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SYNTHESIS AND CHARACTERIZATION OF ZSM-5 ZEOLITE USING ETHELINEDIAMMINE AS ORGANIC TEMPLATE: VIA HYDROTHERMAL PROCESS

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ABSTRACT

Zeolite can be synthesized from different substances but because of the environmental issues researchers have currently drawn their attention to cost effective and eco-friendly materials that can be used in the synthesis of various zeolites. Kaolin is one of these materials because of their nonhazardous and easy handling property. The uniqueness properties of the material gives it wide range of applications in different fields such as gas separation, adsorption and catalysis.. ZSM-5 Zeolite was prepared by addition of (ethylenediamine) as organic template. This experiment was conducted at the optimum conditions at 160 0c for a period of 44hr. Zeolite synthesized from Kaolin is also a crystalline micro porous aluminosilicate solid consisting of pores and routes of a molecular size. The synthesized material was found to have high SiO2 content of 42.95% and the alumina content of 2.65% which gives the SiO2/Al2O3 ratio of 16.2.In order to obtain a comprehensive picture of morphology of the synthesized material, spectroscopic analysis were performed sing X-ray powder diffraction (XRD) shows peaks at 2θ = 7-9° and 22- 25°, which correspond to the specific peaks of ZSM-5. Fourier-transform infrared spectroscopy (FTIR) which shows the absorption band near 450 cm-1 is due to the T-O bending vibrations of the SiO4 and AlO4 in tetrahedra. scanning electron microscope (SEM) in this zeolite was crystallized in spherical to cubical shape.

Keywords: ZSM-5, structure directing agent, template.

INTRODUCTION

Kaolin is one of the low cost and available silica rich raw materials used in zeolite synthesis. Literatures reported that the essential components of a material to qualify for zeolite synthesisare silicon oxide (SiO_2) and aluminum oxide (Al_2O_3) (Querol *et al.*, 2001). The synthetic zeolites obtained by harnessing kaolin indicates that the material has a great potential as a cost-effective, eco-friendly solution that can be used efficiently as heterogeneous catalysts.

Zeolite was a Greek word meaning "boiling stone" because when heated water was released (Cejka, *et al.,* 2007). Over forty natural zeolites are reported to be in existence as they formed naturally. Tschemich *et al.,* 1992, reported that the first zeolite was discovered in 1756. Natural zeolite consist of large amount of impurities and their surface areas is low which limit their catalytic activity and absorption capability, as such this narrow their applications. Researchers begin to develop synthetic zeolites, like ZSM-5 in the 1970s and discovered that it has very efficient catalytic chemical conversion, mainly in isomerization, alkylation, and aromatization process (Ren *et al.,* 2017). Since then zeolites became widely used in various applications (Auebach, *et al.,* 2003). Therefore, further research was carried out and many synthetic zeolites were developed. International Zeolite Association reported that, there are now 231 known zeolite framework structures. Zeolite Socony Mobil–five (ZSM-5) is a crystalline micro porous aluminosilicate substance consists of SiO4 and AlO4 tetrahedral with pores and channels of a molecular size. The building block of ZSM-5 is a three-dimensional framework and the structure units contain eight five-member rings with uniform pore size and it has high thermal stability, many acid sites, high selectivity, well adsorption property etc. It has reported that this type of zeolite has very important chemical properties, which makes the material very useful in many industries such as selective absorbent, ion-exchange resin, and high activity catalyst (Kusuma, *et al., 2*013).

ZSM-5 Zeolite can also be prepared with the addition of a templating agent such as tetrapropylammonium (TPA) bromide, iodide, or hydroxide (Argauer *et al.,* 1972), mono or polyhydric alcohols with ammonia (Planck *et al.,* 1980) or diamines such as ethylenediamine (ED) or hexamethylenediamine (Deane *et al.,* 1977). Systematic synthesis of zeolite was first established by Richard Barrer and Robert Milton in the 1940s by investigating the conversion of known mineral phases at high temperatures (70–270 °C) (Auerbach *et al.,* 2003). These materials were later determined to be zeolite ZK-5 with a KFI structure. The synthesis conditions were later optimized by Milton and co-workers in late 1940s when zeolites A, X and P were produced hydrothermally at low temperature (i.e. below 100°C) under autogenous pressures. Significant developments in zeolite synthesis then occurred over the few decades particularly when quaternary ammonium cations were introduced as structure directing agent for the formation of zeolites. Following the first successful synthesis of high silica zeolite, zeolite beta with Si/Al ratio ranging from 5 to 100, the ZSM-5 zeolite was synthesized using tetrapropylammonium cation (TPA^+) (Argauer *et al.,* 1972). The high cost of TPA as compared with other templating agents makesthe research to alternatively used ethylene diamine (ED) to serve as structure directing agent as it decrease the cost of ZSM-5 production.

Jiang, *et al.,* 2014, as successfully synthesized ZSM-5 hydrothermally in acid solution using natural zeolite Palygorskite with TPABr as template at 180 ℃ for 48 hours. ZSM-5 zeolite has also been successfully synthesized from natural alumina-silica in alkaline solution through sub molten systems (Yue *et al.,* 2014). In this work, we focused on synthesis of ZSM-5 zeolite using silica gel as sources of silica and natural Kankara kaolin as a source of alumina. Liu *et al., 2*015, reported that prior to the synthesis; depolymerized zeolite framework of ZSM-5 was carried out through sub molten system in alkaline solution at temperature 523 K. However, prior to our synthesis beneficiation was carried out then followed by calcinations. Synthesis of ZSM-5 can be carried out through single template methods using tetrapropylammoniumhidroxyde (TPAOH) as structure directing agent (SDA) (Lupulescu, *et al.,* 2012). Moreover, in the some researches Ethylene diamine was used as structure directing additive while it was used also by some researchers as a template for borosilicate and boroaluminosilicate (Perego *et al.,* 2003; Kester *et al.,* 2018).

MATERIALS AND METHODS

The chemical used includes silica gel Fluka (Merck), ethylenediamine (BDH ltd England), concentrated sulphuric acid (Pure chem. product ltd), sodium chloride (Pure chem. product ltd), local kaolin (Kankara, Katsina State, Nigeria).The materials and equipment used includes Autoclave STI9T (Dixon's Surgical instrument), Scanning Electron Microscope (Model 440i), FTIR Spectrophotometer Cary 630 (Agilent Tech), XRF Rigaku ZSX-100 etc.

Pretreatment of Kaolin

The kaolin is obtained from mining site in Kankara Local Government and preheated at 600-700℃. The amorphous preheated metakaolin phase was washed with acid to further remove anypossible impurities (Khatamian, *et al.,* 2007).

Synthesis of ZSM-5 Zeolite

ZSM-5 was synthesized hydrothermally. The following reagents were used for the synthesis of zeolites; the obtained kaolin was used as alumina source, Silica gel as silica source and ethelendiammine as structure directing agent.

Two solutions were prepared separately as follows; 1.5 g of sodium hydroxide, 6.03 gof silica gel, 3ml of ethelenediammine were added to 15ml of distilled water and the mixture was stirred for 1 hour using magnetic stirrer to get solution A (stirred at 2,600 revelation per minute).In another container, 0.6579 g of metakaolin was mixed thoroughly with 15ml of distilled water and 1.5ml of concentrated sulfuric acid was added to get solution B. The mixture of solution A was added to solution B; the mixture was stirred until a gel was formed. The stirring continued for another 2hrs until a homogenous mixture is obtained. The mixture was transferred to a stain-less steel autoclave with 70mm long tube having 41 mm and 5 mm thickness. The sealed autoclave with Teflon internal vessel was heated with the autogenously pressure in an air oven maintained at 433k for 44 hrs.

RESULT AND DISCUSSION

Table 1: XRF result of the synthesize ZSM-5

FORMULA	SiO_2	SO_3	Na_2O	Al_2O_3	MgO	CaO	P_2O_5	K_2O	Fe_2O_3	Cl	TiO_2
COMPOSITION (wt%)	42.95	42.41	7.5	2.65	1.1	1.08	0.90	0.51	0.42	0.28	0.12

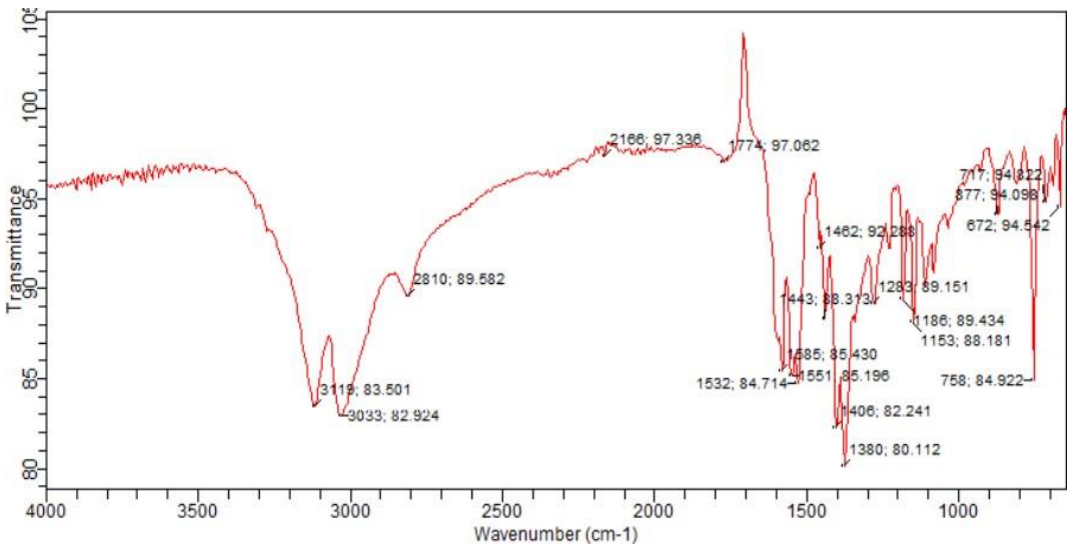

Fig.1: Show the FT-IR analysis of the synthesized ZSM-5 zeolite.

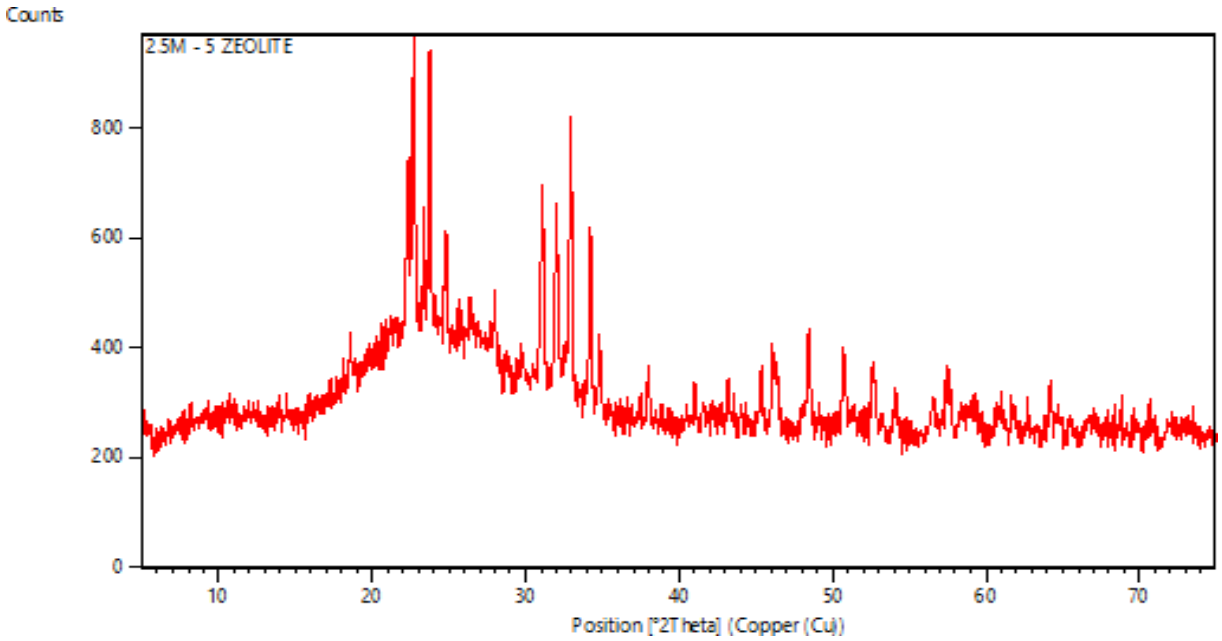

Fig.2: Shows the XRD result of synthesized ZSM-5 zeolite.

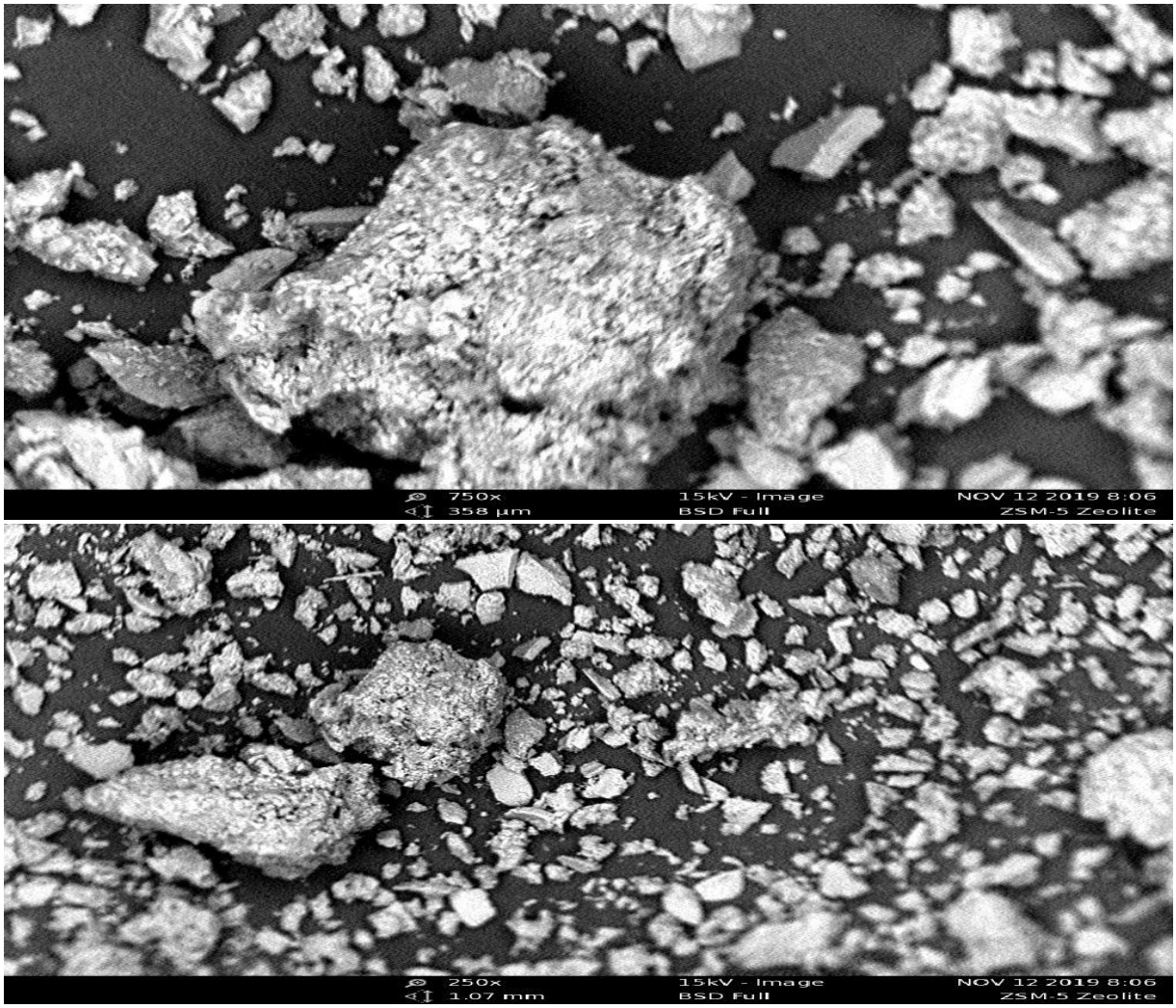

Plate: 1: Shows the SEM micrographs of ZSM-5 X750 and X250

It was observed from Table 1, that the kaolin composed of high SiO_2 content of 42.95%. Na_2O and SO_3 constitute7.5 and 42.41% respectively, while the alumina content was found to be 2.65%. Those are the major chemical composition of most common zeolites. The Si/Al ratio is an important factor in Zeolite synthesis, the crystal size of the ZSM-5 zeolite decreases with increasing the SiO_2/Al_2O_3. In this work, the SiO_2/Al_2O_3 ratio was 16.2. After crystallization the ratio reduces remarkably and this may be due to alkaline nature medium of the gel during synthesis with pH range of 10-11. Moreover, alkalinity enhance dissolving more silica in the liquid phase and therefore, less silica was usually left and become incorporated into the crystalline solid phase; so a considerable decrease in the Si/Al ratio takes place after crystallization.

The FT-IR spectra of the synthesized zeolites were recorded in the range 4000-400 cm^{-1} Figure 1.0. The Figure shows infrared spectra of the synthesized zeolite at 160°C using ethelendiammine as SDA. In the zeolite sample the fundamental vibrations of T (Si/Al) O4 tetrahedra of the zeolite framework has been observed in the region 400-1300 cm-1. Bands around 790, 1080 and 1219 cm- 1 are characteristic of SiO4 tetrahedron units as well. The external asymmetric stretching vibration near 1219 cm-1 is due to the presence of structures containing four chains of five-member rings arranged around a two-fold crew axis, as in the case of ZSM-5 structure. The absorption band around 1080 cm-1 is attributed to the internal asymmetric stretching vibration of Si-O-T linkage of zeolite ZSM-5. The absorption near 790 cm-1 assigned to the symmetric stretching of the external linkages. The absorption band near 450 cm-1 is due to the T-O bending vibrations of the SiO4 and AlO4 in tetrahedra. The presence of absorption bands around 542 and 450 cm-1 are characteristic of the ZSM-5 crystalline structure and the ratio of the intensities of these two peaks provides an approximate estimate of the degree of crystalline of a given zeolite sample and these are band characteristic of double ring, and is present specifically in ZSM-5

zeolite.

The analysis of the X-ray diffraction patterns of ZSM-5 zeolite powder synthesized at 160°C using ethelinediammine as SDA with a crystallization time (44 hrs) was also carried out. From Figure 2, the result showed that crystallization is almost complete in less than 2 days. Therefore, increasing the crystallization time does not lead to better crystallization, but usually causes decomposition of the ZSM-5 crystal phase. The XRD pattern for ZSM-5(44 hrs) shows peaks at 2θ = 7-9° and 22- 25°, which correspond to the specific peaks of ZSM-5 according to ASTM data. As such No other peak could be observed. This indicates the high purity of product. The relative crystallinity of ZSM-5 was calculated based on the intensity of the peaks of angle 2θ=22-25°. Average crystal size measured about 21 nm for ZSM-5(44 h) by Scherer's equation (D= K alpha 57.32 /beta cosθ) from XRD peaks between 2θ = 7-9°. The relative intensities are affected by the Si/Al ratio and the distribution of these atoms in the unit cell. The synthesized sample of ZSM-5 show peaks at 2θ=7°−9° and 22°−25° that are characteristic of typical ZSM-5 zeolites.

The scanning electron micrograph (SEM) of ZSM- 5 was shown in Figure 2.The intensity of emission of both secondary and backscattered electrons is very sensitive to the angle at which the electron beam strikes the surface, i.e. to topographical features on the specimen. The crystallite size and shape is often influenced by different synthesis parameter (Szostak, 1992). The silica to alumina ratio, source of silica, alumina and templating agent, influences the crystal morphology (Guisnet and Gilson, 2002). From the image it can be seen that this zeolite was crystallized in spherical to cubical shape. The SEM photograph of the sample shows bigger crystal size which may increase the surface properties of the zeolites for different applications. No amorphous phase is observable, indicating high purity of the sample although slight agglomeration was observed.

CONCLUSION

A ZSM-5 zeolite was synthesized from amorphous metakaolin prepared by H_2SO_4 for the leaching of a kaolin mineral from Kankara mining, Katsina State Nigeria. The syntheses were conducted with organic template (ethelinediammine) as SDA type and the optimum condition was at temperature of 160°C for a period of 44hrs. The synthesized material was found to have high SiO_2 content of 42.95% and the alumina content of 2.65% which gives the SiO_2/Al_2O_3 ratio of 16.2. The FT-IR spectra show some important absorption bands which indicate Si-O-T and T-O linkages. the X-ray diffraction patterns of the zeolite shows that crystallization is almost complete, while SEM micrographs implies that the sample crystallized in cubical shape with some agglomerations that occur.

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