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Synthesis of Zeolite Y from Kaolin Using Novel Method of Dealumination

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Abstract
In this study Zeolite Y was successfully synthesized from local kaolin in Ado-0do Ota, Ogun state Nigeria through a novel process of dealumination. The thermal activation of kaolin was achieved through the process of metakaolinization at 850 ^oC for 6 hours in a furnace and dealumination with H_2SO_4 in order to achieve a desire silica/alumina molar ratio between 3 and 8. Zeolitization involved alkaline attack of dealuminated metakaolin and its consequent transformation into Zeolite Y crystal. Silica/Alumina molar ratio of 5.84 of metakaolin was synthesized under hydrothermal treatment with aqueous NaOH at atmospheric pressure. It was then aged for 7 days at room temperature and crystallized at 100 ^oC for 24 hours; Zeolite NaY of molar ratio of 3.46 was achieved and then modified to its hydrogen form by ion exchange with NH_4Cl. The molar ratio of Zeolite Y in hydrogen form is 3.22. The samples were characterized with X-ray Fluorescence (XRF), X-Ray Diffraction (XRD), and Scanning Electron Microscope (SEM). The result showed that zeolite Y was synthesized from Arobieye mined kaolin with a molar ratio of $6SiO_2 : Al_2O_3 : 9Na_2O : 24H_2O$ by ageing at room temperature for 24 hours and crystallized at 100 ^oC for 24 hours.

Keyword; Arobieye mined kaolin, Crystallization, Hydrothermal Reaction, Novel dealumination, Zeolite Y

INTRODUCTION

Zeolites are crystalline microporous, aluminosilicate minerals, with a unique three or two dimensional structural pattern of arrays of uniform pores, cavities and channels in molecular dimensional order. They are referred to as solid acids with fascinating chemisorptions, high selectivity and thermal stability properties [1]. Zeolites are synthesis traditionally by hydro gel of Sodium aluminate and silicate [2]. The production of zeolite from clay as a source of silica and alumina are been investigates with positive achievement [3-4]. The benefits of using kaolin as an aluminosilicate source in zeolite production are widely known [5].

MATERIALS AND METHOD

Materials

Kaolinite clay used in the course of synthesis of zeolite Y was procured from Arobieye village in Ado-Odo, Ota, Ogun state. Sodium hydroxide pellets (Sigma-Aldrich, Lobal Chemie, ≥98 %) and concentrated sulfuric acid (Sigma-Aldrich, Lobal Chemie, 98%) were used in this work for zeolite Y preparation. The chemical composition (XRF) and mineralogical analysis of Arobieye kaolin are shown in Table 1.0.

Experimental procedure for the synthesis of zeolite Y

Arobieye clay was thoroughly purified by a clay-split method. The purified kaolin was calcined and converted to metakaolin at 850 ^oC for 6 hours. The metakaolin was dealuminated by using concentrated sulphric acid. Novel method of dealumination was used in this research work. Sodium hydroxide pellets (Sigma-Aldrich, Lobal Chemie, ≥98 %) was reacted with dealuminated kaolinite in a ratio of 2.5: 1 by weight and molar composition of $6SiO2 : Al_2O_3 : 9Na_2O : 24H_2O$ [6]. The gel obtained was aged for 7 days at room temperature and then hydrothermally crystallized at 100 ^oC for 24 hours. Figure 1.0 shows the flow diagram of the processes involved in the synthesis of zeolite Y from kaolin.

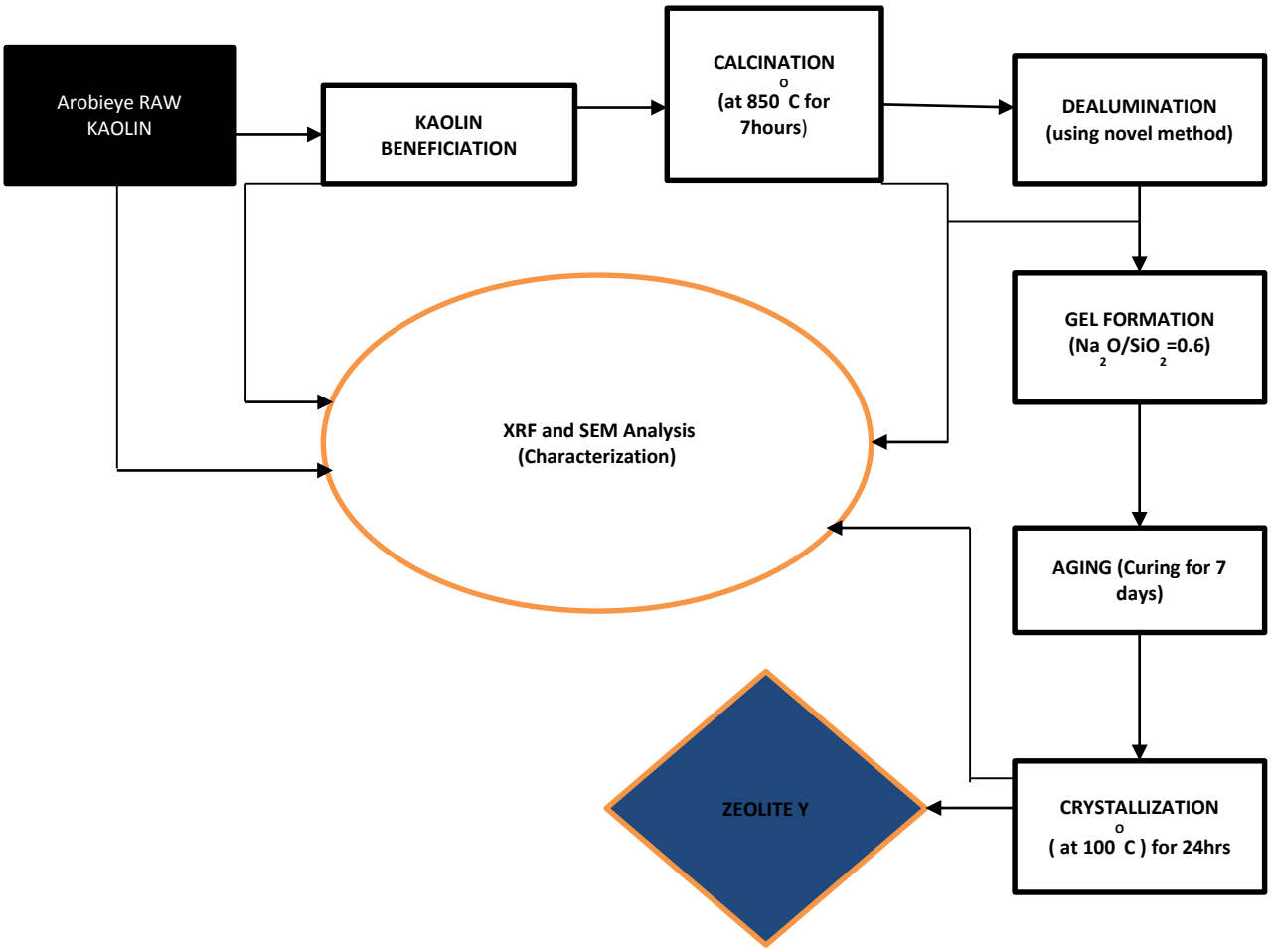


Figure 1.0: Flow diagram of zeolite Y synthesis from Arobieye mined clay [7]

Transformation of zeolite NaY to his hydrogen form (zeolite HY)

The synthesized zeolite NaY produced from Arobieye kaolin was modified to its hydrogen

form by ion exchange reaction. 0.1M NH_4Cl solution was prepared and mixed with zeolite NaY at room temperature using a ratio of 100ml of solution to 10g of zeolite NaY and stirred vigorously using a magnetic stirrer for 10 minutes. This operation was carried out twice to obtain optimum ammonium exchange. The sample was filtered from the slurry and washed with deionized water until the solid was free of chloride. The zeolite NH_4Y was dried at room temperature for 24 hours and then transferred into a crucible and charged into a furnace at 450^{o}c for residence time of 4 hours in order to remove ammonia and leave the zeolite Y in its hydrogen form.

Characterization

In order to know the crystal structure and the relative crystallinity of zeolite, the X-ray diffraction (XRD) patterns were recorded on an X-ray diffraction machine (Cubic 3 Cement PAN analytical) using Cu-ka radiation with a wavelength of 1.540598. To determine the morphology of zeolite, the scanning electron micrograph (SEM) was analyzed by Phenom prox SEM, manufactured: 2012, model number: 800-07334, part number: MVE0224651193. Chemical composition of kaolin was analyzed by X-ray machine (Axios Pananalytical).

RESULTS AND DISCUSSION

Table 1.0 show that Arobieye mined kaolin is rich in oxides of iron, calcium and titanium. It indicates that there are large quantities of quartz in the sample. It also indicates that it is rich in the oxides of iron and Calcium but poor in the oxides of potassium and manganese.

Pure raw kaolinite clay is expected to have silica/Alumina ratio of 1 to 2 [8, 9]. Table 1.0 shows that SiO_2/Al_2O_3 ratio of Arobieye mined clay is to 1.45, and it is within the theoretical value.

Table 2.0 shows the XRF analysis of the Synthesized Zeolite NaY and Zeolite HY. The results show that the silica/alumina ratio of 3.46 and 3.22 respectively are typical of zeolite Y.

Table 1.0: Chemical and mineralogical analysis of the Arobieye mined kaolin

Chemical composition of Arobieye kaolin		Mineralogical composition	
Oxide	Conc. Wt.%	Mineral	%
SiO_2	48.79	Kaolinite	40.68
Al_2O_3	33.58	Quartz	52.28
Fe_2O_3	2.65	Illite/mica	6.89
CaO	2.98	Palygorskite	0.18
MgO	0.58		
SO_3	0.04		
Na_2O	0.07		
K_2O	0.01		
TiO_2	1.48		
P_2O_5	0.10		
Mn_2O_3	0.01		
Si/Al (wt%)	**1.45**		

Table 2.0: XRF analysis of the synthesis Zeolite NaY, Zeolite NH_4Y and Zeolite HY

Oxide	Synthesis zeolite NaY Conc. Wt.%	Synthesis zeolite NH_4Y Conc. Wt.%	Synthesis zeolite HY Conc. Wt.%
SiO_2	37.57	38.58	39.71
Al_2O_3	18.44	18.68	20.94
Fe_2O_3	2.03	2.00	2.26
CaO	3.14	3.08	3.15
MgO	0.23	0.24	0.28
SO_3	7.30	6.46	6.76
Na_2O	33.27	30.07	28.47
K_2O	0.07	0.07	0.06
TiO_2	1.39	1.42	1.67
P_2O_5	0.07	0.07	0.07
Mn_2O_3	0.02	0.01	0.02
Si/Al (Mol ratio)	**3.46**	**3.51**	**3.22**

Figure 2(a-b) shows the XRD pattern of the synthesized Zeolite NaY and Zeolite HY. The Zeolite peaks could be observed in both XRD patterns at Bragg's angles of 14, 19, 21, 24, 26.8, 31.9, 34.9, 39.9, 49.8, 51°. The intensities of the peaks at Bragg's angles of 14, 19, 21, 24, 26.8, 31.9, 34.9, 49.8 and 51° corresponding to 980, 589, 2500, 500, 8000, 500, 500, 980 and 510 counts, respectively and characteristic of zeolite Y [10-11].

The XRD patterns of Zeolite NaY and zeolite HY are identical which indicated that modification of Zeolite with the exchange solutions did not lead to significant structural changes but there are differences in intensities.

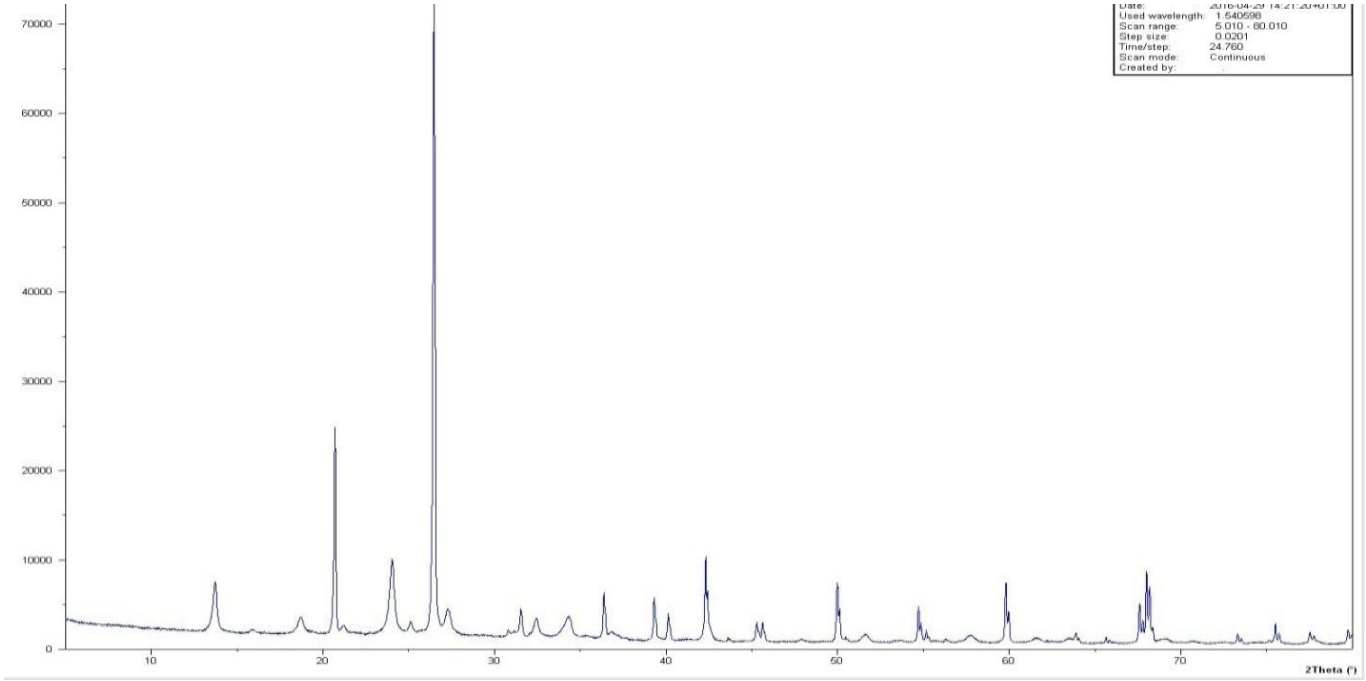


Figure 2a: XRD pattern of the zeolite NaY

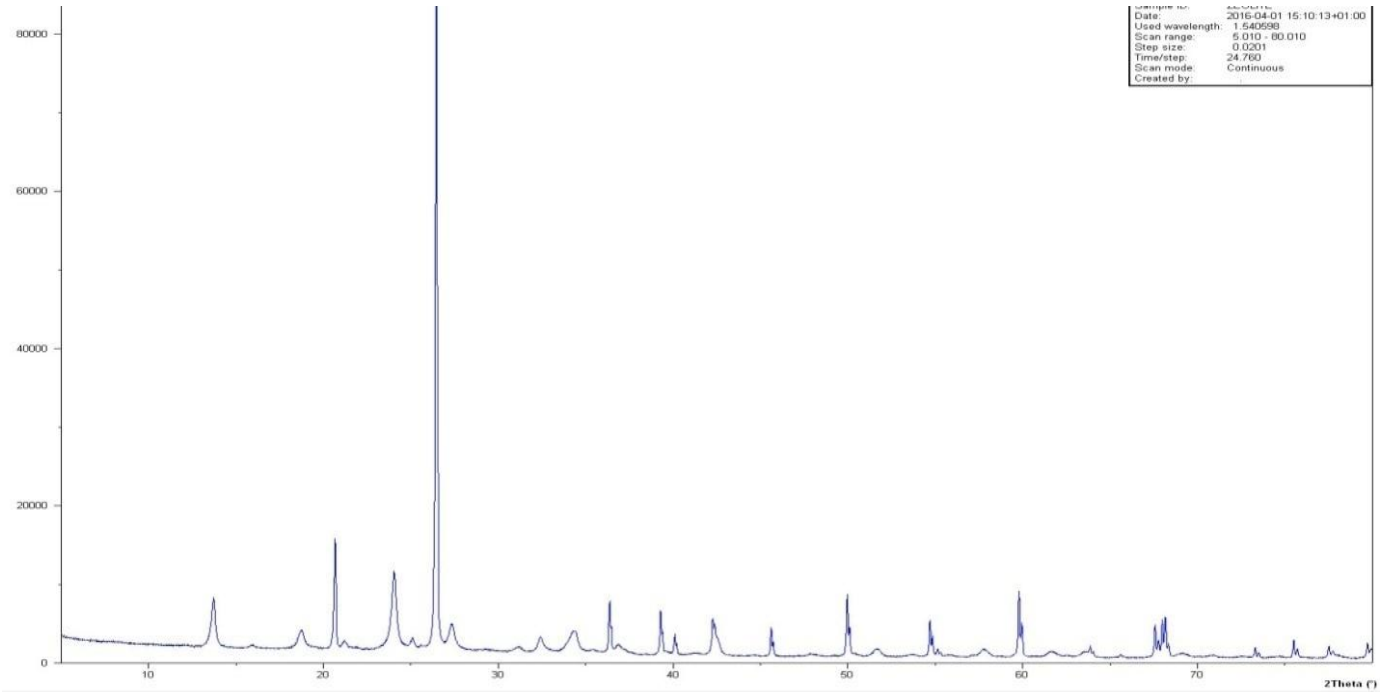
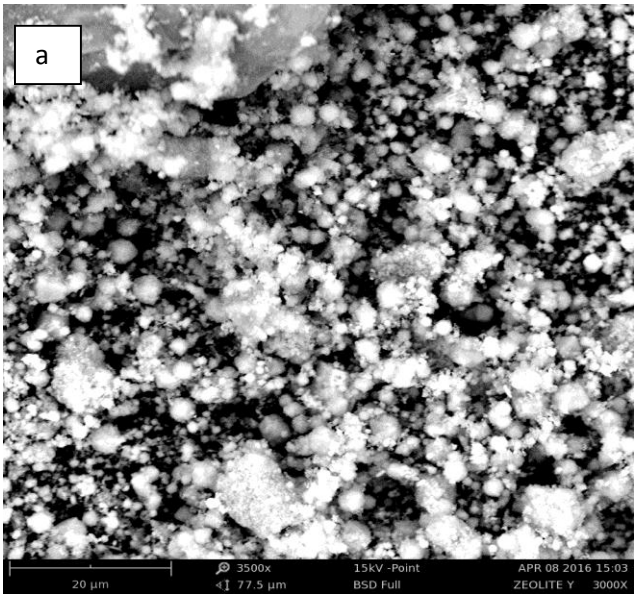
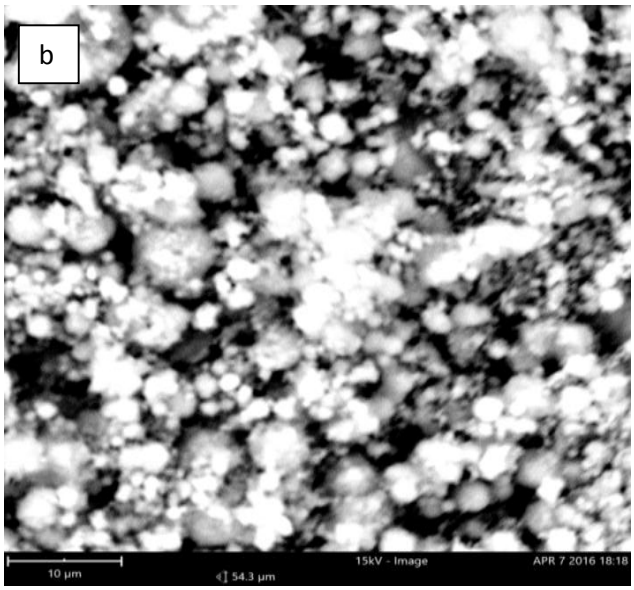
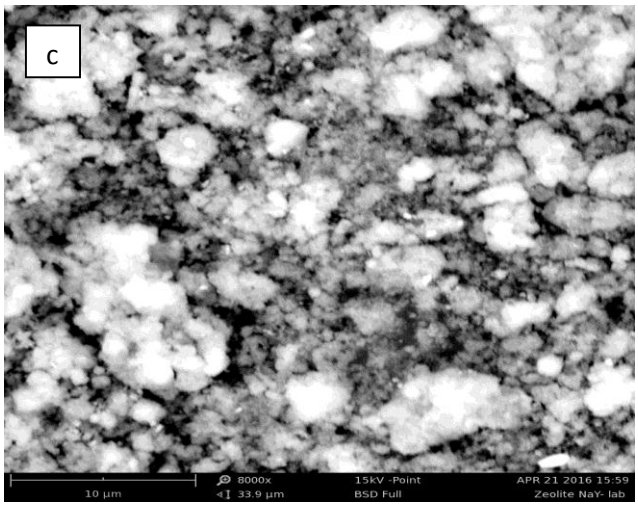


Figure 2b: XRD pattern of the zeolite HY

Figures 3(a- d) and 4(a-d) show the structural morphology of the synthesized Zeolite NaY and Zeolite HY at different magnifications of 3500, 5000, 8000 and 10000 respectively. The clear structural boundaries and shapes are evident of clear crystal formation of zeolite Y.







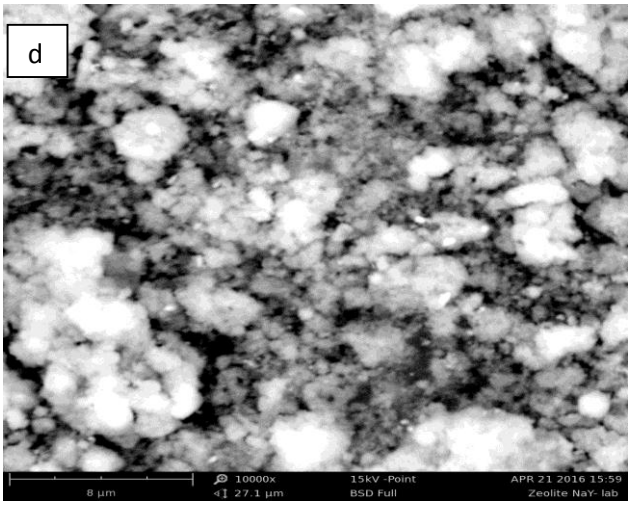
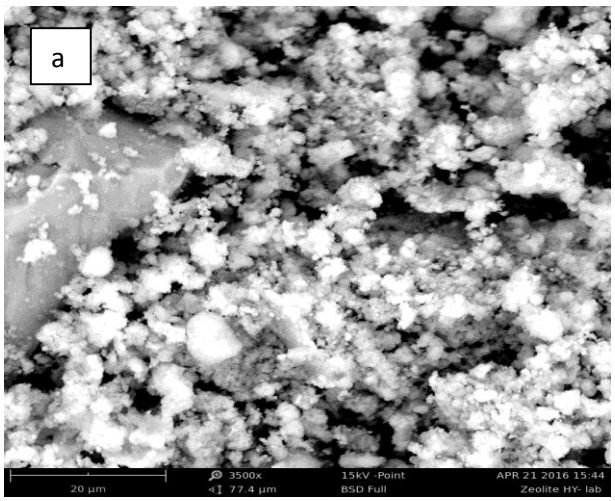
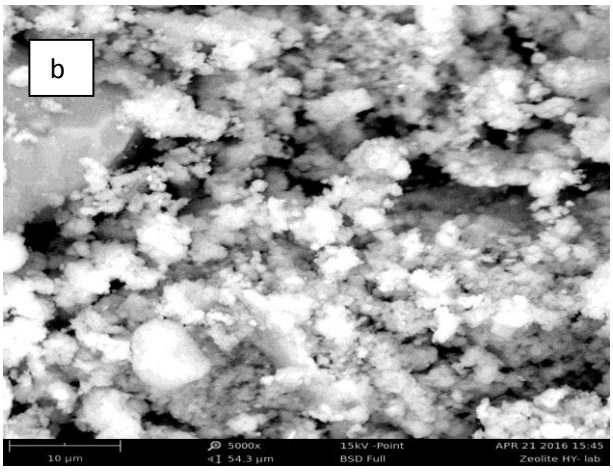


Figure 3(a-d): SEM images for the synthesized zeolite NaY at various magnifications (a) 3500; (b) 5000; (c) 8000; (d) 10000





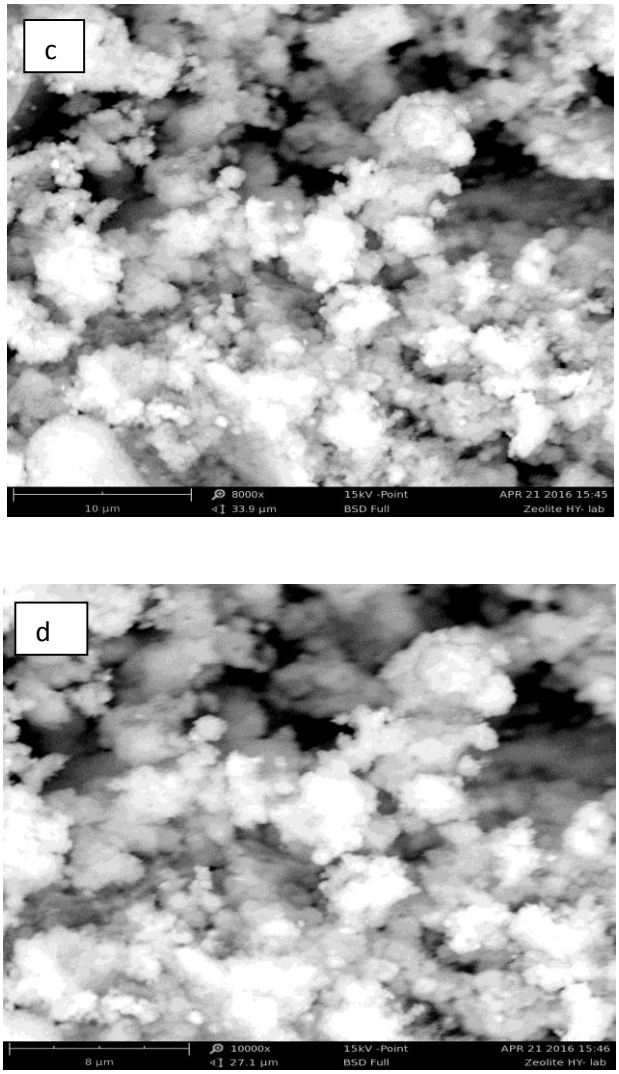


Figure 4(a-d): SEM images for the synthesized zeolite HY at various magnifications (a) 3500; (b) 5000; (c) 8000; (d) 10000

CONCLUSION

Zeolite Y was successfully synthesized from Arobieye mined clay from Ota, Ogun state, Nigeria. Zeolite Y with $SiO_2/Al2O_3$ molar ratio of 3.46 was achieved from dealuminated metakaolin of $SiO_2/Al2O_3$ molar ratio 5.84 by treatment with sodium hydroxide and ageing for 7 days under proper condition. The zeolite NaY was modified by ion exchange (NH_4Cl) and give a SiO_2/Al_2O_3 molar ratio of 3.22. The ion exchange decreased the peak intensities of zeolite HY. The results of XRF analysis show that the major components of synthesized zeolite are SiO_2, Al_2O_3, SO_3 and Na_2O, along with a small quantity of CaO and trace amounts of K_2O, Fe_2O_3, TiO_2, P_2O_5, Mn_2O_3 and MgO. The XRD analysis pattern refers to nearly crystalline of zeolite Y type, indicating the formation of zeolite NaY and HY.

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