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Utilization of Nagarparker Kaolin for the Synthesis of Zeolite-zsm, A Value Added Product

H. Mahar[1], S. A. Soomro[2], A. R. Memon[2], S. Holmes[3]*

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Abstract

Nagarparker arid zone of Pakistan. It has large deposits of Kaolin (China Clay) approximately 4.3 million tons. Crystal zeolite ZSM produced and characterized. Material ground, calcined dehydrated using ball mill, autoclave and furnace. Due to dehydration kaolinite converted into Metakaolin with a weight loss of about 3.9% and 8 M solution of Sodium hydroxide added with the ratio of 1:5 at 100 °C with vigorous stirring for 1 h. Fusion carried out at 100 °C for 1 h, sample washed 3 times to make its pH normal. Fourier Transform Infrared Spectroscopy (FTIR) characteristic studies showed the presence of Si-O-Al , OH, Al-OH and Si-OH at different band widths 1000 cm^{-1}, 1434 cm^{-1} , 1100 cm^{-1} and 1250 cm^{-1} respectively. Scanning Electron microscopy showed clear morphology of zeolite ZSM. X-ray diffraction showed the synthesis of Zeolite ZSM with absence of amorphous materials and revealed orthogonal shaped crystal structure. Crystal size 0.68 Å calculated using Xperts Highscore. The results show that the Nagarparker kaolin is suitable for the synthesis of Zeolite ZSM as value added Product.

Keywords: Nagarparker Kaolin, Synthesis, Zeolite ZSM, Utilization

1. Introduction:

Nagarparker is the region containing reserves of approximately 3.67 Million Tons [1]. Muslim et at reported geological map of Nagarparker area in 1997 [2]. Kaolin deposits as shown in Figure 1. vary from 1.50 to 10.0 m in thickness and average overstretch thickness is 2.10 m [3]. Clay minerals like kaolinite, sepiolite, mica, palygorskite, smectite and vermiculite groups are naturally occurring minerals. Out of these kaolinite ($Al_2Si_2O_5(OH)_4$) is one of the most important material to be used for the production of zeolites [4-6]. Zeolites are found naturally [7, 8] and can be made synthetically[9-11].

Kaolin obtained from silicate rocks as a weathering product of silicate its color varies from whitish powder to earthy having some degree of plasticity. It is an industrial mineral used as base material for ceramics and production of refractories, sometimes used as material for industrial filling of paints, rubber, plastic, dyes and paper [4, 6, 12]. Additionally, kaolin can be utilized for waste management [13, 14] and in the preparation of geo polymers and geo polymer-based composites [15, 16] zeolites [17, 18] and interpolates [19, 20].

Kaolin is a natural mineral from the clay family and

[1] *Department of Chemical Engineering, NFC Institute of Engineering & Technology, Multan*

[2] *Department of Chemical Engineering Mehran University of Engineering & Technology, Jamshoro*

[3] *Department of Chemical Engineering and Analytical Sciences, University of Manchester UK.*

Corresponding Author: hidayatullah@nfciet.edu.pk

can contain a number of impurities, like zircon, feldspar, quartz, tourmaline etc., which obtained from the parent rock. Initially properties and structure of kaolinite was studied by Brindley and Robinson [21]. They determined lattice parameters by analysis of reflections using patterns obtained from X-ray diffraction. Karmous [22] showed lattice energy -827.4eV in kaolinite by applying technique of computational energy minimization. The total lattice energy in kaolinite is equal to standard. While the primitive cell volume is 321.30 Å. Kaolinite elastic constants were calculated by using first principle calculations by Militzer *et al.,* [23]. Also discussed possible application areas of kaolinite. With Rietveld refinement, Young and Hewat [24].

Though a few researchers, like Edomwonyi-Out *et al*. [25-27] have explored Kankara kaolinite of Nigeria by checking its influence of thermal treatment. Possible application areas of kaolinite deposits and its in-depth properties are still lacking. Worldwide kaolin production is $38*10^6$ Metric Ton. Literature suggest that kaolin is best material to produce various types of zeolite like Mia synthesized zeolite-A [28], and activated waste kaolin [29].

Figure 1: Map of Pakistan Showing Nagarparker Kaolin deposits

used by Iran to produce zeolite-ZSM-5 [33]. Jordon kaolin was used to produce zeolite A [34]. Tunisian kaolin was studied by [35] and used to produce zeolite LTA [36] and NaX zeolite [37]. Literature suggests use of kaolin to synthesize zeolite [38, 39]. Ugal *et al*., [39] synthesized zeolite 4A from Iraqi kaolin. Ion exchange technique used to insert sodium to the structure and water adsorption purposes, identified by conducting tests on the zeolite. Zhao *et al*., [40] also used halloysite mineral to produce well-ordered NaA zeolite [41, 42]. Researchers have used Nagarparker kaolin as base material for the synthesis of Zeolite Y using hydrothermal treatment method [43].

Zeolite materials are applied as an additive for foaming in asphalt technology [44]. As a feed additive zeolites were used for dairy cows [45]. Water treatment is carried out using zeolite sorbent for the removal of heavy metal ions [46]. In the hydrocarbons and volatile organic compounds zeolites have good adsorption effect on various liquid and gas adsorbates [47].

According to literature survey, the scientists did not synthesize any zeolite ZSM-5 using Nagarparker kaolin reserves found in Pakistan. The objective of this research is thus, to synthesize and to study the characteristics of Zeolite ZSM-5.

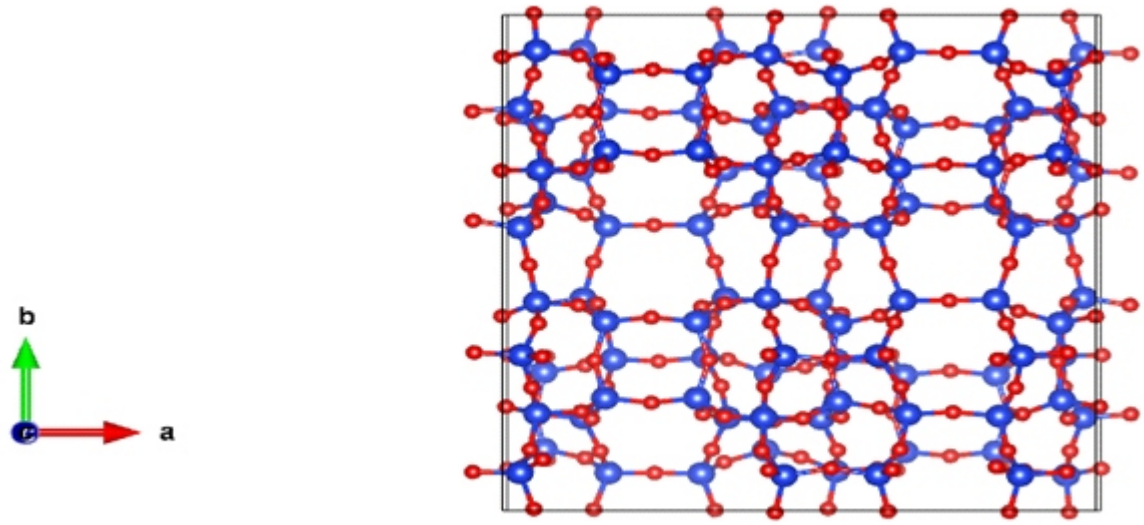


Figure 2: Single component Crystal structure of Zeolite ZSM obtained from International Zeolite Association.

2. Methods And Materials :

2.1. Material collection

Samples of kaolin collected from Nagarparker area of Pakistan having longitudes and latitudes Sindh (24° 15' to 24° 30' N, 70° 37' to 71° 07' E. Major Oxides of Nagarparker kaolin mentioned in Table1. Physical properties are such as density, specific gravity, plastic limit; Liquid limit, Plastic index and shrinkage index given in Table 2.

2.2. Calcination:

Calcination of Kaolin clay carried out for 4 h at 700 °C. Due to this clay activated and metakaolinite formed with the loss of 3% by weight percentage. Alkali-activated paste was made of eight Molarity by adding NaOH in to water. Thus, a more active amorphous Metakaolin with a small amount of quartz obtained as a product. The alkali-activated paste samples were synthesized using 4 ml of a 5-10 M solution of NaOH and 5 g of metakaolin. Mechanically the solution mixed with solids at room temperatures for several minutes. The fresh pasta was poured into a silicone mold and activated at 100 ° C. for 4 hours.

2.3. Gel formation:

The autoclave filled with various concentrations of sodium hydroxide; distilled water and Metakaolin added to obtain a solution. A gel-like glossy solution obtained. Agitation and aging Agitation at 90 °C for 60 minutes

2.4. Crystallization and post treatment:

The gel crystallized at 100 °C. for 24 hours. After crystallization, filtration and washing carried out with water demonized from zeolite crystals obtained until the pH was lower than 10

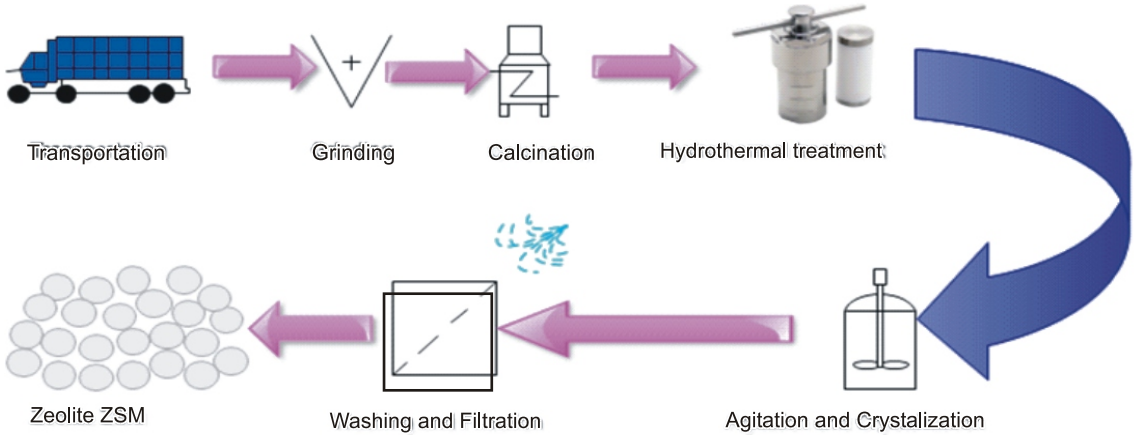


Figure 3: Zeolite Synthesis from Nagarparker kaolin

2.5. Characterization

The starting material and synthesized product characterized by FTIR, SEM, XRF and XRD techniques, as follows. High-speed solid-state linear (X'Celerator) carried out X-ray powder diffraction (XRD) analyses with a P Analytical X'Pert Pro MPD (PW3040/60) diffractometer applying linear detector. Using Cu-Ka radiation (l = 1.5406 A°) on powdered samples in y/y scanning mode randomly Ni Kb filter. X-ray powder patterns collected. The scan range was 5° to 75° 2y, with the following instrumental conditions: 1/4° anti-scatter slit, 1/8° divergent slit, Fourier transform infrared spectrometry (FTIR) employed a Perkin Elmer 1760 X FTIR spectro-meter in the 4000-400 cm^{-1} range with samples prepared as KBr discs.

Scanning electron microscopy (SEM) analyses carried out on a Zeiss LEO 1430 microscope. The samples sputtered with gold using Emitech K 550 equipment 0.02° 2y step size and 20 s per step.

3. Results And Discussions:

3.1. XRD pattern:

Phase compositions analyzed by X-ray Powder Diffraction

Table 1: Composition of major oxides of raw and washed kaolin of Nagarparker.

Oxides	SiO_2	TiO_2	Al_2O_3	FeO_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI
Raw Kaolin of Nagarparker	52.9	1.3	24.7	0.7	0	0.2	4.8	1.4	0.3	0	13.7
washed kaolin of Nagarparker	45.1	0.7	35.1	0.7	0	0.6	1.8	1.2	0.2	0	14.8

(XRD) X'Perts system (CuKá radiation). Range of 2è degree angle of 5-90° with a step of 0.007 for 2 hr. X'Pert High Score Plus application used to identify phases with the use of an and the International Centre for Di?raction Data. The bands intensity ratio of 550 and 450 cm^{-1} utilized to estimate the crystallinity of zeolite. Considering value of 0.70 for well crystalline ZSM, the observed value of 0.68 for the products as the XRD graph presented in Figure 5, which clearly suggests that, the framework of the zeolite.

Table 2: Physical properties of Nagarparker kaolin

Locality name	Density g/cm3	Sp. Gravity	Plastic Limit%	Liquid Limit %	Plastic Index %	Shrinkage Limit %
Nagarparker kaolin	2.53	2.54	24.9	39.5	14.61	1.67

3.2. FTIR Analysis:

Fourier Transform and Infrared Spectroscopy was done of raw kaolin obtained from Nagarparker named as sample hk1 and the product synthesized called zeolite ZSM is shown in Figure 4 and Figure 5 respectively. 1400-400 cm^{-1} are wavenumber regions of solid-state reaction product. The course of the spectra subsequently confronted with structure and the character of bonds in these zeolites

Shift of the band at around 1435 cm^{-1} toward higher wavenumbers observed with the products of the solid-state reaction, indicating that the reaction has slightly influenced the bonding strength of the zeolite framework. Figure 4 describes clearly that (Al, Si) O bonds were estimated by tetrahedrons stretching vibrations at wavenumbers 400-1100 cm^{-1} for the kaolin samples obtained from locality of Nagarparker. OH, groups of water molecules observed through stretching vibrations at wavenumbers 1590-1670 and 3400-3700 cm^{-1}. Wavenumbers 300-500 and 1100-1250 cm^{-1} having external vibrations shows (Al, Si) O. Tetrahedrons.

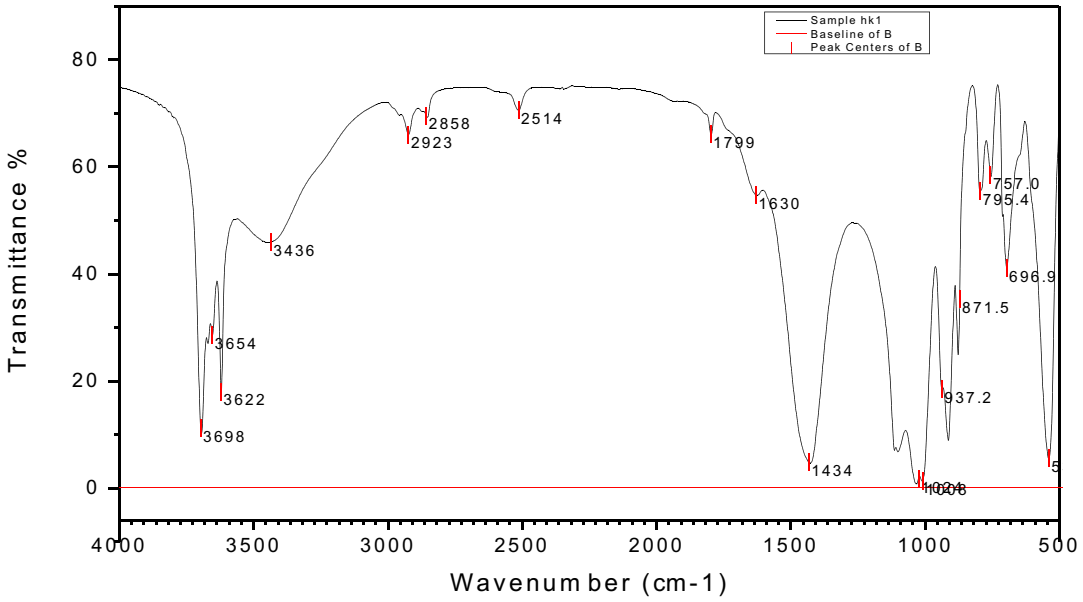


Figure 4: FTIR Spectrum of Nagarparker kaolin

In Figure 5 the tetrahedrons vibrations were observed (wavenumbers 300-500 and 1100-1250 cm^{-1}) Figures 5 containing three parts (a), (b), and (c) shows the FTIR spectra of the products obtained after 1h. Bands at around 3600 cm^{-1} and 1600 cm^{-1}, attributed to zeolitic water, observed in all the products. In addition, a band at around 1000 cm^{-1} observed, characteristic of the Si-O-Al bonds in TO_4 tetrahedral, which confirmed the presence of zeolitic material. Another band observed at around 531 cm^{-1} for all the products obtained. Also, a band at around 1000 cm^{-1} was observed, characteristic of the Si-O-Al bonds in TO_4 tetrahedral [48], which confirmed the presence of zeolitic material. Another band observed at around 531 cm^{-1} for all the products obtained.

3.3 SEM Analysis:

Scanning Electron Microscopy analysis taken at three magnifications (a) at x2500, (b) at x5000 and (c) at x10000. Morphology clearly indicate presence of particles with pores. Direct imaging technique applied on the surfaces of particles of zeolite, types of pores existing revealed by SEM technique. Distribution of atoms on zeolite can by visualized on their surfaces by conjunction analysis by cross-sectional observations as described in Figure7.

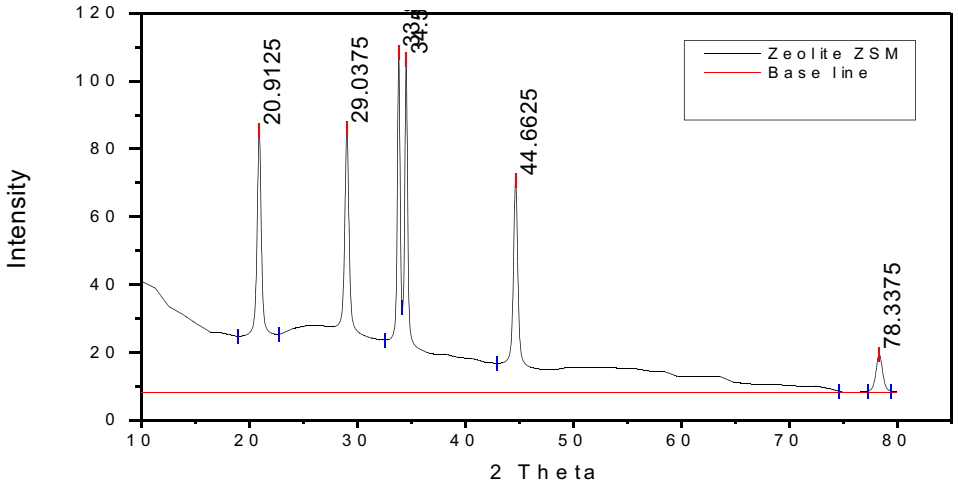


Figure 5:. XRD Pattern of Zeolite ZSM produced from Nagarparker kaolin.

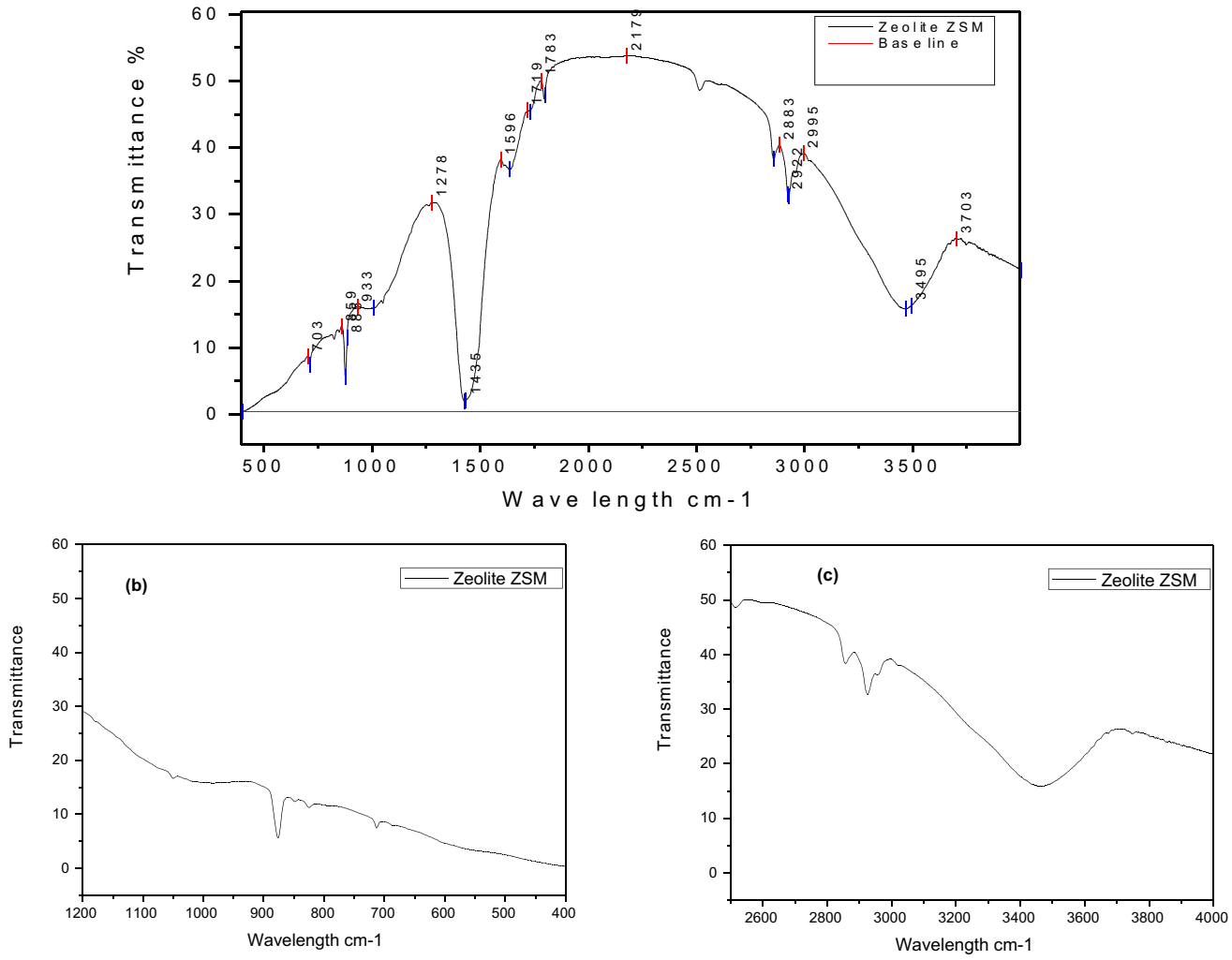
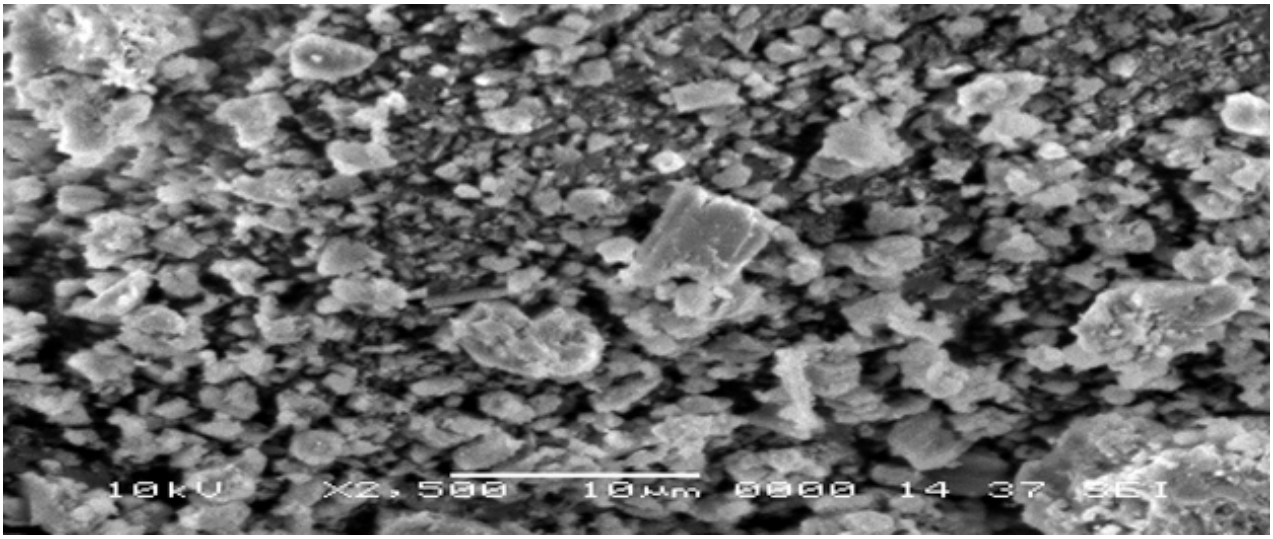


Figure 6: FTIR Pattern of Zeolite ZSM prepared from Nagarparker Kaolin.
(a) Zeolite ZSM prepared from Nagarparker kaolin. FTIR range of wavelength is from 1200 cm^{-1} to 400 cm^{-1}.
(c) Zeolite ZSM prepared form Nagarparker kaolin. FTIR range of wavelength 2500 cm^{-1} to 4000 cm^{-1}.



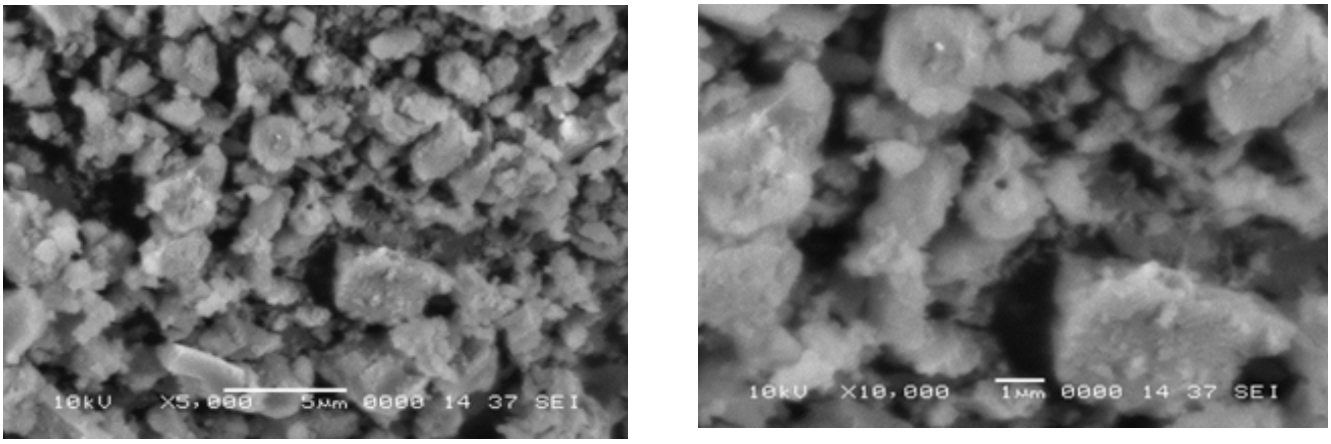


Figure 7: SEM of Zeolite ZSM produced from Nagarparker kaolin (a) Resonance focus of X2500 (b) Resonance focus of x5000 and (c) Resonance of x10000

4. Conclusion:

Zeolite ZSM-5 synthesized using the Nagarparker kaolin as a base material. Crystallinity of synthesized zeolite observed from XRD and calculated using XPert HighScore that is 0.68 Å. FTIR study also revealed band at around 1000 cm^{-1} characteristic of the Si-O-Al bonds in TO_4 during the synthesis of zeolite. Moreover, SEM depicted crystal morphologies resulting no any amorphous substances or other crystalline nor uniform size distribution. There is a significant environmental advantage to use unexplored reserve of kaolin as raw materials. The value of reserve enhanced by such a scientific approach. Definitely, it would aid realistic economic and social development of the region.

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