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ORIGINAL RESEARCH ARTICLE

CHARACTERIZATION OF SYNTHESIZED ZEOLITE SOCONY MOBILE 5 (ZSM-5) FROM BULARAFA DIATOMITE

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ABSTRACT

In this study, a highly siliceous ZSM-5 zeolite with elemental silicon to aluminium ratio of 250 was synthesized using Bularafa diatomite as silica source. The diatomite was used to produce silica sol which was used with alumina in the presence of organic template (tetrapropyl ammonium bromide, TPABr) to form ZSM-5 under hydrothermal reaction at low temperature and atmospheric pressure in alkaline medium. The synthesized ZSM-5 was characterized using X-ray diffraction (XRD), Fourier transformation infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), N_2 adsorption and X-ray fluorescence (XRF). The Brunauer, Emmet and Teller (BET) method revealed that the ZSM-5 produced from Bularafa diatomite have very high specific surface area of 619 m^2 g^{-1}.

1.0 Introduction

Diatomite rock is a loose, earthy or loosely cemented porous and lightweight rock of sedimentary origin, mainly formed by fragments of armor (skeletons) of diatom algae: (diatomea and radiolaria). Diatomite is a microscopic diatom alga whose size ranges from 0.75 to 1500 m; sometimes this rock is called infusorial earth, kieselguhr, or mountain meal (Arik, 2003). The important properties of diatomite are related to physical structures and an aggregate of fine particles perforated by a regular pattern of very small holes (Aliev et al., 2011). Diatomite's highly porous structure, low density and high surface area resulted in a number of industrial applications as filtration media for various beverages and inorganic and organic chemicals as well as an adsorbent for oil spills (Bakr, 2010). It can be used as an alternative source of amorphous silica for the production of silicon-based materials with industrial and technological interests. Diatomite is another interesting material because of its low cost and its advantage over other materials such as clays, iron oxides, molecular sieves, activated carbon and rice husk due to the highly reactive amorphous state of its silica skeletons, which makes it unnecessary to carry out thermal activation to transform an unreactive state into a reactive state (Chaisena and Rangsriwatananon, 2005). It has been shown that kaolin clay and diatomaceous earth are two suitable and inexpensive sources of silica materials. Some studies reported that rice husk ash contains high amount of silica that is amorphous or crystalline depending on the combustion temperature (Shen et al., 2011, 2018; Habeeb and Mahmud, 2010). Other studies were conducted on the synthesis of zeolites from rice husk ash, namely MCM zeolite and ZSM-5 (Chiarakorn et al., 2007; Fernandes et al., 2005; Mohammed et al., 2008) for possible use in catalytic refinery and petrochemical processes. However, preparation of zeolites with higher SiO_2/Al_2O_3 molar ratios such as ZSM-5 requires either an increase of the amount of silica or partial removal of aluminium. The first alternative implies using an additional source of silica with high solubility, e.g. sodium silicate or silica sol as reported in the research works of Khatamian and Irani 2009, Kovo et al., 2009. However, in the work of Li et al., 2015, ZSM-5 zeolite was synthesized directly from diatomite after calcination, but the synthesized zeolite has low quality which could be due to the presence of impurities such as

iron oxide, potassium etc. Also, in the previous works ZSM-5 took longer synthesis times up to seven days and above at elevated temperature.

In this study, we synthesized a highly siliceous ZSM-5 by using silica sol prepared from Bularafa diatomite for the first time.

2.0 Materials and methods

2.1 Materials

Bularafa diatomite as a silica source was collected in lump from Bularafa village in Gubja Local Government area of Yobe State. Activated alumina (fused 99%, Sigma, USA), pellets of sodium hydroxide (98 wt.%, Sigma, USA), tetrapropyl ammonium bromide (TPABr) (Sigma, USA), Sulphuric acid (98 wt.%, Sigma, USA) and distilled water were used as the starting materials in the initial mixture for the synthesis of ZSM-5.

2.2 Methods

The Bularafa diatomite was characterized using Empyreal PANalytic Diffractometer X"pert 3 with Cu Kα radiation (PHILIPS BW 1710, Netherlands) for XRD and Munipal 4 Energy Dispersed- X ray fluorescence (ED-XRF, USA) machines and gas adsorption measurement with N_2 (BET isothermal).

The diatomite was treated with 1M hydrochloric acid (Merck) to remove impurities such as iron and calcium before sodium silicate extraction. Sodium silicate was extracted from acid treated diatomite following the methods of Panda et al., (2004), Mandal and Benergee, (2004) and Anjum et al., (2010). Sodium silicate obtained was used in silica sol production via neutralization of alkaline sodium silicate solution with sulfuric acid (Malewski et al., 2006; De sousa1 et al., 2009) and Kalaphaty et al., (2000).

2.2.1 Synthesis of ZSM-5 from silica sol

ZSM-5 was prepared according to hydrothermal procedure as reported previously (Lisensky et al., 2008). 1.2g of sodium hydroxide in 7.5ml of de-ionized water, 0.09g of an activated alumina was added with additional 0.1g of NaOH pellets and mixture was stirred. Then 1.2g tetrapropyl ammonium bormide was added to 0.51 ml of 96 wt. % of 1 M H_2SO_4 and mixture stirred. The mixtures were simultaneously added to 25ml of silica sol prepared from kaolin in a polypropylene bottle and the mixture shaken vigorously for 5 minutes, and then the mixture was stirred vigorously for 30 minutes and then tightly closed. It was then aged in an oven at 95°C for 4 days. After 4 days, the polypropylene bottle was removed and the cap was opened and the liquid was carefully decanted manually. The solution was filtered using a filter paper, and the white solid was washed with de-ionized water several times until the pH is about 8. The solid product was dried in an oven at 100°C for 12hrs. The dried sample was calcined at 500°C for 2 hours using a Gallen kamp 6B77A tube furnace in the presence of nitrogen.

2.3 Zeolite Characterization

The calcined sample was analyzed using the following equipment, Empyreal PANalytic Diffractometer (XRD), using Cu Kα radiation, X-ray fluorescence (XRF) by a Munipal 4 Energy Dispersed- X ray fluorescence (ED-XRF), Phenom ProX desktop (34250) SEM, USA, and Shimadzu 8400S spectrometer (FTIR), Japan. In addition, the specific surface areas of sample were measured by the Brunauer, Emmet and Teller (BET) method using nitrogen adsorption–adsorption data were recorded with a Quantachrome (Novawin-Data Acquisition and Reduction Version 11.03) 2013 equipment, USA.

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3.0 Results and Discussion

3.1 XRD Analysis of zeolite

The XRD patterns of Buralafa diatomite, diatomite based ZSM-5 and referenced ZSM-5 are shown in (Figure 1) as illustrated in Figure 1a, the XRD pattern of diatomite has a diffraction peak at 2Θ of 26.7 with small amount of quartz and broad band of 2Θ = 22-30° corresponding to amorphous silica as reported by Li et al., 2015 and Yi et al., 2006 respectively. This confirms that diatomite was amorphous originally. When Figure 1(a) was compared to the XRD pattern of the synthesized ZSM-5 in Figure 1(b) a distinct peak at 2Θ of 7.88, 23.23, 8.8, 23.63, 23.85 and 24.33° ascribing to ZSM-5 were observed. It can be seen that Figure 1 (b) compared well with XRD pattern reported by Treacy and Higgins, 2001 in Figure 1 (c), since all the characteristic peaks of ZSM-5 were observed in Figure 1 (b) and no other unknown phase in the XRD patterns, this indicated that the synthesized powders were pure ZSM-5 zeolite crystals.

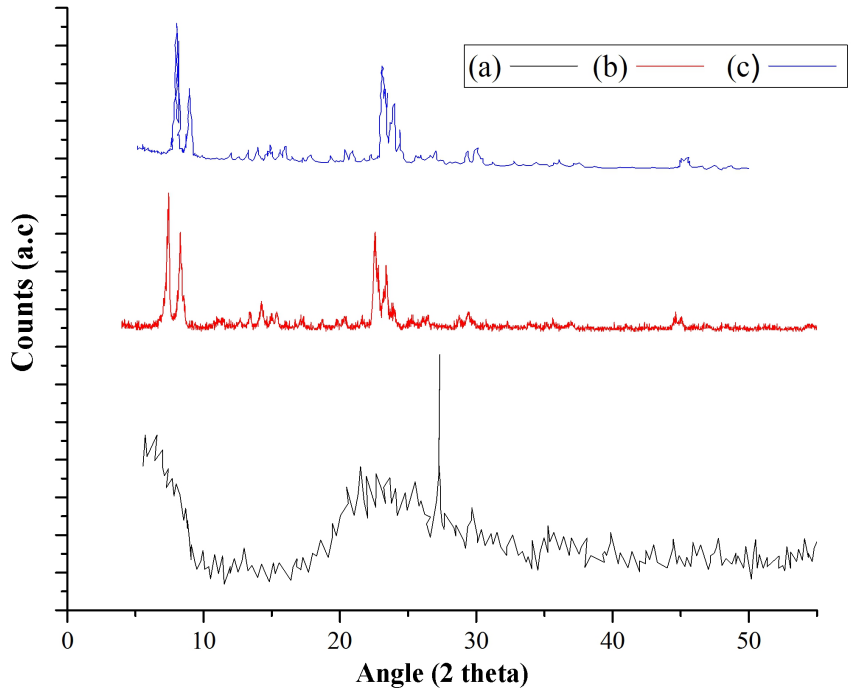

Figure 1: XRD pattern of (a) Diatomite (b) diatomite based ZSM-5 and (c) Reference ZSM-5

3.2 Fourier Transform Infra- Red (FTIR) Analysis

FTIR could help us understand the active sites and subsequently the mechanisms involved in zeolite catalysis. We know that the lattice vibrations characteristic to H-ZSM-5 zeolite usually appear in the range of 400–1200 cm^{-1}, while the bands corresponding to OH bond vibrations appear at wave numbers higher than 3200 cm^{-1} (Shaik et al., 2015). Figure 2 presents the FT-IR spectra recorded in the 4000–400 cm^{-1} range for diatomite based synthesized ZSM-5. The IR spectra of ZSM-5 zeolite showed general spectral features at 1221, 1092, 795, 548 and 448cm^{-1} which were assigned to different vibrations of tetrahedral and framework atoms in ZSM-5 zeolite (Ibraheem et al., 2012). The bands at about 1090 and 456 cm^{-1} are due to internal vibrations of (Si, Al)O_4 tetrahedra of ZSM-5, which are insensitive to framework structure. The other bands at about 1234, 800 and 557 cm^{-1} are due to vibrations related to external linkages between tetrahedra and hence sensitive to framework structure. The presence of infrared band around 557.45cm^{-1} for diatomite based ZSM-5 indicated the characteristic vibrational modes of the ZSM-5 zeolite framework. According to (Shaik et al., 2015) the spectral bands appearing at 3450 and 3700 cm^{-1} in Figure 2 may be attributed to the presence of hydroxyl groups in this ZSM-5 (Lercher et al., 1999), which may be responsible for catalyzing cracking (Bhan et al., 2008; Kotrel et al., 2000). The evidence for the formation of ZSM-5 zeolite could be seen in Figure 2 from the appearance of the bands at 557.45 and 1234.40 cm^{-1}.

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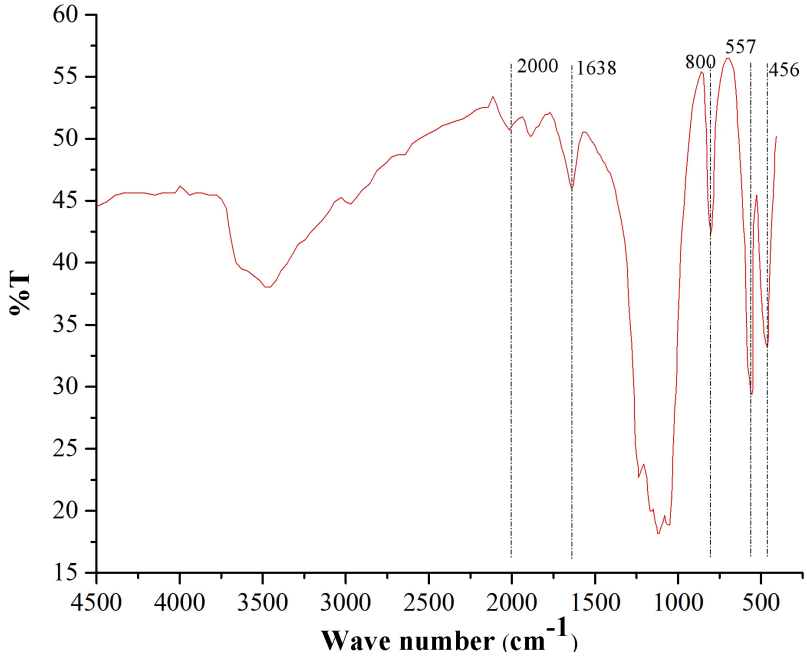

Figure 2: FTIR spectra for Bularafa diatomite based ZSM-5

3.3 Scanning Electron Micrograph (SEM) Analysis

The SEM technique was used to observe the crystals as shown in Figures 3 (a), (b) and (c). It was observed that the sample was ellipsoidal in shape. The sizes of these samples were uniformly distributed and did not contain amorphous substances or other crystalline impurities as can be seen in the SEM image of raw diatomite in Figure 3a; (Chaisena and Rangsriwatananon, 2005). The uniformity in morphology of the synthesized ZSM-5 suggested that good crystallization was obtained, as shown in the XRD pattern 1b. From the high-resolution SEM micrographs (Figure 3c), it was observed that the surface of the large particle was composed of many small crystals. These small primary crystals appeared to be tightly packed together to form the polycrystalline particles.

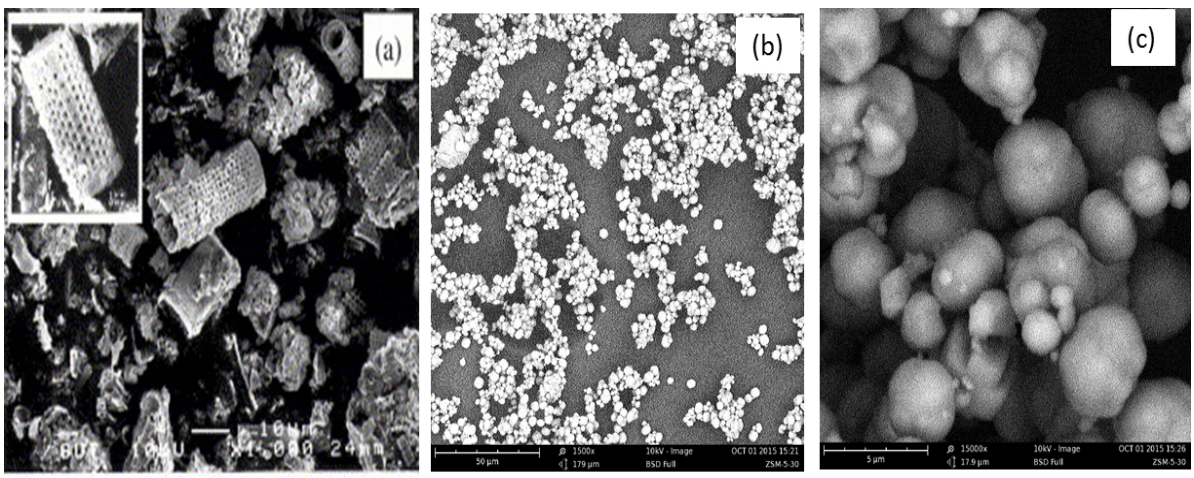

Figure 3: SEM images for (a) raw diatomite, (b) ZSM-5 from diatomite at low magnification (c) ZSM-5 from diatomite at high magnification.

3.4 X-Ray Fluorescence (XRF) Analysis

Chemical compositions of raw Buralafa diatomite and diatomite based synthesized ZSM-5 were determined using XRF technique as shown in Table 1. It could be observed that ZSM-5 synthesized from diatomite contained small impurities, this may be due to the acid treatment of the raw diatomite and preparation silica sol from the diatomite used, which greatly minimized

metal oxides contents such as Fe_2O_3, CaO, MgO and CuO. These oxides could also cause a decrease in BET surface area as observed in Li et al., 2015 who recorded a low BET surface area of 223 $m^2 g^{-1}$ as compared to 619 $m^2 g^{-1}$ obtained in this work. The impurities reduce the surface area of the synthesized zeolite by filling up some of its pores. Si to Al ratio was another very important parameter that could be used to measure the catalytic activity of the zeolite and it was determined by the XRF analysis as shown in Table 1. It could be seen that Si to Al ratio of diatomite based ZSM-5 was 250. Generally, Si to Al ratio of a zeolite determine its chemical and thermal stability, the literature value of Si to Al ratio of ZSM-5 zeolite is from 10 to 500 (Al-Bogami, 2013).

Table 1: Chemical analysis (XRF) of Raw Diatomite and ZSM-5 from Diatomite

Oxides	Raw Diatomite (wt.%)	ZSM-5 from Diatomite (wt.%)
SiO_2	89.30	99.20
Al_2O_3	0.62	0.35
CaO	0.53	0.261
TiO_2	0.86	0.010
MnO	0.007	0.006
Fe_2O_3	5.73	0.095
CuO	0.063	0.023
K2O	0.46	-
LOI	1.03	-
Si/Al		250

3.5 Surface Analysis of ZSM-5

Nitrogen adsorption-desorption data were recorded with a Quantachrome (Novawin-Data Acquisition and Reduction Version 11.03) 2013 equipment to determine the BET specific surface area (SSA), micro pore size and micro-pore volume of the synthesized ZSM-5. The N_2 adsorption isotherm of ZSM-5 synthesized from Buralafa diatomite is shown in Figure 4. It was type I based on IUPAC's classification with a large nitrogen uptake at low pressure and the desorption matched with the adsorption isotherms. Also, the knee portion of the isotherm was higher indicating its higher surface area, as shown in Table 2.

The specific surface area (SSA) of the synthesized ZSM-5 was determined using the BET techniques, while the micro-pore volume and pore diameter were determined using Horvath-Kawazoe (H-K) and Sato Foley (SF) methods. The BET SSA obtained in this work for the sample prepared from Bularafa diatomite was 619 m^2/g which is two times more than that obtained in the study by Aguilar -mamani et al., 2014 (298 m^2/g), who employed leached diatomaceous earth directly as silica source. Also, Li et al synthesized ZSM-5 using purified diatomite and sodium aluminate as silica and alumina sources respectively, where BET surface area of 223 m^2/g was obtained as shown in Table 2. Both micro-volume and pore sizes of the synthesized ZSM-5 were quite comparable with the ones got in the previous works of Aguilar -mamani et al. (2014), Li et al. (2015) and Al-bogami (2013) as indicated in Table 2.

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Table 2: Texture properties of synthesized ZSM-5 from Diatomite using different methods

Samples	BET Surface area (m^2g^{-1})	Median pore Diameter (nm)	Micro pore volume (cm^3g^{-1})	Reference
As- synthesized ZSM-5 from Bularafa Diatomite	619	0.45a	0.013a	This work
As- synthesized H- ZSM-5 from Kaolin	411	0.61b	0.12c	Al-bogami, 2013
As- synthesized ZSM-5 from Diatomite	223	0.54	0.06	Li et al., 2015
As- synthesized ZSM-5 from Bolivian Diatomite	298	-	0.15	Aguilar-Mamani et al., 2014

a Data are determined by applying the Saito-Foley method
b Data are determined by applying the Horvath-Kawazoe method
c Data are determined by applying the t-plot method

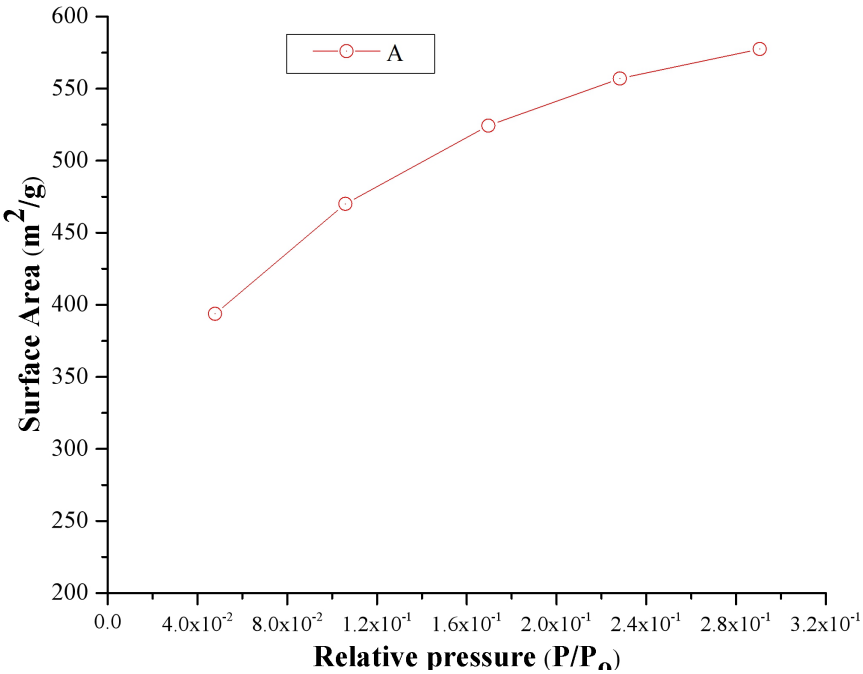

Figure. 4: N_2 Adsorption-desorption Isotherms of the Synthesized ZSM-5 from Buralafa Diatomite

4.0 Conclusions

The ZSM-5 was successfully synthesized from Bularafa diatomite via the hydrothermal process. The utilization of diatomite as inexpensive raw material for ZSM-5 zeolite synthesis is remarkable. From the XRD result, it was observed that well crystalline ZSM-5 was successfully synthesized from diatomite without using additional silica source. SEM images of the ZSM-5 also confirmed uniform particles distribution. In addition, FTIR analysis showed that the ZSM-5 were pentacyclic with typical absorption band at about 550 cm^{-1}. The BET method revealed that the ZSM-5 produced from Bularafa diatomite have very high specific surface area that is suitable for zeolite application. Also, the ZSM-5 had least metal oxide impurities due to the acid treatment carried out on the Buralafa diatomite which has greatly reduced the metal oxides.

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