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Low cost approach for synthesizing zeolite ZSM-5 from Kankara clay

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Abstract
Zeolites are advanced microporous materials that have played significant roles in our daily lives especially as it relates to adsorption, ion-exchange, catalysis and even in most petrochemical applications. In modern times, research findings have been geared towards improving and enhancing the effectiveness of Zeolite ZSM-5 as a catalyst. So, environmentally friendly, cheaper alternative have been sought. However, a locally sourced Kaolin from Kankara have been found to be precursor for zeolite synthesis as it comprises the required constituents for an aluminosilicate zeolite material. The raw material was hydrothermally activated with NaOH to synthesized zeolite ZSM-5. the method for economic purpose used conditions which included $23.4Na_2O:Al_2O_3:83.4SiO_2:4.2(TPA)_2O:3750H_2O$, The gel obtained was left to age for a period of 48 h at room temperature and hydrothermally treated at a temperature between 100-170^oC using Teflon-line autoclave at crystallization time of 72 h. The SEM reveals a well crystallized ZSM-5 sample with large, high quality hexagonal morphology and surface area of 96 m^2/g. The transformation of the starting material into Zeolite ZSM-5 was evaluated using X-Ray diffraction, scanning electron microscopy and Fourier transformed infra-red spectroscopy to elucidate the crystallization process of Zeolites.

Keywords: hydrothermally, precursor, adsorption, ion-exchange, catalysis

Introduction
Kaolinite is a clay mineral with a chemical composition $Al_2Si_2O_5(OH)_4$. (http://www.asdn.net/asdn/chemistry/zeolites.shtml 2015) and have been known by man for several centuries. They have properties which can be used for a lot of technological applications (Agbendeh, *et al*., 2021) [2]. Its chemical composition includes replacement of Si, Al, and Mg by other cations and water content (Agbendeh, *et al*, 2021) [2]. Kaolinite clay have numerous characterizing parameters which make them useful and have wide applications (Owate and Edike, 1984). They include: plasticity, resistant to temperature, malleability and complex formulation (Agbendeh, *et al*, 2021; Owate and Edike, 1984) [2].
Apart from the numerous applications in both industrial and domestics purposes, kaolinite clay serve as a good source from which zeolite can be prepared. However, it is only those zeolites that are laboratory well prepared can give optimum performance during application (Kovo and Edoga, 2011) [14].
Zeolites are highly crystalline microporous aluminosilicate materials which have defined topological network of uniformly linked cavities and pores of molecular dimensions that give rise to molecular sieving properties (http://www.asdn.net/asdn/chemistry/zeolites.shtml 2015). The term molecular sieve can be attributed to a material that has the capacity to selectively sort molecules on the basis on size exclusion. They can be referred also as hydrated aluminosilicate minerals which have micro-porous structures.
Zeolites have a unique feature of "open" structure that can host a variety of cations to include Na^+, K^+, Ca^{2+}, Mg^{2+} and others. These positive charged ions are loosely held and can easily be exchanged when they come into solution. Some of the most common mineral zeolites are: analcime, chabazite, heulandite, natrolite, phillipsite, and stilbite (http: www.iza-online.org 2015). The general formula of a zeolite is $M\ x/y\ [(AlO_2)\ x(SiO_2)\ y]\ wH_2O$. *M* is the cation; w is the number of molecules of water and the ratio *x/y* is the dependent parameter of the structure between 1 and 5.
Natural Zeolites can be formed from volcanic rocks where the ash layers react with alkaline groundwater. Also, Zeolites crystallize in post-depositional environments over long period of time ranging from thousands to millions of years in shallow marine basins. These Zeolites which occur naturally are most times not pure and contaminated with varying degrees of other minerals, metals, quartz and sometimes other types of zeolites. This has resulted to the reason why natural Zeolites are not essentially used for many commercial applications where uniformity and purity are needed.
More than 70 novel, distinct framework structures of zeolites are known (Kulprathipanja 2010) [6]. They exhibit pore sizes from 0.3 to 1.0 nm and pore volumes from about 0.10 to 0.35 cm^3/g. Typical zeolite pore sizes include: (i) small pore zeolites with eight-ring pores, free diameters of 0.30–0.45 nm (e.g., zeolite A), (ii)

medium pore zeolites with ten-ring pores, 0.45–0.60 nm in free diameter (ZSM-5); (iii) large pore zeolites with twelve-ring pores of 0.6–0.8 nm (e.g., zeolites X, Y) and (iv) extra-large pore zeolites with fourteen- ring pores (e.g. UTD-1). The zeolite framework should be viewed as somewhat flexible, with the size and shape of the framework and pore responding to changes in temperature and guest species. For example, ZSM-5 with sorbed neopentane has a near-circular pore of 0.62 nm, but with substituted aromatics as the guest species the pore assumes an elliptical shape, 0.45 to 0.70 nm in diameter. Some of the more important zeolite types, most of which have been used in commercial applications, include the zeolite minerals mordenite, chabazite, erionite and clinoptilolite, the synthetic zeolite types A, X, Y, L, "Zeolon" mordenite, ZSM-5, beta and MCM-22 and the zeolites F and W (Kulprathipanja, 2010) [6].

Synthetic zeolite is conventionally developed by hydrothermal crystallization under alkaline conditions which has been reported by several patents and technical articles. Recently, the classic alkaline hydrothermal synthesis has been improved by using sophisticated treatments, which include an alkaline fusion step followed by hydrothermal treatment, the application of micro-wave- assisted zeolite synthesis and a method for synthesizing zeolites under molten conditions without any addition of water.

The preparation of zeolites is generally expensive and, therefore, their use and applications is restricted due to prohibitive costs (Rios, 2008b) [10]. Cost limitations can be overcome by using low-cost materials for zeolite synthesis, such as kaolinite (KAO) clay. The use of these materials in the zeolite synthesis needs to be evaluated, and their potential applications explored. The experimental work in zeolite synthesis is particularly important in understanding and predicting applications of the raw materials under real-world conditions, because many applications are used under conditions quite distinct from typical laboratory conditions. To draw attention to unaddressed issues that deserve experimental attention, it is particularly needful to study the synthesis of zeolites under a wide range of experimental conditions. Studies should be carried out to investigate the types of zeolites that form, from specific raw materials under different conditions, assessing the interacting influences of different factors, the genesis of the alteration process, the succession of zeolite formation and the nucleation (Rios 2008a) [11].

Materials and Methods

Materials used were standard materials for synthesis of Zeolite ZSM-5 as presented in our work somewhere. Also, the sample collection, processing and metakaolin was also presented there (Agbendeh, *et al*, 2021).

Synthesis of Zeolite ZSM-5

A complete synthetic procedure for zeolite ZSM-5 is presented in a schematic diagram below.

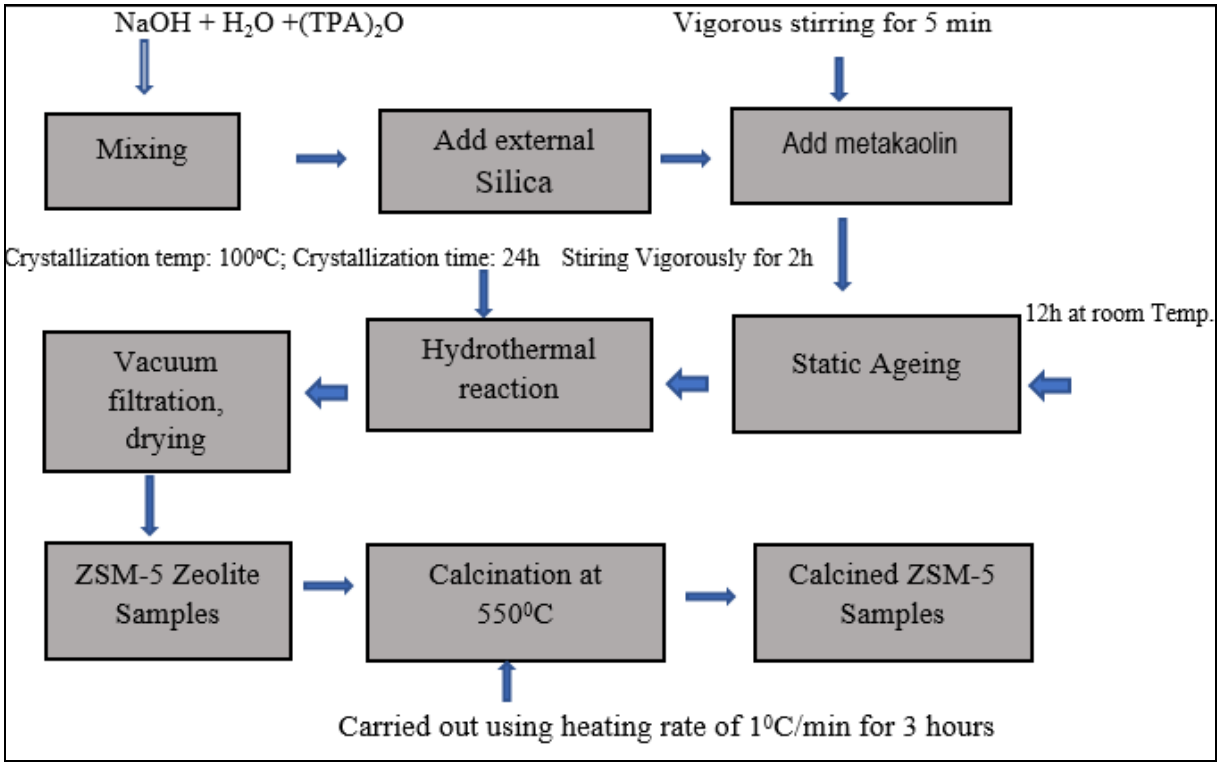

Fig 1

The composition of the synthesis gel was taken based on the work done by Abdmeziem and Siffert (1994) and Kovo, 2011 as:

$23.4Na_2O:Al_2O_3:83.4SiO_2:4.2(TPA)_2O:3750H_2O$

Results and Discussion

Synthesis, Properties and Characterisation of Zeolite ZSM-5

The production of ZSM-5 has been on the increase yearly for different industrial applications especially in refining, petrochemical and fine chemical production. The preparation of such material for use in the adsorption of heavy metals from wastewater using a low-cost material such as kaolin for the first time is a welcome development especially from a Nigeria's perspective.

Effect of Ageing

Ageing promotes the dissolution of different source materials, which will include, metakaolin, colloidal silica and SDA. However, this is expected to occur before the hydrothermal reaction proper. The XRD pattern in figure 1a, 1b and 1d shows that the ZSM-5 phase was crystallized by the different precursor materials, this is evident to the fact that all of them showed a diffraction peaks at 2-theta= 7- 9 and 23-25 there occur slight differences in intensities. This is matched with the reference ZSM-5 zeolite as shown in the figure 1c. The peaks are sharp and well- resolved which makes for a good crystallization between the KNK metakaolin and external colloidal silica. All the ZSM-5 produced from different precursor and method showed increased purity and high crystallinity which is evident from the fact that quartz or any amorphous materials. This might be as a result of the refinement process used which is effective and that all the impurities present in the source materials were reduced to minimal prior to further synthesis. Hence in this work, ageing time of 12 h was chosen as ideal ageing time for the formation of ZSM-5 from KNK. This has not been reported before, the reason is as discussed earlier. The SEM images in plates Plate I – IV also corroborate the results of XRD. However, a well crystallized ZSM-5 sample with large quality hexagonal morphology with very minor impurities was obtained at fused KNK material. Other materials especially as indicated by their image analysis revealed that the material did not react fully at the 12 hours of ageing (plate XI) or the method employed in (plate XIV D) was not effective.

Effects of Crystallisation time

ZSM-5 was synthesized from different source materials and conditions at an ideal time of 12hours. Immediately the crystallization time started, it was monitored and discovered that even at 12 hours of crystallization, the XRD pattern of the samples compared well with that used as reference and those in literature (Kovo, 2011) as was seen to be 100% crystalline.

It was discovered that though other findings presented co-crystalline phases and noted mordenite peaks. Ours did not, however, the position in the peaks correspond to the reference ZSM-5 sample.

Effects of Crystallization Temperature

Crystallisation temperature is known to reduce the induction period and accelerate the rate of nucleation and crystallization (Feng, *et al*, 2009). Therefore, crystallization temperature was employed to establish the formation of ZSM-5 from KNK. The ideal time which is adopted in this study is 100^{o}C, and the XRD are shown in figure 4.6a- 4.6d, and the SEM analysis revealed that our unfused kaolin and fused KNK with other conditions had amorphous and had some irregular shape. This is evident that these materials probably need additional temperature for fully crystallization to take place. However, our fused material prompted the use of this temperature which agrees with the aim of this work that required low

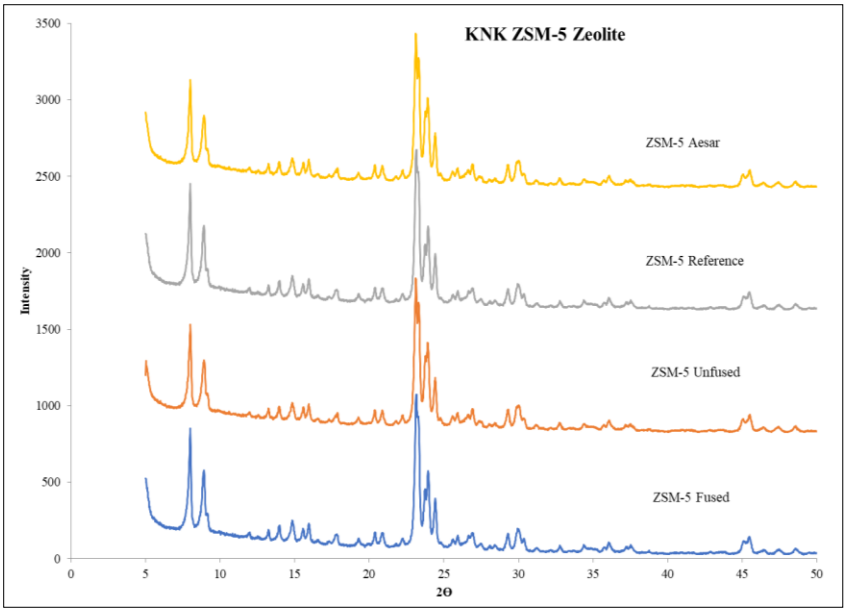

Fig 2: XRD pattern showing variation of preparation process and aluminosilicate material, a) Zeolite A obtained from fusion process, b) Zeolite A without fusion, c) Standard Zeolite A used for reference, d) Zeolite A from Aesar

SEM analysis of Zeolite ZSM-5

The SEM reveals a well crystallized ZSM-5 sample with large, high quality hexagonal morphology as presented in the literature for fused KNK sample. Others seems to have clear pictorial representation of the SEM analysis, but there occur some poor quality and irregular shape as shown in b,c and d which might be as a result of the minor impurities which still persisted as a result of the unreacted metakaolin in the unfused sample and analysis on other aluminosilicate material.

However, our method of synthesis showed a defined morphology of ZSM-5 unlike others in the figure. This establishes the reason why our method is effective and that all silicon and aluminium species from kaolin reacted (Rios, 2011)

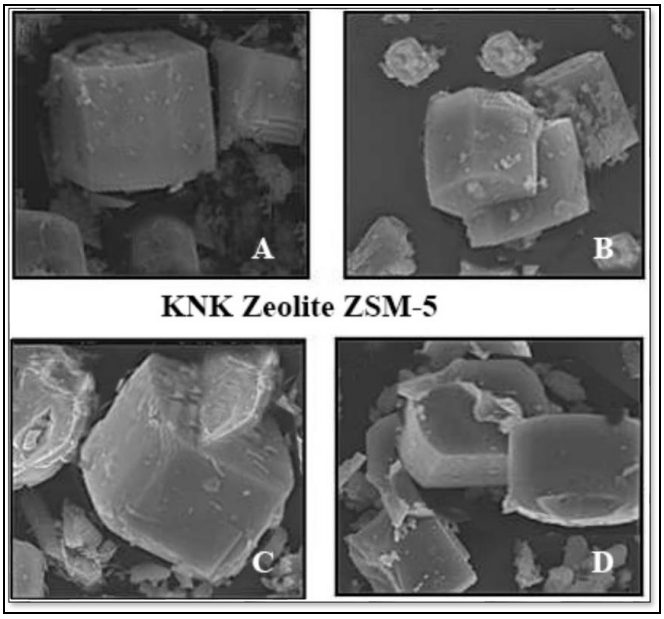

Plate I: (A): SEM of Reference ZSM-5 sample, (B): SEM of Zeolite ZSM-5 using fused standard kaolin sample, (C): SEM of ZSM- 5 obtained from fused KNK sample, (D): SEM of ZSM-5 obtained from unfused KNK sample, FTIR of Zeolite ZSM-5

The FTIR spectra of the ZSM-5 zeolite sample is given in figure 4.10. The IR spectra of these samples showed the characteristic adsorption bands corresponding to those obtained from literature (Pichat, *et al*.,1975). Bands at 920-1250 cm^{-1} and 1050-1150 cm^{-1}, due to internal symmetric and asymmetrical stretches, and bands at 500-650 cm^{-1}, due to ring vibrations, and bands at 420-500 cm^{-1}due to T-O bends were clearly observed and were in accordance with the band assignments reported in the literature (Özvatan and YÜrÜm, 2010). However, the extra peaks observed in the fingerprint region of the spectrum are probably due to the slight crystalline changes, different extra-framework cations, and presence of some impurities. The appearance of a new peak at the hydroxyl region corresponding to the presence of OH groups was also in agreement with the reports in literature (Özvatan and YÜrÜm, 2010).

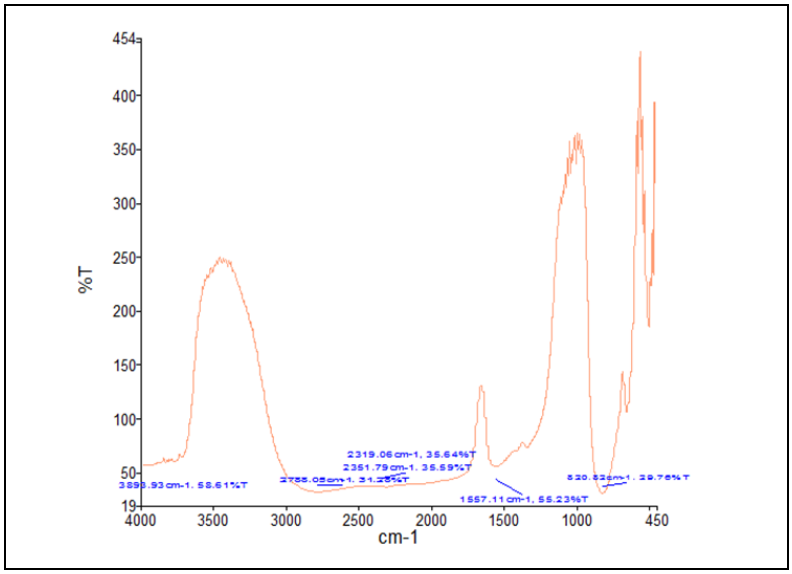

Fig 3: FTIR of Zeolite ZSM-5

Nitrogen adsorption isotherm and BET surface area

Figure 2 present the N_2 gas adsorption/desorption isotherm for zeolite ZSM-5 at 77 K. The isotherm curves for Zeolites ZSM-5 conforms to type IV in accordance with the IUPAC classification. The curve initially convex to the relative pressure and then level off with increase in pressure. The Brunauer-Emmett-Teller (BET) surface area of ZSM-5 have been experimentally determined to be 96 m^2/g which is significantly larger than those for natural porous materials, such as clay and other types of zeolite and porous carbons (Rouguerol *et al*., 2002; Xiaoming & Erdong 2007)

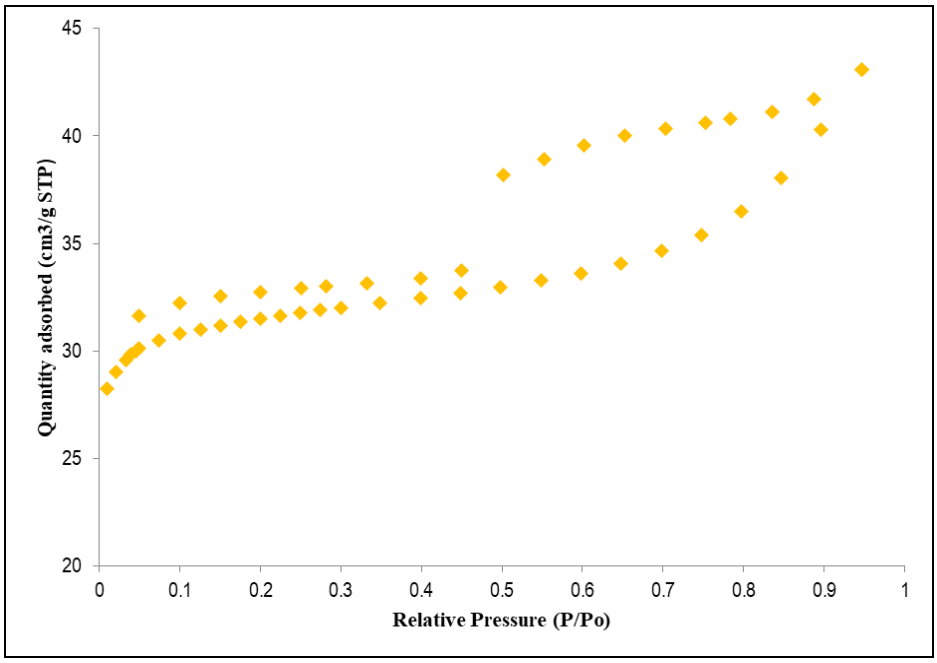

Fig 4: Adsorption and Desorption of Zeolite ZSM-5

Conclusion

The Kankara Nigerian Kaolin (KNK) has been used as a source of raw material for the preparation of zeolite ZSM-5. The processes of synthesis adopted facilitated the hydrothermal conditions and larger amounts of aluminosilicates were dissolved in the process. Also, the alkaline fused method employed in the synthesis enhanced effective extraction of silicon and aluminium species from the kaolin. The morphology of the synthesized materials compared well with those presented in literature. However, our modified method of synthesis showed better textural features as compared to other conditions and other aluminosilicates used in this research. *Zeolite ZSM-5* presented a high-quality hexagonal morphology which possesses required features for its application.

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Declaration of conflicting interests

The authors declared no potential conflicts of interest

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