Synthesis and Characterization of Zeolite Y Catalyst from Ethiopian Ansho Kaolin for Heavy Hydrocarbon Cracking

By: - Adane Tilahun Beshir

A Thesis Submitted to

The Department of Chemical Engineering

School of Mechanical, Chemical, and Material Engineering

Presented in Partial Fulfillment of the Requirement for the Degree of Master's in Chemical Engineering (Specialization in Process Engineering)

Office of Graduate Studies

Adama Science and Technology University

Adama, Ethiopia

July 2020

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Approval of Board of Examiners

Submitted by

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Name	Signature	Date

As thesis research advisors, we hereby certify that we have read and evaluated this thesis prepared under our guidance by Adane Tilahun Beshir. We recommended the paper to be submitted as fulfilling the requirements for the Degree of Master in Chemical Engineering (Specialization in Process Engineering).

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Advisor	Signature	Date
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Co-Advisor	Signature	Date

We, the undersigned, members of the Board of Examiners of the final open defense by **Adane Tilahun Beshir** have read and evaluated his thesis entitled **"Synthesis and Characterization of Zeolite Y Catalyst from Ethiopian Ansho Kaolin for Heavy Hydrocarbon Cracking"** and examined the candidate. This is, therefore, to certify that the thesis has been accepted in partial fulfillment of the requirement for the Degree of Masters in Chemical Engineering (Specialization in Process Engineering) complies with the regulation of the University.

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Declaration

I hereby declare that this MSc Thesis entitled **" Synthesis and Characterization of Zeolite Y Catalyst from Ethiopian Ansho Kaolin for Heavy Hydrocarbon Cracking"** is my original work and has not been presented for a degree in any other university for the award of any degree, and all sources of material used for this thesis have been duly acknowledged.

Name: Adane Tilahun Beshir

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This MSc Thesis has been submitted for examination with my approval as thesis advisor/ dissertation Supervisor.

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Abstract

Zeolites are inorganic materials widely used in the chemical industry as catalysts. In this study, kaolin based Zeolite Y and P1have been synthesized successfully in the laboratory at 110^{o}C, 24hrs. crystallization temperature and time respectively. The Synthesis process involves several steps, including collection of Ethiopian Hosanna kaolin, calcination of kaolin, dealumination to get the desired Si/Al ratio and final hydrothermal synthesis. Calcination of kaolin carried out with different temperature range to convert kaolin into the reactive metastable amorphous phase metakaolin. Amorphous metakaolin was obtained at a temperature of above 550^{o}C at residence time of 3hrs. Dealumination technique; both conventional and novel methods were used to arrange metakaolin silica alumina ratio good enough for zeolite synthesis. The complete silica analysis results show that the composition of the Hosanna metakaolin changed considerably during dealumination by both the novel and conventional method.

The zeolite Y was synthesized with hydrothermal method using teflon lined stainless steel autoclave reactor. A kaolin calcined at a temperature of 675^{o}C was used as a source of silica and alumina. The stoichiometric amount of NaOH, metakaolin and water were used for the zeolite gel synthesis. Then the gel aged for 1 days at ambient condition and crystallize hydrothermally in an autoclave reactor at temperature of 110^{o}C for 24 hrs. Finally, the synthesized zeolites were characterized by atomic absorption spectrophotometry (AAS), X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). The results found from characterization confirms that zeolite Y synthesized successfully.

The effects of calcination temperature of kaolin (ranging from 450^{o}C up to 1050^{o}C), gel aging time (1 up to 9 days) and crystallization time (1 up to 4 days) have been investigated. As a results, the kaolin calcination temperature above 550^{o}C have found suitable for zeolite synthesis regardless of zeolite type. Zeolite transformation from zeolite Y to P1 took place by changing the gel aging and crystallization time in zeolite Y synthesis. This transformation was observed by powder X-ray diffraction. The performance of the zeolite Y was evaluated by decomposing polyethylene (PE) using TGA. The results obtained showed a decrease in the decomposition temperature, for all PE/Catalyst mixtures, as a results of the use of each of the additional catalyst dosage with respect to pure PE. Moreover, the PE-30 mass % zeolite Y mixture was reduced the

decomposition temperature of T_{10} (temperature at which 10% of sample mass decomposed) by 53^{o}C relative to the pure.

CHAPTER ONE

1. INTRODUCTION

1.1. Background

Even though Ethiopia is endowed with a variety of mineral resources, i.e. Geological surveys proved that Ethiopia has an abundant natural resource of i) metals and precious metals; ii) coal, and iii) industrial minerals [1] , it has not utilized the resources to a reasonable amount regardless of the resources importance to its economy. This is often due to different reasons such as, inadequate research on the geological location and deposit of the mineral, inadequate knowledge on the types of the mineral and its benefits, and therefore the lack of promotion are the causes for having a weak mineral industry in Ethiopia.

To the contrary, Ethiopia has registered impressive economic growth for several years, ranging between 8 to 12 percent [1] to sustain this growth the Government of Ethiopia (GoE) follows a series of integrated five-year development plans, called Growth and Transformation Plans (GTP) to guide the state-led industrial development. Growth and transformation plans two, covering 2016–2020, sets the general target to realize a mean growth of 11% within the next five years and lays the ground to achieve lower-middle-income status by 2025 [1].To realize these goals, the GoE continues to take a position heavily in large-scale social, infrastructural and energy projects and also the mining sector remains one among the priority sectors in GTP II, with main strategic directions of attracting sizable foreign direct investment (FDI) for exploration and extraction of minerals, increase (tenfold) foreign exchange earnings of the sector and focus on production of mineral inputs for the manufacturing sector that promote import substitution. Mining operations within the country are expected to be a crucial economic catalyst for the Government's export-orientated development strategy. Since the mining and quarrying sector is very underdeveloped and its contribution to the Gross Domestic Product (GDP) is limited to 2% in 2016/17 the goal is to bring the minerals sector to a level of larger than 10% GDP contributions within 10 years [2].

The Geological Survey of Ethiopia conducted in 2011 and found opportunities for kaolin resource development, from a total reserve of 960,062 tons, with pure kaolin amounting to 291,355 tons [3]. According to the world mining data report in 2019, Ethiopia produced 373,600 metric tons of

industrial minerals. This totally fetched 35 million USD (United State of America Dollar) foreign currency to the country by 2017. Within the same year, Ethiopia produced 4,600 metric ton of kaolin which is 1.23 % of the total production of industrial mineral (Table1.1) the growth of the sector was less than expected. Thus to curve this problem Ethiopian Ministry of Mines recently handed over its first mining survey license for Kaolin to China Communications Constructions Company Ltd. (CCCC) [3]. This shows that the Ethiopian government's commitment to utilizing the kaolin resources for the implementation of the GTP II goal. Besides, the involvement of investors within the kaolin sector will reduce the number of imported minerals and enable the utilization of the mines within the country. In line with this, most of the kaolin produced within the country is consumed by the ceramics industries. To extend the consumption rate of the kaolin resource trying to find another application area is mandatory [4]. Now a day's production of zeolite from natural kaolin gets bigger attention because the conventional zeolite synthesis system that employs pure sodium silicate and sodium aluminate are expensive, with the negative impact on the environment and hence not sustainable in comparison to kaolinite-based zeolites synthesis [5].

Table 1. 1 World mining data report 2019 G.C (Ethiopian kaolin production)

Years	2013	2014	2015	2016	2017
Kaolin (In metric tons)	3534	4530	4600	4600	4600

Zeolites are highly crystalline, porous aluminosilicate earth metal minerals based on a three-dimensional network of tetrahedral $[SiO_4]^{4-}$ and $[Al_4]^{5-}$ whose framework are open structures with cations positioned within the material's pores. The cation neutralizes the charge on the lattice [5]. Zeolites have been classified based on silica-alumina ratios into three types, viz., low, intermediate, and high silica/alumina zeolites. Typical example of the low silica/alumina ratio zeolites are A, X, and sodalite, which possess Si/A1 ratios between 1 and 1.5. Examples of the intermediate silica/alumina zeolites (Si/Al = 2 to 5) are Y, L, large pore mordenite and omega, while examples of high Si/Al zeolites (Si/Al = 10 to many thousand) are ZSM-5, ZSM-11, EU-1, EU-2, Dealuminated Y, mordenite, and erionite.

There are several uses of zeolites in industry, among them, the most important being is as a catalyst, but others include gas separation, ion exchange, and as a medicine. A unique property possessed by zeolites making them useful as catalysts for interesting applications is shape selectivity, which is that the ability to restrict or prevent the passage of molecules based on size or stearic effects. The catalytic conversion of heavy hydrocarbons like crude oil, linear chain plastics (PE) and biomass are often converted to the lower molecular chain by the zeolite catalytic activities this in-turn help to crack the crude oil to useful products and reduce the plastic waste from the environment by changing it in to fuel.

The increasing world demand for energy has intensified the processing of heavy hydrocarbon feedstock. Catalytic Cracking is a crucial refining process utilized in upgrading these heavy hydrocarbons to a high valued product. Since this process came into existence, it has continuously undergone changes and major improvements associated with the technology were made because of the catalyst. Approximately 1,100 tons of catalyst is manufactured a every day to be used worldwide in over 200 Fluid Catalytic Cracking Units (FCC) [6].

Associated with this, Ethiopia is richly endowed with an enormous reserve of crude oil and natural gas as shown on (Table 1.2) and also it begins producing oil at Kalub and Hilala fields within the eastern part of the country which, according to the Ministry of Mines of Ethiopia, is proven to possess 6-8 trillion cubic meters of crude oil [2]. The Chinese company Poly-GCL Petroleum Investment Limited is liable for the extraction of both crude oil and natural gas in the Ogaden area. The other Chinese firm Communications Construction Company Ltd (CCCC) is the first company to obtain a license for kaolin exploration and beneficiation. Thus, these may be shows the integrated plan to utilize the Ethiopian kaolin (a mineral containing the silica and alumina) for the synthesis of zeolites Y to the heavy hydrocarbon cracking process.

Beside to the crude oil and natural gas, the plastics and plastic packaging are an integral and important part of the global economy. Plastics production has surged over the past 50 years, from 15 million tons in 1964 to 311 million tons in 2014, and is predicted to double again over the subsequent 20 years, as plastics come to serve increasingly many applications. Its seemingly countless applications include plastic packaging, life-saving medical devices, clothes, toys, various industrial and agricultural uses, and so on.

Table 1. 2 Natural gas - proved reserves (m^3), Country (Source CIA world fact book 2019)

Rank	Country	Value (billion m^3)
70	Mauritania	28.32
71	Croatia	24.92
72	Ethiopia	24.92
73	Ghana	22.65
74	Japan	20.9

*Date of information Jan 1st, 2018 G.C

Since most plastic in use today comes from hydrocarbons derived from crude oil, natural gas and coal. Thus, this work used polyethylene plastic as a hydrocarbon to crack and show the performance of the synthesized zeolite Y. Accordingly polyethylene is the main plastic used as a packaging materials and the most important application; currently, packaging represents 26% of the entire volume of plastics used. Plastic packaging not only delivers direct economic benefits but also can contribute to increased levels of resource productivity, as an example, plastic packaging can reduce food waste by extending shelf life and may reduce fuel consumption for transportation by bringing packaging weight down [7]. While delivering many benefits, the present plastics economy also has important drawbacks that are getting more apparent by the day. Today, 95% of plastic packaging material value, or 80–120 billion USD annually, is lost to the economy after short first use. Plastic packaging generates significant negative externalities, conservatively valued by UNEP (United Nations Environment Program) at 40 billion USD, and expected to extend with strong volume growth during a business-as-usual scenario. Each year, a minimum of 8 million tons of plastics leak into the ocean, which is like dumping the contents of one garbage truck into the ocean every minute. If no action is taken, this is often expected to increase to two per minute by 2030 and four per minute by 2050.

Estimates suggest that plastic packaging represents the major share of this leakage [7].We have already known that the buildup of plastic in Ethiopia's landfills, lakes, and rivers represents a growing environmental risk. More recently, we have come to know that plastic poses an urgent even deadly threat to public and animal health, too. Yet, Ethiopia's efforts to deal with the plastic crisis remain consistently focused on the wrong end of the life cycle: waste management. Ministry's Solid and unsafe Waste Compliance Director Girma Gemechu told The Ethiopian Herald that the Ministry has found alarming results from the study conducted on the status of plastic pollution in about 24 areas in Ethiopia. Plastic pollution constitutes 9 to 14 percent portion of the entire waste, and nearly 50 percent of it is not properly disposed of. He added, "Malpractices in plastic disposal, like burning them easily release dangerous chemicals like CH_4 and CO_2 to the soil and air. It also spoils the aesthetic value of the environment, since plastic do not easily decompose, they cause floods by clogging ditches and sewers [8].

The fossil driven heavy hydrocarbons are mostly non-biodegradable and remain within the environment for many years. Conventional recycling methods like sorting and grinding can recycle only a small amount of total plastic waste. Nowadays, different new technology is being used to treat heavy-hydrocarbons materials like crude petroleum, waste plastic (i.e. PE, PP, PVC, etc.) and biomass. Among such process cracking and pyrolysis are worthy to mention and therefore the above-mentioned potential problems are often tackled using these processes. Although many researchers have worked on zeolite synthesis from different kaolin sources of the planet, no such effort has been observed on the use of Ethiopian natural kaolin for zeolite Y synthesis and applying it as a catalyst for heavy hydrocarbon cracking.

Therefore, this thesis is all about the synthesis and characterization of zeolite-Y from locally available kaolin and evaluation of the performance of the synthesized catalyst by doing catalytic cracking of heavy hydrocarbon like polyethylene using thermogravimetric analysis (TGA). In addition, the study deals with the factor affecting the catalytic cracking process like catalysts dosage, which is, evaluated intimately using TGA graphs. The effect of calcination temperature of kaolin in to metakaolin, gel aging and crystallization time on zeolite Y catalysts synthesis examined under different synthesis conditions. In this regard, atomic absorption spectrophotometry (AAS), X-ray diffraction pattern (XRD), scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FTIR) and TGA were used for characterization. The

characterization were showed the chemical composition, the crystallinity, the morphology, the structural groups and the thermal stability of the raw material and the synthesized zeolite Y respectively.

1.2 Statement of the Problem

In the past couple of decades a number of researches have been conducted to confirm the potential of Ethiopian kaolin for different zeolite synthesis like zeolite A and X, however, no such attempt has been carried out on the utilization of Ethiopian natural kaolin for the purpose of zeolite Y synthesis. On the other hand, having recognized the importance of kaolin for production of zeolite in the mineral sector and for the inclusive economic development of Ethiopia, identification of a new application area for kaolin resource is necessary. Thus to fill this gap, this paper tries to show a new application area for Ethiopian kaolin in the field of catalyst synthesis specially zeolite Y. In addition, environmental crises of plastic waste accumulation got a bigger attention in developing countries. To alleviate this problem reprocessing the waste plastic to useful forms such as fuels are essential. Since, the crude oil refining process depends greatly on zeolite catalyst, it is essential to synthesis zeolite Y for cracking application too. In line with this and to achieve the above-mentioned objectives, zeolite Y is synthesized, characterized and evaluated from Ethiopian kaolin for application of heavy hydrocarbon cracking as a catalyst in the thermogravimetric analysis (TGA).

1.3 Significance of the Study

About 99% of the world's petroleum that is sourced from crude oil is dependent on the use of zeolite as a catalyst, this catalytic property of zeolites is as a result of the combination of the intrinsic properties found in zeolite and these properties are responsible for its overall behavior [9].

The interest in the use of kaolin to develop zeolites is attributed to the fact that it provides a cheaper and easy means of obtaining zeolite rather than the usual expensive process involving the use of synthetic chemicals such as soluble salt of silica and alumina [10]. Due to the above facts, Ethiopian Ministry of Mines (MoM) has extended its first mining survey license for Kaolin to China Communications Constructions Company Ltd (CCCC) [3]. However, the Chinese company

(CCCC) launches its exploration of kaolin in Ethiopia might not be a coincidence with the beginning of Ethiopian crude oil development instead it is probably a deliberate or a well-organized movement to check whether or not Ethiopian kaolin can be used for synthesis of zeolite Y for application of a catalyst in the fluidized catalytic cracking process (FCC) in petroleum industry.

Ethiopia for the first time ever began producing crude oil at Kalub and Hilala fields in the eastern part of the country. A groundbreaking trial-production ceremony saw three oil wells spewing 150 barrels, each raising the nation's hopes of generating the badly needed hard currency and creating employment. The Chinese company Poly-GCL Petroleum Investment Limited is responsible for the extraction of both crude oil and natural gas in the Ogaden area, Somali regional state in eastern Ethiopia [2].Thus, the potential of Ethiopia to produce petroleum in the near future and the environmental threat that waste plastic accumulation pose will initiate the consumption of local kaolin. The production of zeolite Y from this natural kaolin not only reduce or cease the imported synthetic zeolite Y, for the application of petroleum refinery as a catalyst to the catalytic cracking process, but also mitigate the waste plastic problems and generate a foreign currency too.

1.4 Objectives of the Study

1.4.1 General Objective

Synthesis and characterize zeolite Y catalyst from Ethiopian Ansho kaolin for heavy hydrocarbon cracking, especially PE.

1.4.2 Specific Objectives

i. To synthesize and characterize Zeolite Y catalyst from Ansho kaolin.
ii. To study the effects of calcination temperature of kaolin to metakaolin, gel aging time in gel formation and crystallization time in crystallization of zeolite Y synthesis.
iii. To evaluate the performance of zeolite Y catalyst, related to catalyst dosage and cracking temperature in Polyethylene catalytic cracking using TGA.

1.5 Scope of the Study

The scope of this work covers the laboratory scale preparation, characterization and evaluation of zeolite Y catalyst produced from Ethiopian Ansho Kaolin as a catalyst for a heavy hydrocarbon such as Polyethylene (PE) cracking using thermogravimetric analysis (TGA).

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Historical Background of Zeolite

Zeolites are a family of crystalline aluminosilicate minerals. The history of zeolites began in 1756 when the Swedish mineralogist Cronstedt discovered the first zeolite mineral. The word Zeolite is from two Greek words zein and lithos meaning “boiling" and “stone” respectively. Since then, zeolite has been recognized as a separate group of minerals, in which it is one of the most abundant on earth [11]. Zeolites are microporous crystalline materials with regular structures consisting of molecular-sized pores and channels. The structure of zeolites contains aluminum, silicon, and oxygen in regular frameworks with cations and water in the pores. The silicon and aluminum are tetrahedrally coordinated with each other through shared oxygen atoms. Each AlO_4 tetrahedron in the framework bears a net negative charge balanced by cations such as Na^+, Ca^{+2}. Chemically, the structural formula of a crystallographic unit cell of the zeolite may represent as:

$$Mx/n\ [(AlO_2)\ x\ (SiO_2)\ y].\ wH_2O$$

where M is the cation of an alkali or alkaline earth atom, n is the charge on that atom, x and y are the total numbers of tetrahedral per unit cell, w is the number of water molecules per unit cell and the ratio y/x usually has values of 1 to 5. In the case of the high silica zeolite, y/x can be ranging from 10 to 100 or even higher. The tetrahedral form of the structural framework in zeolites with centrally located Si or Al atoms and corners occupied by oxygen atoms being shared between SiO_4 and AlO_4, oriented in such a way that the framework develops voids or pores in the form of cages and channels. As an example, zeolite X also called Na-X [i.e., $Na88\ (AlO_2)88\ (SiO_2)104.\ 220\ H_2O$, where x is 88, y is 104 and hence y/x is 1.2 which is between 1 and 5 [12, 13].

There are two kinds of zeolites: natural zeolites and synthetic zeolites. About fifty natural zeolites have been known. Each of them has a different chemical composition and structure. The most common are analcime, chabazite, clinoptilolite, heulandites, erionite, ferrierite, laumontite, mordenite, and phillipsite. There are more than two hundred those have been synthesized for

specific applications such as molecular sieves, cation exchangers, and industrial catalysts and as adsorbent materials [13, 14].

From the early 1940s onwards, systematic synthesis studies on zeolites were started. Due to the unique properties of zeolites, extensive attempts for zeolite synthesis were begun. Milton, in 1949, had successfully prepared zeolites A, X, and Na-P by the end of the year 1949. The golden age of zeolite development, i.e. the period between 1954 to early 1980, saw a massive exploration of zeolites with high, medium and low Si/Al ratios [15].Nowadays, the increasing interest in zeolite synthesis from low-cost materials has promoted the development of various studies on their conversion into zeolitic materials, giving rise to comprehensive literature. Clay minerals such as kaolinite have been used as the sources of Al and Si for the synthesis of several types of zeolites such as zeolite X and zeolite Y with faujasite structure [16].

2.2 The Framework Structure and Properties of Zeolite

All zeolites are composed of an elementary structure of an aluminosilicate framework, which comprises of a tetrahedral arrangement of silicon cations (Si^{4+}) and aluminum cations (Al^{3+}) that are surrounded by four oxygen anions (O^{2-}). Each oxygen ion within the Si-O and Al-O bonds connects two cations and is shared between two tetrahedrons as shown in figure 2.1 a and b, thus yielding a macromolecular three-dimensional framework of SiO_2 and AlO_2 tetrahedral building blocks. In this arrangement of atoms, each tetrahedron consists of four O atoms surrounding a-Si or Al cation, resulting in a three-dimensional structure of silicate tetrahedral with a Si : O ratio of 1:2 [17].

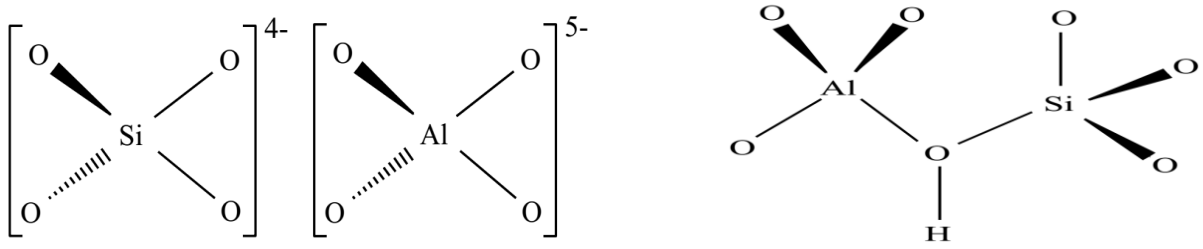


Figure 2.1 a) The tetrahedral arrangement of the SiO_4 and AlO_4 molecules forming unit blocks of a zeolite b) The tetrahedral arrangement of the Si-O and Al-O bonds forming a unit block of zeolite

The crystal structures of zeolites are normally categorized into primary building units (PBUs) and secondary building units (SBUs). The PBUs are the $(SiO4)^{4+}$ and $(AlO4)^{5+}$ tetrahedral. These combine by sharing oxygen with adjacent tetrahedral to form a spacial arrangement of simple geometric forms – the SBUs. The SBUs come in a variety of forms – some being single rings, double rings, polyhedra or even more complex units, which are linked together in a variety of ways to produce a unique system of channels and cages. A zeolite's unit cell always contains an integral number of SBUs. At present, 23 different types of SBUs are known to exist. An example of how SBUs are linked together to produce a unique zeolite structure is shown in Figure 2.2 and Figure 2.3 [17].

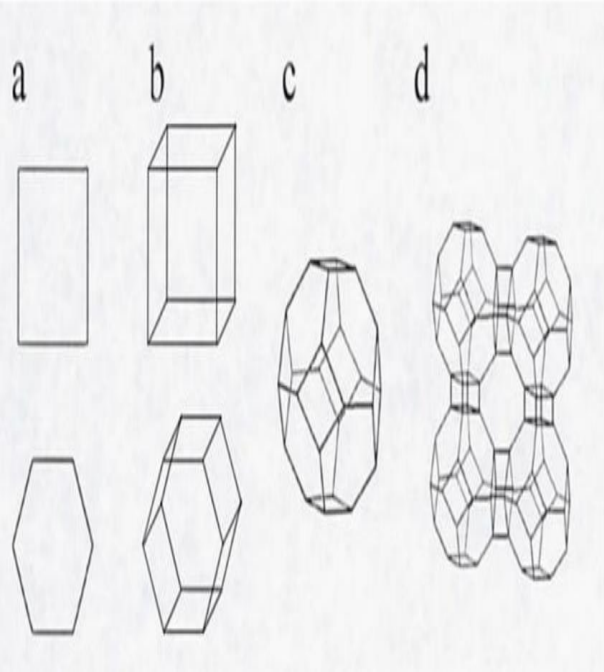


Figure 2.2 Different orientations of secondary building unites (SBUs) the intersections of lines Represent the centers of tetrahedral cations (Al or Si).
a) Single 4- and 6- rings; b) Double 4- and 6- rings;
c) Truncated cubo-octahedrons composed of 4- and 6- rings; d) Four truncated cubo-octahedrons linked together by four, double 4- rings.

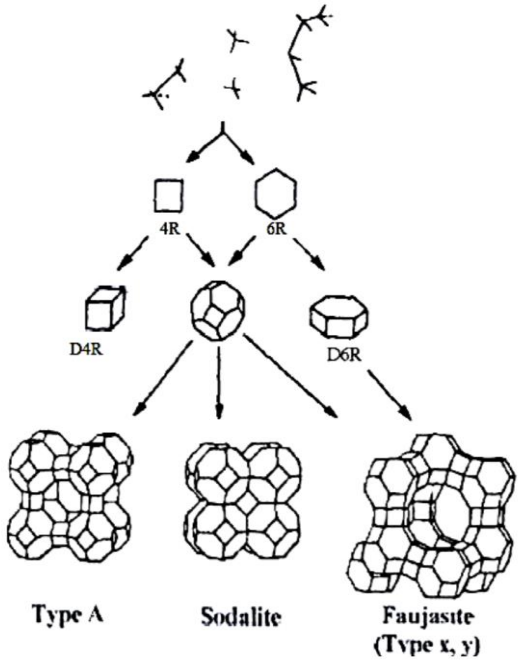


Figure 2.3 Structures of three different zeolites and there micropore system.

Over the year's zeolites have attracted a great deal of attention among researchers and scientists due to their flexibility and adaptability. Following their discovery in 1756 by Axel Fredrik Cronstedt, zeolites were found to be good adsorbents, ion exchangers and molecular sieves. The molecular sieve properties of zeolites, in particular, are extensively employed in the industry. Zeolites have been used in the separation of straight-chain hydrocarbons from branched-chain hydrocarbons, chemical sensors in industrial process control, environmental and indoor air-quality monitoring, effluent, and auto-exhaust control, medical monitoring, air separation and removal of heavy metals to mention but a few [17].

Zeolite Y

Zeolite Y is a synthetic sodium aluminosilicate often also referred to as zeolite NaY. Zeolite Y is a member of the Faujasite family very similar to zeolite X. Zeolite Y exhibits the Faujasite (FAU) structure as shown in the Figure 2.3. It has a 3-dimensional pore structure with pores running perpendicular to each other in the x, y and z planes similar to each other in the x, y and z planes similar to Linde Type A (LTA) frameworks structure and is made of secondary building units 4, 6 and 6-6. The pore diameter is large at 7.4Å, aperture defined by a twelve (12)-member oxygen ring and leads into a larger cavity of diameter 12Å. The cavity is surrounded by 10 sodalite cages (truncated octahedral) connected on their hexagonal faces. Its unit cell is cubic (a= 24.7Å) with face diagonal-3m symmetry. Zeolite Y has a void volume fraction of 0.48 and Si/Al ratio of 2-5. It decomposes at 793˚C [18]. Applications include its use as a cracking catalyst. It is used in acidic form in petroleum refinery catalytic cracking units to increase the yield of gasoline and diesel fuel from crude oil feedstock by cracking heavy paraffin into gasoline grade naphtha [19]. Zeolite Y is known to supersede X in this use because it is both more active and more stable at high temperatures due to the higher Si/Al ratio.

2.3 Method Used In Zeolite Synthesis

Crystalline solid-state materials production can be classified into two groups. There are those whose reaction occurs in solid state and those where it occurs in a liquid state. This solid-state reactions often occurs at temperatures above 300°C to overcome the difficulties that arises from the transportation of the reactants to the sites where this reaction takes place, while in the other group the reactions occur in the liquid phase, in the presence of a solvent [20] and since the

transportation of molecules is much easier in the liquid phase than in the solid phase, these syntheses are carried out at a relatively lower temperature, much lower than 300°C. Hence, the syntheses of zeolites are carried out in the liquid phase and there are three methods used in the synthesis of zeolites and they include [9].

2.3.1 Hydrothermal Methods

A hydrothermal method is the earliest method of synthesis of zeolite in which synthesis is carried out in the presence of water as a solvent, base solution as mineralizer and a temperature range of 90–180°C. The reactants are usually put inside a Teflon-lined Autoclave with hydrothermal synthesis pressure (up to 15 bars) for optimum zeolite production. Since the temperatures required for the hydrothermal synthesis of zeolite is much lower, this method is much easier and cheaper than other methods [20]. Nucleation and crystallization of the crystals do not necessarily occur in solution but can take place at the gels present in the mixtures.

2.3.2 Solvothermal Methods

Solvothermal method of zeolite synthesis involves the use of a solvent to produce the zeolite. Based on this broad description, the hydrothermal method can also be said to be a member of this classification, since water is by far the most common solvent. There are however other solvents such as alcohols, hydrocarbons, pyridine, etc. that had been used successfully for zeolite synthesis. The solvents used in the solvothermal method of zeolite synthesis varies from nonpolar and hydrophobic to polar and hydrophilic [20].

2.3.3 Ionothermal Methods

Ionothermal is another special category of solvothermal synthesis method in which the solvent used are mainly ionic compounds and are not molecular in nature as in the case of the solvothermal solvents. The solvents used in the Ionothermal method of zeolite synthesis are called ionic liquids and their ionic nature has an effect on some particular properties such as low vapor pressures [20].

2.4 Hydrothermal Synthesis of Zeolite

Synthesis of zeolite through the hydrothermal route is a multiphase reaction-crystallization process, usually encompassing at least one liquid phase and both amorphous and crystalline solid

phases. From the time when it was introduced by Barrer in the year 1948, the hydrothermal synthesis process has to turn out to be the rudimentary route for zeolite synthesis. Byrappa and Yoshimura described the hydrothermal synthesis as an in-situ reaction occurring above room temperature in an aqueous solution under pressure (approximately 14.5038 psi) [5].

Aluminosilicate zeolites are usually synthesized under hydrothermal conditions owing to some advantages prescribed by different researchers which include, the high reactivity of reactants, low energy consumption, low air pollution, easy to control the solution, formational of metastable phases, and unique condensed phases. However, different world scientist has reported an alternative zeolite synthesis route based on fluoride containing compositions as mineralizing media. Nevertheless, Cundy and Cox maintained that the major synthesis route for many zeolites and zeotypes is the hydrothermal process. Although the intricacy of the hydrothermal process underscores the necessity for cautious observation and analysis of the synthesis mechanism, *this present work is principally concerned with the hydrothermal synthesis of zeolites from Kaolinite natural resources* [5].

2.5 Materials of Zeolite Synthesis

The synthesis of zeolites is usually carried out using the hydrothermal synthesis method using commercial chemicals as the primary source of SiO_2 and Al_2O_3. The production process of these chemicals is expensive leading to complications and high cost of zeolite synthesis, resulting in a limitation in commercialization and uses of these zeolites in many industrial applications. As a result the use of cheap and relatively abundant raw materials which serve as combined sources of silica and alumina for the synthesis of zeolite is highly desirable [9].

Synthetic zeolites made from natural or synthetic raw materials having a wide range of chemical properties, pore size, and better thermal stability are commercially widely used compared to natural zeolites because they are of higher purity and have a more uniform particle size [9].

The preparation of synthetic zeolite from silica and alumina chemical sources are expensive, yet cheaper raw materials such as clay minerals, natural zeolite, municipal solid waste, coal ashes, industrial slag, incineration ashes, etc. are being used as starting materials for zeolite synthesis. Presently a lot of researches are ongoing with respect to the use of clay and other raw materials in

zeolite synthesis, which has the advantage of being relatively cheaper, readily available and more abundant [9].

Table 2. 1 Tabular representation of cheap, abundant and readily available raw materials that have been used to synthesize zeolite and the type of zeolite synthesized [9].

Name of raw materials	**Types of zeolite synthesized**
Kaolin	NaX, NaA, Y, ZSM-5, RHA, hydroxysodalite, β
Rice husk ash	Analcime, Y
Fly Ash	X-type Zeolite
Waste Perlite	Na-P1
SiO_2 Sinter and Perlite glass.	Zeolite Y, P, and gmelinite
Template-free batches of macro-porous α-alumina disks	ZSM-5
Halloysite mineral	NaA
Lithium Slag	NaX-1
Brazilian chrysotile and rice husk.	NaA
Coal Fly Ash	hydroxysodalite or Na-P1
Silicic acid and Sodium aluminate	ZSM-5

2.5.1 Kaolin

Kaolin is a white colored substance, which is also known as China Clay. Its fine particles size and color are the physical properties, which differentiate kaolin from other industrial clay base mineral. In kaolin, mineral such as feldspar decomposed to form a hydrous aluminum silicate or mineral

kaolinite, which is the main component of kaolin. There are many applications of kaolin. Kaolin is primarily used in papermaking industries to improve the appearance of paper such as brightness, smoothness, and gloss. The excellent characteristic in color, gloss, and hardness of kaolin make it a valuable substance for ceramic ware and other tableware manufacturing. Kaolin also has been used in many industries including paint, rubber, cable insulation, specialty film and fertilizers [21, 22].

Kaolin is a type of clay whose major mineral component is kaolinite. Kaolinite has a chemical formula $Al_2Si_2O_5$ (OH) $_4$ [23]. Kaolinite has a structure built of SiO_4 in the tetrahedral sheet bonded to similar Al $(OH)_4$ octahedral sheet to form the silica gibbsite layer. The sheets of kaolinite are a single tetrahedral and octahedral i.e. 1:1 layer. Each layer consists of a sheet of SiO_4 tetrahedra forming six-membered silicate rings connected via common oxygen atoms to a sheet of AlO_6 octahedral building four-membered aluminate rings. Kaolinite is formed by rock weathering. It is made up of tiny, thin, pseudohexagonal, flexible sheets of triclinic crystal with a diameter of 0.2–12 μm. It has a density of 2.1–2.6 g/cm3 [24].

Kaolin is made reactive through dehydroxylation or a process called metakaolinization. Metakaolinization implies the removal or loss of the Hydroxyl group. When kaolin is heated, a series of transformations occur. This is accompanied by the rearrangement of the octahedral layer to the tetrahedral orientation in the calcined clay. Calcination has been undertaken at different temperatures and different times. The process occurs between the temperatures of 500 – 900 °C. Some major applications of kaolin include the production of the following: paper, paint, ceramics, rubber, ink, plastics, fiberglass, Portland cement and as a catalyst. Modification of clay minerals by converting them to zeolites was reported as early as 1935 [25].

2.5.2 Ethiopian Kaolin

Economic kaolin resources of Ethiopia are mostly associated with acidic intrusive rocks e.g., granites and pegmatites and gneissic rocks. Kaolins hosted by sedimentary rocks are reported in Blue Nile river basin, Ogaden basin and Mekele Outlier [26]. Based on World mining data report 2019, Ethiopia's domestic production of kaolin varied from 3534 tons and 4600 tons per year between 2013 and 2017. Moreover, according to Geological Survey of Ethiopia, there are a number

of kaolin deposit have found in the country (i.e. In Sidamo, Shoa, and Harerge). Among them, the following are worthy to mention:

The Bombowha kaolin is the most geologically investigated and processed kaolin site so far. Its occurrence is located in Oromia regional state Bombowha area (Adola greenstone region) and geographically located at a point coordinates of 38° 46' 30" E and 06° 05' 20" N [27]. Kaolinite is the dominant mineral in the kaolinitic clays of Bombowha clay. Traces of illiite/muscovite, feldspar and quartz are common characteristics. Gibbsite and halloysite, as minor constituents, are typical of the Bombowha kaolin [26].Three deposits (i.e. Bombowha I, II and III) are recognized in Bombowha area. Bombowha kaolin occurs on kaolinized pegmatites and granites [28]. All the pegmatites and granites occur in deformed metamorphic rocks. The kaolin morphology of the Bombowha deposit is dominantly elongated with books and plates of kaolinite. The halloysites are up to 4–5 μm in length and 0.25 μm in diameter. They are mostly tabular in shape but some tend to be platelet. The Bombowha kaolin contains books of kaolinite up to 8 μm in length. Alumina is generally above 35% for the Bombowha kaolin with impurity elements such as iron (<1%), total alkali and titanium accounting for less than 3% [26].

Kombolcha kaolin is one of the kaolin deposit of Ethiopia, which is located, Kombolcha town, at about 18 km north of Harar. The Kaolinized granite occurrences are located within 4-10kms radius of Kombolcha town. There are four kaolin deposits: Gende Errer, Gende Moli, and two other localities [29]. The Geological Survey of Ethiopia has previously studied three of these occurrences in detail. Considering the mineralogy of Kombolcha kaolin, Kaolinite is the dominant mineral in all kaolinitic clays. Traces of illiite/muscovite, feldspar and quartz are common characteristics. The Kombolcha Kaolin consists of well preserved, expanded books of Kaolinite. The length of books may be up to 15μm and individual flakes are less than 5μ (usually less than 1-3μ). The Kombolcha Kaolin consists of some partly altered feldspar with pitted surfaces [26]. According to Haile Michael et al [26], the Kombolcha Kaolin bears lower alumina, and higher total alkali and iron, averaging 33.24%, 2.54% and 2.63%, respectively.

Belesa Kaolin is among one of Ethiopia kaolin, its occurrence is situated 10 km Northeast of Hossaina town [29]. Kaolinite is the predominant clay mineral contained in the Belesa kaolin. Quartz is the only non-clay mineral contained in minor amount in the kaolinitic clays of Belesa

area. The presence and absence of quartz in the clay did not influence the crystal structure of the kaolinite. The Kaolin occurrence do not have any impurities such as iron coating, Fe and Ti minerals and other non-clay minerals such as mica and feldspar [30].

Ansho kaolin is the second deposit in the Hossaina area apart from Belesa kaolin. Its occurrence is located in Hadiya zone and is geographically located at a point coordinates of 35°09'20" E, and 8°16'00'' N. Ansho areas is located 50 km southwest of Hossaina, in Gimbichu sub sheet 0737D1. Gimbichu is located 32 km far away from Hossaina and can be accessed via a gravel surfaced all weather road [29]. The kaolin occurrences are found approximately 18km south of Gimbichu, and can be accessed through a dry weather road. Ansho kaolin occurrence is generally fine grained, yellowish grey to white on the surface and at depth respectively. Both quartz bearing and non-quartz varieties [29].

Kaolin production was entirely from the processing plant in Bombowuha to two main customers, the Tabor Ceramics Factory and Awash Melkasa Aluminium Sulfate and Sulphuric Acid Factory. The aluminium sulphate is used for water purification, but this is under threat from substitution by cheaper, imported polyelectrolyte. The Tabor Ceramics factory is currently favoring kaolin from Hossaina (Ansho), despite lack of consistency in delivered material from this deposit. The quality of product from the Bombowuha plant is low.

2.6 Synthesis of Zeolite from Kaolin

The searching for cost-effective, environmentally friendly and sustainable starting material required for production of zeolite leads to the study on modification of kaolinite minerals for zeolite production. Youssef et al. as a more cost-efficient system, recommend kaolinite-based zeolites that are produced from cheap natural resources as against the conventional process that employs pure sodium silicate and sodium aluminate which are expensive, with a negative impact on the environment and hence not sustainable. Likewise, Rocha et al. Roozeboom et al. emphasize that zeolite production from cheap raw natural resources is of economic significance and hence its synthesis parameters need to be optimized [5].

Kaolinite is a clay mineral of chemical formula $Al_2O_32SiO_2.2H_2O$ that has a structure of 1:1 uncharged dioctahedral layer where each layer consists of a single silica tetrahedral sheet and

single alumina octahedral sheet. The early work of Barrer provides the essence for the use of kaolinite as a suitable starting material for the production of zeolite. Ever since quite appreciated research has been carried out on the transformation of kaolin into the zeolite. Basically, there are two steps in producing zeolite from kaolinite: (i) metakaolinization – which involves transforming kaolin to metakaolin by chemically activating the kaolin clay using heat, and (ii) zeolization – treatment of the metakaolin with an aqueous alkali solution to form zeolite.

Kaolinite	500°C-900°C	Metakaolinite	Water
$Si_2Al_2O_5\ (OH)_4$	→	$2SiO_2.Al_2O_3$ +	$2\ H_2O$

The transformation of four hydroxyl groups into two water molecules will occur as described in the reaction below.

$$4(OH^-) \rightarrow 2H_2O + 2O^{2-}$$

However, Dion et al. argued that metakaolinization occurs according to first order and diffusion processes. The first order process aided the realization of water from the two contiguous hydroxyl groups, while the latter is responsible for the transport of water. The metakaolin will then go through hydrothermal handling in a solution of NaOH (aqueous solution) to synthesize the required zeolite [5].

2.6.1 Calcination of Kaolin (Metakaolin)

This is the process used to put the beneficiated clay to a more reactive phase -metakaolin (semi-amorphous) as kaolin in its natural state is less reactive and forms hydrosodalite when reacted with sodium hydroxide .Various authors reported calcinations temperature to range between 500-900°C and time range of 1 to 8 hrs. .

The process of metakaolinization involves the loss of hydroxyl group and is followed by rearrangement of the octahedral layer to tetrahedral orientation in the calcined kaolin. Kaolin is an aluminosilicate and the Al^{3+}ion can be in the form of IV and VI coordination state and it is essential in zeolite formation that $Al^{3+}$is in IV coordination, hence metakaolin with IV Al coordination and amorphous in nature is a necessary path toward zeolite synthesis from kaolin [31, 32]. Wardle and Brindley describe the metakaolinization reactions as follows:-

Kaolinite	500°C-900°C	Metakaolinite	Water

$$Si_2Al_2O_5(OH)_4 \rightarrow 2SiO_2.Al_2O_3 + 2H_2O$$

2.6.2 Dealumination of the Calcined Kaolin

To increase the SiO_2:Al_2O_3 ratio of the starting material, dealumination is an alternative route to reduce the alumina content from the metakaolin sources. The dealumination reaction given as:

$$Al_2O_3(s) + 3H_2SO_4(aq) \leftrightarrow Al_2(SO_4)_3(aq) + 3H_2O\ldots. \quad \text{Dealumination}$$

Dealumination of metakaolin by using sulfuric acid reaction is carried out by two methods. These methods are a non- heating method known as Novel approach and a heating method known as Conventional approach. The extent of dealumination is determined by varying the reaction times.

2.6.2.1 Conventional Method of Dealumination

This method often requires the input of an external source of thermal energy to facilitate the needed kinetic energy for effective collision and successful reaction between the metakaolin and sulfuric acid. In all cases, dealumination was done by using three fold of the stoichiometric amount of 60-wt % sulfuric acid required. This was done to enhance mass transfer and to reduce cake formation tendencies [33].

2.6.2.2 Non-Heating (Novel) Method of Dealumination

This method of dealumination reaction does not require an external source of thermal energy to facilitate the dealumination of the metakaolin, but instead it employs the heat released when sulphuric acid was mixed with water.

2.6.3 Gel Formation

Conventional zeolite syntheses are performed from a reaction medium containing an aqueous phase of dissolved reagents and solid species, which may exist as gel particles and be suspended in solution. The gel is formed from copolymerization or condensation-polymerization mechanism.

2.6.4 Crystallization of zeolite

The crystallization process is a most important step in zeolite synthesis and it involves a condensation reaction taking place between silicate and aluminate in a strong basic solution. The process of zeolite crystallization can be divided into two major steps. These are nucleation and crystal growth.

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

Crystal growth is the series of processes by which an atom or a molecule is incorporated into the surface of a crystal, causing an increase in size. Nucleation and crystal growth are promoted by several parameters such as incubation time and history of the system. Again, the size of the crystal can be controlled based on the choice of conditions of the crystallization [34].

2.7 Zeolite Characterization

Zeolite characterization used to identify the crystalline product by comparing its properties to those of known standards. X-Ray diffraction, Scanning electron microscopy, thermogravimetric analysis, compositional analysis (X-Ray florescence) and the crystal size of the synthesized zeolite are methods used to describe a particular type of zeolite.

2.7.1 Atomic absorption spectrometry (AAS)

AAS is one of an analytical technique that measures the concentration of an element. It is the process involving the absorption of light by free atoms or ions of an element at a wavelength specific to that element. In atomic absorption spectroscopy, emission, absorption and fluorescence energy is put into the atom population by thermal, electromagnetic, chemical and electrical forms of energy and is converted to light energy by various atomic and electronic processes before measurement. It is useful not only for the identification but also for the quantitative determination of many elements present in samples. The technique is specific, in that individual element in each

sample can be reliably identified and it is sensitive, enabling small amounts of an element down to parts per billion of a gram in a sample.

2.7.2 X-Ray diffraction (XRD)

X-ray diffraction (XRD) is an essential tool in the identification and characterization of zeolites at various stages in their syntheses, modifications, and uses as catalysts. X-ray diffraction is commonly used to identify the presence and quantitatively determine the amount of crystalline zeolite present. It provides the unit cell parameters of the product. X-ray diffractometer is based on the elastic scattering theory. The diffraction patterns differ for all types of zeolites. The purpose of XRD patterns is to be able to determine the unit cell parameters and thus its unit cell volume [15]. Powder X-ray diffraction measurements use Cu-Kα radiations to determine zeolite crystallinity. Phase identification can also be performed by XRD. During this activity, the zeolite sample is subjected to an x-ray beam ray. The intensity of the emergent rays is recorded as a function of the deflection angle 2Ɵ.

Using Wulff Bragg‟s law, i.e.

$$n\lambda = 2d \sin\theta$$

Where n is an integer,

λ is the wavelength

d is the lattice spacing and

θ is the deflection angle

For crystals with cubic symmetry e.g. FAU, the size of the unit cell a_0 can be determined from the angular positions of the reflection.

$$a_0 = \frac{\lambda\sqrt{h^2 + k^2 + l^2}}{2\sin\Theta}$$

hkl is an orientation indicated by the Miller's indices

2.7.3 Fourier transform infrared spectrometry (FTIR)

The FTIR measures vibrations caused by internal stretching of the framework tetrahedra and vibrations related to the external linkages between the tetrahedra. The spectrometer has two mirrors, a fixed mirror and a moving mirror, a detector and a beam splitter. A radiation from the IR source is directed to the beam splitter, which splits the beam into two parts, one to the fixed mirror and the other to the moving. FTIR is operated based on the principle of diffuse reflectance. An incident beams emits a spectra of both absorbance and reflectance features. A detector records radiations that pass through the sample. Calibrations on the detector enable radiations to be read in the form of energy signals.

2.7.4 Scanning Electron Microscopy (SEM)

SEM is a versatile advanced instrument, which is largely employed to observe the surface phenomena of the materials. It has played a major role in the understanding of zeolitic materials. SEM is used to determine the morphology of the zeolites. The size of zeolites studied with this apparatus is between 20nm and 20μm. Information gathered from the SEM picture of material includes: Morphology indicates the shape and size, while topography indicates the surface features of an object or "how it looks", its texture, smoothness or roughness. According to zeolite: crystal form i.e. type of zeolite and crystal form and size, external surface such as relative roughness and purity of phase i.e. presence of other zeolite types. The crystal size is an estimate of the crystallite size and or the aggregate particle size [35].

SEM consists principally of an electron gun, electron lenses, scan coils and detectors. The electron gun generates a beam of electrons from a cathode or filament usually made of tungsten. The electrons escape at high voltage from the filament. The final size of the beam is controlled by the electron lenses. Scan coils make the beam scan over the sample or target. When the electrons hit the target, they collide with electrons in the inner atomic shells. Back scattered and secondary electrons that escape from the sample are detected. If there is no detection, the image will be black [36].

2.7.5 Thermogravimetric Analysis (TGA/DTG)

TGA is one of the basic methods in thermal analysis. The mass of a substance is measured as a function of temperature or time while a substance is subjected to a controlled temperature program in a technique. This measurement provides information about physical phenomena, such as phase transitions, absorption and desorption; as well as chemical phenomena including chemisorption, thermal decomposition, and solid-gas reactions (e.g., oxidation or reduction).

DTG is difference thermogravimetric ratio of measurement of dm (weight loss or weight increase) at heating/cooling/isotherm, interpretation by dm over T or time (-dm/dt). In majority cases subsequent decomposition process give overlapping decomposition stages. In most of cases, a reliable qualitative and quantitative evaluation of the TG curve is impossible without having its first derivative (i.e. DTG curve). The DTG peak height at any temperature gives the rate of mass loss (dm/dT in mg/min unit). With DTG curve Ti, Tf and Tmax (the temperature of the maximum mass loss rate) can be precisely determined in overlapping reactions.

2.8 Application Area of Zeolite

The structure of zeolite generally consists of many channels, cavities and interconnected voids, which are occupied by cations and water molecules. Synthetic zeolites are crystalline molecular sieves with pores of molecular dimensions and with well-defined structures, which have a high total surface area that makes them effective in a wide range of applications such as catalysis, ion exchange, and selective adsorption. Industrial applications make use of synthetic zeolites of high purity, which have larger cavities than the natural zeolites. These larger cavities enable synthetic zeolites to adsorb or hold molecules that the natural zeolites do not. Synthetic zeolites are used in a variety of applications as a catalyst in petrochemical cracking, ion exchange in water softening and purification, and adsorption in the removal of heavy metals [37].

Zeolites are a component of about 130 catalysts on a total of 840 catalysts used in the world. Compared to other types of catalysts, zeolites exhibit exceptional properties with respect to both activity and selectivity because of their ability to absorb and transform molecules in their inner pore volume. An important class of reactions performed by zeolites is the acid-catalyzed reactions. For that, the zeolite framework needs to contain protons, which give rise to high Brønsted acidity.

Synthetic zeolites of the type X and Y have an important role in the cracking of heavy crude oil into lighter highly valuable products, resulting in a major increase in the yield of gasoline [38].

2.9 Related Literature and Previous Works

Faujasite zeolites (A zeolite mineral consisting of sodalite cages connected through hexagonal prisms) has been synthesized using kaolin samples from Kankara Nigeria by Atta et al. Sodium hydroxide was fused into the kaolin and the resulting mixture was allowed to age for 3 days and subsequently crystallized at 100˚C for 24 hrs. The resulting product was a zeolite having a mixed phase of zeolite X and zeolite Y [9].

L.Ayele et al.[39] have synthesized zeolite A from Ethiopian kaolin. In order to evaluate the potential of the raw kaolin, an attempt to purify it has been carried out by separation and sedimentation for the removal of quartz, and ultrasonic suspension and magnetic separation for the removal of iron. Finally, both raw and the purified kaolin were calcined in air at 600^{o}C for 3hrs. to yield metakaolin. Then the metakaolin mixed in sodium hydroxide to produce the synthesized gel. Crystallization of the gel using hydrothermal treatment to produce zeolite was done at a temperature of 100˚C for 6 hrs. and the final solids are washed and dried overnight to get zeolite A.

Htay and Oo produced zeolite Y from kaolin by fusing kaolin with sodium hydroxide at a temperature of 850˚C for 3hrs. The fused mixture was hydrothermally crystallized at 100˚C for 16 hrs. and the products were mixed phases of zeolite Y and zeolite P [9].

Ma et al. [9] synthesized zeolite type X using kaolin as the precursor material and the conventional method of zeolite synthesis by the fusion of the kaolin with sodium hydroxide at a temperature of 90˚C for 8 hrs.

Atta et al. [40] studied the synthesis of Faujasite Zeolites from Kankara kaolin Clay. The clay being unreactive was transformed into a more reactive (amorphous) form by subjecting it to heating at 600^{o}C before using it as a reactant. Dealumination of metakaolin was affected by leaching out the structural alumina with Sulphuric acid, to meet the silica-alumina mole ratio 65, 66 required for the targeted zeolite.

Kovo et al. [9] investigated the synthesis and characterization of zeolite Y and ZSM-5 from Nigerian Ahoko Kaolin using a novel, lower temperature, metakaolinization technique. In their study, 30 kg of a raw representative sample of kaolin clay was used along with sodium hydroxide, which was obtained from Sigma-Aldrich (99% analytical grade). From the study, it was concluded that reactive metakaolin could be produced at very short exposure times, of the order of 10 minutes, to a temperature of 600^{o}C. This is a significant reduction in both time and temperature on previous studies and represents both a reduced energy requirement and the potential for a continuous production process.

L.Ayele et al. [41] compared the conventional and the alkali fusion synthesis of zeolite A from low-grade Ethiopian kaolin. Synthesis of zeolite A using low-grade Bombowha kaolin from Ethiopia has been carried out by two methods: the conventional hydrothermal synthesis and alkali fusion followed by hydrothermal treatment. In the synthesis process, the metakaolinization was achieved by calcination of the kaolin at 600 °C for 3 hrs. for the conventional method and for the alkali fusion method, the activation of the raw kaolin was done by alkali fusion for only 1 hr. Zeolite A was the main product obtained using 3 M NaOH concentration, 100 °C reaction temperature and 3 hrs. crystallization time in both methods. The molar gel composition for the best synthesis conditions for both methods was Na_2O: Al_2O_3: $2SiO_2$: $37H_2O$. The main advantage of the alkali fusion method is that it allows using low-grade virgin kaolin without purification, whereas the conventional method only yields good quality zeolite A when the raw kaolin is purified.

Htay and Oo prepared zeolite Y catalyst from kaolin by fusing kaolin with sodium hydroxide at a temperature of 850˚C for 3 hrs. for application of petroleum cracking. The prepared zeolite NaY was modified by exchanging with ammonium ion and hydrogen ion. The catalytic activities of prepared zeolite NaY, NH4Y and HY were investigated by using the simplified laboratory scale fixed-bed catalytic cracking unit. In this study, the feed was heavy gas oil. The cracking process was carried out with a catalyst to oil ratio of 3 at the reaction temperature of 450-510˚C. The degree of catalytic activities of the prepared zeolite NaY, NH_4Y and HY were determined in terms of conversion yield and formation of gasoline. The conversion yield by NaY, NH_4Y, and HY were 74%, 83.3%, and 82% respectively. The gasoline contents in the cracked products were 26%, 31% and 43% respectively [42].

Vinıcius et al. studied the Polyethylene catalytic cracking by thermogravimetric analysis. In this work, the authors compare the interactions between the polymeric molecules and the contact surface of zeolitic catalysts (hierarchical and standard Beta zeolites, Y zeolite, ZSM-5, ZSM-12 and MCM-22) with different properties, in the catalytic cracking reactions of low-density polyethylene. In cracking reactions, the polymeric macromolecules mainly react in the external surface of the catalysts due to the several diffusional limitations imposed. Based on this process, zeolites with larger external area values (hierarchical Beta, standard Beta, ZSM-5 and MCM-22) promoted the lower values of degradation temperature with high efficiency of conversion [43].

An extensive search to get additional published documents about the zeolite synthesis from Ethiopia kaolin was carried out with a lot of dedication and commitment but could not get any other. However, many other Ethiopian researchers have synthesized zeolite from different raw material such as rice husk, fly ash, rice husk ash, and coal fly ash etc.

CHAPTER THREE

3. MATERIALS AND METHOD

In this chapter, the materials and methods of experiments conducted are reported. The main purpose of this part is to develop a chemically and thermally stable and most probably commercially viable Zeolite Y catalyst for cracking of higher hydrocarbon molecules e.g. polyethylene into a lower one and more economic value e.g. gasoline. The first step to achieving this goal was to identify different materials suitable for the synthesis of zeolite materials and it is explained as shown in Table 2.1. As a results the kaolin clay was found to be suitable, particularly the one from Ansho.

The series of work adopted in this part includes all the experiments starting from collection of raw Ansho kaolin clay to the refinement of the raw samples, metakaolinization, dealumination, up to the actual synthesis of Zeolite Y and its characterization. Afterwards, the performance of the synthesized zeolite Y have been evaluated using thermogravimetric analysis (TGA).

Ansho kaolin was procured and subjected to refinement by beneficiation process. Then the calcinations of kaolin followed before application in zeolite products formulations. The formulated products were strictly monitored at stages involved by carrying out analysis using instrumental equipment such as atomic absorption spectrometer (AAS), x-ray diffractometer (XRD), scanning electronic microscope (SEM), fourier transform infrared (FTIR) and thermogravimetric analysis (TGA). Other allied characterization methods were employed to identify crystallite type and the determination of other utility properties. These procedures are detailed in the following section.

3.1 Materials

a) Ansho Kaolin supplied from Tabor Ceramic Products Share Company, located in Hawassa city. However, the kaolin was originally sourced from Ansho area around Hadiya zone.

b) Reagents

In carrying out the experiments, the materials and equipment listed hereunder were used.

3.1.1 Beneficiation equipment/chemicals

The equipment and chemicals used for beneficiation of Ansho Kaolin are listed in Table 3.1.

Table 3. 1 List of Materials/equipment and chemicals used during Beneficiation

Equipment/material	**Quantity**
Plastic Bucket	15 Liters (2 Nos)
Sieve	230 MESH (63 µm)
Plastic carpet	1pcs.
Chemicals	**Quantity**
Raw Ansho Kaolin	3Kg
Distilled Water	10 liter
Hydrochloric Acid (HCl)	500ml

3.1.2 Calcination equipment/materials

The equipment/materials used for calcination of Ansho kaolin are presented in Table 3.2

Table 3. 2 List of Materials/Equipment used during Calcination

Equipment /Materials	**Quantity**
Locally fabricated crucible	0.1 liter (3 Nos)
Electric Muffle furnace	2 (SX-2.5-12)
Desiccator with silica gel	1

3.1.3 Dealumination material/chemicals

The equipment/materials used in carrying out dealumination of metakaolin are presented in Table 3.3.

Table 3. 3 List of Materials/equipment and chemicals used during Dealumination

Equipment/Materials	**Quantity**
Electronic Weighing Machine	1
85-2 Heating mantle with Magnetic stirrer	1
Three neck-round bottom flask, thermometer and reflux condenser	1set
Micro Processor pH-mV meter	1
White-man filter paper	2 packs
Chemicals	**Quantity**
Ansho Kaolin (calcined @ 296,450,650,675,700,900,1050ºC)	1/2 Kg
Sulfuric Acid (H_2SO_4)	2, 98 Wt.% and 60 Wt.%

3.1.4 Gelation material/chemicals

The equipment and chemicals used for gelation of Ansho Kaolin are listed in Table 3.4.

Table 3. 4 List of Materials/equipment and chemicals used for Gel formation and actual synthesis of zeolite Y

Equipment/Materials	**Supplied by**	**Quantity/ Model**
Teflon Lined Hydrothermal Autoclave Reactor	Techinstro	1
Electrically driven magnetic stirrer	Sinossource	85-2 Magnetic Stirrer
Drying oven	Clifton, England	NE9-56S
Solids Handling	Armfield, England	CEN-MKII-11
Micro Processor pH-mV meter	Spectronics, India	SL-145
Chemical	**Supplied by**	**Quantity**
Dealuminated Metakaolin with Silica/Alumina ratio of 7.6.	Tabor Ceramic Products Share Company Hawassa	1/2 Kg
Sodium Hydroxide (NaOH)	Alphax Chemical, India	2 pcs (500gm each)
Deionized Water	Material Science and Engineering Department, ASTU.	

3.3 Methodology

The methodology utilized in this study for the synthesis of Zeolite Y from kaolin was conventional hydrothermal synthesis method. Aluminosilicate zeolites are usually synthesized under hydrothermal conditions because, it has some advantages prescribed by different researchers

which include, the high reactivity of reactants, low energy consumption, low air pollution, easy to regulate the solution, formational of metastable phases, and unique condensed phases.

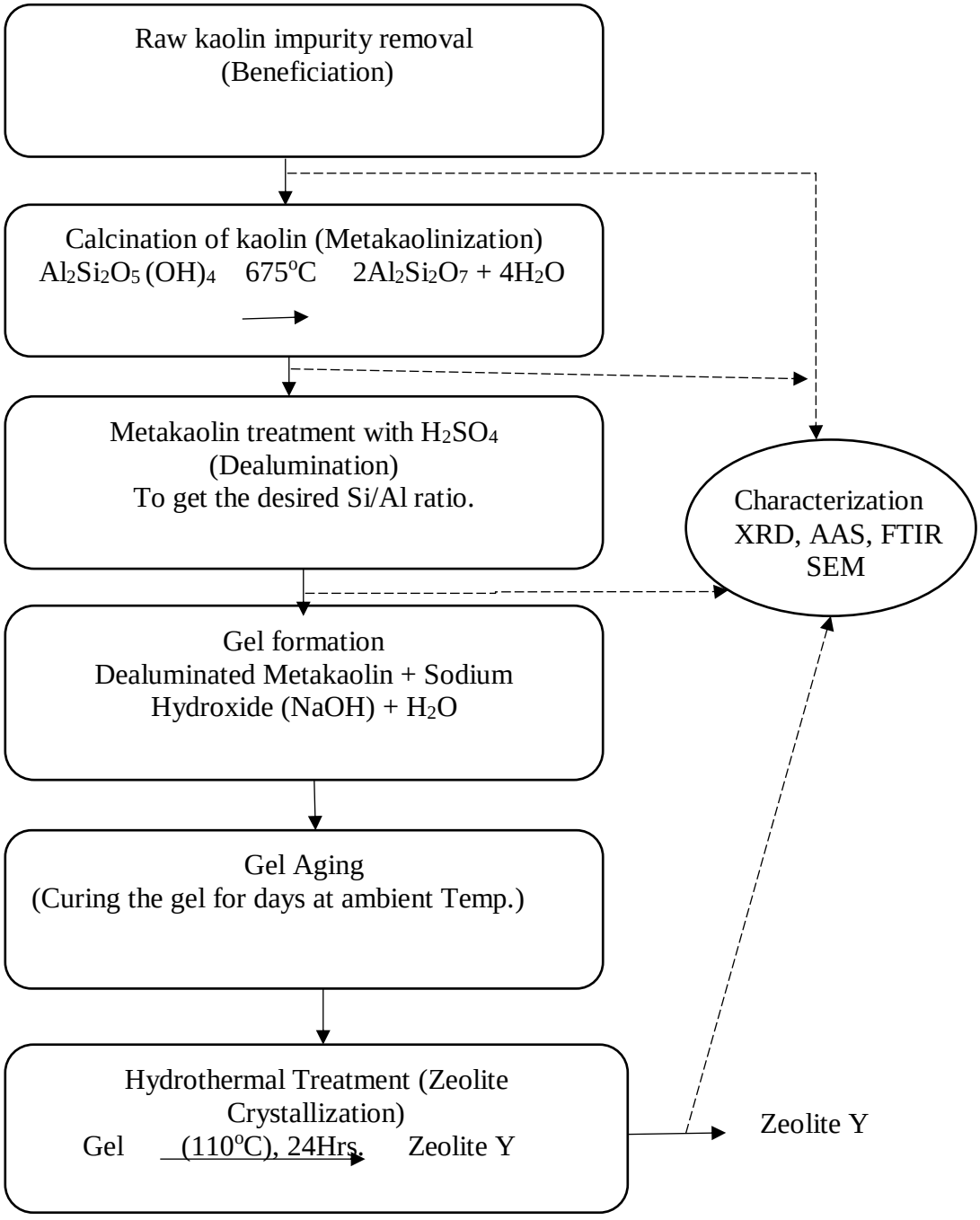


Figure 3.1 Overall flow diagram for production of zeolite Y from kaolin using conventional hydrothermal synthesis method [6, 39].

3.4 Synthesis of Zeolite Y from Ansho Kaolin

To synthesize zeolite Y from kaolin there are a variety of individual process steps were followed as shown in the Figure 3.1:-

3.4.1Kaolin Beneficiation and Drying

The raw kaolin was first treated with Hydrochloric acid (HCl) to remove non- structural iron, impurities and improve the whiteness of the starting raw kaolin, and then washed with distilled water for the removal of impurities like those that sand and soluble salts present within the raw kaolinite clay.

The beneficiation was carried out; as such at the beginning, 500gm of raw kaolinitic clay was treated in 300ml of 1 M HCl for 24hrs. at ambient temperature (Figure 3.2), and after decantation of the acid was completed, the slurry remaining at the bottom was then soaked in a bucket of water for 2 days at normal condition. During the soaking period, the clay was masticated at intervals to break it into small lumps. The floated dirt was also removed by discarding the water on top and therefore the fresh water was added afterwards for further impurities removal. The mixture was decanted several times to urge obviate of the sand, stony particles, heavy impurities and soluble salts presented. The slurry was dried in an oven at 100^{o}C for 24 hrs. to remove the water contents. Then the dried sample was grind using mortar and pestle. After grinding, the samples were sieved under dry conditions, the size fraction of less than 230 meshes or 63 microns collected for zeolite synthesis, and the remaining (Oversized) samples were recycled for same size reduction process.

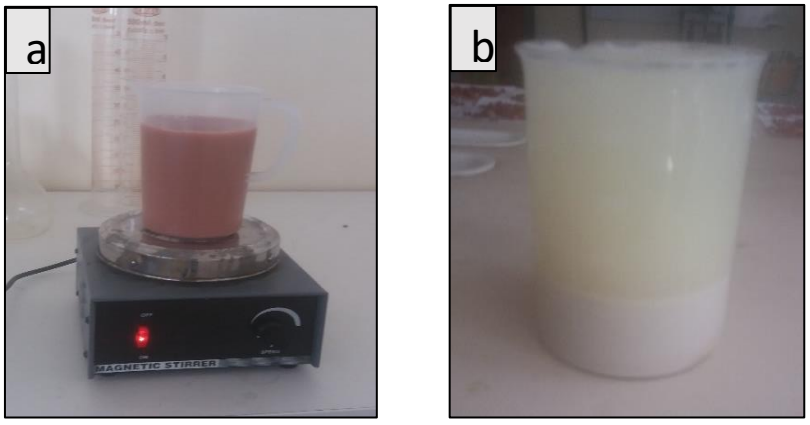


Figure 3.2 Beneficiation of Raw Kaolin using a) water and b) acid (HCl)

3.4.2 Metakaolinization (Calcination of Kaolin)

The Si-O or Al-O structures in kaolin are inactive in nature, which is difficult to directly synthesize zeolites. Therefore, kaolin was pre-activated to change this inert structure. The most effective way to activate such natural clays are thermally transform (calcine) the inert phase into the active phase at different temperature. In order to get the optimum calcination temperature for metakaolinization process the Design Expert Version 11 software was used. According to the analysis, the following temperature of calcination were tested at 450,550,600, 650,675,700,900 and 1050ºC. (Figure 3.3) shows the calcination process to convert kaolin to metakaolin.

$$2Al_2Si_2O_5(OH)_4 \rightarrow 2Al_2Si_2O_7 + 4H_2O \quad \text{……Metakaolinization}$$

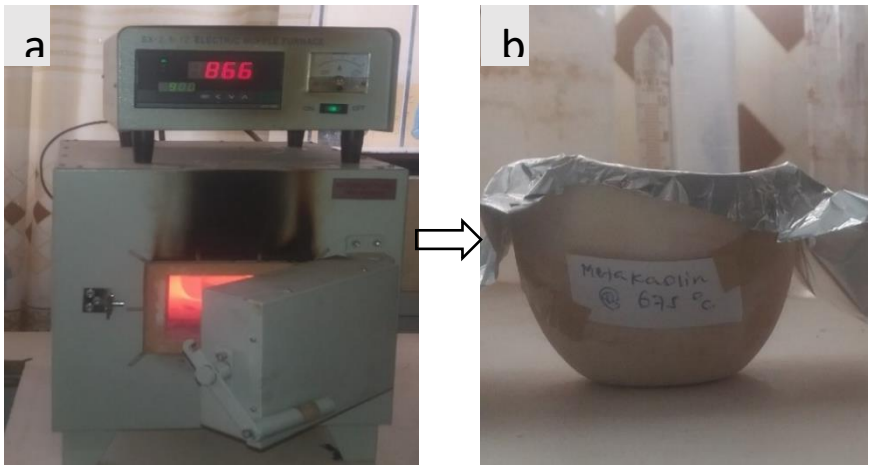


Figure 3.3 Calcination of Kaolin using muffle furnace a) kaolin calcination at 675ºC b) metakaolin

3.4.3 Dealumination

The prepared metakaolin was then treated using H_2SO_4 in order to get the desired Si/Al ratio of 2.5-5 by reducing the alumina contents in the metakaolin. This is because each types of synthetic zeolite depends on the Si/Al ratio for its synthesis. The dealumination reaction carried out as such:-

$$Al_2O_3(s) + 3H_2SO_4(aq) \xleftrightarrow{90\text{-}100^oC} Al_2(SO_4)_3(aq) + 3H_2O \quad \text{….Dealumination}$$

In this study, the conventional dealumination method was used in the dealumination of the metakaolin as shown in the Figure 3.4. The method involved the reaction of the metakaolin with Sulphuric acid (H_2SO_4) and deionized water, with the application heat. Fifty gram of the metakaolin was mixed with approximately 62 ml of distilled water and approximately 107 ml of 60 Wt. % H_2SO_4 (Sulphuric acid based on the dealumination calculation) then added for reaction to commence and proceed for a specified reaction time of 10 minutes. As soon as the reaction time elapsed, the reaction was terminated by adding 450 ml of distilled water. The resulting mixture then stirred and left to completely settle before the supernatant formed would pour off leaving the dealuminated metakaolin. Dealuminated metakaolin obtained was then washed with distilled water to remove unreacted Sulphuric acid that may be present. (Please refer to Appendix A for detail dealumination calculation).

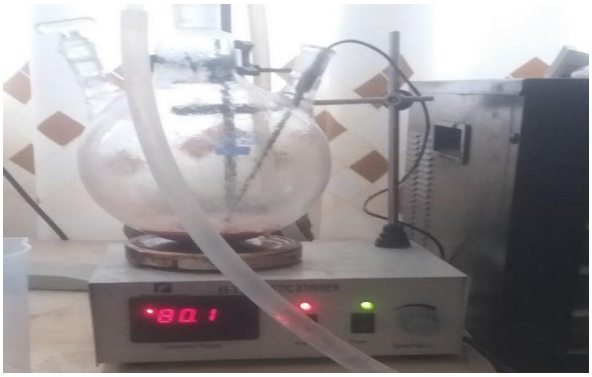


Figure 3.4 Dealumination of metakaolin using three necked round bottom flask setup.

3.4.4 Gel Formation

Here the mass of sodium hydroxide and volume of water required for gellating of dealuminated metakaolin were calculated. At this stage, gelation was achieved with a desired molar composition using the following equations.

$$\frac{SiO_2}{Al_2O_3} = 19.7; \quad \frac{Na_2O}{SiO_2} = 0.6; \quad \frac{H_2O}{Na_2O} = 30$$

$$Na_2O + H_2O \rightarrow NaOH$$

The theoretical silica alumina (SiO_2/Al_2O_3) ratio calculation:

Given mass from the Table 4.3

Given mass SiO_2 = 80.78 gm Molecular mass SiO_2 = 60.09 gm/mole

Given mass Al_2SO_3 = 6.94 gm Molecular mass Al_2SO_3 = 102 gm/mole

Moles of SiO_2

$$\text{Moles} = \frac{\text{Given mass}}{\text{Molecular mass}} \rightarrow$$

n_{SiO2} = (Given mass SiO_2)/(Molecular mass SiO_2) = $\frac{80.78\text{gm}}{60.09\text{gm/mole}} = 1.344\text{moles}$

Moles of Al_2SO_3

$n_{Al2SO3} = \frac{6.94\text{gm}}{102\text{gm/mole}} = 0.068\text{moles}$

Silicon Aluminium ratio becomes $\rightarrow n_{\frac{SiO2}{Al2SO3}} = \frac{1.344 moles}{0.068} = 19.76$

The Silica/Alumina (SiO_2/Al_2O_3) ratio used in this work is obtained from the compositional analysis of the dealuminated samples as shown in Table 4.3, while the ratio of Sodium oxide to Silica (Na_2O/SiO_2) and that of water to Sodium oxide (H_2O/Na_2O) were found from standard constant for zeolite formation. The volume of water and the mass of sodium hydroxide required for gellating 20gm of dealuminated metakaolin was obtained as 99.36 ml and 14.72gm respectively. Twenty gram of dealuminated metakaolin put in a conical flask and mixed with half of the required quantity (49.68ml) of deionized water until the dealuminated sample was dissolved completely. The required quantity (14.72gm) of sodium hydroxide was then added to the solution and stirred vigorously before the remaining quantity (49.68ml) of deionized water was added. Then the content was continuously stirred with magnetic stirrer for 30 minutes. Finally, the resulting aluminosilicate gel was put in a Teflon lined autoclave reactor, sealed and left to age for days at room conditions. (For detailed gel formation calculation, please refer Appendix A)

$$NaOH(s) + H_2O(l) + 2Al_2Si_2O_7(s) \rightarrow Na_2O.Al_2O_3.SiO_2.H_2O(aq)\ldots\ldots \text{ Gel Formation}$$

The zeolite Y synthesized from Hosanna kaolin with a batch molar composition of the gel was:

6.93 Na_2O: Al_2O_3: 11.5 SiO_2: 207 H_2O

3.4.5 Gel Aging

Gel aging can be considered as, an interval after the composition of the reaction gel and the crystallization process. In this synthesis, the gel was kept undisturbed (aged) at ambient temperature. To study the effect of gel aging time the samples were prepared to age at various times (1, 2, 3 4, 5, 7, and 9 days) and crystallized for 1 day at 110^{o}C as the optimum crystallization condition for Zeolite Y synthesis

3.4.6 Crystallization

The enclosed gel found in the autoclave reactor was then placed in the electric oven as shown on the Figure 3.5 (a) at 110^{o}C for 24 hrs. for crystallization of Zeolite to take place, since; this condition was the optimum for zeolite Y synthesis according to literature. The reactor was then quenched using ice bath to cool and cease the crystallization process as shown in the figure 3.5 (b). Then the crystallized solution formed a layer inside the Teflon thus, the precipitate was separated from the supernatant by filtration. The zeolite Y filtrate was washed thoroughly several times, to make free of excess sodium hydroxide, using deionized water. The pH was monitored, while washing, using Micro Processor pH-mV meter to obtain neutral pH. The precipitated solid after washing was dried at 100 ^{o}C for 24hrs. and the crystals were then pulverized in a mortar and pestle to obtain a smooth and evenly distributed powder. Eventually the zeolite powder then sent for characterization.

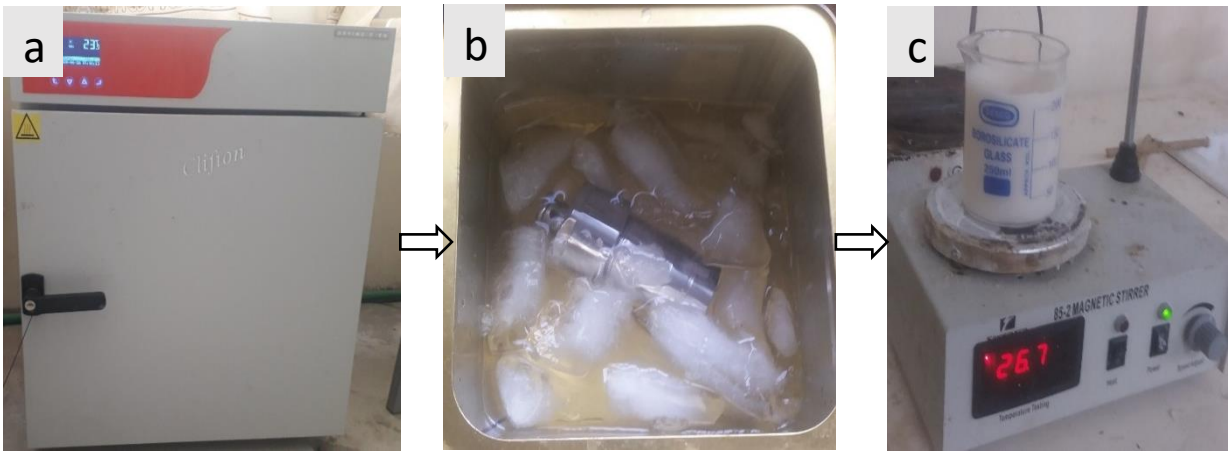


Figure 3.5 Crystallization of Zeolite Y a) Crystallization in the oven b) Ice bathing to stop crystallization c) Washing to reduce the pH to neutral.

3.5 Performance Evaluation of Synthesized Zeolite Y Catalyst Using TGA

The catalytic activities of synthesized zeolites Y was investigated by thermogravimetric analysis (TGA). The low-density polyethylene (LDPE) which is collected from the Municipal Solid Waste (MSW) was washed using distilled water, reduce the size with scissors, and sieved using sieve shaker to get the desired particle size less than 25Mesh (i.e. 700μm), then the composite mixture of LDPE and the zeolite Y were prepared with the application of heat at 200^{o}C in melting mixing process. The LDPE/catalyst composite mixtures and pure LDPE were placed directly in a platinum pan for thermogravimetric analysis. The catalyst proportion were of 10, 15 and 30 mass (%) in the PE-ZY mixture (Polyethylene Zeolite Y mixture) was used from different literature [43, 44]. In order to obtain around 50 mg of total mixture, 5, 7.5 and 15 mg of catalyst were mixed with 45, 42.5 and 35 mg of PE powder respectively in targeting to prepare 10, 15 and 30 mass % PE-ZY mixture composite. Then after 50mg PE was heated by a non-isothermal temperature program, from 30^{o}C to 900^{o}C temperature at 15 ^{o}C/min of heating rate under 50ml/min purge rate of nitrogen atmosphere, DTG-60H Shimadzu instrument with platinum crucible were used. For the catalytic TGA, 10 mg of Catalyst /PE mixture was evaluated at the same temperature program as mentioned above.

3.6 Raw Materials and Product Characterization Technique

3.6.1 Atomic Absorption Spectrometry (AAS)

In this study the chemical composition analysis of kaolin, metakaolin and synthesized zeolite Y were done by atomic absorption spectrometer (AAS) spectry AA-20 plus model at Geological survey of Ethiopia. Apart from the AAS, the LiBO2 Fusion, HF attack, Gravimetric, Colorimetric were carried out for all samples to perform the complete silica analysis at Geological Survey of Ethiopia.

3.6.2 X-ray Diffraction (XRD)

In this study, the analysis of the Ansho kaolins, metakaolins and zeolites powder samples were carried out using the XRD machine model of Shimadzu XRD-7000 X-ray diffractometer using Cu-Kα radiation. The instrument measurement condition for each test at room temperature was voltage = 40 kV, current = 30 mA, in step size of 0.02 degree. The scan range (2Θ) between 5 to

80 degrees and the scan speed of 3 (deg/min) with a continuous scan mode. Samples for the X-ray analysis were prepared by placing 0.2-0.4 g of the powder sample in an aluminum holder. The sample holder surface should be smoothed off to absorb the X-ray beam regularly. The diffraction pattern is plotted within the XRD machine by generating a scan with continuous scanning mode for the intensity of peak (Irel) as the Y-axis versus (2Ɵ) as the X-axis.

3.6.3 Scanning Electron Microscopy (SEM)

The crystallite size and morphology analysis of the kaolins, metakaolins and zeolite Y, P1 samples synthesized from Ansho kaolin of Ethiopia were carried out using JEOL, JCM-6000 Plus (Washington D.C, USA) with the SED detector in high vacuum. The measurement condition for the test at room temperature with applied potential 10-20 kV. With this detector the signal were collected from both secondary and backscattered electrons simultaneously. Although sample coating is important in many SEM analyses, in this case the analysis was done without coating under high vacuum. In addition to the morphological analysis, the particle size of the kaolins, metakaolin and the synthesized zeolite Y and P1 samples were estimated using this technique.

3.6.4 Fourier Transform Infrared Spectrometry (FTIR)

The internal and external chemical bonding (Functional Groups) linkages analysis of the kaolins, metakaolins and zeolite Y samples synthesized from Ansho kaolin were carried out using the JASCO FT/IR-6600typeA. The instruments measurement conditions for each test at room temperature was in the range of 400 to 4000 cm−1 with a resolution of 4 cm−1. Sample for the FTIR analysis were prepared by weighting the amounts of sample, 1 gm, and Potassium Bromide (KBr) powder, 100 gm into an agate mortar. Grind the powders together, with an agate mortar and pestle, until the sample is well dispersed and the mixture has the consistency of fine flour. Then run the test by loading the sample on to the FTIR instrument. The FTIR pattern is plotted within the FTIR machine by generating the transmittance peaks (%) as the Y-axis versus wavenumber (cm-1) as the X-axis.

3.6.5 Thermogravimetric Analysis (TGA/DTG)

The thermal stability of the synthesized zeolite Y and the thermal degradation of the composite formed from the synthesized zeolite Y and polyethylene were carried out using the DTG-60H

model Shimadzu instrument. The instruments measurement condition for each test was a non-isothermal temperature program, from 30^{o}C to 900^{o}C temperature at 15^{o}C/min of heating rate under 50 ml/min purge rate of nitrogen atmosphere. Sample for the TGA analysis were prepared by weighting the amounts of sample, 10-20 mg, and placed in platinum crucible. Then run the test by loading the sample on to the TGA instrument. The TGA curve is plotted within the TGA machine by generating the percentage mass loos in (mg) as the Y-axis versus temperature (^{o}C) as the X-axis.

CHAPTER FOUR

4. RESULTS AND DISCUSSION

In this chapter, results and discussion based on the experimental procedure stated in the previous chapter are presented.

4.1 Raw Materials Characterization

Results found by above-mentioned analytical methods are complete silica analysis of Raw, Beneficiated, Calcined Ansho Kaolin and Zeolite Y (Table 4.1).

The results on Table 4.1 show that raw Ansho kaolin contains contaminations of oxides of, iron, titanium, potassium and magnesium. This is not true on the case of beneficiated kaolin, since the HCl attacked most of metallic oxides, then the value of metallic oxide reduced significantly, but the value of SiO_2 increased from 51.68% to 52.64% due to compensation of the whole proportion while the amount of Al_2O_3 did not show significant change because the HCl has law affinity to Al_2O_3. The Table 4.1 also indicates that Ansho kaolin is ferric in nature due to its high content of iron oxide as compared with that of potassium. It can also be observed that there is removal of Na_2O and K_2O following the purification processes. The reductions have occurred because of washing off soluble salts of sodium and potassium during the purification. Pure raw kaolinite clay of Ethiopia has a Silica/Alumina ratio of between 2 to 3 were mentioned in various literature [26, 39]. Table 4.1 shows that the SiO_2/Al_2O_3 ratio of 2.64 and 2.73 for the raw and beneficiated kaolin respectively are within theoretical value as mentioned in the literature [26].

Table 4. 1 Compositional analysis results of the Raw, Beneficiated and Calcined Ansho Kaolin

	Ansho Kaolin (Wt. %)		
Oxides	**Raw kaolin**	**Beneficiated Kaolin**	**Calcined (metakaolin)**
SiO_2	51.68	52.64	55.60
Al_2O_3	33.22	32.68	39.68
Fe_2O_3	1.88	1.42	1.38
CaO	0.08	<0.01	<0.01
MgO	0.16	0.02	0.06
Na_2O	0.01	<0.01	<0.01
K_2O	1.18	<0.01	<0.01
MnO	0.01	<0.01	<0.01
P_2O_5	0.06	0.05	<0.01
TiO_2	0.27	0.27	0.35
H_2O	1.21	0.81	0.57
LOI*	12.72	12.69	1.84
SiO_2/Al_2O_3 (n/n)	**2.64**	**2.73**	**2.40**

*Loss of Ignition

4.1.1 Kaolin

Powder X-ray diffraction (XRD) of kaolin, metakaolin and zeolite Y were used to determine the sample crystallinity throughout this work.

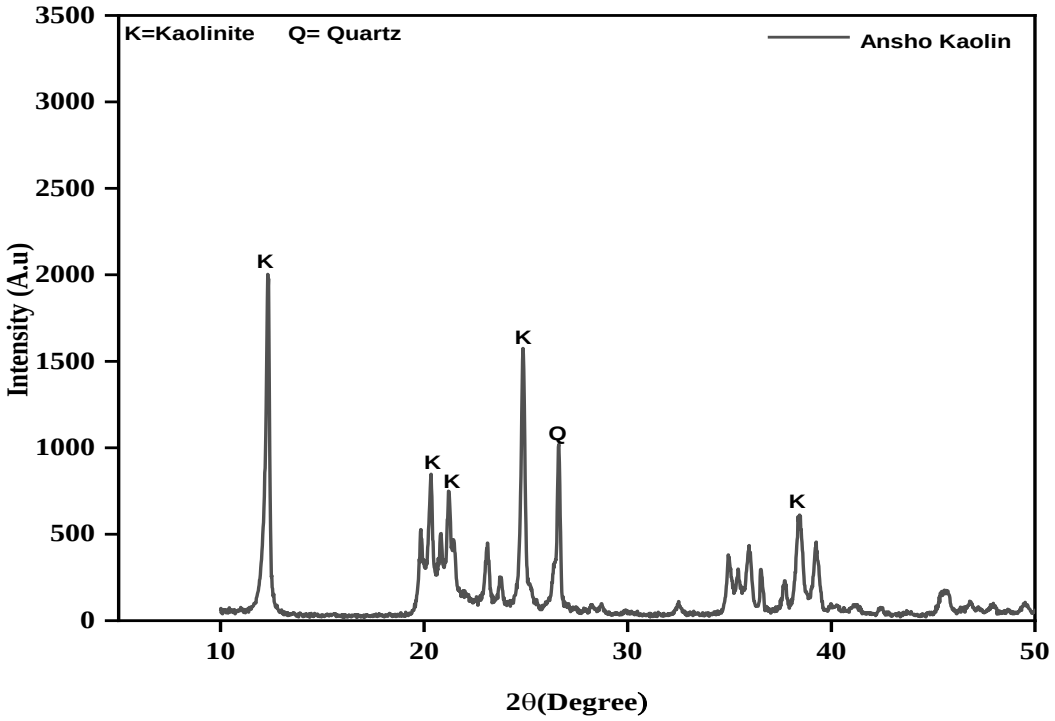


Figure 4.1 XRD of Raw Ansho Kaolin

As shown in the Figure 4.1 the raw Ansho Kaolin has many sharp peaks, which contains the kaolinite the main minerals and the quartz impurity. The x-ray diffraction analysis of the peaks shows a sharp peak with high intensity at 2Θ = 12.34º. This is the main peak used in identification of kaolinite clay. Beside the kaolinite the 2Θ angle at 26.67º profiles, correspond to that of quartz impurity .These results are in agreement with [39]. Kaolinite and quartz are the dominant characteristics of natural kaolin [45].

The scanning electron micrographs (SEM) analysis of the raw Ansho kaolin (Figure 4.2) showed the presence of platy like morphology of kaolinite crystals. Different researchers have reported the same results too [39].

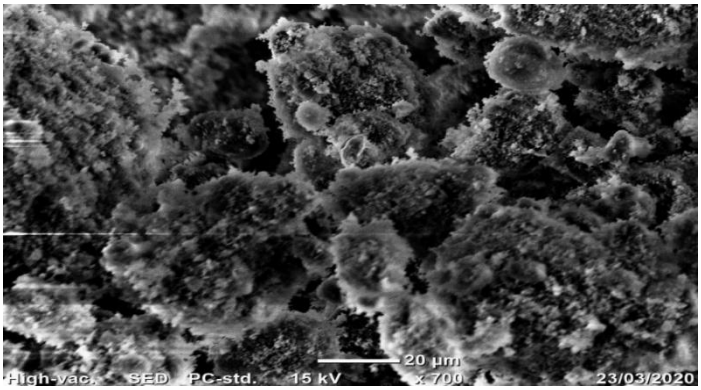


Figure 4.2 SEM micrographs of Ansho Kaolin

4.1.2 Metakaolin (Calcination of Kaolin)

To determine the specific temperature at which the crystalline kaolin changed to form the amorphous metakaolin were investigated at a temperature range from ambient to 1050^{o}C. As a result, the calcination of Ansho kaolinite from room temperature to 450^{o}C caused an increased intensity of the main peak reflections. From Figure 4.3, the increased intensity was 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 peak reflection at 550^{o}C leaving only a small holes which indicate the formation of a non- crystalline phase. This is in good agreement with results of Franco et al. [46], which show the formation of metakaolin at a temperature around 550^{o}C. The XRD pattern of Ansho kaolin shown on the figure 4.3 indicates at and above 550^{o}C, the kaolin clay is amorphous as all the kaolinite peaks was converted to metakaolin. The peaks at $2\Theta = 12.34^{o}$ (kaolinite peak) disappeared but the peak at $2\Theta = 26.67^{o}$ was not affected by the thermal treatment, attributed to the presence of quartz. Therefore, metakaolin can be described as an amorphous material containing free silica, free alumina as reported by Brindley [47].

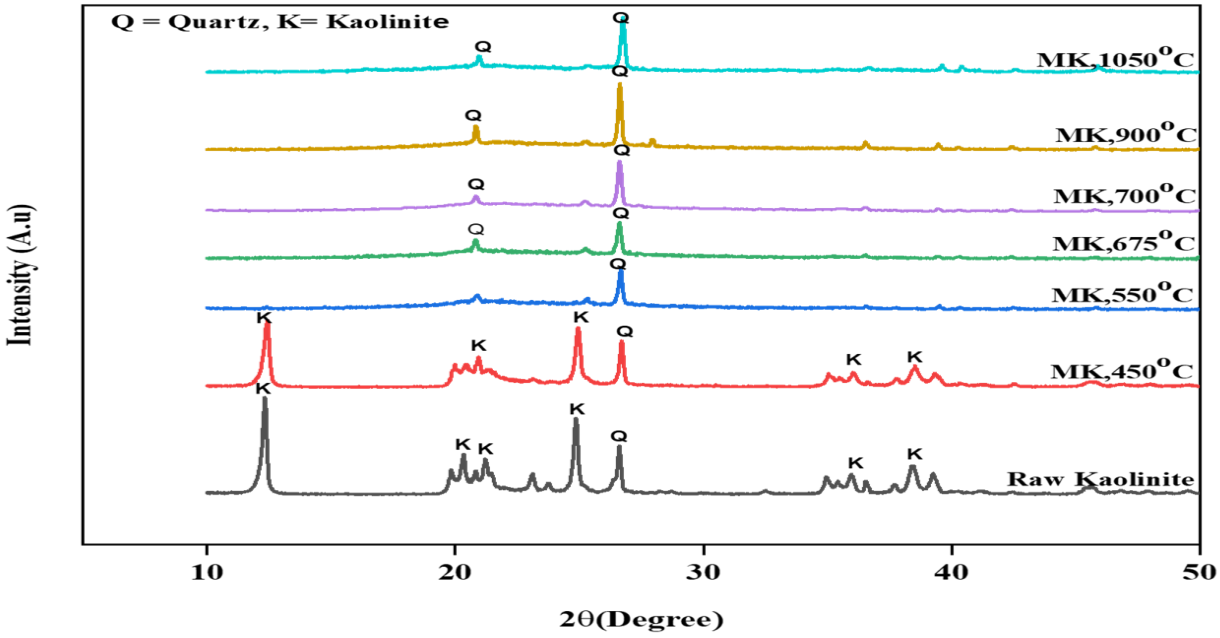


Figure 4.3 The XRD pattern of kaolin transformation to metakaolin with various temperature.

4.1.3 Crystallinity difference

From Origin Lab 2019b analysis software, the areas of different samples Like BRK, MK-675°C and Zeolite Y synthesized from metakaolin at 675°Cwere calculated.

- BRK: - Beneficiated Raw Kaolin

Area of crystalline peaks =3731.48

Area of all peaks (Crystalline + Amorphous) =5945.56

$$\text{Crystallinity} = \frac{\text{Area of crystalline peaks}}{\text{Area of all peaks (Crystalline+Amorphous)}} * 100$$

$$\text{Crystallinity} = \frac{3731.48}{5945.56} * 100 = 62.76\%$$

- MK-675°C: - Metakaolin

Area of crystalline peaks = 644.96 Area of all peaks (Crystalline + Amorphous) = 2813.7

$$\rightarrow \text{Crystallinity} = \frac{644.96}{2813.7} * 100 = 22.92\%$$

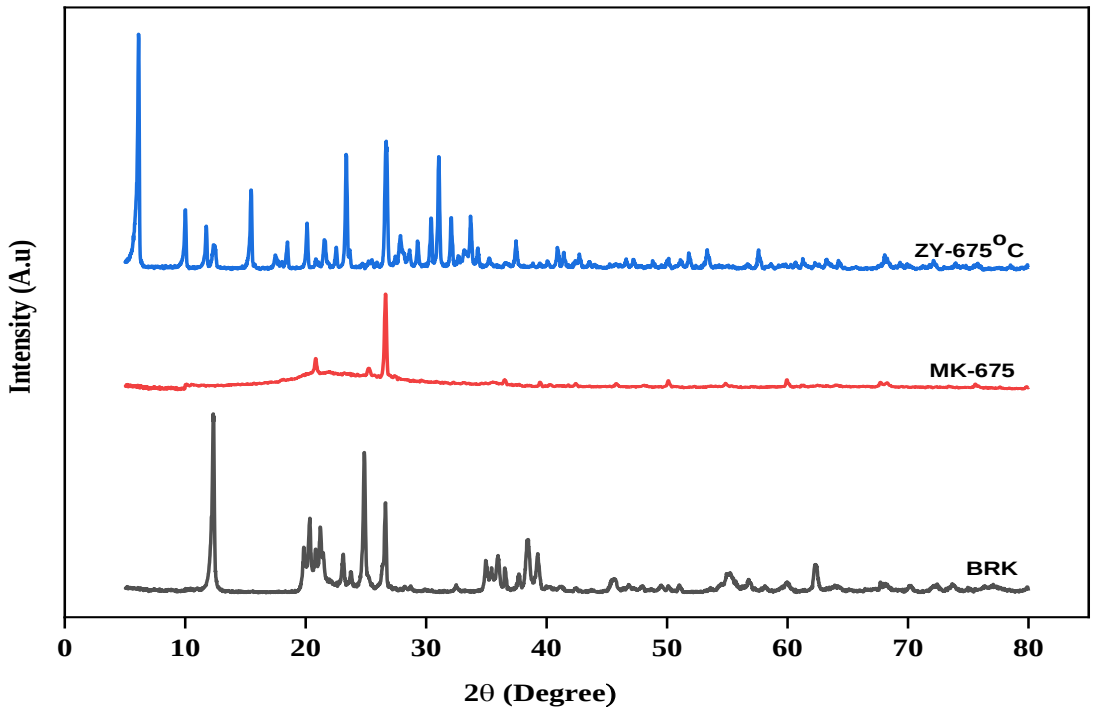


Figure 4.4 The XRD pattern of BRK, MK-675°C and ZY-675°C.

- ZY: - Zeolite Y synthesized from metakaolin at 6750°C

Area of crystalline peaks = 3950.14

Area of all peaks (Crystalline + Amorphous) = 4806.84

Crystallinity = $\frac{3950.14}{4806.84} * 100$ = 82.17%

Table 4. 2 Percentage crystallinity of Ansho Kaolin, Metakaolin and Synthesized Zeolite Y

Chemicals	**Crystallinity (%)**
Beneficiated Raw kaolin	62.76
Metakaolin @675°C	22.92
Zeolite Y	82.17

4.1.4 Dealumination of Metakaolin

Dealumination is an alternative route to reduce the alumina content from the metakaolin, as a results it increases the SiO_2:Al_2O_3 ratio of the starting material. Adjusting the silica to alumina ratio was the key steps in the starting gel of high silica zeolite Y synthesis. As mentioned above the dealumination was carried out using Sulphuric acid (H_2SO_4). Therefore, to determine the optimum concentration of acid required to effect the extraction (leaching) of alumina from the clay, various literature were reviewed and obtained 60wt.% acid concentration was good for efficient dealumination. In this study to dealuminated, 50 grams of Ansho metakaolin 107 ml of 60Wt. % H_2SO_4 and 62 ml of deionized water were used to get the Silica /Alumina ratio of 5 [48]. The dealumination reaction is mentioned in section 3.2.3 and detail dealumination calculation is given in Appendix A.

Table 4.3 Atomic absorption spectroscopy (AAS) compositional analysis of Dealuminated Metakaolin using Novel and Conventional method with various dealumination time

Ansho Kaolin (Wt. %)					
Dealumination		**Novel Method**		**Conventional Method**	
Oxides	**Metakaolin**	**5 Minutes**	**10 Minutes**	**5 Minutes**	**10 Minutes**
SiO_2	55.60	49.06	62.28	52.04	80.78
Al_2O_3	39.68	34.18	34.72	30.84	6.94
Fe_2O_3	1.38	0.94	0.70	0.34	0.20
CaO	<0.01	<0.01	<0.01	0.38	0.04
MgO	0.06	<0.01	0.12	1.14	<0.01
Na_2O	<0.01	<0.01	<0.01	0.24	0.28
K2O	<0.01	<0.01	<0.01	0.02	<0.01

MnO	<0.01	0.08	<0.01	<0.01	<0.01
P_2O_5	<0.01	0.13	0.04	0.15	0.05
TiO_2	0.35	0.29	0.35	0.31	0.40
H_2O	0.57	1.88	0.51	0.27	6.62
LOI	1.84	13.64	2.60	13.59	5.57
SiO_2/Al_2O_3(n/n)	**2.40**	**2.44**	**3.05**	**2.87**	**19.76**

The acid treatment of metakaolin results in selective leaching of alumina and iron contents from the octahedral sheet, thus lowering the alumina content of Ansho metakaolin. The XRF results presented in Table 4.3 shows that the composition of the Ansho clay changed considerably during dealumination by both the novel and conventional method. The Fe_2O_3 content was reduced from 1.38 to 0.2, Alumina reduced from 39.68 to 6.94 and on the contrary, TiO_2 increased from 0.35 to 0.4 and similar result is also observed by Belver et al., [49]. It was also observed that both novel and conventional methods increased the SiO_2/Al_2O_3 ratio with increase in the time of reaction. For instance, for novel method at 5 minutes the silica –alumina ratio was 2.44 whereas at 10 minutes it was 3.05 and for conventional method at 5 minutes 2.87 whereas at 10 minutes it was 19.76 with a corresponding decrease in alumina content. However, the leaching of the alumina contents of Ansho metakaolin ultimately alters the chemical composition and thus changes the structure of the parent starting material.

4.2 Product Characterization

4.2.1 X-ray diffraction Analysis of Zeolite Y

Powder X-ray diffraction was used to determine the sample crystallinity. The formation of zeolite Y from Ethiopian Ansho kaolin was confirmed by comparing its XRD pattern to document by International Zeolite Association (IZA) powder pattern identification diffractograms table indicating a FAU structure. According to Treacy and Higgins within a range of $2\theta = 5\text{-}50^{\circ}$, the first

peak for zeolite Y will appear within 6-10˚. The first three strongest peak for each zeolite Y was observed at 2θ=6.26, 23.45 and 31.13 then 2θ = 6.33˚, 26.8 and 31.2, finally, 2θ=6.25, 26.70 and 31.06, with approximately similar d-spacing shown in the Table 4.4 ,for Zeolite Y at 1day, 2days and 3 days gel aging time respectively. Small zigzag peaks refer to the presence of amorphous material. Strong peaks represent full crystallization. The SEM and FTIR graphs shown below on Figure, 4.6 and 4.7 have also confirmed the successful synthesis of zeolite Y. Synthesized zeolite Y gave similar SEM morphology and FTIR spectrum pattern to that of the referenced literature [10] and [9] respectively.

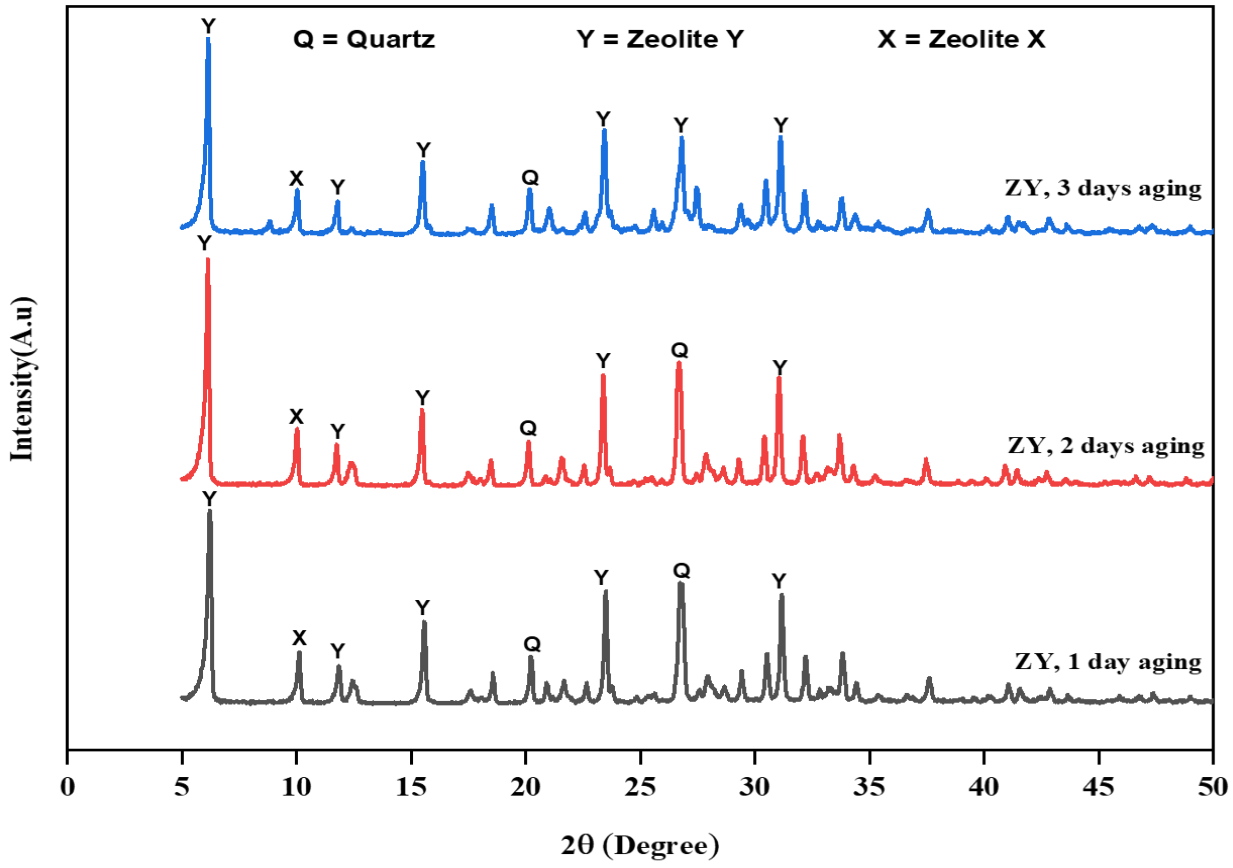


Figure 4.5 XRD Pattern of Synthesis Zeolite Y from Ansho Kaolin for 1, 2 and 3-day aging.

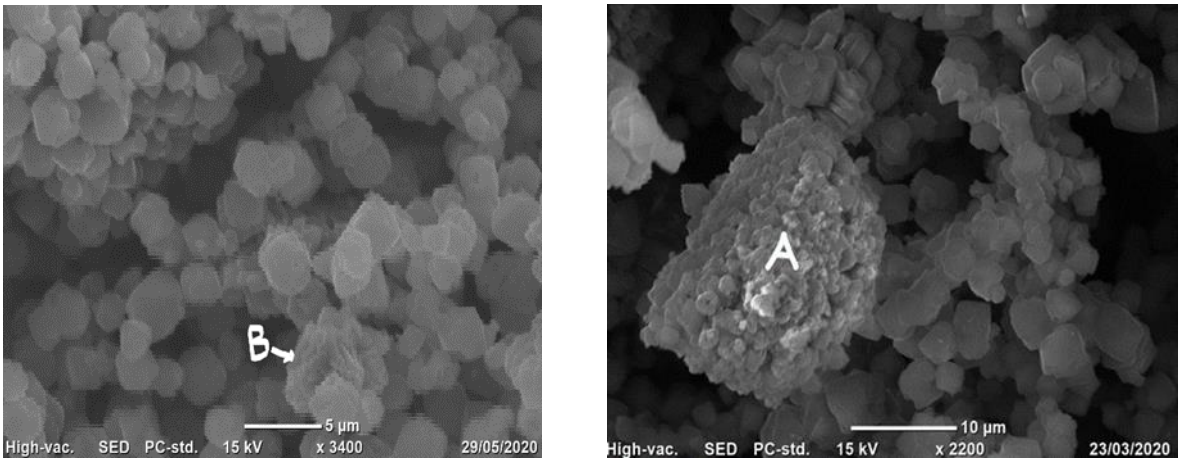
Table 4. 4 Comparison of lattice spacing, between the developed Zeolite Y from Ansho kaolin and standard Zeolite NaY from International zeolite Association (IZA)

Zeolite Y prepared from Ansho Kaolin		**Standard Zeolite Y (IZA) By Treacy and Higgins**	
Angle (2theta) degree	d, spacing (A^o)	Angle (2theta) degree	d, spacing (A^o)
6.3304	13.9209	6.33	13.965
10.09	8.759	10.34	8.55
15.5465	5.695	15.97	5.549
23.453	3.790	23.26	3.82
26.807	3.323	26.31	3.387
30.2396	2.9548	30.239	2.955
31.18	2.866	31.380	2.850

4.2.2 SEM micrographs of the synthesized zeolite Y

To characterize the general features of zeolite crystals (e.g., size, shape, etc.); Scanning Electron Microscopy (SEM) was used. For this work, the crystallite size and morphology were studied by using Scanning Electron Microscopy from JEOL, JCM-6000 Plus (Washington D.C, USA) with applied potential 10 - 20 kV. Figure 4.6 is the SEM image of the developed zeolite Y. It reveals clear zeolite Y morphology with a hexagonal shape structure. The image also shows low concentration of impurities (quartz) in the sample labeled “A” and “B” which corroborated the XRD findings that few impurities are present in the dealuminated kaolin which transforms to zeolite. This compared well with similar images of zeolite Y in the literature [10]. The hexagonal

ordering of SEM images of the zeolite Y with different gel aging time (a) 2 days (b) 3 days respectively signifies a typical zeolite Y.



a) Zeolite Y, 2 days aging time b) Zeolite Y, 3 days aging time

Figure 4.6 SEM image of general morphology of faujasite zeolite Y crystallites

4.2.3 FTIR Analysis of Raw Kaolin, Metakaolin and Zeolite Y

Most compounds exhibit very complicated absorption or transmission when subjected to the whole range of the infrared spectrum. This absorption or transmission reflects the rotation of molecules and all of the various modes of interatomic vibration within the molecule, which cause bonds to be deformed by stretching, bending, twisting, etc. Each of these types of rotatory and oscillatory motion absorbs or transmits its characteristic amount of radiant energy, and a large number of them may be detected at various frequencies in the spectrum of a given compound. On this study, the JASCO FT/IR-6600typeA measurements were performed in the range of 400 to 4000 cm−1 with a resolution of 4 cm−1.The general infrared assignments as proposed by Flanigen [50] and Blackwell [51] is shown in the table below:

Table 4. 5 General Infrared Assignment

Internal tetrahedra (cm-1)

Asymmetric Stretching	1250-950
Symmetric Stretching	720-650
T-O Bending	500-420

External linkages (T-O linkage)

Asymmetric Stretching	1050-1150
Symmetric Stretching	820-720
Double ring	650-500
Pore Opening	420-300

Figure 4.7, shows the FT-IR spectra of kaolin (RK); metakaolin (MK) and Synthesized Zeolite Y crystals respectively, the kaolin and metakaolin were characterized by different vibration belong to Si-O, Al (VI)-O, Al (VI)-OH and Si-O-Al bonds. Two bands around 3650 cm^{-1} and one band at 914 cm^{-1} related to Al (VI)-OH and Al (VI)-O stretching vibration respectively. With calcination of kaolin these bands disappear and 4-coordination vibration of Al (IV)-O appear at around 812 cm^{-1} band. The broad bands at about 3454 cm^{-1} and 1635 cm^{-1} show adsorbed atmospheric water. The Si–O stretching vibration at 1065 cm^{-1}, Si–O–Al vibration at 812 cm^{-1} and Si–O bending vibration at about 470 cm^{-1} also present in kaolin IR spectrum. The shoulder near 914cm-1 arises from the quartz impurity. The band centered at 1065 cm^{-1} in the IR spectrum of kaolinite, corresponding to the Si–O-Si or Si-O-Al bond became broad due to decreasing of crystallinity kaolinite structure during calcination and formation of metakaolin. Characteristic peak of kaolinite in 542 cm^{-1} due to Si-O-Al (VI) bond are reduced after calcination process and will disappear in metakaolin. The broad bands in the region of 1635–3447 cm^{-1} are character of stretching and deformation vibrations of O-H and H–O–H groups from the weakly bound water molecules, which are reduced in infrared spectra of metakaolin. Similar results was reported by Soleimani et al. [52].

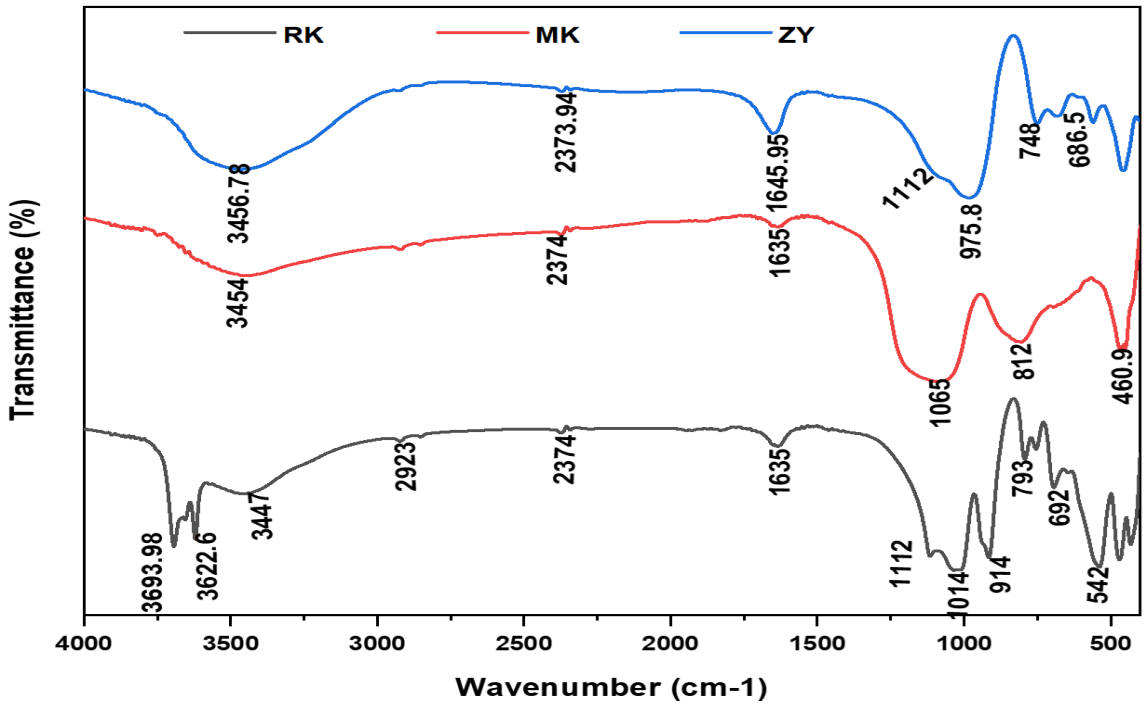


Figure 4.7 The FTIR spectra of the Raw Kaolin, Metakaolin and Synthesized NaY zeolite crystals.

The framework vibrations of zeolites are observed in the spectral region 1,400–300 cm^{-1} [50]. In the FTIR Figure 4.7, the blue line (ZY) corresponds to zeolite Y spectra. Narrow band in the regions 1250-950 cm^{-1} attributed to the internal tetrahedron vibrations of Si-O-Si and Si-O-Al. This should be the strongest vibration band and assigned to a T–O (T= Si, Al) asymmetric stretching mode, which was shown at about 975.8 cm^{-1} in the FTIR spectrum of synthesized zeolite Y and a shoulder located at 1112 cm^{-1}. It was the characteristics of structural sensitive T-O external linkages. The weak peaks below 950 cm^{-1} wavenumber are possibly due to the vibration involving the ≡Al-OH nests created by the cation vacancies. The peaks found at 748 cm^{-1} shown in the FTIR spectral region (820-720 cm^{-1}) corresponds to the symmetric stretching vibration of SiO_4 groups while the bands around 450-650 cm^{-1} are related to either bending vibration of SiO_4 groups or in the vibration modes of the 4-membered rings of the silicate chains as reported by Mgbemer et al. [53]. The water-bending vibration at 1,645.95 cm^{-1} indicates the presence of adsorbed water in zeolites. The broad band with a peak at 3456.78 cm^{-1} was due to the hydrogen bonding of water with OH groups, the bands in the hydroxyl spectral region (3,000– 4,000 cm^{-1}) are generally structureless and broad.

4.2.4 Effects of Calcination Temperature of Kaolin on Zeolite Types

Zeolite synthesizing process is very complex because the system is sensitive to a large number of modifiable factors, which may include: impurities originating from the starting materials, the composition of the slurry gel, pH, water content, reaction temperature and time (calcination and crystallization), formation of intermediate metastable phases, Si/Al ratio, Alkalinity, organic template, nucleation and growth of more stable phases and aging conditions among others [5].

In this study the effects of calcination temperature of kaolin on zeolite types was carried out. As shown in the Figure 4.3, the XRD pattern of kaolin with various temperature formed amorphous phase of metakaolin with the exception of at 450^{o}C, which shows incomplete metakaolinization. This incompletion also confirmed by XRD pattern shown in the Figure 4.8, which shows no zeolite formation within 4 days aging time and 1 day crystallization time. According to literature [54] and from our observation, calcined natural kaolinite to metakaolin at 400–600 ^{o}C for 2 hrs, it was learned that the formation of metakaolinite at a temperature lower than 600 ^{o}C is not suitable because the product obtained is relatively reactive; hence, it might not produce adequate silica content required for zeolite synthesis.

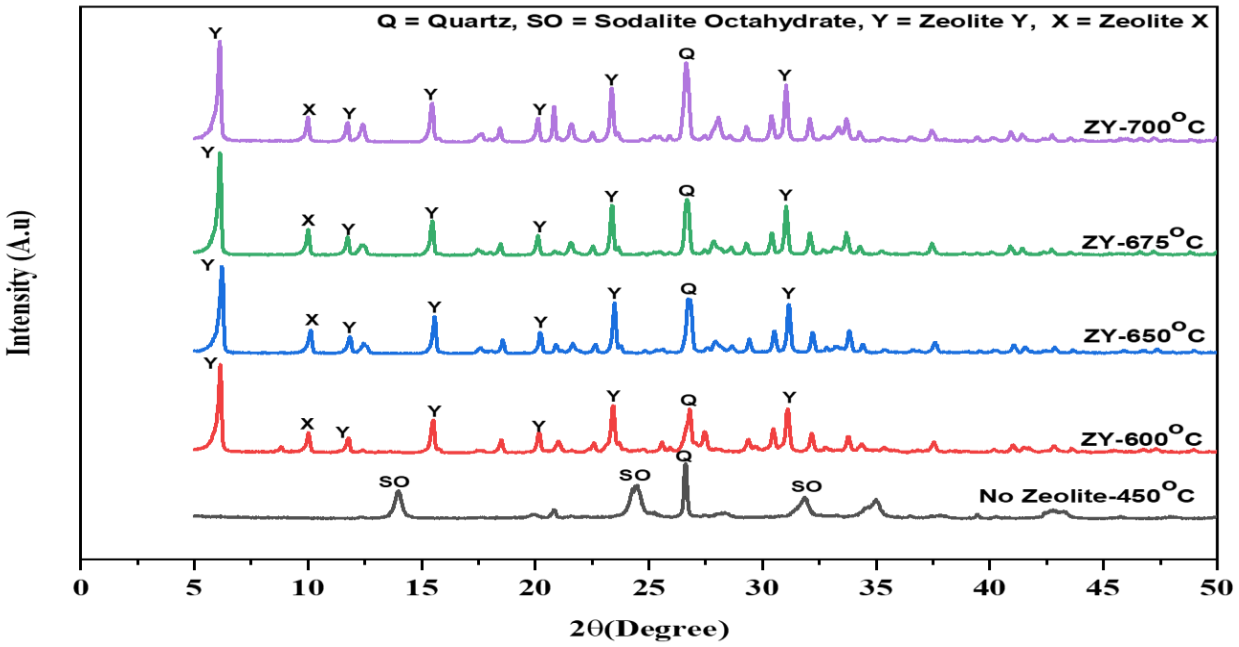


Figure 4.8 XRD patterns of zeolite Y synthesized with different calcination temperature compared with the patterns of no zeolite at 450^{o}C calcination temperature.

The x-ray diffraction pattern in the Figure 4.8 shows, the successful synthesis of zeolite Y with different kaolin calcination temperature (i.e. 600,650,675,700 ^{o}C for 3hrs.) in comparison with no zeolite at 450^{o}C for 3hrs. kaolin calcination temperature. Thus, based on the above presented fact, the calcination temperature of kaolin to metakaolin does not have much effect on the zeolite types that can be synthesized from the resulted metakaolin. At a temperature between 550^{o}C-950^{o}C, it is possible to synthesis any types of synthetic zeolite irrespective of the metakaolinization temperature. Madani et al. [55] studied the alkali treatment of kaolinites heated between 400 ^{o}C and 1000 ^{o}C by NMR and reported that at above 500^{o}C calcination temperature, kaolin transformed into metakaolin and the tetrahedral sheet got broken resulting a high degree of disorder, a condition suitable for quick polymerization of aluminosilicate species in the solution, which in turn will induces nucleus formation for the zeolite framework construction [5].

4.2.5 Effects of Gel Aging Time on Zeolite Synthesis

In the study of gel aging time effects on zeolite synthesis, the zeolite crystallizations temperature and time were made constant at 110^{o}C and 24hrs. respectively, this is because it was the optimum condition when the zeolite Y synthesized. The Figure 4.9 shows that XRD patterns of the sample prepared at aging time of 1, 2, 3 and 4-days. On the figure, the aging time of 1, 2 and 3-days were matched with that of Y standards from International Zeolite Association (IZA) powder pattern identification diffractograms table by Treacy and Higgins [45] indicating a FAU structure but, 4 days aging time sample pattern were transformed to zeolite P1. The P1 zeolite XRD pattern also confirmed with the same way as zeolite Y confirmed. The spectrum of the 1, 2 and 3-days aging sample was similar to that of standard zeolite Y from (IZA), with the exception of some quartz impurity, any other peaks indicating that the pure phase of Y was obtained.

When the aging time increased, as shown on the figure 4.9 the zeolite P1 peaks at 12.52, 21.6, and 28.17 (2Ɵ) degrees with low intensity emerged in the products from 4-day aging times and the zeolite Y peaks were lost except at 15.52^{o}. The positions of those extra peaks were the characteristic peaks of P1, indicating that a longer aging time than 3 day might causes the transformation of zeolite Y to P1. The transformation was not significant at these conditions. It was found that the transformation occurred at 5 and 7 days of aging time shows a sharp zeolite P1

peaks with some impurities of quartz and gmelinite this also supported by SEM micrographs of figure 4.10 and 4.11.

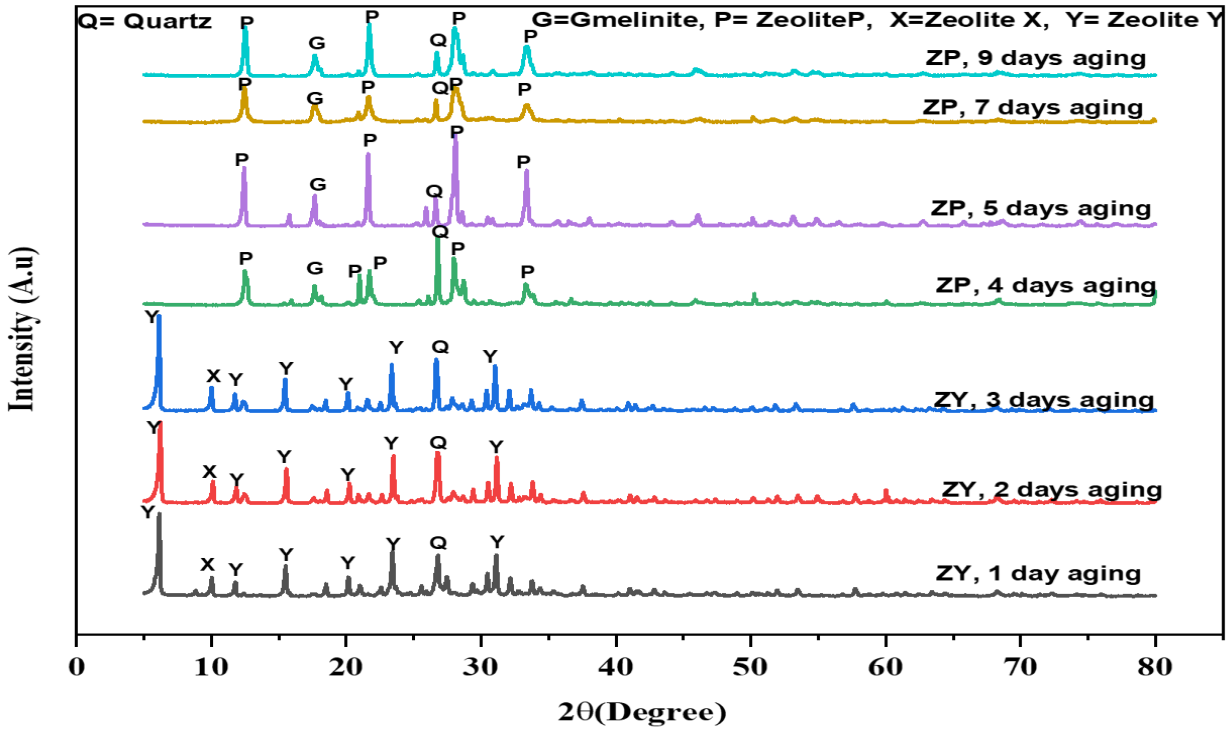


Figure 4.9 XRD patterns of zeolite synthesized with different aging times compared with the patterns of Y and P1.

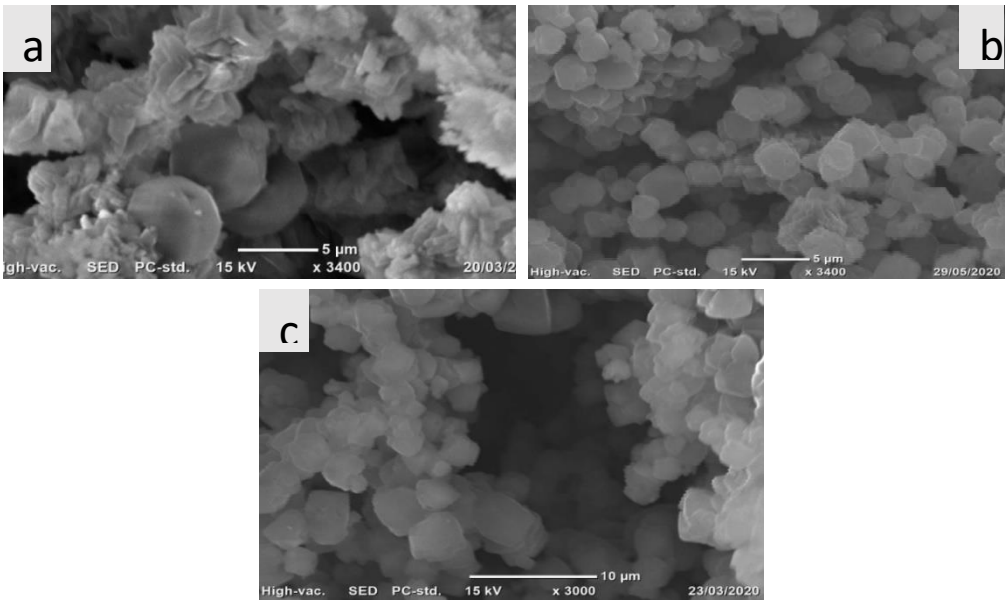


Figure 4.10 SEM micrograph of zeolite Y a) 1day b) 2 days c) 3 days aging time

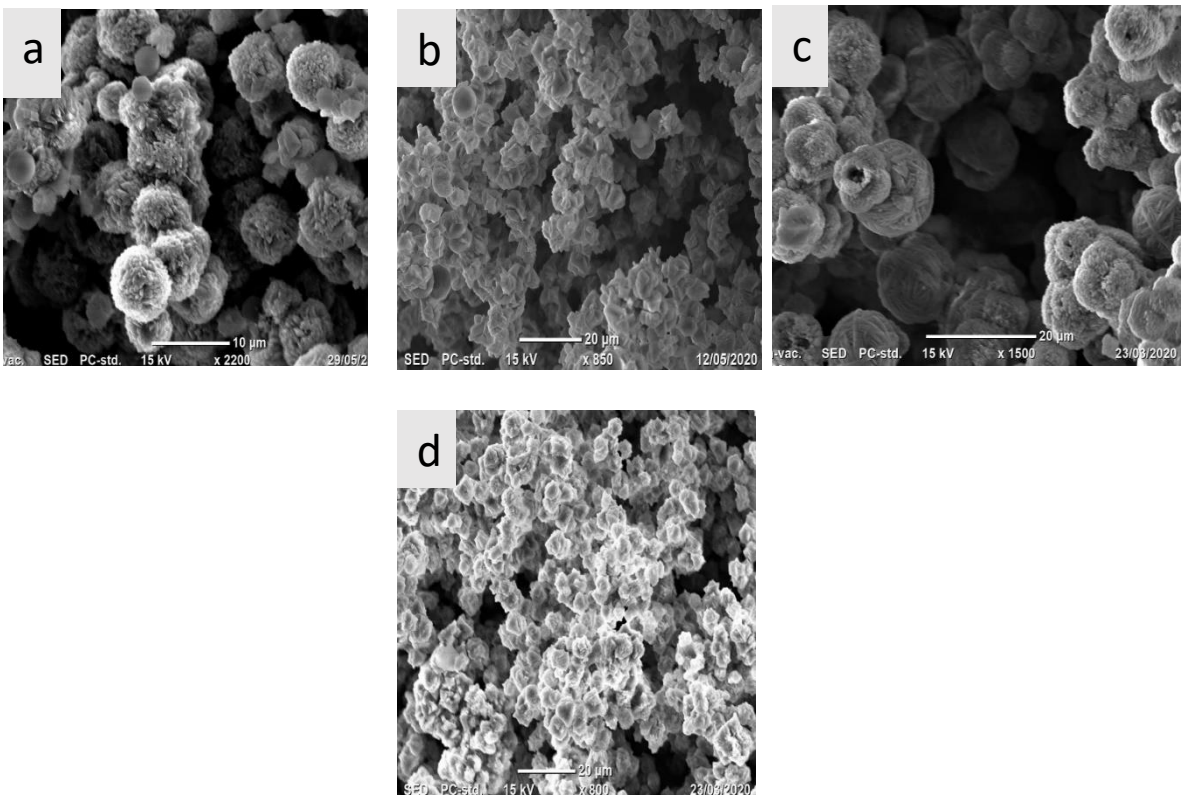


Figure 4.11 SEM micrograph of zeolite P1 a) 4 days b) 5 days c) 7days and d) 9 days, aging time

4.2.6 Effects of Crystallization Time on Zeolite Synthesis

Temperature and time are the most important crystallization conditions necessary for the synthesis of a particular type of zeolite because the intended zeolite phase can only be synthesized under a defined temperature range [5].

The effect of crystallization time on the transformation of zeolite Y to P1 was investigated with the aging time of 2 day because it showed no effect on the transformation. The XRD patterns of the products with a crystallization time from 1 to 3 days are displayed in Figure 4.12. The products with the 1 day and 2 days crystallization time showed the pure phase of Y with the 3–strongest peaks at 6.28, 15.55, and 23.44 and 6.42, 15.70 and 23.59 degrees. These 6 peaks had almost the same positions as those of zeolite Y reported in IZA (International Zeolite Association, 2001, 4th edn) file by M.M.J. Treacy and J.B. Higgins [45]. Characteristic peaks of P1 started to emerge in the sample with the 3-day crystallization time and the intensities of those peaks might be increased with a longer crystallization time [56]. The main peak of zeolite Y was not observed, except at 6.27 degree, after crystallization for 3 days and zeolite P became a major component. Because

there was another phase along with NaP, this condition was not suitable for the synthesis of zeolite P. The formation of zeolite P also confirmed with the same way as zeolite Y confirmed. The 2θ at 12.53, 21.67 and 28.13 degrees had the same position with the peaks of zeolite P from IZA powder pattern identification file [45].

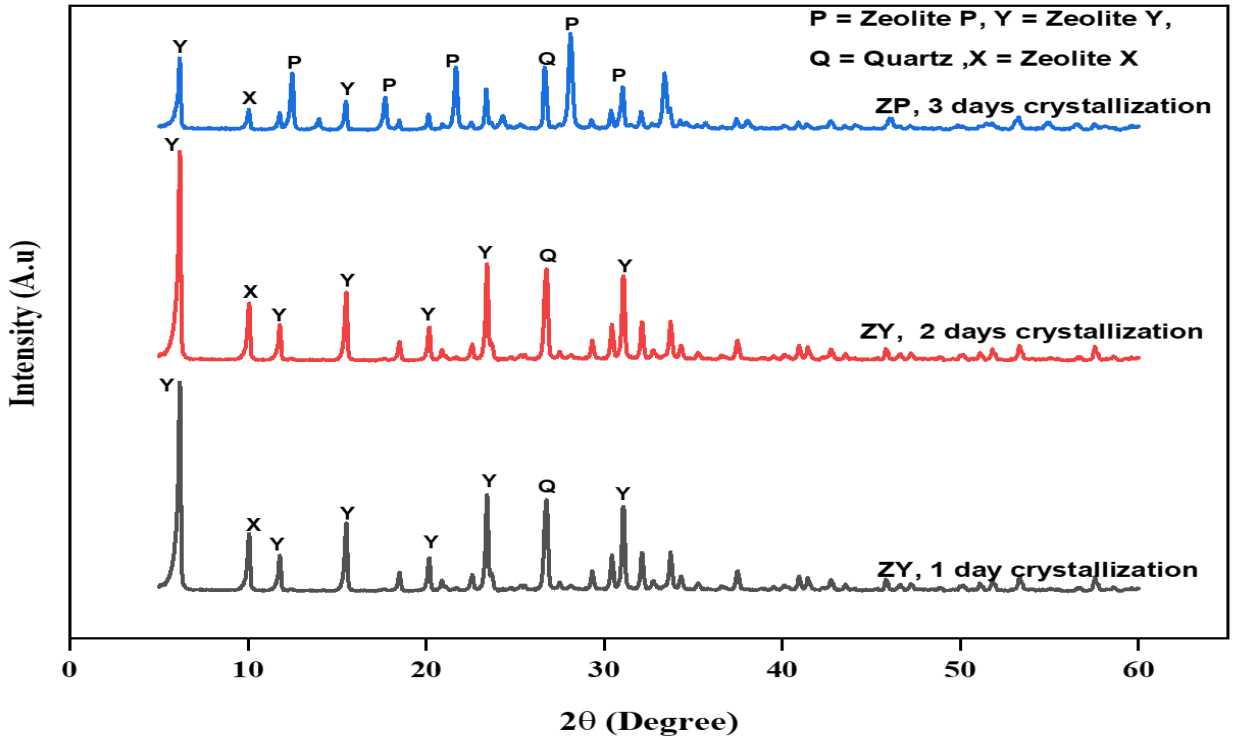


Figure 4.12 XRD patterns of zeolite synthesized with different crystallization times compared with the patterns of Y and P1.

4.2.6 Performance Evaluation of Prepared Zeolite Y Catalyst for LDPE Catalytic Cracking Using TGA

4.2.6.1 Thermogravimetric analysis (TGA) of the PE/ZY mixture

TGA provides a useful and convenient information for comparing a wide range of materials for their thermal and catalytic degradation properties. In this work the DTG-60H Shimadzu instrument with platinum crucible were used to study the performance of zeolite Y catalyst in the PE catalytic decomposition. Thermogravimetric (TGA) curves show events of mass loss corresponding to the cracking of the polymer, associated with the evaporation or volatilization of lighter products. The

thermogravimetric curves for thermal and catalytic degradation of low-density polyethylene under heating rate of 15°C min^{-1} are shown in Figure 4.11 as well the thermogravimetric values obtained from these curves are listed in Table 4.6. At the beginning of the TGA curve, the slight improvement in thermal properties of PE is observed at lower concentration of Na ZY (10% and 15%) unlike higher concentration (30%). This is may be due to the presence of sufficient catalytic active site at higher concentration that results the starting of PE cracking at lower temperature. It is interesting to note on the graph at T_{10}, PE with PE-30ZY, relation shows the addition of the catalyst decreases the polymer degradation temperature from 394°C to 341°C. As a result, the PE-30ZY sample reduced the decomposition temperature by 53°C relative to the pure PE. The final decomposition temperature of all PE/Catalyst mixtures were decreased by the use of each of the catalyst dosage with respect to pure PE.As shown in the Table 4.6 the TGA residual analysis results 10%, 15% and 30% PE-ZY were observed to be 8.2%, 12.6% and 31.5% respectively. These discrepancies might be due to measurement error during PE-ZY mixture preparation.

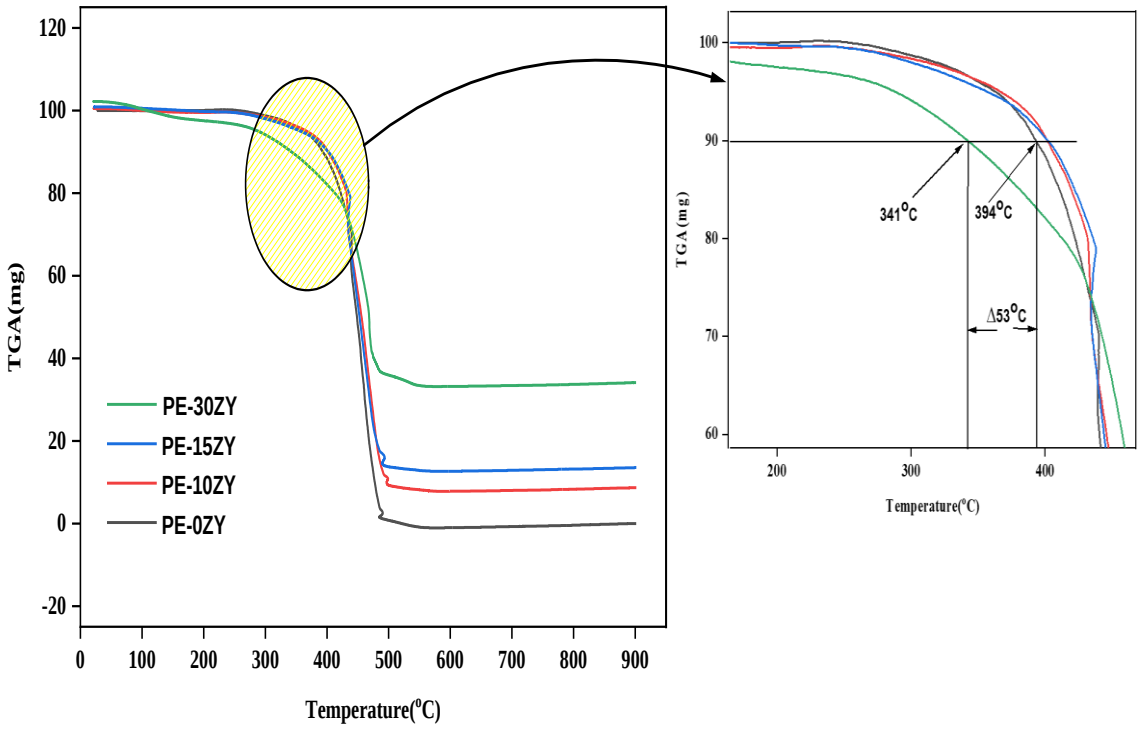


Figure 4.13 Normalized TGA curves of the polymer (PE) weight loss vs. temperature for: a) PE-0ZY b) PE-10ZY c) PE-15ZY and d) PE-30ZY.

Table 4. 6 TGA values obtained in the degradation of LDPE with zeolites Y, under heating rate of 15ºC min^{-1}.

Samples	T^{a}_{intial} /ºC	T^{a}_{final} /ºC	$T_{max,degra}$ a /ºC	Mass loss [c]/mass%	Residual mass [c]/mass%
PE-0ZY	431.7	497	473	98.3	1.7
PE-10ZY	437.5	491	472	91.8	8.2
PE-15ZY	435	475	469	87.4	12.6
PE-30ZY	412	485	465	68.5	31.5

[a] Obtained in DTG curve. [c] Until the temperature of 900ºC

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

This chapter present the conclusion and recommendations of this thesis based on the obtained results.

From the results of this study, the following conclusions can be drawn.

- ✓ Zeolite Y has been synthesized successfully from Ethiopian Ansho kaolin.
- ✓ The XRD, SEM, FTIR results obtained from the analysis totally agreed with the standards. Therefore, this thesis work confirms the successful preparation of zeolite Y.
- ✓ The process variables effect studies, the analysis results obtained shows crystallization time has more effect than gel aging time for zeolite Y transformation to zeolite P1.
- ✓ According to this study results, the dealumination process was optional since, zeolite Y synthesized successfully with or without the dealumination process
- ✓ The results obtained showed that the decomposition temperature of all PE/Catalyst mixtures decreased by the use of additional catalyst dosage with respect to pure PE.

5.2. Recommendation

Due to financial and time constraints, the scope of this work was limited. Based on the present study, some recommendations can be made for future work.

- ✓ A lot of work has been done in this area and has successfully produced high quality as-synthesized zeolite like zeolite A and X from Ethiopian kaolin especially from Bombowha and Ansho. However, Ethiopia has commenced its first natural gas and oil development in Kalub and Hilala. Consequently, zeolite Y synthesis will have a greater role as a catalyst on the petroleum refinery process.
- ✓ Using natural raw material like Kaolin will cut down cost considerably as local materials are cheaper than purchasing chemicals.
- ✓ It should be recommended that to set up pilot plant and industrial plant to produce zeolite Y and transforms to commercialization.

- ✓ Ethiopian kaolin grade would be suitable to synthesized expensive zeolite like ZSM-5 (zeolite Mobile -5) for catalytic cracking process.
- ✓ This thesis recommended that the specific condition, temperature and Time, required for the development of Zeolite-Y from Ansho kaolin clay.
- ✓ Finally, this thesis recommend and confirm that the Ansho kaolin clay as a good deposit for the production of Zeolite-Y.

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APPENDICES

Appendix A

Dealumination Calculation

Calcined Hosanna kaolin (Hosanna Metakaolin)

SiO_2 =62.28

Al_2O_3 =34.72

Dealumination calculation

Let us take; - 50gm metakaolin

For Silica

62.28 wt.% SiO_2

X= $\frac{62.28*50}{100} = 31.14\text{gm } SiO_2$

Molecular mass of SiO_2 =60gm/mol

Therefore, no of moles of SiO_2 in 50gm metakaolin is:

$n = \frac{m}{M} = \frac{31.14\text{gm}}{60\ gm/mol} = 0.519\text{mol } SiO_2$

For Alumina

34.72 Wt.% Al_2O_3

X=$\frac{34.72*50}{100} = 17.36\text{gm } Al_2O_3$

Molecular mass of Al_2O_3=102gm/mol

Therefore, no of moles of Al_2O_3 in 50gm Hosanna metakaolin is:

$$n = \frac{m}{M} = \frac{17.36\text{gm}}{102\text{gm/mol}} = 0.170\text{mol } Al_2O_3$$

Since, the silica/alumina ratio requirement for zeolite Y is between 3 to 10 then, we assumed it to be 5.

As thus $\frac{SiO_2}{Al_2O_3} = 5 \quad \rightarrow 5Al_2O_3 = SiO_2$

i.e. $Al_2O_3 = \frac{SiO_2}{5} = \frac{0.519mol}{5}$ =0.1038mol.

weight of Al_2O_3 left after dealumination is expected to be: -

0.1038mol *102gm/mol =10.5876gm Al_2O_3 left after dealumination.

Thus, leaching out 17.36 – 10.5876 =6.7724gm.

Leaching out Al_2O_3 amount to be 6.7724gm.

Equation of reaction for dealumination is

$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O$

To determine the quality of H_2SO_4 required for this leaching with 98% purity thus:

From the reaction stoichiometry, 102gm Al_2O_3 will require

102gm of Al_2O_3 = requires 294gm of H_2SO_4 with 100% purity while 98% purity yields

$x = \frac{100*294}{98} = 300\text{gm of } 98\% \ H_2SO_4 \text{purity}$

Therefore, to leach out 6.7724gm Al_2O_3 from 50gm hosanna metakaolin will require

$$\frac{300\text{gm} * 6.7724\text{gm}}{102\text{gm/mol}} = 19.918\text{gm of } 98\% \ H_2SO_4$$

To avoid complete dealumination of the metakaolin the required acid strength is 60%.

Therefore, the need to convert to 60% H_2SO_4

i.e. $\frac{19.981\text{gm}*98}{60} = 32.5327\text{gm } 60\% \ H_2SO_4$

To convert the mass of acid to volume, theoretical values of density for H_2SO_4:

Density of 60% H_2SO_4 at 25 ^oC = 1.494 gm/cm^3

Density of 98% H_2SO_4 at 25 ^oC = 1.8437 gm/cm^3 but,

$$\text{Density} = \frac{mass}{volume} \quad \rightarrow \quad \text{volume} = \frac{mass}{density}$$

Therefore, volume of 98% H_2SO_4

$V_{98} = \frac{m}{\rho} = \frac{19.918\text{gm}}{1.8437\text{gm/cm3}} = 10.803\text{cm3 of } 98\% \ H_2SO_4$

Conversion from 98% to 60% to the component balance

$V_{60} * \rho_{60} * 60 = V_{98} * \rho_{98} * 98$

Therefore, $V_{60} = \frac{10.803cm3 * 1.8437 \ gm/cm3}{1.494 \ gm/cm3 * 60} * 98$ V_{60} = 21.775 cm^3

To avoid slurry formation, which may reduce efficient heat and mass transfer during dealumination, the volume of acid calculated above is multiplied by factor 3.

V_{60} = 3* 21.775 cm3 = 65.325cm3 of 60%H_2SO_4.

The volume of 98% H_2SO_4 required is

$V_{60} * \rho_{60} * 60 = V_{98} * \rho_{98} * 98$

$V_{98} = \frac{65.325cm3 * 1.494 \quad {}^{gm}/_{cm3}}{1.8437 * 98} * 60$ V_{98} = 32.409cm3 of 98% H_2SO_4

Dilution calculation

$$V_{60} * \rho_{60} = V_{98} * \rho_{98} + V_W * \rho_W$$

Where

V_W = volume of water

ρ_W = density of water = 1gm/cm^3 = 1000gm/cm^3

$$V_W = \frac{V_{60} * \rho_{60} - V_{98}\rho_{98}}{\rho_W}$$

$$V_W = \frac{(65.325 * 1.494) - (32.409 * 1.8437)}{1}$$

V_W =<u>37.84cm^3</u>

<u>Summary</u>

To dealuminated 50gm of Hosanna metakaolin, we used the followings

32.409 cm^3 of 98% H_2SO_4 or 65.325cm^3 of 60% H_2SO_4

37.84cm^3 of deionized water.

<u>Other option</u>

Required Sulfuric acid concentration 60 Wt. %

60 Wt. % H_2SO_4 was prepared by mixing 85 cm^3 of 98% Wt. % H_2SO_4 with 99 cm3 of deionized water Or 85ml of 98Wt. % H2SO4 with 99ml of deionized water.

To Dealuminated 50gm of Hosanna metakaolin we used the following

106.698 cm^3 of 60Wt. % H_2SO_4 / 52.9348 cm3 of 98Wt. % H_2SO_4 61.810 cm^3 of deionized water.

Gel Formation Calculation

$\frac{SiO_2}{Al_2O_3} = 7.46$ from XRF compositional analysis test results

$\frac{Na_2O}{SiO_2} = 0.6$, the ratio should be $0.6 - 0.8$ from standared

$\frac{H_2O}{Na_2O} = 30$, standared from the zeolite Y standard formula molecular composition

2 Calculation for batch composition

Molar mass of Z-5 = (60*7.46) + 102+94=643.6gm/mole

Mole of Z-5 in 20gm of Z-5

$$\frac{20gm}{643.6gm/mol} = 0.03mole$$

Mole of SiO_2 in 20gm of Z-5

=0.03*7.46=0.23mol

3 Calculation for Na_2O need in batch composition

$\frac{Na_2O}{SiO_2}$ is 0.6 , from the standared formula (given)

$$\frac{Na_2O}{SiO_2} = 0.6$$

$Na_2O = 0.6*SiO_2 = 0.6*0.232 = 0.14$ mole

From reaction

$2NaOH \rightarrow Na_2O + H_2O$

$2 \rightarrow 1$

$X \rightarrow 0.14$ NaOH = 0.28 mole of NaOH

11.14gm of NaOH, will be needed

20gm Z-S of 11.14gm → fused

Calculation for H_2O

$$\frac{H_2O}{Na_2O} = 30 - - - - - - given$$

$H2O = 30*Na_2O = 30*0.14 = 4.2$ mole

From molar mass of water, mass of water will be 4.2 mole *18gm/mole =75.6gm

Since density of water is 1gm/cm3

1gm → cm3

75.6gm → 75.6cm3 = 75.6ml of water will be added.

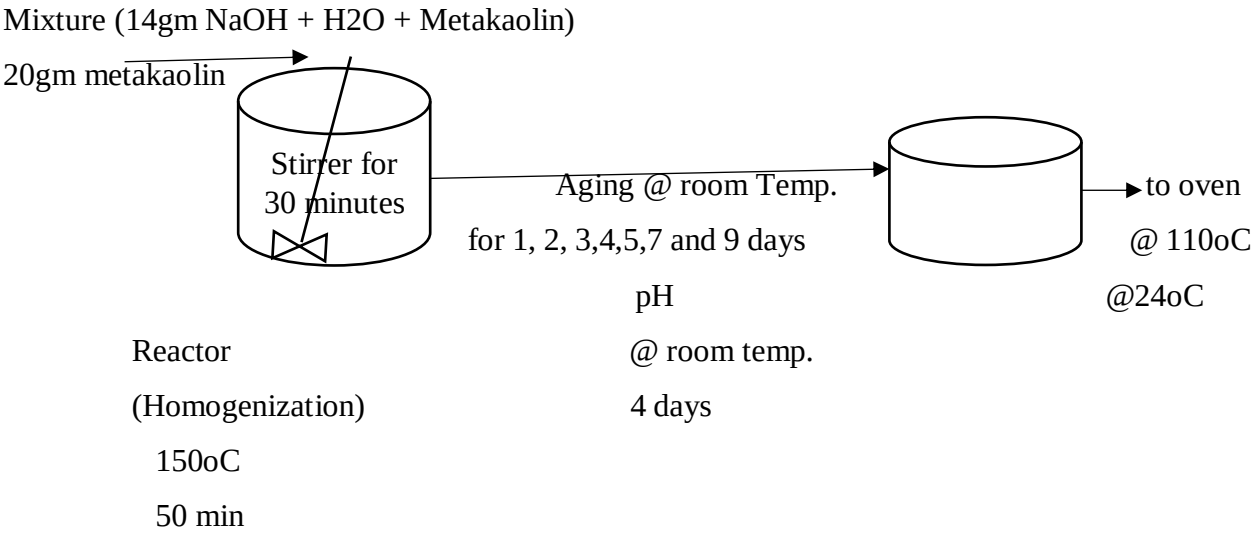
Gel formation process

Mix 20gm of Z-S with 11.14gm of NaOH (use uniform mixer)

Form uniform solid mixture and use ball mill

Fused the mixture in furnace at 650oC for 3hr.

Grind cooled mixture



Finally, the synthesized Zeolite Y molar Chemical Composition from the above compositional calculation is as follows

$6.93Na_2O: Al_2O_3: 11.5\ SiO_2: 207H_2O$ --- molar composition of synthesized Zeolite Y

This is only the representative zeolite Y molar chemical composition but for each zeolite Y synthesis from kaolin, it is possible to calculate its own molar chemical composition.

Appendix B

Pictorial Presentation of the Zeolite Production Process

- Beneficiation of Raw Hosanna (Ansho) Kaolin

Purpose:-to remove impurities such as soluble salt, quartz etc.

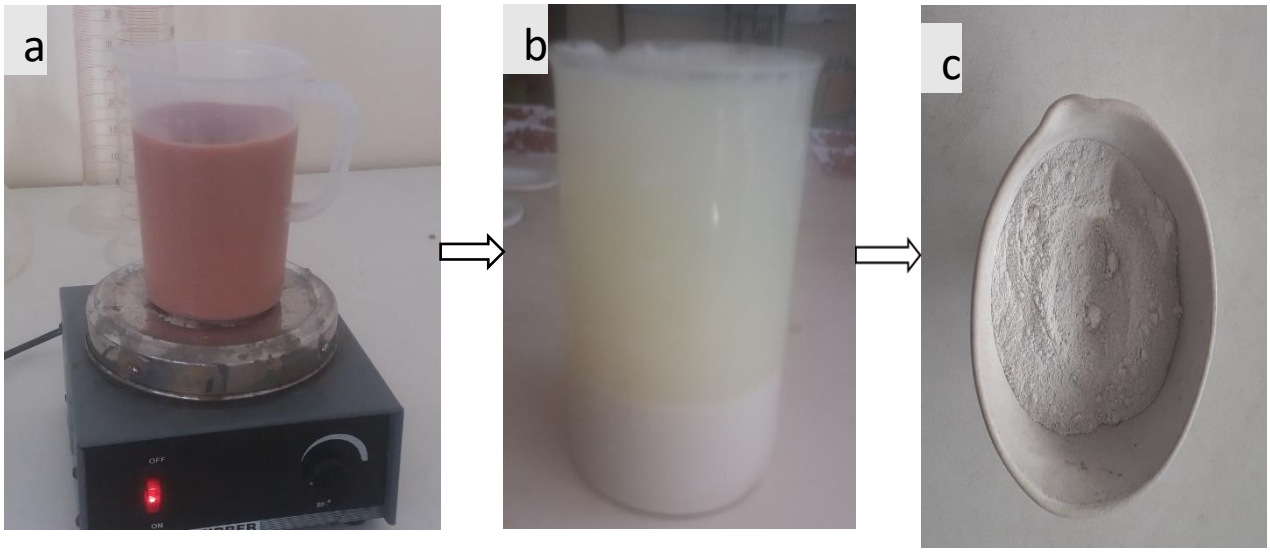


Figure a) Washing using water b) Washing with water and acid (HCl) c) Oven dried kaolin

- Calcination of Kaolin to Metakaolin

Treatment of the raw and beneficiated kaolin with heat using muffle furnace to convert the inactive and crystalline kaolin phase to active and amorphous phase of metakaolin.

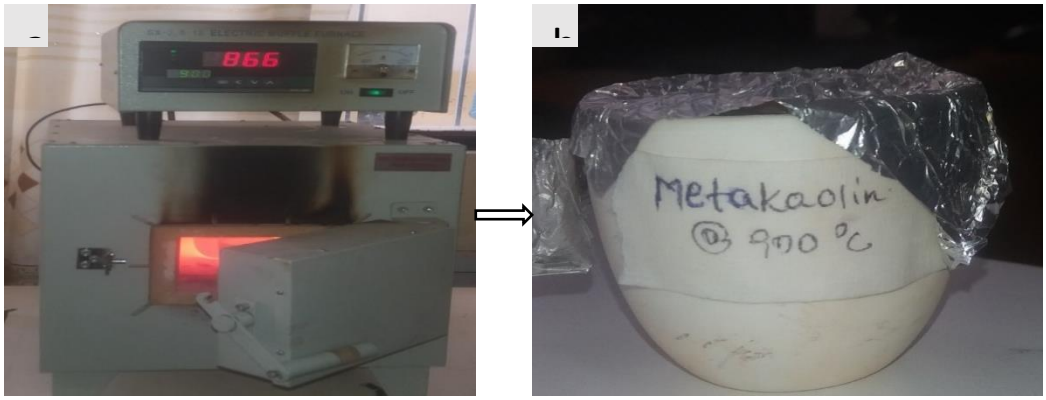


Figure a) calcination of kaolin with muffle furnace b) metakaolin at 900^{o}C

- Zeolite Formation Steps

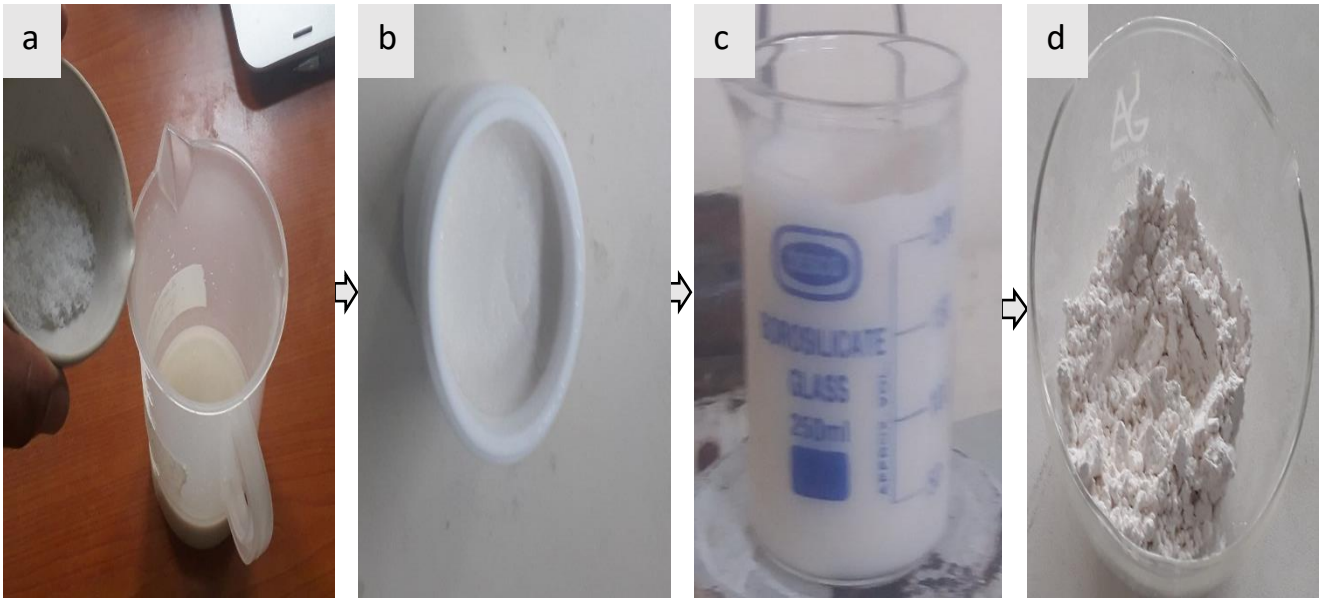


Figure a) Gel formation (H_2O + NaOH + Metakaolin) b) zeolite crystallization in side Teflon c) washing zeolite to reduce the pH level to 8 d) Oven dried zeolite Y

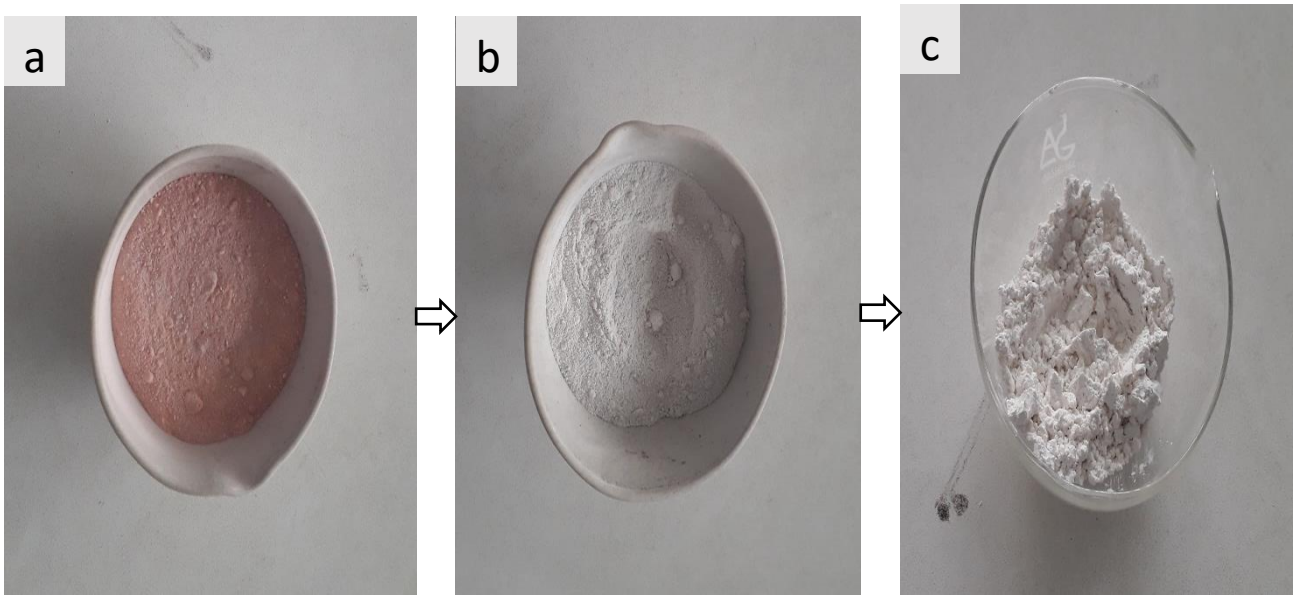


Figure a) water washed raw Hosanna Kaolin b) Water and acid washed Hosanna kaolin c) Zeolite Y synthesized from Hosanna kaolin.

XRD pattern of synthesized Zeolite P1

Details about Zeolite P1 Synthesized from Hosanna Kaolin.

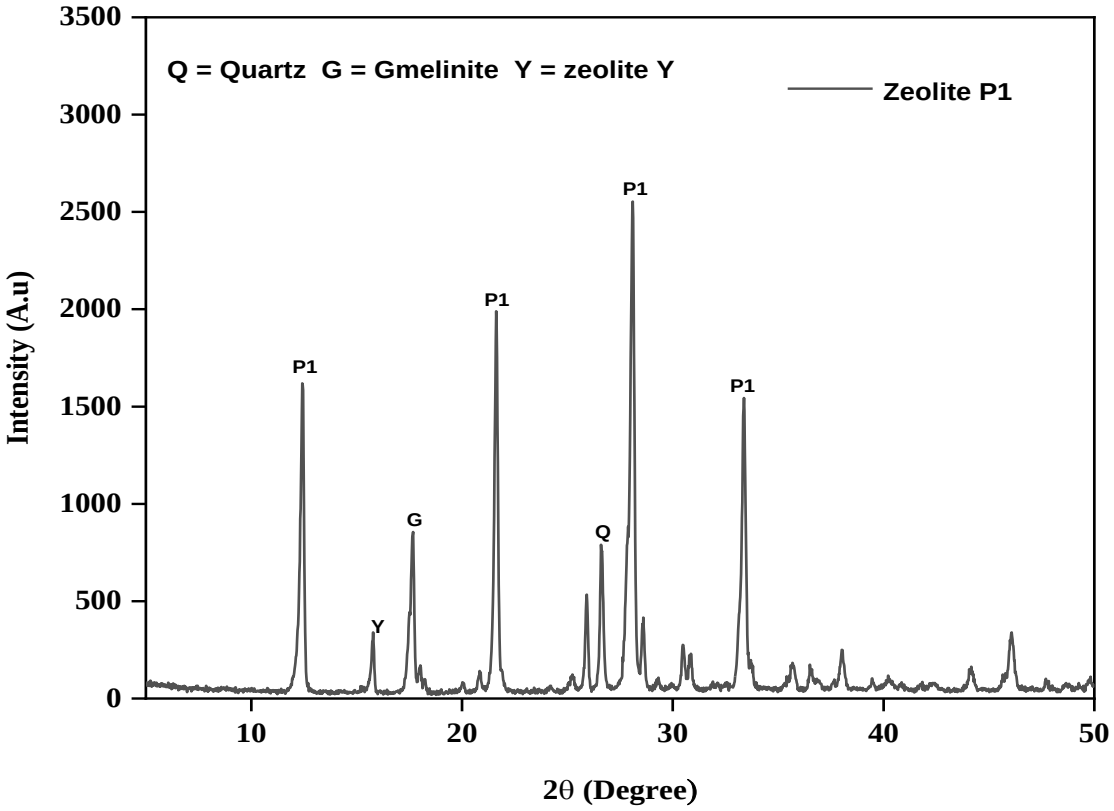


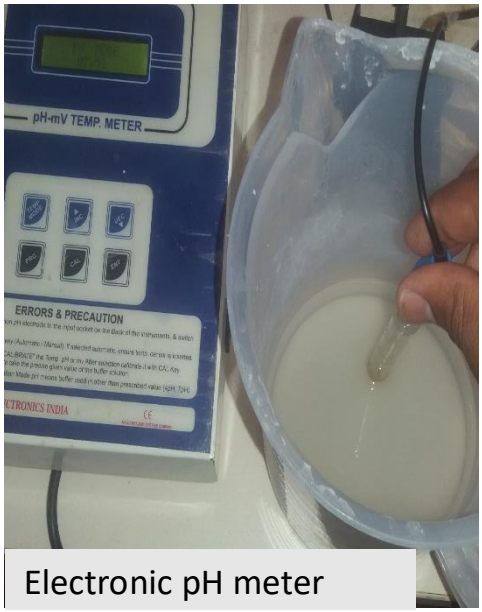
Figure XRD Pattern of Synthesis Zeolite P1 from Hosanna Kaolin for 5 days aging.

Table:-Comparison of lattice spacing, between the developed Zeolite P1 and standard Zeolite P1 from International Zeolite Association (IZA).

Zeolite P1 prepared from Hosanna Kaolin		Standard Zeolite P1 (IZA)	
Angle (2theta) degree	d, spacing (A^o)	Angle (2theta) degree	d, spacing (A^o)
12.4889	7.08188	12.46	7.101
17.6856	5.01093	17.66	5.022
21.6597	4.09967	21.67	4.100
26.8105	3.2254	25.08	3.551
28.1049	3.17244	28.10	3.176
33.3873	2.68160	33.38	33.38

Picture of laboratory equipment used in the preparation of Zeolite from kaolin.

Digital weighing



Electronic pH meter

Stainless steel
Autoclave reactor

Reverse Osmosis
Distill water source

Muffle Furnace

Digital Oven


Ice Bath