeolite Y Films from ANK using Modified In-situ and Secondary Growth Method on Non-porous Stainless Steel Supports

Zeolite Y films was also produced using the two techniques and the molar composition of the starting aluminosilicate was taken from the study on zeolite Y powder synthesis in
chapter 4 as $15\text{Na}_2\text{O}: \text{Al}_2\text{O}_3:15\text{SiO}_2:450\text{H}_2\text{O}$. Sodium metasilicate (Aldrich) serve as source of additional silica in addition to other reagents used as before.

### 5.11.3.3.1 Preparation of Zeolite Y using Modified In-situ Method

Zeolite Y films was synthesised using the MIM technique as follows: 0.1g of the required metakaolin used to prepare zeolite Y was used to coat the supports following the similar procedure like zeolite A and ZSM-5. The synthesis gel was then prepared as follows, An alkaline solution was initially prepared by adding 0.5 g of NaOH to 29.9 g of deionised water. The solution was then divided into two parts. To one part, 5.8 g of sodium metasilicate which act as additional silica in zeolite Y synthesis from kaolin was added and stirred for 10 min and to the second part, 0.9 g of the outstanding metakaolin was added and also stirred for 10 min. The two solutions were mixed and then aged 48 h at room temperature. After the ageing of the aluminosilicate gel, the coated support was put into the Teflon line autoclave in vertical position with the aid of the Teflon holder and the synthesis gel was carefully pour into it making sure the gel does not strike the support surface. Hydrothermal synthesis was carried out at 100°C and time of crystallization was varied between the range of 3, 6, 9 and 12 h. The film and excess powder obtained was washed and dried and kept for analysis.

### 5.11.3.3.2 Preparation of Zeolite Y using Secondary Growth Method

Colloidal seeds was also prepared from commercial zeolite Y (Zeolyst, USA) and followed by coating on the supports using the same procedure as described for zeolite A earlier.

The synthesis of zeolite Y film by SGM is similar to the description given for the zeolite Y film preparation by MIM except that instead of using 0.9 g outstanding metakaolin to prepare the synthesis gel, 1 g of metakaolin was used while the rest procedure are the same.
5.11.3.3 Synthesis of Zeolite Y Membrane on Porous Stainless Steel Supports using Modified In-situ and Secondary Growth Method from ANK

The most favourable condition for the synthesis of zeolite Y films was chosen as 9 and 9 h for MIM and SGM and was repeated to prepare zeolite membrane on etched and oxidised support using the same procedure as the earlier zeolite Y films synthesised.

5.11.3.4 Quality Testing of the Synthesised Zeolite Membranes from ANK.

The zeolite membranes synthesised from ANK such as zeolite A, zeolite Y and ZSM-5 membranes on the modified porous stainless steel were evaluated in term of their separation performance and defect appearance. A laboratory pervaporation cell was designed and built to test the quality of the developed membrane. The diagram of the designed pervaporation cell is given in figure 5.6 and description of the experimental procedure for the testing of the zeolite membrane is presented.

![Diagram of pervaporation cell](image)

Figure 5.6: A simplified pervaporation set up used in testing zeolite membranes from ANK

Two set of experiment were performed using the pervaporation rig in figure 5.6. The first experiment was carried using a bulk molecule triisopropylbenzene (TIPB) to test the
coherence of the fabricated zeolite membrane and the second experiment involved
determination of the separation performance of the synthesized zeolite membrane by using
a constant concentration of ethanol/water mixture.

In the first experiment, a feed of constant composition of 95wt % of TIPB in water was
prepared and put in the feed container above the membranes while the second experiment
was carried out following the work of Holmes et al [201] with some modification. The
water/ethanol mixture solution with constant composition of 5wt %/95wt% was prepared
at constant temperature and was well mixed to avoid the problem of temperature and
concentration polarization. The feeds were put into the feed container and permeation was
performed with the vacuum pump creating the necessary driving force causing permeation.
The flux and the separation performance was evaluated by removing the permeate from the
liquid nitrogen trap followed by weighing and compositional analysis using GC.

The key parameters used in evaluating the efficiency of zeolite membrane are the flux (J)
and selectivity (α).

The flux is defined and calculated using the following equation:

\[ J = \frac{w}{tA} \tag{5-1} \]

Where

- W is the total weight of the permeate (g)
- t is the collection time (h)
- A is the effective membrane separation area (m²)

The selectivity or separation factor is defined by the equation:

\[ selectivity (\alpha) = \frac{x_w}{x_e} \frac{permeate}{feed} \tag{5-2} \]

Where \( x_w \) and \( x_e \) are the weight fraction of water and ethanol component
5.12 Results and Discussion

This section presents the outcome of the investigation carried out on the development of supported zeolite films and membranes using Ahoko Nigerian kaolin (ANK) as the source of zeolite synthesis precursor.

5.12.1 Stainless Steel Supports Characterization

The significance of supported zeolite films and membranes over free-standing zeolite films and membrane is the presence of a support which facilitate the mechanical stability and sufficient permeability for material passing through the zeolite membranes.

In this study, stainless steel was chosen over other supports such as alumina, zirconia, because they are cheap and show compatibility with most zeolite films precursors. However the synthesis of zeolites films and membrane on the surface of metals is difficult and sometime require long exposure time to obtain a good synthesis, in addition, the presence of impurities such as grease and other organic materials can retards nucleation of zeolites taking place on the support. Therefore modification of support plays a significant role in zeolite films and membrane formation as it influences the nucleation, crystal growth and films adhesion [264]. The interaction between the support surface and the zeolite crystals is vital hence it is important to modify the support used in zeolite coatings preparation in order to promote bonding between the supports and the zeolite synthesis gel.

Non-porous stainless steels were used to fabricate zeolite films from kaolin and the outcome of the investigation was used to prepare zeolite membranes on porous stainless steel. Non-porous stainless steel was used because it is cheap and help to initially study synthesis conditions of film formation on stainless steel before using the expensive porous support. The as-received stainless steel based on SEM (not shown) have contaminant deposits which can potentially interfere or impede the crystallization of zeolite layer on support surface, hence it is important to carried out a good cleaning before the actual pre-treatment. The SEM of the washed support reveal clean and smooth surfaces of stainless steel with no visible impurities or organic contaminants. The XRD of the stainless steel revealed that only iron phase is present in the surface at standard 2-theta = 43.5° (appendix C).
The SEM images for the modified non-porous and porous stainless are shown in figure 5.7 and 5.8 while the XRD patterns of the modified stainless steel are shown in figure 5.9 and 5.10. The SEM images of both modified stainless steels reveal that both have rough surfaces which are known to promote zeolite nucleation [278]. It has been revealed that metal imperfection can act as a growth centre for zeolite crystal formation and etching of the stainless steel generally create a number of imperfect points on the surface of the steel.

While there might be change in the microstructure of the stainless steel after etching in 37% HCl and 2 M of KOH as shown in the XRD of the etched support (figure 5.9 and 5.11), oxidation of the stainless steel at 550°C for 10h causes a visible change of colour to dark brown indication that oxidation has indeed taken place.

The XRD pattern of the oxidised supports (figure 5.10 and 5.12) shows the transformation of the stainless steel into haematite phase [264] which is a crystalline iron oxide.

The two modified support was used for the synthesis of zeolite A, ZSM-5 and zeolite Y membrane.
Figure 5.9: XRD pattern of etched non-porous stainless steel

Figure 5.10: XRD pattern of oxidised non-porous stainless steel
The chemical composition of the support used in this work was also analysed by EDAX to understand the effect of modification on the chemical reactivity of the support. The result is shown in table 5.9. Again the chemical analysis shows the transformation taking place...
similar to the work carried out by Chau et al [264]. The chemical analysis of the cleaned support indicate that the support mainly contain Fe, Cr, Ni and O\textsubscript{2}. The modification of the supports indicate that oxidised supports shows evolution of oxide layer as there was an increase in the composition of oxygen in the oxidised stainless steel than in the cleaned support in all cases i.e. both the non-porous and porous stainless steel. This indicate that the Fe at the surface of the oxidised support mostly exist as Fe\textsubscript{2}O\textsubscript{3} corroborating the earlier result of the XRD analysis which show the transformation of Fe into haematite phase.

The etching of the support with HCl removes both organic and inorganic contaminant still present in the support. Significantly, as shown in table 5.9, the etching process remove the native oxide layer and in the process expose the underlying the metal.

<table>
<thead>
<tr>
<th>Stainless steel</th>
<th>C</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cleaned non porous</td>
<td>0.00</td>
<td>18.06</td>
<td>72.49</td>
<td>7.99</td>
<td>1.47</td>
</tr>
<tr>
<td>Etched non porous</td>
<td>0.00</td>
<td>18.45</td>
<td>68.51</td>
<td>8.35</td>
<td>4.68</td>
</tr>
<tr>
<td>Oxidised non-porous</td>
<td>0.00</td>
<td>17.86</td>
<td>67.41</td>
<td>7.30</td>
<td>7.43</td>
</tr>
<tr>
<td>Cleaned porous</td>
<td>0.00</td>
<td>18.79</td>
<td>68.65</td>
<td>10.41</td>
<td>1.41</td>
</tr>
<tr>
<td>Etched porous</td>
<td>0.00</td>
<td>17.11</td>
<td>65.03</td>
<td>13.08</td>
<td>3.64</td>
</tr>
<tr>
<td>Oxidised porous</td>
<td>0.00</td>
<td>19.80</td>
<td>63.43</td>
<td>8.55</td>
<td>7.32</td>
</tr>
</tbody>
</table>

### 5.12.2 Zeolite Films and Membranes from ANK

Practically every research on the synthesis of zeolite films and membranes have focused on the use of commercial chemicals as a silica and alumina source for it preparation. In this work, attempt is made for the first time to prepare not only zeolite A which have been reported twice before [238, 279] but also other zeolite film and membrane such as zeolite Y and ZSM-5 film and membrane from ANK. The unique structure of kaolin and the reactivity of metakaolin make it an ideal source of making zeolite membrane and has been
described as a having a potential of making pinhole-free film because of it platelet structure [279].

Two methods was used to prepare the membrane on porous supports with the synthesis condition especially crystallization time obtained after carrying experiments on the synthesis of zeolite films on non-porous support. The influence of support pre-treatment on the formation of coherent membrane was also investigated. The discussion of the results obtained using the two methods of zeolite films and membrane on the pre-treated support are presented in section 5.12.2.1 and 5.12.2.2.

5.12.2.1 Synthesis of Zeolite A Films and membranes from ANK using Modified In-situ method (MIM) and Secondary Growth Method (SGM)

5.12.2.1.1 Preparation of Zeolite A film by Modified In-situ Method

The XRD pattern of zeolite A films samples obtained from both etched and oxidised supports are presented in figure 5.13 and figure 5.16. The XRD analysis of the excess powdered samples obtained in both etched and oxidised support are also presented in appendix C.

In the case of the etched supports, after 3 h of crystallization, no trace of zeolite A can be detected on the stainless steel support as shown in the XRD pattern. This is as a result of formation of a gel layer on the surface of support which will be followed by crystallization of zeolite A crystals.

Zeolite A coatings with low XRD peaks intensity at 2 theta = 7.20°, 10.18°, 23.90°, 27.11° was formed after 6 h of crystallization. Increase in the time of crystallization to 9h appear to make the peak assigned to zeolite A to be clear but still with low intensity, additional increase of crystallization time to 12 h clearly displayed all the peaks of zeolite A. The low reflection of the diffraction peak of stainless steel at 2 theta = 43.3° indicate high degree of coverage and probably formation of thick zeolite layer after 12 h of crystallization [280].

The quartz peak in the parent metakaolin was not detected in the film of zeolite A produced. Quartz impurities must have been removed during the hydrothermal synthesis because it is insoluble and cannot anchor or attach to the support used in the synthesis of
the film. This is significant result as it indicates that pure phase zeolite A film can be produced from kaolin containing quartz impurity.

The XRD pattern of the powdered sample as shown in appendix C provided information on the possible mechanism of the formation process of the zeolite film. The XRD results show that the formation of zeolite A films from the aluminosilicate gel started in the bulk phase as evidenced by the crystallization of zeolite A at 3h while at the same time, there was no sign of zeolite formation on the support surface.

The morphology of the zeolite A coatings on the etched support was also monitored with SEM. Figure 5.14 shows the SEM images of the zeolite films obtained from 3 h to 12 h crystallization time. Compact membrane was obtained after 9 h of crystallization as shown in the SEM.

The surface of the etched stainless steel was almost free of any zeolite A crystals after 3h of crystallization. Increase in crystallization time to 6 h lead to increase in the coverage of the support with the zeolite crystallites but there was obvious lack of intergrowth of the crystals which is important for any good zeolite film. Full coverage and intergrowth zeolite A crystal was observed when a crystallization time of 12 h was reached which again corroborate the result of the XRD analysis. The edge view of the final zeolite A coatings obtained at 12 h of crystallization was observed by the SEM and shown in figure 5.15. At the end phase of zeolite A crystallization (12 h), the zeolite A crystals have grown into cubic shape and giving rise to apparently continuous films. There is no obvious sign of significant pinhole or defect.

The EDAX analysis of the films obtained shows the presence of Na, Si, Al and O along with Fe. Most importantly the Si/Al ratio of the synthesised zeolite A crystals on the support varies from 0.99 to 1. And this is within the range of commercial zeolite A confirming the actual formation of zeolite A films.

Examination of the edge section of the zeolite A films produced by SEM generally reveal that the thickness of the zeolite layer decrease with increase in the crystallization time. This is likely due to mass transport of gel or deposition that took place on the support surface and this is soon replaced by the evolution of gel into compact zeolite and forming more excess powder in the process.
Figure 5.13: XRD pattern of Zeolite films on non-porous stainless steel by MIM from ANK (A) etched stainless steel (B) zeolite A film sample 3 h (C) zeolite A film sample 6 h (D) zeolite A film sample 9 h (E) zeolite A sample 12 h

Figure 5.14: Zeolite A films on etched stainless steel by MIM A. 3 h B. 6 h, C. 9 h and D. 12 h. Scale bars = 50 µm
The XRD and SEM (figure 5.16 and 5.17) analysis of zeolite A coatings on oxidised stainless steel using the MIM indicate slight advantage in terms of the time of zeolite A coatings production and the quality of the deposition. Zeolite A crystals was clearly observed on the oxidised support after 6h of crystallization unlike etched support. The morphology of the coatings on the oxidised support shows the progressive transformation of zeolite A into a more compact and crack-free in the support after 9h of crystallization.
The strength of the interaction or bonding between the zeolite A crystallites and the support was carried out by soaking the zeolite films and membrane films in acetone and sonicated for 30 min at room temperature. The results are shown in table 5.10. There is generally a minimal loss of zeolite crystals during adhesion test for both the film on etched
and oxidised support. This shows there is a bonding between the zeolite crystal and the supports. What remains unclear is the type of bonding that took place between the zeolite crystals and the support. There are two type of bonding which can take place during zeolite crystallization, these are chemical or physical anchorage. Based on the results in table 5.10, the strength of the zeolite A crystal adhesion on both etched and oxidised is not in doubt because of minimal loss of zeolite crystal during the adhesion test, therefore it is likely that chemical bonding exist between the support and the zeolite crystallites. Finally, zeolite A films on oxidised support suffers less loss of zeolite crystals than the film on the etched supports.

The weight gain of the zeolite crystals was used to monitor the deposition of the crystal on the support. The weight gain was measured by weighing the weight of support before and after the hydrothermal synthesis and the result obtained is shown in table 5.10.

The range of deposition of zeolite crystals on the two support indicate that increase in the synthesis time lead to corresponding increase in the deposited zeolites crystals on the supports. However, zeolite A crystal seem to deposit more in oxidised support than in etched support over the entire synthesis time range. For example, after 12 h of crystallization, the weight gain of zeolite A on oxidised support was 1.139 mg/g while that on etched support was 0.4242 mg/g. This is expected because there is better interaction between the oxidised surface and the synthesis gel leading to strong bonding. The outcome of adhesion test also attested to this fact. Loss of zeolite crystal was more in the etched support than oxidised support, see table 5.10.

In summary, the best result was obtained when the surface oxidation of the stainless steel was used. The crystals were seen to be attached to the surface of the support in most cases, however the increase in crystallization time favoured good continuity and high coverage as evidence in the result obtained. 100% coverage was achieved when the synthesis time was increased to 12 h. More work is required to understand the formation process of zeolite membrane and to predict which mechanism controls the zeolitization process.
Table 5.10: Some physiochemical properties of synthesised zeolite A films

<table>
<thead>
<tr>
<th>Zeolite films/coatings</th>
<th>Method of synthesis</th>
<th>Synthesis time (h)</th>
<th>Modification techniques</th>
<th>Si/Al Weight gain in zeolite coating mg/g</th>
<th>Adhesion test (weight loss) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite A</td>
<td>MIM</td>
<td>3</td>
<td>Etched</td>
<td>0.757</td>
<td>0.3468</td>
</tr>
<tr>
<td></td>
<td>MIM</td>
<td>6</td>
<td>Etched</td>
<td>1.020</td>
<td>0.4034</td>
</tr>
<tr>
<td></td>
<td>MIM</td>
<td>9</td>
<td>Etched</td>
<td>1.061</td>
<td>0.4134</td>
</tr>
<tr>
<td></td>
<td>MIM</td>
<td>12</td>
<td>Etched</td>
<td>1.089</td>
<td>0.4242</td>
</tr>
<tr>
<td></td>
<td>MIM</td>
<td>3</td>
<td>Oxidised</td>
<td>0.812</td>
<td>0.3529</td>
</tr>
<tr>
<td></td>
<td>MIM</td>
<td>6</td>
<td>Oxidised</td>
<td>0.949</td>
<td>0.3635</td>
</tr>
<tr>
<td></td>
<td>MIM</td>
<td>9</td>
<td>Oxidised</td>
<td>1.111</td>
<td>0.4101</td>
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<tr>
<td></td>
<td>MIM</td>
<td>12</td>
<td>Oxidised</td>
<td>1.139</td>
<td>0.4331</td>
</tr>
</tbody>
</table>

5.12.2.2 Synthesis of Zeolite A films by Secondary Growth Method

Secondary (seeded) growth method was also investigated in this study to synthesize zeolite A films and membrane using kaolin as a precursor. Secondary growth method is an established procedure used in the synthesis of different type of zeolite membrane, and it has continued to attract attention as the best in the fabrication of zeolite membranes mainly because of reproducibility of the method and the huge chance it give to produce good and quality membrane in a shorter period. However it has not being used to prepare zeolite films and membrane from kaolin based on the literature.

In this work, commercial zeolite A powder was obtained and was ball milled as explained in the experimental section, from which colloidal seeds were produced. The particle size and pH of colloidal zeolites which was used in the seeding process during the SGM synthesis was determined by Malvern zetasizer 3000 HS. The result of the analysis show that the particle size of the zeolites A seed produced is 297.3 nm. This indicate that the zeolite seeds which was expected to form the nucleus for zeolite growth are thin and it is most likely to obtain zeolite films and membranes that are thinner than those prepared using MIM.
Zeolite A films was prepared by the secondary growth method (SGM) using the colloidal seed of zeolite A as explained in the experimental section. Seeding was carried out by first dip coating the modified supports (etched and oxidised) in the colloidal zeolite A seeds for 30 min followed by drying at 60°C. The seeded supports were put vertically into an autoclave using Teflon holder and the synthesis gel was carefully poured into the autoclave. The synthesis gel was prepared from chemical composition similar to the type used in MIM earlier. Hydrothermal treatment was carried out at constant crystallization temperature and ageing time of 100°C and 12 h respectively at varying crystallization time.

The XRD analysis of both zeolite films produced at different crystallization of 3, 6, 9, and 12 h for the two supports (etched and oxidised) are shown in figure 5.19 and 5.22 respectively. The excess powder obtained from the autoclave are also analysed by XRD and the results are shown in appendix C for etched supports and oxidised supports.

The formation of zeolite film did not commence until after 6 h of hydrothermal synthesis for the two support when the diffraction peak corresponding to zeolite A was clearly noticed. There was a further increase in the diffraction peak of zeolite A indicating higher crystallinity. In this case of zeolite A film on etched support, there was a quick transformation of zeolite A crystal into a dense phase called zeolite P as shown in figure 5.19 even though the seeding obviously reduced the crystallization of zeolite A from ANK by 3 h, increase to crystallization of 12 h will lead to co-crystallization of undesirable zeolite phase. When compared with powder sample from the bulk phase. It is obviously clear that the hydrothermal synthesis reaction is initially controlled by homogenous nucleation as can be seen by the early formation of zeolite A in the first 3 h of crystallization, however unlike the MIM, heterogeneous nucleation took place faster because of the presence of zeolite seed on the surface of the support region. This causes an early formation of zeolite A film, hence zeolite A films was formed 3 h faster than the same film using MIM. There was no immediate change of zeolite A phase on oxidised support. This can still be attributed to the fact that oxidised support offer a better media for zeolite crystallization as earlier explained.

The transformation that happens in the support surface was not noticed in the bulk phases. This indicate that during the crystal growth, most of the crystallization process was taking place on the surface of the support and probably because some seeds are transported up into the bulk phase by the aluminosilicate gel and the seed suppresses the transformation of
zeolite into different phase. The XRD pattern also shows that peak corresponding to the Fe phase was reduced as the crystallization time increase. This is known to be indicative of the degree of coverage of the support by the crystallizing zeolite phase as previously explained.

The SEM image of zeolite A film sample on the etched and oxidised support obtained using SGM are shown in figure 5.20 and 5.23 for different crystallization time at 3h, 6h, 9h and 12h while the edge view of the sample obtained at 9h of crystallization is shown in figure 5.21 and 5.24.

The morphology of the zeolite A film was observed using SEM for all the sample prepared from 3 h to 12 h. Initially the surface of the etched and the oxidised support was partially covered with zeolite crystals that seem to be well bonded to the support surface. This is probably caused by the initial coating of the surface with zeolite A seed and which seem to favour and promote the crystal growth. Progressive improvement in the support coverage was observed when the crystallization time was increased from 3 h through 6 h to 12 h. The support was completely covered by the first 6 h and further increase in the coverage when the synthesis time was increased to 9 h and 12 h. This is similar to the observation by other author on the synthesis of zeolite A films in which mostly cubic zeolite A crystals are formed [281]. The edge view shown in figure 5. 21 and 5.24 for the etched and oxidised samples reveal the continuity of the zeolite A layer and there seem to be absence of any visible cracks and pinholes.

The edge view of the grown zeolite A film using the SGM at 9 h for both the etched and oxidised support also tend to reveal that zeolite grew from the surface and are firmly attached to the supports. This corroborate the earlier postulation that heterogeneous nucleation tend to dominate the crystallization process when SGM is used.

Kondo et al [282] has also produced zeolite A membrane using SGM but they used sodium metasilicate nonahydrate and aluminium hydroxide as silica and alumina sources, however short time of crystallization (3 h) was reported. The difference between their work and this study can be traced to the fact that the commercial chemical such as sodium metasilicate can easily dissolve and allow early crystal growth, it took a bit of time to cause the kaolin which supply the silica and alumina to go into solution before condensation/polymerization reaction take place.
Figure 5.19: XRD pattern of zeolite A films on etched non-porous stainless steel by SGM from ANK (A) etched stainless steel (B) zeolite A film sample 3h (C) zeolite A film sample 6h (D) zeolite A film sample 9h (E) zeolite A sample 12h

Figure 5.20: SEM image of zeolite A films sample on etched stainless steel by SGM using ANK A.3 h, B.6 h, C.9h D. 12 h. Scale bar =50 μm
Figure 5.21: SEM image of zeolite A films sample on etched stainless steel by SGM using ANK 12 h (edge view). Scale bar= 400 µm

Figure 5.22: XRD pattern of zeolite A films on non-porous stainless steel by SGM from ANK (A) oxidised stainless steel(B) zeolite A film sample 3 h (C) zeolite A film sample 6 h (D) zeolite A film sample 9 h (E) zeolite A sample 12 h
Some other important characteristic behaviour of the zeolite film was also monitored during the synthesis. These properties such as the Si/Al ratio, the weight gained by the support and adhesion test of the synthesised film is vital in a potential industrial application of the films and even when they are produced as membrane. The Si/Al ratio of all the samples on etched and oxidised sample were determined with the aid of EDAX while the weight gain was obtained by measuring the differential in the weight of the support before
and after the hydrothermal synthesis. The adhesion test is vital and is used to know the degree of bonding between the support and the zeolite crystals. While it is not clear exactly the type of interaction or bonding that take place between the synthesis gel of zeolite and the support during the synthesis proper, adhesion test indicate the compatibility of the heterogeneous species needed for the film formation.

The results of the analysis are shown in table 5.11. The Si/Al ratio of the developed zeolite films from ANK fall within the range of 0.944 to 1.008 and this conform with reported literature value of standard zeolite A crystal. This again supports both the XRD and SEM analysis which confirm that zeolite A crystal was indeed synthesised on both the etched and oxidised support. The result also shows that the Si/Al ratio marginally increase with increase in growth time. This is because increase crystallization only lead to corresponding increase dissolution of the silica component of the metakaolin and thereby incorporating more into the already formed zeolite framework. The weight gain also increase with increase time which indicate the coverage of the support surface as the crystallization time increase. It is difficult to know exactly the optimum weight gain, uniform distribution of the zeolite crystal on the support is vital to get a continuous zeolite layer. On the other hand, the result of the adhesion test show that the loss of the zeolite crystal after soaking in acetone for 30 min in a sonicator was low and decrease with time. It is also clear from the result that the weight loss in etched support is a bit higher than those of oxidised support. This again suggests that oxidised support interact more positively with zeolite synthesis gel.
Table 5.11: Physiochemical properties of synthesised zeolite A by SGM

<table>
<thead>
<tr>
<th>Zeolite films</th>
<th>Method of synthesis</th>
<th>Synthesis time</th>
<th>Modification techniques</th>
<th>Si/Al</th>
<th>Weight gain in zeolite coating mg/g</th>
<th>Adhesion test (weight loss) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite A</td>
<td>SGM</td>
<td>3</td>
<td>Etched</td>
<td>0.944</td>
<td>0.3848</td>
<td>0.19</td>
</tr>
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<td></td>
<td>SGM</td>
<td>6</td>
<td>Etched</td>
<td>1.043</td>
<td>0.4749</td>
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<td></td>
<td>SGM</td>
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<td>Etched</td>
<td>1.106</td>
<td>0.4803</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>SGM</td>
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<td>1.130</td>
<td>0.4867</td>
<td>0.09</td>
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<td>0.912</td>
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<td>Oxidised</td>
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<td>Oxidised</td>
<td>1.008</td>
<td>0.4507</td>
<td>0.05</td>
</tr>
</tbody>
</table>

5.12.2.3 Synthesis of Zeolite A membrane by Modified In-situ and Secondary Growth Method

The outcome of the experiment on the synthesis of zeolite A films on non-porous stainless steel was then used to develop zeolite A membrane using MIM and SGM and again using ANK metakaolin as a combined source of silica and alumina. The porous support was also modified by etching and surface oxidation. Crystallization time of 9h was selected to prepare zeolite A membranes on the substrates.

Figure 5.25 presents the XRD patterns of zeolite A membrane on etched support while figure 5.28 shows the XRD pattern of zeolite A membrane on oxidised support using MIM. The XRD pattern of zeolite A membrane synthesised by SGM is shown in figure 5.31 and 5.34 for etched and oxidised support respectively. It can be seen that the diffraction peak of zeolite A appears in both the etched and oxidised support after 9 h of hydrothermal synthesis for the two techniques used. The XRD pattern of zeolite A was similar to the pattern obtained for zeolite A films on non porous stainless steel and compared with zeolite A membrane in the literature [222].
The results also show that the intensity of zeolite A peaks for the membrane prepared on etched support was low compared to strong peak intensity observed for the membrane prepared on oxidised support using the MIM.

The XRD pattern of zeolite A membrane obtained using SGM was also compared with the membrane prepared using MIM. The intensity of the diffraction pattern of zeolite A membrane is stronger than using MIM in all cases. This indicates that crystallization is increased because of the seeding of the support using colloidal silica.

The morphology of the zeolite A membrane developed using MIM was thereafter observed by SEM for both etched and oxidised support. Figure 5.26 and 5.27 show the top and edge view of zeolite A membrane on etched support while figure 5.29 and 5.30 show the top and edge view of zeolite A membrane on oxidised support.

There was good coverage for both cases of modified stainless steel however the intergrowth in the oxidised is visibly more pronounced than that of etched porous stainless steel. The results also confirm that continuity of the zeolite A layer. The Si/Al ratio of the zeolite crystallites was measured using EDAX and the result shown in table 5.12. The value of 0.956 was obtained for membrane on etched support while 1.02 was obtained for the membrane on oxidised support. The adhesion test carried out similar to the zeolite films show a strong interaction between the zeolite crystal and the support.

Figure 5.32, 5.35 and 5.36 shows the SEM images of the top view and the edge view of zeolite A membrane using SGM on etched and oxidised support respectively. The images reveal a cubical shape and excellent intergrowth of zeolite A crystals similar to the several zeolite A membrane synthesised from commercial chemical [222, 280] and the edge view shows a good continuous zeolite A membrane layer. The edge view also reveals the likely process of the membrane formation. The zeolite crystals seem to grow from the surface of the support as result of the seeds. This is why the adhesion between the zeolite crystal and the support surface look strong. EDAX analysis of the developed membrane was also measured just like it was done for the zeolite film. The Si/Al ratio of ca. 1 was obtained for all the zeolite membrane on both oxidised and etched support. The adhesion test carried out on the membrane as shown in table 5.12 indicates that there is minimal weight loss. This generally confirm the existence of strong adhesion between the zeolite crystal and the support, however oxidised support was a better support because it has less weight loss than etched supports.
Figure 5.25: XRD pattern of zeolite A membrane on etched porous stainless steel from ANK using MIM (A) etched porous stainless steel (B) zeolite A membrane sample at 9 h

Figure 5.26: SEM image of zeolite A membrane on porous etched stainless steel by MIM 9 h scale bar = 50 µm
Figure 5.27: SEM image of zeolite A membrane on porous etched stainless steel by MIM for 9 h (edge view). Scale bar = 400 µm

Figure 5.28: XRD pattern of zeolite A membrane on oxidised porous stainless steel from ANK using MIM (A) oxidised porous stainless steel (B) zeolite A membrane sample at 9h
Figure 5.29: SEM image of zeolite A membrane on porous oxidised stainless steel my MIM for 9 h. Scale bar = 50 µm

Figure 5.30: SEM image of zeolite A membrane on porous oxidised stainless steel in-situ method 9 h (edge view). Scale bar= 400 µm
Figure 5.31: XRD pattern of zeolite A membrane on etched porous stainless steel from ANK using SGM (A) etched porous stainless steel (B) zeolite A membrane sample at 9 h

Figure 5.32: SEM image of zeolite A membrane on porous etched stainless steel by SGM for 9 h. Scale bar = 50 µm
Figure 5.33: SEM image zeolite A membrane on porous etched stainless steel by SGM for 9 h (edge view). Scale bar = 400 µm

Figure 5.34: XRD pattern of zeolite A membrane on oxidised porous stainless steel from ANK using SGM (A) oxidised porous stainless steel (B) zeolite A membrane sample at 9 h
Figure 5.35: SEM image zeolite A membrane on porous oxidised stainless steel by SGM on ANK 9 h. Scale bar= 20 µm

Figure 5.36: SEM image zeolite A membrane on porous oxidised stainless steel by SGM for 9 h (edge view). Scale bar= 200 µm

Table 5.12: Some physiochemical properties of synthesised zeolite A membrane

<table>
<thead>
<tr>
<th>Zeolite membrane</th>
<th>Method of synthesis</th>
<th>Synthesis time</th>
<th>Modification techniques</th>
<th>Si/Al</th>
<th>Weight gain in zeolite coating mg/g</th>
<th>Adhesion test (weight loss) %</th>
</tr>
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<tr>
<td>Zeolite A</td>
<td>MIM</td>
<td>9</td>
<td>Etched</td>
<td>0.959</td>
<td>0.1628</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>MIM</td>
<td>9</td>
<td>Oxidised</td>
<td>1.020</td>
<td>0.2361</td>
<td>0.06</td>
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<tr>
<td></td>
<td>SGM</td>
<td>9</td>
<td>Etched</td>
<td>1.00</td>
<td>0.1435</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>SGM</td>
<td>9</td>
<td>Oxidised</td>
<td>1.01</td>
<td>0.2143</td>
<td>0.54</td>
</tr>
</tbody>
</table>
Performance Evaluation of Zeolite A Membrane Synthesised by Modified In-situ and Secondary growth method

The performance of the zeolite A membrane prepared from ANK using the MIM and SGM on the modified stainless steel were examined by pervaporation process. The pervaporation experiment was carried out at room temperature with fixed feed composition using the pervaporation apparatus as described in section 5.11.3.5. The permeate which is obtained as a vapour was collected over liquid nitrogen.

In the first experiment on the performance evaluation of the synthesised zeolite A membrane, a mixture of 1,3,5 tri-isopropylbenzene (TIPB) and water was used as a material to test the presence of defect and coherence in the membrane prepared. TIPB has a kinetic diameter of 0.87 nm larger than the pore size of most zeolitic materials, so has emerged as a good organic molecule used in the testing of the continuity and coherence in zeolite membrane [244]. Figure 5.37 show the pervaporation performance of zeolite A membrane synthesised by the MIM and SGM using both etched and oxidised supports. The flux of TIPB/water mixture passing through both membranes was measured and the composition analysed by offline GC. The result shows a flux of 47.84 g/m²h (99.99 wt% H₂O) and 39.78 g/m²h (99.02 wt % H₂O) for zeolite A membrane on oxidised and etched support using MIM and 55.69g/m²h (99.99 wt% H₂O) and 44.55 g/m²h (99.95 wt % H₂O) for oxidised and etched support using SGM. The result generally indicate extremely low flux of TIPB through zeolite A membrane meaning the membrane prepared from ANK is coherence and defect formation in the membrane is nearly absent. Zeolite A has a kinetic of 0.41 nm and in theory, a heavy molecule such as TIPB will be rejected by the small molecule zeolite by the mechanism of molecular sieving, but in some case when the transport pathway in the zeolite material is a combination of the zeolitic pores and the defect, heavy molecule such TIPB will permeate through the membrane. An almost defect free membrane can be said to have been developed from ANK using MIM and SGM on oxidised and etched stainless steel since the synthesised membrane performed well when tested with TIPB. The presence of non zeolitic pore larger than 0.85 nm could have lead to some permeation of the organic material. What was predominantly obtained is a selective permeation of the water component and this prove the absence of non-zeolitic pore which are effectively called defect or pin holes. The non permeation of TIPB does not necessary mean there is no defect since most defect can either be micro, meso or macropore. Micro defect with pore
less than 2nm might be present but such defect does not influence the membrane negatively.

The second experiment on the performance evaluation of the synthesised zeolite A membrane was on the pervaporation of 95 wt % ethanol/water mixture. The experiment was also carried out at room temperature. Permeate was also collected over liquid nitrogen and weighed to determine the flux. The separation performance was calculated after analysing the permeate in an offline GC. The result is shown in table 5.13.

Zeolite A membrane developed by MIM from ANK metakaolin show a low flux of permeate as 204 g/m$^2$h for oxidised support and 186 g/m$^2$h for etched support. The flux is low and is likely due to the high thickness of the membrane obtained in this work. The selectivity (the ratio of the composition of water to ethanol in permeate divided by the same composition in the feed) obtained however was better than some reported zeolite A membrane. The selectivity for zeolite A membrane synthesised using oxidised and etched stainless steel support are 2210 and 10682 respectively. For example, the pervaporation performance especially the selectivity of 95 wt% ethanol/water mixture at room temperature is higher than the zeolite membrane prepared by Kondo et al [282]. Even though they reported higher permeation flux as 2350 g/m$^2$h compared to the flux obtained in this study. It is noteworthy that they used tubular support and the analysis was done at higher temperature, the vacuum pressure was not reported. The pervaporation study in this work was carried out at room temperature and a vacuum pressure of 748 mmHg was attained.

The result for zeolite A membrane produced using SGM show a flux of 213 g/m$^2$h for oxidised support and a flux of 200 g/m$^2$h was obtained for the membrane developed on the etched support. On the other hand, the etched support membrane has a high selectivity toward water than the membrane on oxidised support. This is as result of difference in the thickness of the zeolite layer, while oxidised support allows the formation of thinner membrane with a thickness of 19.45 µm which favour higher flux, the thickness of the membrane on the etched support was obtained as 23.54 µm allow lower flux but higher separation performance. These results show the inverse relationship existing between the thickness of membrane and the flux and separation performance. While both parameters (flux and selectivity) are important in membrane separation processes, the thickness of membrane should be selected in order to have a trade-off between the two parameters.
Although the result in table 5.13 showed difference in the separation performance for etched and oxidised support using SGM and MIM technique, the GC error of 3.6% might account for the difference.

The membrane preferentially allow water to pass while stopping the ethanol from permeating [201]. Generally zeolite membrane perform separation by three mechanism mainly molecular sieving, selective adsorption and diffusion rate variation but in this case specifically, it has been established selective adsorption and diffusion and driven by the hydrophilicity of zeolite A is responsible for the selective permeation of water. Water permeate filled the pore pathway of zeolite A membrane and this is mainly caused by the strong hydrophilicity of zeolite A [283] and in the process move faster than the organic component.

The zeolite A membrane produced using SGM showed a better performance than MIM in term of permeation with MIM having a better selectivity. This is expected because thick zeolite layer are formed using MIM and this show high selectivity as earlier explained.

![Figure 5.37: Evaluation of the quality of the synthesised zeolite A by pervaporation of TIPB/water mixture (M1, M2, M3, M4 represent zeolite A membrane synthesised on oxidised, etched for MIM and oxidised and etched for SGM respectively)](image)
Table 5.13: Evaluation of the quality of the synthesize d zeolite A membrane by pervaporation of water/ethanol mixture

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Method</th>
<th>Crystallization time h</th>
<th>Thickness μm</th>
<th>Pre-treatment method</th>
<th>Flux g/m²h</th>
<th>Ethanol/water wt% (feed)</th>
<th>Ethanol/water wt% (permeate)</th>
<th>Separation factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite A membrane</td>
<td>MIM</td>
<td>9</td>
<td>30.21</td>
<td>Oxidised</td>
<td>204</td>
<td>95/5</td>
<td>0.08/99.92</td>
<td>10682</td>
</tr>
<tr>
<td>MIM</td>
<td>9</td>
<td>34.65</td>
<td>Etched</td>
<td>186</td>
<td>95/5</td>
<td>0.17/99.82</td>
<td>22102</td>
<td></td>
</tr>
<tr>
<td>SGM</td>
<td>9</td>
<td>19.45</td>
<td>Oxidised</td>
<td>213</td>
<td>95/5</td>
<td>1.53/98.47</td>
<td>1224</td>
<td></td>
</tr>
<tr>
<td>SGM</td>
<td>9</td>
<td>23.54</td>
<td>Etched</td>
<td>200</td>
<td>95/5</td>
<td>1.49/98.51</td>
<td>1258</td>
<td></td>
</tr>
</tbody>
</table>

*Although differences in the separation factor are observed, these could be accounted for by GC error.

5.12.3 Synthesis of ZSM-5 Films and Membrane from ANK using Modified In-situ and Secondary Growth Method

5.12.3.1 Synthesis of ZSM-5 Films using Modified In-situ Method

ZSM-5 zeolite layer were hydrothermally grown on the surface of etched and oxidised support. The composition of the reacting mixture was based on the earlier work on ZSM-5 synthesis from ANK. During the synthesis of the ZSM-5 film, the crystallization time was varied while holding other parameters such as ageing time and crystallization temperature at 48 h and 170°C respectively. Several synthesis of ZSM-5 films and membrane using commercial chemical silica and alumina sources have been reported [284] till date no report on the preparation of ZSM-5 from kaolin exist in the literature.

Figure 5.38 show the XRD of all the samples of ZSM-5 film produced on etched support and while figure 5.41 show that of films deposited on oxidised support. The SEM images of surface and edge view of the films are presented in figure 5.39, 5.40, 5.42 and 5.42 for etched and oxidised support respectively.
Figure 5.38: XRD pattern of ZSM-5 films on non-porous stainless steel by MIM from ANK (A) etched stainless steel (B) ZSM-5 film sample 24 h (C) ZSM-5 film sample 36 h (D) ZSM-5 film sample 48 h (E) ZSM-5 sample 72 h

Figure 5.39: SEM image ZSM-5 films on etched stainless steel by MIM A.24 h, B.36 h, C.48 h, D.72 h. Scale bars = 50 µm
Figure 5.40: SEM image ZSM-5 film on etched stainless steel by MIM method 72 h (edge view). Scale bar = 400 µm

Figure 5.41: XRD pattern of Zeolite films on non-porous stainless steel by MIM from ANK (A) oxidised stainless steel (B) ZSM-5 film sample 24 h (C) ZSM-5 film sample 36 h (D) ZSM-5 film sample 48 h (E) ZSM-5 sample 72 h
Figure 5.42: SEM image of ZSM-5 films on oxidised stainless steel by MIM A24h, B36h, C48h, D72h. scale bars = 50 µm

Figure 5.43: SEM image of ZSM-5 film on oxidised stainless steel by MIM (edge view) scale bar = 300 µm

To verify the films as ZSM-5, the XRD pattern was compared with ZSM-5 films studied by Oankhanond [285] and standard ZSM-5 XRD pattern. After 24h of hydrothermal treatment, there was weak peaks at 2theta = 7.93°, 8.84°, 23.12°, 23.27°, 23.93° respectively in both films synthesised on the etched while for the oxidised support, the diffraction peak of ZSM-5 starting appearing after 36 h of crystallization. The ZSM-5 films seem to behave differently from zeolite A film since etched support interact faster than the oxidised support. The outcome of the XRD analysis generally confirms that the samples
are that of ZSM-5 zeolite phase. Increase in the synthesis time leads to increase in the intensity of the ZSM-5 diffraction peaks for the synthesis on both etched and oxidised support. Increase in the time of crystallization is known to increase crystallization rate and allow more crystal to grow forming interlocking films and eventually obtain a continuous films. Maximum crystallinity is obtained at 72 h within the range of the crystallization time studied for the two set of ZSM-5 film. On the other hand, the intensity of the iron phase at 2 theta= 43.3° has reduced considerably as a result of the coverage of the surface of the support for the two support. The influence of synthesis time is significant as it leads to variation in the characteristic of the film such as thickness, orientation and homogeneity of the films. The crystallization time was changed to study the time required to obtained sufficient crystal growth on the support surface. The crystallization time was also seen as one of the most important parameter that control crystal growth on zeolite films. The XRD pattern of the excess powder samples (appendix C) also indicates that ZSM-5 is the predominant phase with little or no amorphous phase and there is no sign of any other zeolitic phase. The result also show mechanism similar to zeolite A films described earlier. i.e homogenous nucleation in the bulk phase forming the zeolite phase faster and subsequent heterogeneous nucleation on the support to grow the zeolite films.

SEM was used to monitor the surface morphology, the thickness of zeolite layer and confirm the quality of the zeolite film developed from ANK. The morphology of the top view on the two supports show that ZSM-5 crystallites were uniformly distributed even after 36h of crystallization corroborating the result of XRD analysis. The morphology of the ZSM-5 membrane is similar to those obtained by Algieri et al [286].However increase in crystallization time from 24 h to 72 h causes the ZSM-5 crystals to inter-grow and form continuous layer as confirmed by the edge view of the ZSM-5 films.

The edge view as seen by the SEM image of the film produced at 72 h show the zeolite crystal and support are tightly bonded together (figure 5.40 and 5.43). This confirms that there is high degree of adhesion of zeolite film produced from ANK. This was further investigated by carrying out an adhesion test on the ZSM-5 films. Similar results were obtained for the oxidised support however ZSM-5 zeolite crystals were quick to intergrow compared to etched support films. This is due to stronger interaction between the oxidic layer and the synthesis gel. The thickness of the ZSM film was estimated from the edge view using SEM. It shows that as the crystallization time increase, the thickness was decreasing with value ranging from 570.10 to 59.43 µm. It was also noticed that unlike
zeolite A films, ZSM-5 films are formed more easily on the two modified supports. Previous work [227] corroborates the ease with MFI films and membrane are formed, irrespective of the type of support, compared to other zeolites.

EDAX analysis of all the ZSM-5 films sample were also carried out to determine their Si/Al ratio. The results shown in table 5.16 indicate that Si/Al increase with increasing synthesis time with the highest Si/Al obtained after 72h of hydrothermal synthesis to be 16.133 for film on etched support and 19.98 for film on oxidised support. The result confirm the incorporation of more silica into the ZSM-5 framework as the synthesis time increase due to increasing dissolution/polymerization reaction involving silica from both the metakaolin, colloidal silica and other components. The presence of Al in the ZSM-5 which solely come from the metakaolin change the zeolite into having some element of hydrophilicity unlike the other member of the MFI group, silicalite, that is completely free of Al and are wholly hydrophobic.

An adhesion test to further examine the strength of interaction between the zeolite crystallite and the substrate as explained earlier was carried out similar to zeolite A films adhesion test. The results shown in table 5.16 confirm a very strong bonding exists between the crystallites and the support as almost all the sample show a very low weight loss. ZSM-5 films developed on oxidised support showed lower weight loss because there is better interaction between the oxidised support and the aluminosilicate gel than on etched support. The oxidised support provides –OH on the surface for crystal adhesion in addition the pore size which creates ideal site allowing adhesion to take place for both etched and oxidised support.
Table 5.14: Some physiochemical properties of synthesised ZSM-5 films

<table>
<thead>
<tr>
<th>Zeolite films/coatings</th>
<th>Method of synthesis</th>
<th>Synthesis time</th>
<th>Modification techniques</th>
<th>Si/Al</th>
<th>Weight gain in zeolite coating mg/g</th>
<th>Adhesion test(weight loss) %</th>
</tr>
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<tbody>
<tr>
<td>ZSM-5</td>
<td>MIM</td>
<td>24</td>
<td>Etched</td>
<td>3.286</td>
<td>0.988</td>
<td>0.05</td>
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<tr>
<td></td>
<td>MIM</td>
<td>36</td>
<td>Etched</td>
<td>3.933</td>
<td>1.038</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>MIM</td>
<td>48</td>
<td>Etched</td>
<td>7.741</td>
<td>1.144</td>
<td>0.03</td>
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<tr>
<td></td>
<td>MIM</td>
<td>72</td>
<td>Etched</td>
<td>16.133</td>
<td>1.189</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>MIM</td>
<td>24</td>
<td>Oxidised</td>
<td>3.467</td>
<td>1.046</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>MIM</td>
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<td>Oxidised</td>
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<td>Oxidised</td>
<td>7.860</td>
<td>1.237</td>
<td>0.02</td>
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<td>MIM</td>
<td>72</td>
<td>Oxidised</td>
<td>19.893</td>
<td>1.337</td>
<td>0.01</td>
</tr>
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</table>

5.12.3.2 Synthesis of ZSM-5 Films using Secondary Growth Method

The XRD pattern of the calcined ZSM-5 films on etched support are shown in figure 5.44. The XRD pattern shows a new peak on the support after 24h of crystallization at 7-9° and 23-25°. These peaks correspond to the specific peak of ZSM-5 zeolite. This reveals the coating layer to be ZSM-5, furthermore, the intensity of the peak of zeolite ZSM-5 increase with increase in crystallization time up to 48 h and started to decrease at 72h. The result show that in secondary growth, there is increase crystallization rate compared to the modified in-situ crystallization method similarly used to prepare ZSM-5 films. The peak assigned to the support decreases as the crystallization time increases revealing the covering of the surface of the supports. The XRD patterns of the excess also support the formation of ZSM-5 phase in the bulk phase (appendix C).
The SEM image (figures 45 and 5.46) clearly show the presence of ZSM-5 zeolite crystals on the etched stainless steel. The results show that after 24h of reaction time, the ZSM-5 crystal was not homogenously distributed. The zeolite crystals were randomly accumulated and were not strongly bonded to the support and to each other. However an increase in time of crystallization leads to the formation of good intergrowth of the crystals after 36 and 48h leading to formation of good intergrowth zeolite crystals and complete coverage of the support surface. The edge view (figure 5.87) also shows the absence of space between the zeolite layer and the support indicating a strong interaction between the zeolite crystals and the etched support at 48 h of crystallization continuity in the ZSM-5 layer.

The XRD pattern of the ZSM-5 zeolite films on oxidised stainless steel are shown in figure 5.47. ZSM-5 films was formed on the oxidised surface after 24 h just like etched support and increase in the crystallization time to 48 h lead to increase in the relative intensity of the ZSM-5 peak and further increase cause decrease in the intensity probably an onset of transformation of the ZSM-5 phase to a different phase hence 48 h is the ideal time of crystallization of ZSM-5 films from ANK using SGM.

The SEM images shown in figure 5.48 and 5.49 for the film on oxidised supports show the formation of well intergrown ZSM-5 crystals after 24 h of crystallization. The surface of the oxidised was fully covered. The edge view shows in figure 5.49 the continuity of the zeolite layer on the supports and the bonding between the zeolite crystals and the support to be strong. The bonding can said to be chemical in nature rather than a physical anchorage. The weight gain analysis was used to further illustrate the level of coverage of the support by the zeolite crystals. The result shown in table 5.15 shows that increase in crystallization time lead to increase in the weight gain, however the increase between each time of synthesis was not much which tends to indicate that the support was covered early during the synthesis and further synthesis only lead to better coverage. The adhesion test carried out on the films produced reveal little or no loss of crystal after sonication for 30min, this corroborate the SEM result of the edge which illustrate a complete chemical bonding between the zeolite crystal and the supports for both etched and oxidised support.

EDAX was used to analyse the Si/Al ratio of the ZSM-5 films and the result also shown in table 5.15 indicate that the Si/Al ratio increase with synthesis time and range from 7.89 – 20.52 for films on etched support while the range for oxidised support is between 11.05-22.40. The Si/Al obtained generally agrees with literature value of Si/Al for ZSM-5 zeolite,
the result also confirm the incorporation of Si from both metakaolin and the external silica when the synthesis time is increased. The synthesis time of 72 h recorded highest Si/Al ratio for the films on the etched substrate but from the XRD result, the ZSM-5 phase is transforming into a more stable phase of the zeolitic material. Therefore the insertion of excess silica might have help in the transformation process.

Figure 5.44: XRD pattern of Zeolite films on non-porous stainless steel by SGM from ANK (A) etched stainless steel (B) ZSM-5 film sample 24 h (C) ZSM-5 film sample 36 h (D) ZSM-5 film sample 48 h (E) ZSM-5 sample 72 h
Figure 5.45: SEM image of ZSM-5 films on etched stainless steel by SGM A. 24 h, B. 36 h, C. 48 h, D. 72 h. Scale bar = 50 µm

Figure 5.46: SEM image of ZSM-5 film on etched stainless steel by SGM 72 h (edge view). Scale bar = 500 µm
Figure 5.47: XRD pattern of zeolite films on non-porous stainless steel by SGM from ANK (A) oxidised stainless steel (B) ZSM-5 film sample 24 h (C) ZSM-5 film sample 36 h (D) ZSM-5 film sample 48 h (E) ZSM-5 sample 72 h

Figure 5.48: SEM images ZSM-5 films on oxidised stainless steel by SGM A. 24 h, B. 36 h, C. 48 h, D. 72 h. scale bar = 50 µm
Figure 5.49: SEM image of ZSM-5 film on oxidised stainless steel by SGM 72 h (edge view) scale bar = 200 µm

Table 5.15: Physiochemical properties of synthesised ZSM-5 film by SGM

<table>
<thead>
<tr>
<th>Zeolite films/coatings</th>
<th>Method of synthesis</th>
<th>Synthesis time</th>
<th>Modification techniques</th>
<th>Si/Al</th>
<th>Weight gain in zeolite coating mg/g</th>
<th>Adhesion test (weight loss) %</th>
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<tbody>
<tr>
<td>ZSM-5</td>
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<td>24</td>
<td>Etched</td>
<td>7.897</td>
<td>1.177</td>
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<td>36</td>
<td>Etched</td>
<td>15.563</td>
<td>1.276</td>
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<td>Etched</td>
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<td>1.407</td>
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<td>0.01</td>
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<td>48</td>
<td>Oxidised</td>
<td>18.176</td>
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<td>22.40</td>
<td>1.444</td>
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</table>
5.12.3.3 Synthesis of ZSM-5 membrane using Modified In-situ and Secondary Growth Method

ZSM-5 membrane was prepared from ANK using the outcome of investigation of ZSM-5 films on non-porous stainless steel by MIM and SGM. The XRD patterns of the membranes developed by the two techniques on both etched and oxidised support are shown in figure 5.50, 5.53, 5.55 and 5.58 for etched, oxidised support by MIM and etched and oxidised support by SGM. The pattern shows the ZSM-5 peaks at the range of 2 theta = 7.9 and 23-25° which correspond to the specific peak of ZSM-5 zeolite phase. The peak corresponding to the support at 43.5° greatly decreases mainly because of the high coverage of the support surface by the ZSM-5 crystals. The XRD pattern of the excess powder obtained (Not shown) gave a clear indication of the quality and possible mechanism of the reaction taking place as earlier explained for the films of zeolite A and ZSM-5. The results identified all the possible diffraction peaks of ZSM-5 with low background indicating absence of impurities or amorphous materials.

The SEM images for the membranes on etched and oxidised support synthesised using MIM as shown in figure 5.51 and 5.54, reveal 100% coverage of the support however, the intergrowth in etched support is not as good as that of oxidised support. The analysis of Si/Al ratio by EDAX (table 5.16) shows a high Si/Al ratio for the two membrane with a value of 19.54 and 22.40 for etched and oxidised support respectively while the adhesion test indicate a very strong chemical bonding between the zeolite crystals and the support with zero weight loss.

The SEM images of ZSM-5 zeolite membrane for synthesis on both etched and oxidised support using SGM are shown in figure 5.56 and 5.59. There was complete coverage of the support surface as well as a strong intergrowth. The SEM micrograph of the ZSM-5 on oxidised support is clearly more compact and well intergrown than the film on etched support. The possible for this behaviour have been stated in the other synthesis carried out so far.

The edge view for membrane synthesised on etched support show the formation of clearly well grown zeolite/support composite with no clear inter-facial distance between the zeolite crystal and the support. This was clear indication of chemical bonding and the continuity of the zeolite layer was not in doubt.
The Si/Al ratio as was done previously were analysed by EDAX and the result (table 5.16) indicate that the Si/Al of the ZSM-5 film obtained from ANK was 27.22 and 28.62 for the membrane on etched and oxidised support respectively. The Si/Al ratio of the synthesised ZSM-5 membrane sample confirms the formation of that zeolitic phase. The weight gain was found to be 1.41 mg/g and 0.258 mg/g for the membrane on etched and oxidised support. This shows that thin membrane is formed on oxidised support.

The adhesion test clearly shows that ZSM-5 is well bonded to the support than zeolite as 0.00% weight was recorded for the two membranes after sonication. This might because of more positive interaction between ZSM-5 and the support than zeolite.

In summary, the developed membrane seem to follow the same pathway of crystallization as the film grown on non porous support, however the SEM reveal a completely intergrown zeolite crystal on the support. The better intergrowth is most likely due to the presence of sufficient active site in the porous support than the non porous support. The thickness of the support was generally high and this is basic problem noticed in the use of kaolin as precursor to ZSM-5 membrane synthesis. This probably can be reduced if the ageing time of the aluminosilicate gel is increase and an influence of the alkali concentration is undertaken since the dissolution of the silica phase of the kaolin can greatly be enhanced by increasing the concentration of alkali present in the starting material.
Figure 5.50: XRD pattern of ZSM-5 membrane syntheses on etched porous stainless steel by MIM using ANK

Figure 5.51: SEM image of ZSM-5 membrane on etched porous stainless steel by MIM scale bar = 50 µm
Figure 5.52: SEM image of ZSM-5 membrane on etched porous stainless steel by MIM (edge view). Scale bar = 400 µm

Figure 5.53: XRD pattern of ZSM-5 membrane syntheses on oxidised porous stainless steel by MIM using ANK
Figure 5.54: SEM image of ZSM-5 membrane on oxidised stainless steel by MIM. Scale bar = 50 µm

Figure 5.55: XRD pattern of ZSM-5 membrane synthesises on etched porous stainless steel by SGM using ANK.
Figure 5.56: SEM image of ZSM-5 membrane on etched stainless steel by SGM at 48 h. Scale bar = 100 µm

Figure 5.57: SEM image of ZSM-5 membrane on etched stainless steel by SGM at 48 h (edge View). Scale bar = 500 µm
Figure 5.58: XRD pattern of ZSM-5 membrane synthesises on oxidised porous stainless steel by SGM using ANK

Figure 5.59: SEM image of ZSM-5 membrane on oxidised stainless steel by SGM at 48 h. Scale bar = 100 µm
Table 5.16: Some physiochemical properties of synthesised ZSM-5 membrane

<table>
<thead>
<tr>
<th>Zeolite membrane</th>
<th>Method of synthesis</th>
<th>Synthesis time h</th>
<th>Modification techniques</th>
<th>Si/Al gain in zeolite</th>
<th>Adhesion test (weight loss) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5 MIM</td>
<td>72</td>
<td>Etched</td>
<td>19.54</td>
<td>0.986</td>
<td>0.00</td>
</tr>
<tr>
<td>MIM</td>
<td>72</td>
<td>Oxidised</td>
<td>22.40</td>
<td>1.209</td>
<td>0.00</td>
</tr>
<tr>
<td>SGM</td>
<td>48</td>
<td>Etched</td>
<td>27.22</td>
<td>1.406</td>
<td>0.00</td>
</tr>
<tr>
<td>SGM</td>
<td>48</td>
<td>Oxidised</td>
<td>28.63</td>
<td>0.258</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Performance Evaluation of the ZSM-5 membrane Synthesised by Modified In-situ and Secondary Growth Method

Again the ZSM-5 membranes developed or synthesised were tested by pervaporation measurement of 95% constant composition of TIPB and 95 wt % ethanol/water mixture. The TIPB permeation as earlier explained for zeolite A membrane was used to check the quality of the synthesised membrane while the permeation of ethanol/water mixture give the performance of the membrane in a separation process.

The permeate side of the pervaporation set up was always kept under vacuum using vacuum pump achieving pressure of 748 mmHg. The driving force for the pervaporation is the pressure difference across the permeation cell.

The result shows that the total flux of the TIPB/water permeating through the zeolite layer are 19.09 g/m²h (99.95wt% H₂O) and 15.91 g/m²h (99.67wt % H₂O ) for synthesised membrane on oxidised and etched support using MIM. A total flux of 20.68 g/m²h and 12.73 g/m²h for oxidised and etched support using SGM was also obtained.

The flux of TIPB through the ZSM-5 membrane is generally low. This confirms that synthesis of almost defect-free and coherent zeolite membrane was achieved. The small value of flux obtained can be attributed to the existence of non zeolite pore in the membrane which probably came about from the detemplating carried out and this is known to cause cracking if not well handled. Since the pore size of the ZSM-5 is 0.58 nm, the
permeation of large sized-molecule is not expected but because of the presence of few non zeolitic pore mostly occasioned by the presence of pinhole and defect lead to permeation of the large molecule through the pore created by the presence of defect. The pore size of the possible generated from the calcination was not measured, it is believed the low amount of flux of TIPB in the permeate indicate that defect if present is not large enough to prevent the us of the membrane for the separation ethanol/water mixture.

The flux and selectivity of ethanol/water mixture across the membranes synthesised by MIM and SGM is shown in table 5.17 The results obtained using MIM show that the total flux across the ZSM-5 membrane on oxidised support is 112 g/m²h while the selectivity (ratio of ethanol to water composition in permeate divided by the same ratio in the feed) was calculated to be 0.3. The flux across the ZSM-5 membrane etched support was obtained as 104 g/m²h while the selectivity was calculated as 0.5. The result of the analysis of the permeate and feed for membrane prepared using SGM are also shown in table 5.17. The result show total flux of 115 g/m²h (selectivity = 1.4) for oxidised stainless steel support while the flux for etched support is 109 g/m²h (selectivity =1.20). The flux of membrane on oxidised supports is higher than that on etched support, this is mainly due to the formation of a thinner zeolite layer in the oxidised support compared to the etched support.

The flux of ethanol and water was generally low compared to value reported in the literature for ZSM-5 membrane [243]. The low value of flux indicates the influence of the high thickness on the permeation rate. High thickness of zeolite layer imposes low flux of chemical species across the membrane.

The permeation of ethanol/water mixture through the ZSM-5 zeolite membrane have been described by the principle of selectively adsorption/diffusion and desorption at the permeate side. Since the pore size of ethanol and water are smaller than the pore of the ZSM-5 separation layer (0.58 nm), the principle of molecular sieving is out of place in the separation but because ethanol is organophilic, ethanol is selectively adsorbed on the feed side and diffuses through the membrane and are desorbed on the permeate.

The Si/Al ratio of the developed also influences the selectivity of ethanol/water mixture. Water is allow to penetrate the pore of the ZSM-5 zeolite because small degree of hydrophilicity as result of the presence of Al in the framework of ZSM-5 zeolite. Silicalite-1, analogue of ZSM-5 zeolite with all silica framework is completely hydrophobic and will
not allow water through it pore. The value obtained as selectivity using ZSM-5 zeolite will be far higher if the silicalite-I was used instead and can be used as dehydrating agent, a direct opposite of behaviour of zeolite A membrane.

The separation property of ZSM-5 grown on stainless steel has been known to show separation property selectively removing organic species in mixture at room temperature therefore, this confirm that ZSM-5 zeolite produced from ANK is as good as those produced from commercial silica and alumina sources.

![Graph showing TIPB permeation through ZSM-5 membrane synthesised using MIM and SGM](image)

Figure 5.60: TIPB permeation through ZSM-5 membrane synthesised using MIM and SGM (M9, M10, M11, M12 represent ZSM-5 membrane synthesised on oxidised, etched for MIM and oxidised and etched for SGM respectively)
Table 5.17: Evaluation of the quality of the synthesised zeolite ZSM-5 membrane by pervaporation of water/ethanol mixture

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Method</th>
<th>Crystallization time</th>
<th>Thickness (µm)</th>
<th>Pre-treatment method</th>
<th>Flux (g/m²h)</th>
<th>Ethanol/water wt% (feed)</th>
<th>Ethanol /water wt% (permeate)</th>
<th>Separation factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5</td>
<td>MIM 72</td>
<td>59.43</td>
<td>Oxidised</td>
<td>112</td>
<td>95/5</td>
<td>83.04/16.96</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MIM 72</td>
<td>84.38</td>
<td>Etched</td>
<td>104</td>
<td>95/5</td>
<td>90.05/9.95</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SGM 48</td>
<td>49.73</td>
<td>Oxidised</td>
<td>115</td>
<td>95/5</td>
<td>96.41/3.59</td>
<td>1.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SGM 48</td>
<td>68.43</td>
<td>Etched</td>
<td>109</td>
<td>95/5</td>
<td>95.84/4.16</td>
<td>1.20</td>
<td></td>
</tr>
</tbody>
</table>

5.12.4 Synthesis of Zeolite Y Films and Membrane from ANK using Modified In-situ and Secondary Growth Method

5.12.4.1 Synthesis of Zeolite Y Films using Modified In-situ Method

Figure 5.61 shows the XRD pattern of the zeolite Y films obtained between 3 to 12h of crystallization for film produced on etched support while figure 5.64 present the XRD pattern of the film on oxidised supports.

Formation of zeolite Y did not start until 9 h of crystallization. Pure phase of zeolite Y crystal was obtained after 9 h of crystallization as confirmed by the appearance of main diffraction peak of zeolite Y at 2-theta = 6.18°, however there might be an immediate transformation of the zeolite Y phase when there was a further increase of crystallization time beyond 12 h as a result Otswald’s law of successive transformation leading to the formation of zeolite P. The peak corresponding to the stainless steel at 43.3° was observed after 3 and 6 h of crystallization probably because the support was not completely covered by the aluminosilicate gel, however after 9 h of crystallization, there was an appearance of the diffraction peak of the stainless steel. The quality of the XRD pattern of the zeolite Y film on etched support looks inferior to that on oxidised support especially after 9 h of crystallization. Again this can be ascribed to the fact that oxidised support show a better interaction with zeolite synthesis gel and are more widely used [247].
The result of the XRD analysis of powder samples (appendix C) shows growth of the zeolite Y crystal started early in the bulk solution just like was obtained for zeolite A film and ZSM-5 synthesis from ANK using MIM. This indicates that zeolite Y film formation shared a similar possible mechanism with the film earlier produced. Any route of limiting nucleation and crystal growth in the synthesis solution will ultimately promote the formation of zeolite crystal on the support surface. There is no yet any clear techniques that inhibit zeolite formation in the solution/support interface rather than the seeding of the support surface prior to the hydrothermal treatment which was also attempted.

SEM image of the zeolite Y films on etched and oxidised support at 3 h, 6 h 9 h and 12 h are shown in figure 5.62 and figure 5.64 for etched and oxidised supports while the edge view of the zeolite Y film obtained at 12 h for both support is presented in figure 5.63 and 5.66. The SEM image of film on etched and oxidised support shows the evolution of crystalline film. This started with initial deposition of amorphous aluminosilicate gel on the support by gravitation force, however zeolite Y was not formed until when the crystallization time was increased to 9 h when a zeolite Y crystal are seen to covered the support surface. Further increase in the synthesis time leads to complete coverage but did not show any obvious transformation but the XRD result indicate the changes that took place. The results for the synthesis of zeolite Y on both etched and oxidised stainless steel show the formation of zeolite Y on the support is feasible and good result are generally obtained after 9 h of hydrothermal treatment. Etched support provide a better rough surface which create nucleation site and favour crystal growth while the oxidised support as discussed earlier has good compatibility with the zeolite Y synthesis mixture because of presence of –OH group in the synthesis solution [247].

According to the SEM image, there is complete coverage of the support by the zeolite crystals by 9 h of growth time. Zeolite Y intergrowth has become viable and it is impossible to isolate zeolite crystal individually.

The SEM was also used to measure the thickness using the edge view images obtained after 9 h of crystallization. Close examination of the edge view figure 5.63 and 5.66 show that thickness range from 202.75 to 39.69 µm for etched support and 195 to 33.98 µm for film on oxidised support. The thickness decreases with synthesis time. The reason for this have been attributed to the process of dissolution/polymerization that continue to progress with time. Thickness was also reduced probably because the alkali allow more kaolin to
dissolve forming more nuclei and more crystallization to zeolite. The thickness obtained is generally high compared to most report in the synthesis of zeolite Y membrane using commercial or pure chemical.

The EDAX analysis of the zeolite Y films was carried out using the SEM to determine the Si/Al ratio. The results shown in table 5.18 reveal that the Si/Al ratio increase with crystallization as expected. The Si/Al ratio of zeolite Y film samples on the etched support increase from 0.975 to 1.791 when the crystallization time was increased from 3 to 12 h. The Si/Al of the zeolite Y film sample on oxidised support obtained was with the range of 1.473-1.927 with the same crystallization time. Generally the Si/Al ratio fall with the value reported for zeolite Y materials. Zeolite Y has cavities with a diameter 1.3 cm and is interconnected by pores of 0.74 nm. It has a Si/Al ratio of 1.5 to 2.0 while another zeolite of FAU group called zeolite X has a Si/Al ratio of 1-1.5.

Table 5.18 show the outcome of adhesion test on the film obtained and the result show that after adhesion, the film on etched support have a weight loss of between 0.25-0.35% while the weight loss for films on oxidised support is between 0.12-0.28%. The support generally show low weight loss after sonication with the oxidised support showing better adhesion. The increase chemical reactivity as result of the etching and oxidisation of the support might be responsible for strong adhesion between the zeolite crystals and the support.

Finally, the result in the end show that zeolite Y can also be synthesised from ANK using MIM and the result strongly depend on the time of crystallization. The formation of zeolite Y can therefore be controlled by varying the crystallization time. A variety of synthesis route can be used to produce zeolite films and membranes; so far there are no perfect routes toward zeolite film production and more techniques like MIM will continue to be utilize to prepare zeolite Y films.
Figure 5.61: XRD pattern of Zeolite Y films on non-porous stainless steel by MIM from ANK (A) etched stainless steel (B) zeolite Y film sample 3 h (C) zeolite Y film sample 6 h (D) zeolite Y film sample 9 h (E) zeolite Y sample 12 h.

Figure 5.62: SEM image of zeolite Y coatings on etched stainless steel using MIM A. 3 h, B.6 h, C.9 h, D.12 h. Scale bar 50 µm.
Figure 5.63: SEM of edge view of zeolite Y film on etched stainless steel by MIM for 12 h
scale bar = 400 µm

Figure 5.64: XRD pattern of Zeolite Y films on non-porous stainless steel by MIM from ANK (A) oxidised stainless steel (B) zeolite Y film sample 3 h (C) zeolite Y film sample 6 h (D) zeolite Y film sample 9 h (E) zeolite Y sample 12 h
Figure 5.65: SEM image of zeolite Y films on oxidised stainless steel from ANK using MIM A.3 h, B.6 h, C.9 h, D.12 h scale bars = 50 µm

Figure 5.66: SEM image of zeolite Y films on oxidised stainless steel using MIM (edge view) scale bar = 400 µm
Table 5.18: Some physiochemical properties of zeolite Y membrane prepared by MIM

<table>
<thead>
<tr>
<th>Zeolite films/coatings</th>
<th>Method of synthesis</th>
<th>Synthesis time h</th>
<th>Modification techniques</th>
<th>Si/Al</th>
<th>Weight gain in zeolite coating mg/g</th>
<th>Adhesion test (weight loss) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite Y</td>
<td>MIM</td>
<td>3</td>
<td>Etched</td>
<td>0.975</td>
<td>0.2584</td>
<td>0.35</td>
</tr>
<tr>
<td>MIM</td>
<td>6</td>
<td>Etched</td>
<td>1.428</td>
<td>0.3031</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>MIM</td>
<td>9</td>
<td>Etched</td>
<td>1.595</td>
<td>0.3286</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>MIM</td>
<td>12</td>
<td>Etched</td>
<td>1.791</td>
<td>0.3529</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>MIM</td>
<td>3</td>
<td>Oxidised</td>
<td>1.483</td>
<td>0.2429</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>MIM</td>
<td>6</td>
<td>Oxidised</td>
<td>1.606</td>
<td>0.2591</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>MIM</td>
<td>9</td>
<td>Oxidised</td>
<td>1.738</td>
<td>0.2994</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>MIM</td>
<td>12</td>
<td>Oxidised</td>
<td>1.927</td>
<td>0.3143</td>
<td>0.12</td>
<td></td>
</tr>
</tbody>
</table>

5.12.4.2 Synthesis of Zeolite Y Films using Secondary Growth Method

The XRD analyses of the synthesized zeolite Y films were performed and the results are shown in figure 5.67 for etched and figure 5.70 for oxidised support.

It is clear from the XRD pattern that the diffraction peak of zeolite Y phase were noticed within the first 6 h of crystallization for both supports. The diffraction peaks of the zeolite Y films obtained correspond to the study by Vladimirov Nikolakis et al. [287]. Further increase in the synthesis time film lead to obvious reduction in the diffraction peak of zeolite Y and a further increase in the growth time led to the co-crystallization of zeolite P, usually the most stable phase of zeolite Y. The increase in synthesis time did not lead to the transformation of zeolite for the films produced using oxidised support. This is because oxidised provide a better site for zeolite nucleation as mentioned in the previous sections.

The peak at 2 theta = 43° correspond to the stainless steel support phase and similar to ZSM-5 films earlier reported, the peak of the support decrease drastically, an indicative of the high degree of the coverage of the support by the zeolite crystals. The XRD analysis of the excess product (Appendix C) recovered from the synthesis can be used to suggest the
possible sequence of event leading to the formation of the zeolite film as was done earlier. The diffraction peak of zeolite Y was formed in the powdered sample after 6 h and 9 h of hydrothermal synthesis while there is also transformation to the stable phase of zeolite P at 12 h of crystallization.

This also adds to the earlier postulation of homogenous/heterogeneous nucleation of the starting synthesis gel during the nucleation phase in the zeolite films formation from kaolin.

The SEM image of the film at each crystallization time was shown in figure 5.68 for film on etched support and figure 5.71 for the film on oxidised support. The images reveal that there was low coverage of the support surface at the first 3h and there was further increase and obtaining full coverage when the synthesis time was increase from 6 h and 9 h. The thickness of the zeolite films was monitored using the edge view of the films sample and it was found that the value varied from 108-32.98 µm for zeolite Y film on etched support and 104.63 to 25.83 µm for the films sample on oxidised support.

The Si/Al ratio of all the films was measured using EDAX and was found to be within the range of 1.46 to 2.45. It is well within the range of value reported zeolite Y in the literature. The adhesion test carried out on the synthesised zeolite Y film as shown in table 5.19 indicate that small amount of zeolite crystals was lost when the sample were sonicated in an acetone solution. This again proves that a well adhered zeolite Y film on etched and oxidised stainless support was produced from ANK. The weight again of zeolite Y crystals on the support used for the synthesis as shown in table 5.19 indicate the progressive attachment of the crystal on the substrate as the synthesis time increases.
Figure 5.67: XRD pattern of zeolite Y films on non-porous stainless steel by SGM from ANK (A) etched stainless steel (B) zeolite Y film sample 3 h (C) zeolite Y film sample 6 h (D) zeolite Y film sample 9 h (E) zeolite Y sample 12 h

Figure 5.68: SEM image of zeolite Y film on etched stainless steel using SGM technique A.3 h, B.6 h, C.9 h, D.12 h. scale bar = 50 µm
Figure 5.69: SEM image of zeolite Y film on etched stainless steel by SGM at 48 h (edge View)

Figure 5.70: XRD pattern of Zeolite Y films on non-porous stainless steel by SGM from ANK (A) oxidised stainless steel (B) zeolite Y film sample 3 h (C) zeolite Y film sample 6 h (D) zeolite Y film sample 9 h (E) zeolite Y sample 12 h
Figure 5.71: SEM image of zeolite Y coatings on oxidised stainless steel using SGM technique A. 3 h, B.6 h, C.9 h, D.12 h. scale bars = 50 µm

Figure 5.72: SEM image of zeolite Y film on oxidised stainless steel by SGM at 48 h (edge View). Scale bar = 200 µm
Table 5.19: Physiochemical properties of synthesised zeolite Y films by SGM

<table>
<thead>
<tr>
<th>Zeolite films/coatings</th>
<th>Method of synthesis</th>
<th>Synthesis time</th>
<th>Modification techniques</th>
<th>Si/Al Weight gain in zeolite coating mg/g</th>
<th>Adhesion test (weight loss) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite Y</td>
<td>SGM 3 Etched</td>
<td>1.456</td>
<td>0.2894</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SGM 6 Etched</td>
<td>1.527</td>
<td>0.3032</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SGM 9 Etched</td>
<td>1.627</td>
<td>0.3803</td>
<td>0.08</td>
<td></td>
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<tr>
<td></td>
<td>SGM 12 Etched</td>
<td>2.087</td>
<td>0.3988</td>
<td>0.05</td>
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</tr>
<tr>
<td></td>
<td>SGM 3 Oxidised</td>
<td>1.640</td>
<td>0.2860</td>
<td>0.11</td>
<td></td>
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<tr>
<td></td>
<td>SGM 6 Oxidised</td>
<td>1.911</td>
<td>0.3223</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SGM 9 Oxidised</td>
<td>1.963</td>
<td>0.3230</td>
<td>0.06</td>
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<tr>
<td></td>
<td>SGM 12 Oxidised</td>
<td>2.143</td>
<td>0.3289</td>
<td>0.03</td>
<td></td>
</tr>
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5.12.4.3 Synthesis of Zeolite Y Membrane by Modified In-situ and Secondary Growth Method

Zeolite Y membrane production was carried out on both etched and oxidised stainless steel as support using MIM and SGM. The crystallization time of 9 h was selected from the results of the synthesis of zeolite Y films on non-porous support. The synthesis was carried out at a temperature of 100°C after ageing the synthesis aluminosilicate gel for 12 h. The growth of zeolite Y layer on the porous stainless steel was then examined by XRD and SEM. The Si/A/ ratio of the synthesised zeolite film was determined by EDAX while the strength of the bonding between the zeolite crystals and support was done by adhesion test in a sonicator.

Based on the XRD result shown in figure 5.73, 5.76, 5.79, 5.82 for the two supports used by MIM and SGM, Growth of zeolite Y crystal on the supports was observed after 9h of hydrothermal synthesis. The diffraction peaks of pure zeolite Y phase at 2 theta = 6.18°, 10.11°, 11.86°, 15.61°, 17.56° is clearly shown for both etched and oxidised stainless steel and is similar to XRD pattern of standard zeolite Y [288]. The XRD pattern of the firm shows a very clear and well resolved XRD pattern of zeolite Y with little or no
background. The high intensity shown by the XRD pattern and low background confirm that highly crystalline zeolite crystals with minimal impurities are formed [289]. There was a reduction of the diffraction peak corresponding to the Fe phase which confirms the high degree of coverage in all the zeolite Y membrane. The result also confirm that zeolite Y was completely formed from ANK after 9 h of synthesis with any possible transformation not taking place except the time of synthesis is increased further.

SEM images of the zeolite Y membrane obtained using MIM on both etched and oxidised porous stainless steel using the two techniques are presented in figure 5.74 and 5.77 for the top surface and figure 5.75 and 5.78 for the edge view. The support was fully covered by the zeolite Y crystals after 9 h of crystallization while the edge view for both support show that a continuous and well intergrown crystalline zeolite layer is formed. The thickness of the zeolite Y was also measured from the edge views of the zeolite Y films and was found to between 36.32 µm and 29.75 µm for the membrane on etched and oxidised support. The EDAX analysis of the films on the two supports indicates that the Si/Al ratio over randomly selected region of the film surface is in the range of 1.74 and 2.14 which is characteristic of the standard zeolite Y powder.

The SEM image of the produced zeolite Y membrane using SGM is shown in figure 5.80 while the edge view is shown in figure 5.81 for etched support. The images show a well intergrown zeolite Y crystal on the support. The morphology of the crystals are essentially octahedral and it seem to emanate from the support which prove the significance of seeding of the support prior to the zeolite fabrication. The seeding was done to suppresses the growth in the bulk phase and promote nucleation and growth in the support. While seeding has not succeeded in stopping the growth in the fluid phase, the growth in the support was obviously promoted.

Several report on the preparation of zeolite Y membrane using commercial chemical are available[290, 291], but this is the first work on the synthesis of zeolite Y film and membrane from kaolin. This can potentially contribute to the reduction of the cost of production of zeolite membrane.

Similar result was obtained for oxidised support. The SEM (figure 5.83 and 5.84) indicate that the surface was completely covered as seen by the near absence of the peak corresponding to the stainless steel.
To test the strength of the bonding between the support and the zeolite crystals, the prepared zeolite Y membrane was soaked in acetone and sonicated for 30 min. The quantity of zeolite Y crystals peeling off after the sonication otherwise known as weight loss was determined by measuring the weight before and after of the support/film similar to test carried out by Clet et al [292]. The result of the experiment is shown in table 5.20. The result indicate a low weight loss generally with zeolite crystal on oxidised support losing less than etched support for the two techniques.

Oxidised support was again found to give a better membrane in term of the characteristic of the final product. The oxidation of support has also be seen as the most appropriate pre-treatment as it will aid the overall coating of zeolite Y on metal substrate.

Figure 5.73: XRD pattern of zeolite Y membrane on etched porous by MIM
Figure 5.74: SEM image of zeolite Y membrane on etched stainless steel using MIM technique. scale bar 50 µm

Figure 5.75: SEM image of edge view of zeolite Y synthesised on etched support
Figure 5.76: XRD pattern of zeolite Y membrane on oxidised porous by MIM

Figure 5.77: SEM image of zeolite Y membrane on oxidised stainless steel using MIM technique
Figure 5.78: SEM image of edge view of zeolite Y membrane on oxidised stainless steel by MIM scale bar = 400 µm

Figure 5.79: XRD pattern of zeolite Y membrane on etched porous by SGM
Figure 5.80: SEM image of zeolite Y membrane on etched stainless steel using SGM technique. Scale bar = 50 µm

Figure 5.81: SEM image of zeolite Y membrane on etched stainless steel by SGM at 48 h(edge View). Scale bar = 500 µm
Figure 5.82: XRD pattern of zeolite Y membrane on oxidised porous by SGM

Figure 5.83: SEM image of zeolite Y membrane on oxidised stainless steel using SGM technique. Scale bar = 50 µm
Figure 5.84: SEM image of zeolite Y membrane on oxidised stainless steel by SGM at 48 h (edge View). Scale bar = 500 µm

Table 5.20: Some physiochemical properties of zeolite Y membrane prepared by MIM

<table>
<thead>
<tr>
<th>Zeolite membrane</th>
<th>Method of synthesis</th>
<th>Synthesis time</th>
<th>Modification techniques</th>
<th>Si/Al</th>
<th>Weight gain in zeolite coating mg/g</th>
<th>Adhesion test (weight loss) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite Y</td>
<td>MIM</td>
<td>6</td>
<td>Etched</td>
<td>1.451</td>
<td>0.2745</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>MIM</td>
<td>6</td>
<td>Oxidised</td>
<td>1.627</td>
<td>0.4233</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>SGM</td>
<td>6</td>
<td>Etched</td>
<td>1.689</td>
<td>0.3248</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>SGM</td>
<td>6</td>
<td>Oxidised</td>
<td>2.143</td>
<td>0.4547</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Performance Evaluation of the Zeolite Y membrane Synthesised by Modified In-situ and Secondary Growth Method

Firstly, the quality of the developed zeolite Y membrane on etched and oxidised support using MIM and SGM was evaluated by pervaporation of 95 wt % 1,3,5 tri-isopropylbenzene (TIPB) mixture. The result of permeation of TIPB through zeolite Y membrane synthesised using MIM as shown in figure 5.85 reveal a flux of 10.18 g/m²h (99.03 wt % H₂O) and 11.30 g/m²h (98.12 wt % H₂O) for the membrane on etched and oxidised support. The result indicate that flux through the zeolite Y membrane are mainly from the water component, therefore the synthesised zeolite Y from ANK on both etched and
oxidised stainless steel were considered as defect-free and coherent. The permeation of TIPB through zeolite Y membrane prepared using SGM indicates that membrane on etched support has a TIPB flux of 30.24 g/m$^2$h while that on oxidised membrane has a TIPB flux of 49.33 g/m$^2$h. The presence of non zeolitic pore might be responsible for the permeation of the heavy molecule with the water component of the mixture. The flux of TIPB is considered generally low because the permeation of the molecule can only take through the non zeolite pore pathway which can be said to be few in this case.

The separation by pervaporation of 5 wt % water/95 wt % ethanol was also used to test the efficiency of the developed zeolite Y membrane. The selectivity (defined in the same way as zeolite A membrane selectivity) and the flux of 5 wt % water/95 wt % ethanol mixture for zeolite Y membrane synthesised using MIM and SGM on etched and oxidised stainless steel are listed in table 5.21. The result for the membrane developed using MIM indicate a total flux for membrane on etched support as 147 g/m$^2$h (selectivity = 9987) while that on oxidised support is 190 g/m$^2$h (selectivity = 3860). The membrane prepared by SGM show a flux of 203 g/m$^2$h (selectivity = 6637) for membrane on oxidised support and 169 g/m$^2$h (selectivity = 9987) for membrane on etched support. Again the result in table 5.21 showed difference in the separation performance for etched and oxidised support using SGM and MIM technique, the GC error of 3.6% might also account for the difference.

The separation factor obtained in this work showed that the synthesised zeolite Y membrane by both MIM and SGM on both etched and oxidised supports is selective toward water. For example, with value of 6637 and 9987 for the membrane on oxidised and etched support respectively using SGM, it indicates that the developed zeolite Y membrane is a good separator. The high selectivity generally is due to the filling of water in the zeolite micropores or intercrystalline pore between the zeolite crystal [293]. The flux is low compared with values reported for zeolite Y membrane synthesised using commercial chemical [293]. This is mainly due to the thickness of the zeolite layer in the membranes. Aside the pore size of zeolite membrane, thickness of the separating layer of zeolite membrane is an important properties that determine the permeability of such membrane [185].

In summary zeolite Y membrane synthesised from ANK using MIM and SGM show relatively good selectivity toward water in ethanol/water mixture but low permeation. The result corroborate the fact that zeolite Y can as well be used to dehydrate alcohol in
aqueous mixture. It has better advantage over zeolite A because zeolite Y can survive harsh acidic condition while zeolite A cannot because of the high Al content.

Figure 5.85: Flux of TIPB through zeolite Y membrane synthesised from ANK by MIM and SGM (M5,M6,M7,M8 represent ZSM-5 membrane synthesised on oxidised, etched for MIM and oxidised and etched for SGM respectively)

Table 5.21: Evaluation of the quality of the synthesised zeolite Y membrane by pervaporation of water/ethanol mixture

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Method</th>
<th>Crystallisation time h</th>
<th>Thickness µm</th>
<th>Pre-treatment method</th>
<th>Flux g/m²h</th>
<th>Ethanol/water wt% (permeate)</th>
<th>Separation factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite Y membrane</td>
<td>MIM 9</td>
<td>29.75</td>
<td>Oxidised</td>
<td>190</td>
<td>95/5</td>
<td>0.49/99.51</td>
<td>3860</td>
</tr>
<tr>
<td>MIM 9</td>
<td></td>
<td>36.32</td>
<td>Etched</td>
<td>147</td>
<td>95/5</td>
<td>0.19/99.81</td>
<td>9987</td>
</tr>
<tr>
<td>SGM 12</td>
<td></td>
<td>23.74</td>
<td>Oxidised</td>
<td>203</td>
<td>95/5</td>
<td>0.29/99.71</td>
<td>6637</td>
</tr>
<tr>
<td>SGM 9</td>
<td></td>
<td>29.64</td>
<td>Etched</td>
<td>169</td>
<td>95/5</td>
<td>0.19/99.81</td>
<td>9987</td>
</tr>
</tbody>
</table>

*Although differences in the separation factor are observed, these could be accounted for by GC error.
5.12.5 Summary

Zeolite A, ZSM-5 and Y films and membranes was successfully fabricated from ANK in this study using two method of synthesis namely modified in-situ method (MIM) and secondary growth method (SGM). The chemical nature of the support used in the preparation of the films and membranes is well known to influence zeolite nucleation, crystal growth and adhesion. Hence in the development of zeolite films and membrane from kaolin, the effect of support/synthesis gel interaction was investigated.

Two support surface modification techniques namely etching and air oxidation of stainless steel was used in the study on the formation of the zeolite films and membranes using kaolin as a precursor in the preparation of the synthesis gel. XRD and SEM analysis was used to monitor the development of zeolite films and membrane. Zeolite films was initially synthesised on non-porous stainless steel and effect of crystallization time was study to obtain the required synthesis time to prepare the zeolite membranes. Three zeolite films and membranes were prepared namely zeolite A, ZSM-5 and zeolite Y from ANK. The results confirm the best modification process to be air oxidation as all the zeolite films and membrane obtained show high intergrowth and complete coverage at the end of the crystallization. Each membrane developed was tested for their coherence and separation performance using TIPB and water/ethanol mixture by pervaporation. The results show that the synthesised membranes are coherent because they stopped the permeation of TIPB. The separation performance and flux for the developed membrane obtained on the pervaporation of water/ethanol mixture shows a promising result in term of the separation performance. The results indicate that the selectivity is quite high for zeolite A and zeolite Y membrane but were low for ZSM-5 membranes. The flux for all the zeolite membranes samples were low compared to reported values in the literature mainly because of the high thickness of the membrane prepared in this work.
CHAPTER SIX

GENERAL CONCLUSIONS AND RECOMMENDATION FOR FUTURE WORK
Chapter 6: General Conclusions and Recommendation for Future Work

6.1 Conclusions

This study involved the development of zeolites and zeolite membranes from Ahoko Nigerian kaolin (ANK) as an easy and excellent source of production of these important industrial materials. The application of zeolites and zeolite membranes especially in the areas of ion exchange, catalysis and separation are well known, hence the use of local raw material such as ANK is meant to offer alternative and cheaper means of producing this unique and functional material. According to the objectives stated in chapter 1, this study encompassed:

- The investigation of refinement and metakaolinization of raw ANK
- The investigation of the synthesis and characterization of zeolite materials from ANK
- A study of the development of zeolite films and membranes from ANK

The objectives of this study have been largely met. Different zeolite materials namely zeolite A, Y and ZSM-5 as well as films and membranes have been synthesised successfully.

Previous studies on the synthesis of zeolite from kaolin utilized two main steps. These are metakaolinization and hydrothermal synthesis. No mention has been made on the refinement of kaolin prior to the synthesis of zeolite. Furthermore, there is ambiguity on the exact temperature and duration of heating required to form metakaolin. For example Chandrasekhar et al [60] used a temperature of 700°C and exposure time of 2h to produce metakaolin from an Indian kaolin and while Park et al [117] used a temperature of 800°C and exposure time of 3 h.

This study is innovative because unprocessed kaolin from Nigeria was used for the first time as a precursor toward zeolites and zeolite membrane production through a process of refinement (basically quartz removal), a novel metakaolinization technique, never reported before [276] and a new zeolitization process of kaolin through dealumination in addition to the conventional route (synthesis of zeolite from kaolin plus the addition of extra silica).
The quartz content of the raw ANK was successfully reduced to less than 2% using sedimentation techniques. The metakaolinization was carried out using preheated a furnace at 600°C and 10 min to produce the reactive metaphase. The constitution of metakaolin is still a hotly debated topic, however it is recognised as excellent raw material for zeolite production [5] because it has a distorted configuration with octahedral coordination making it more reactive than the parent kaolinite with Al in 6-coordination state.

Zeolite A was successfully synthesised from the metakaolin directly because it has the same Si/Al ratio and does not require any extra silica. Different synthesis conditions of crystallization time, temperature and ageing time were found to influence the product. However, in the synthesis of higher silica zeolite such as zeolite Y and ZSM-5, external silica is required to supplement the Si/Al ratio in the kaolin. This will add extra cost to the synthesis hence a new technique called dealumination was introduced. Zeolite Y and ZSM-5 was initially synthesised from ANK using additional silica to generate conditions needed for direct synthesis of the zeolites from dealuminated metakaolin. Highly crystalline zeolite Y was obtained after 6 h with the ageing time fixed at 12h and heating temperature at 100°C. These conditions were used to produce the zeolites from dealuminated metakaolin.

The dealumination process in kaolin zeolitization is a very important step because it generates a material that is more reactive than metakaolin. ZSM-5 zeolite was also produced from the dealuminated kaolin using the conditions from the synthesis of the zeolite using kaolin and external silica. The result of the syntheses of zeolites from ANK was compared with similar synthesis using different kaolin sources. The zeolites formed faster than most synthesis reported using other kaolin. This was mostly likely due to reactivity of the parent material which shows that location of kaolin deposit can have different effect on the outcome of zeolite synthesis. For example zeolite Y was obtained with 9 h whilst other report crystallization time of 72 h [134]. Previous report on ZSM-5 synthesis from kaolin also indicate the use of high crystallization temperature and time such as 170°C and several days to obtain ZSM-5. Using ANK shows that ZSM-5 can be synthesised at lower temperature such as 140°C and much shorter duration between 24-48 h. This will reduce the cost of production generally. A key weakness of the synthesis of ZSM-5 from ANK is the presence of mordenite and quartz impurities.

Films and membranes of zeolite A, ZSM-5 and zeolite Y were also successfully synthesised using the ANK metakaolin. For the first time, a new technique called modified insitu method (MIM) was used to produce zeolite films in addition to the conventional
secondary growth method (SGM). MIM enables the direct formation of metakaolin coated support into zeolite films because the metakaolin acted as growth centre on the support thereby promoting nucleation and subsequent crystal growth. Initially zeolite films were synthesised on a non-porous stainless steel support to understand the conditions necessary to form coherent and continuous films. Non porous stainless steel was chosen because it is cheaper than porous. The only parameter studied in this work was crystallization time and it proved to be a major controller of the synthesis of the films. The films are known not to form easily on a support surface during zeolite film and membrane synthesis[264]. Therefore two methods were used to modify the surface of the support to improve its compatibility with the zeolite synthesis solution. Results showed that high quality zeolite film and membrane were obtained with complete surface coverage and reasonable intergrowth. The permeation experiment carried out using 1,3, 5 tri-isopropyl benzene (TIPB) show a coherent films for the three zeolite membrane developed in this work. The membranes were selective toward ethanol/water mixture during pervaporation experiment used to evaluate the performance of the synthesised zeolite membranes. The fluxes of chemical species through the membrane was generally low compared to values reported for zeolite membranes in the literature. This was attributed to the greater thickness of the zeolite separating layer on the support.

Significantly in the synthesis of zeolite films and membranes, quartz impurities in the parent metakaolin did not appear in the final product. This was ascribed to the fact that during synthesis gravity prevented the transportation of the quartz phase into the surface of the support. Therefore pure zeolite films and membranes can be developed from an impure kaolin starting material. The results also show that oxidised stainless steel generates a better film and membrane than an etched support, however the two modification method is good enough to modify stainless to allow zeolite crystallization on it. The secondary growth method give a better performance than modified in-situ method because zeolite seeds ensure the decoupling of the nucleation and crystal growth phase and faster time is used to produced the films.

It is therefore concluded that zeolite A, Y and ZSM-5 as well as its film and membrane can be synthesised conveniently from ANK. It is clear during the synthesis of zeolite powder that crystallization time and temperature influence the synthesis of zeolite more than ageing of the aluminosilicate gel. This result is significantly different from other
reported synthesis of zeolite from other kaolin sources. Reactivity of the starting and its metakaolin product is most likely responsible and should be investigated further.

It is hoped that results from this thesis will be useful in the development of a potential commercial zeolite powder for Nigerian market, in addition, it can also be used for the development of membrane and other structured adsorbent or catalyst for applications such as separation and adsorption especially in heat pump and as a sensor.

### 6.2 Recommendation for Future Work

The zeolitization process of ANK require a more extensive study because unlike most literature which reported longer crystallization time for the preparation of zeolites from other kaolin deposit, The zeolite developed in this work use lower crystallization time. The main difference is probably reactivity as earlier stated. The determination of the reactivity of the developed metakaolin is necessary to be explored. This can be done by studying the alumina coordination behaviour using nuclear magnetic resonance (NMR) and other in-situ characterization tool which can be use to monitor the zeolitization from ANK real time.

The quartz content of kaolin is going to be major obstacle toward the application of the zeolite produced in chemical processes, hence complete removal is important. Further removal of the 2% remaining in the ANK is recommended. Smaller size fraction can be considered but using sedimentation technique is tedious and time consuming, hence other methods of kaolin refinement such as magnetic separation, selective flocculation, flotation purification can be explored.

Other impurities such as mica present in the parent material and impurities such mordenite which crystallized during ZSM-5 synthesis require further investigation to remove them. Further experiments using a modified vapour phase method in which kaolin can go into autoclave along with the mineraliser and water and keeping a holder with a seeded support inside the synthesis solution should be investigated. Since most of the impurities are dense, it will remain in solution while the Si and Al ion are transported to the seeded support to form a pure crystal of zeolite. This method can as well replace refinement step of zeolite synthesis from kaolin and ultimately reduce cost of production.
A clear picture of the developed membrane is not complete without carrying N\textsubscript{2} adsorption experiment to know the pore and surface area of the membrane. It is recommended other analysis be explored. The improvement of the zeolite membrane synthesised from kaolin can be investigated especially enhancement of the following properties that directly influence the performance of the membrane. For example the thickness of zeolite layer is an important parameter which influences the flux and selectivity of chemical species through the membrane. Reducing this parameter for zeolite films and membrane synthesised from kaolin will aid industrial uses of the membrane. The use of tubular support as a substrate for zeolite membrane synthesis can be studied. Further characterization of the developed zeolite and zeolite film developed in this work should be carried to better understand the mechanism of zeolite and film synthesis from kaolin. Techniques such as NMR, surface techniques, permoporosimetry is important in understanding the structural and pore behaviour of the zeolites and zeolite films. More work is also required to understand the formation process of zeolite membrane and to predict which mechanism controls the zeolitization process.

Finally modelling of the synthesis parameters via factorial design as it influence the synthesis of zeolite from kaolin as well as their possible interactions can be used in order to understand the optimization process involved in the synthesis and can help in any apparent future equipment design for zeolite production from Nigerian kaolin.
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A.S. Kovo, 2010  


APPENDIX A

Cost Comparison of Zeolite Synthesis using Commercial Chemical and Kaolin

Simple cost estimation was carried out to validate the advantage of zeolite synthesis from kaolin over commercial chemicals.

A basis of 1kg of zeolite synthesis starting material for silica and alumina source was used. Other components of the precursor were kept constant. This was used to justify the advantage of kaolin over commercial chemicals.

For example commercial chemical such as sodium metasilicate and aluminium hydroxide was used as a case study (source of silica and alumina) while kaolin serve as a combined source of silica and alumina.

The simple cost analysis based on the current price source from Sigma –Aldrich is shown below.

Commercial Chemical

A  Sodium metasilicate  £ 16.30
    Aluminium hydroxide  £ 41.50

B  Kaolin  £ 24.30

Saving in cost with other parameters constant  A-B  £33.50
APPENDIX B

SEM and TEM images of Refined and Coarse Ahoko Nigerian Kaolin

TEM image of refined ANK

SEM image of coarse ANK
TEM image of coarse ANK
APPENDIX C

SEM and XRD Patterns of Cleaned Non-porous and Porous Stainless Steel used for the Synthesis of Zeolite Films and Membranes

SEM image of cleaned stainless steel. A is the surface view while B is the edge view. Scale bar = 100µm

SEM image of cleaned porous stainless steel. A is the surface view while B is the edge view. Scale bars = 100µm
XRD pattern of cleaned non-porous stainless steel

XRD pattern of cleaned porous stainless steel
EXAMPLES of XRD pattern of Excess Powder of Zeolite Obtained during Films Synthesis

XRD pattern of powder zeolite A samples of film prepared on etched stainless steel by MIM 3-12h from ANK

XRD pattern of powdered zeolite A film prepared on oxidised stainless steel by MIM 3-12h from ANK
XRD pattern of powder zeolite A sample of film prepared on etched non porous stainless steel by SGM crystallization method 3-12h from ANK.

XRD pattern of powder zeolite A sample of film prepared on oxidised stainless steel by SGM 3-9h from ANK
XRD pattern of ZSM-5 powder obtained from ZSM-5 films prepared by MIM on etched stainless using ANK 24-72h

XRD pattern of ZSM-5 powder obtained from ZSM-5 films prepared by MIM on oxidised stainless using ANK 24-72h
XRD pattern of ZSM-5 powder obtained from ZSM-5 films prepared by SGM on etched stainless using ANK

XRD pattern of ZSM-5 powder obtained from ZSM-5 films prepared by SGM on oxidised stainless using ANK 24-72h
Zeolite Y powder from etched stainless steel by MIM 3-12h

Zeolite Y powder from oxidised stainless steel by MIM 3-12h
XRD pattern of Zeolite Y powder on etched stainless steel by SGM 3-12h

XRD pattern of zeolite Y powder synthesised on oxidised stainless steel support by SGM 3-12h
APPENDIX D

Examples of Synthesis Calculation for Zeolite A and Zeolite Y

Zeolite A synthesis from Ahoko Nigerian Kaolin

The recipe used for the synthesis of zeolite A from ANK metakaolin is shown in the table below.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Na$_2$O</th>
<th>Al$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Verified mole ratio</td>
<td>3.75</td>
<td>1.00</td>
<td>2.50</td>
<td>243.70</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>RMM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>22.99</td>
</tr>
<tr>
<td>Al</td>
<td>26.98</td>
</tr>
<tr>
<td>O</td>
<td>16.00</td>
</tr>
<tr>
<td>Si</td>
<td>28.09</td>
</tr>
<tr>
<td>H</td>
<td>1.01</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>RMM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$O</td>
<td>61.98</td>
</tr>
<tr>
<td>NaOH</td>
<td>40.00</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>18.01</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>60.08</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>101.96</td>
</tr>
<tr>
<td>Na$_2$SiO$_3$</td>
<td>122.07</td>
</tr>
</tbody>
</table>

Metakaolin Required for Zeolite A synthesis

Based on the composition of source metakaolin SiO$_2$/Al$_2$O$_3$ ratio obtained from XRF analysis as 2, the ANK metakaolin required for the synthesis of zeolite A can be calculated as 252.215g.
Source of Na$_2$O

NaOH was used to supplied the required Na$_2$O as follow

\[ \text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH} \]

The NaOH used in this synthesis was supplied by Sigma-Aldrich and is 99% w/w.

Therefore 1g is equivalent to 0.99g NaOH

This means that 1g of NaOH gives 0.02475 mole NaOH

Hence x g is equivalent to 7.5 mole NaOH (based on the balance hydration reaction of Na$_2$O and H$_2$O)

Finally x g is given as 303.030g NaOH

Distilled water

The mole of H$_2$O in the recipe will reduced by one (1) mole because of introduction of 1mole of H$_2$O in the synthesis solution by the NaOH. Therefore the amount of H$_2$O required for the synthesis of zeolite A from ANK metakaolin is 4368.60g

For the purpose of synthesis, scale down of the calculated material was carried out and the following value was obtained

| Metakaolin  | 0.693g |
| NaOH        | 0.832g |
| H$_2$O      | 12g    |

Zeolite Y synthesis from Ahoko Nigerian Kaolin using extra silica source and dealuminated kaolin

The molar formula of the growth gel for the synthesis of zeolite Y using additional silica source is give a table below:
Ingredients | Na₂O | Al₂O₃ | SiO₂ | H₂O
--- | --- | --- | --- | ---
Verified mole ratio | 15 | 1.00 | 15 | 450

Based on the SiO₂/Al₂O₃ ratio of the ANK metakaolin of approx 2, the table of the molar formula can be rewritten to reflect the external silica provided by anhydrous Na₂SiO₃. The new table become

| Ingredients | Na₂O | Al₂O₃ | SiO₂ | SiO₂<sub>external</sub> | H₂O
--- | --- | --- | --- | --- | ---
| Verified mole ratio | 15 | 1.00 | 2.00 | 13.00 | 450

**Metakaolin used for the synthesis**

Based on the table, the mass of metakaolin needed for the synthesis of zeolite Y is calculated as 222.12g.

**Additional Silica**

Again, Sigma-Aldrich supplied the anhydrous sodium metasilicate used as extra silica source for the synthesis of zeolite Y and it contain 47% SiO₂ and 52% Na₂O.

Assuming 10g of Na₂SiO₃ is taken, It mean that it contain 4.7g SiO₂ which is the same as 0.078 mole SiO₂.

Therefore if 10g Na₂SiO₃ contain 0.078mol of SiO₂, It then means that x₇ is contained in 13 mol of SiO₂ for the additional silica.

Hence x₇ of Na₂SiO₃ is calculated by proportion as \[
\frac{13 \times 10}{0.078} = 1666.67 \text{g Na}_2\text{SiO}_3
\]

Since the sodium metasilicate contained 52 % Na₂O, it then mean that \[
\frac{52}{100} \times 1666.67 = 866.67g \text{ Na}_2\text{O}
\]

This is equivalent to13.98 mol of Na₂O.
It means therefore that the supplied sodium metasilicate add extra 13.98 mol to the synthesis mixture. This must be taken away from the recipe composition. Hence outstanding Na₂O = 15 -13.98 mol = 1.02 mol.

**Na₂O**

The source of Na₂O is NaOH since Na₂O does not exist and is obtained based on the equation earlier shown i.e.

\[ \text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH} \]

So the supplied NaOH pellet gives 0.099 mol of water based on the balanced equation. This will also be taken from the water composition in the recipe.

The source of Na₂O is NaOH pellet which is 99% w/w (Aldrich)

So if 1g of NaOH is taken, it contain 0.99g actual NaOH which is equivalent to 0.0248mol NaOH solute

Therefore proportion can be used as follows to obtain the corresponding mass equivalent to the composition of the NaOH in the recipe

Hence 1g ≡ 0.0248mol NaOH

\[ x_g = 2.04 \text{ mol NaOH from the outstanding Na}_2\text{O} \]

It become 82.25g NaOH pellets

**H₂O**

Outstanding water is given as 450 - 1.02 = 448.98 mol H₂O = 8081.64g H₂O

Required recipe are therefore stated below

Metakaolin : 222.12g

Na₂SiO₃ : 1666.67g

NaOH : 82.25g

H₂O: 8081.64g
A multiplier factor of 36.406/8081.64 was then used to reduced the quantity of the individual precursor used for the synthesis of zeolite Y as

**Metakaolin: 1g**

\[
\text{Na}_2\text{SiO}_3: 7.4814g \\
\text{NaOH}: 0.3602g \\
\text{H}_2\text{O}: 36.406g
\]

**Zeolite Y using dealuminated Ahoko Nigerian kaolin**

The molar formula of the growth gel for the synthesis of zeolite Y using dealuminated metakaolin produced from Ahoko Nigerian kaolin is give a table below:

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Na\textsubscript{2}O</th>
<th>Al\textsubscript{2}O\textsubscript{3}</th>
<th>Si\textsubscript{O}_2</th>
<th>H\textsubscript{2}O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Verified mole ratio</td>
<td>2.2</td>
<td>1.00</td>
<td>6</td>
<td>140</td>
</tr>
</tbody>
</table>

**Metakaolin used for the synthesis**

Based on the table, the mass of metakaolin needed for the synthesis of zeolite Y is calculated as \(1 \times 101.96 + 6 \times 60.08 = 462.44\text{g}\)

**Source of Na\textsubscript{2}O**

NaOH is used to supplied the required Na\textsubscript{2}O as follow

\[
\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}
\]

The NaOH used in this synthesis was supplied by Sigma-Aldrich and is 99% w/w

Therefore 1g is equivalent to 0.99g NaOH

This means that 1g of NaOH gives 0.02475 mole NaOH

Hence \(x_g\) of equivalent to 4.4 mol NaOH (based on the balance hydration reaction of Na\textsubscript{2}O and H\textsubscript{2}O)

Finally \(x_g\) is given as 177.780g NaOH
Distilled water

The mole of H$_2$O in the recipe will reduced by 2.2 mol because of the introduction of H$_2$O in the synthesis solution by NaOH. Therefore the amount of H$_2$O required for the synthesis of zeolite A from ANK metakaolin is 2480.40g

For the purpose of synthesis, scale down of the calculated material was carried out by a factor of 12/2480.40 and the following value was obtained.

Metakaolin  2.24g
NaOH       0.860g
H$_2$O      12g
APPENDIX E

Calibration curve used for Ethanol/water Analysis by Gas Chromatography

Five external standards were prepared and were analysed three times and their peak area averaged serving as a calibration curve as shown in the figure below. A direct relationship between the peak size and the composition of ethanol existed. The standard was chosen carefully to accommodate the entire range expected in the unknown. The sample was then compared with the peak area to determine the concentration of the permeate.

The correlation coefficient was obtained as $R^2 = 0.9987$ and standard deviation of 3.6% (also called standard error of estimate)
APPENDIX F

PUBLICATIONS AND PRESENTATIONS

PUBLICATIONS


PRESENTATIONS

• **A.S. Kovo** and S. M. Holmes (2008), Preliminary study of refinement of Nigerian Ahoko kaolin for zeolite membrane synthesis, Graduate Research Conference, The University of Manchester, UK.


• **A. S. Kovo** and S. M. Holmes (2009), Synthesis and characterization of zeolite A from Nigerian Ahoko kaolin using novel, lower temperature, metakaolinization technique, presented during the British Zeolite Association Conference at University of Cumbria in August 2009.

• **A. S. Kovo** and S. M. Holmes (2009), Synthesis and characterization of ZSM-5 zeolite from Nigerian Ahoko kaolin using novel, low temperature,
metakaolinization technique, postgraduate student conference, School of Chemical Engineering and Analytical Science, The University of Manchester, UK.


- **A. S. Kovo** (2010), Development of zeolites from Ahoko Nigerian kaolin, oral presentation during postgraduate student conference, School of Chemical Engineering and Analytical Science, The University of Manchester, UK.

**OTHER CORROBORATION**