

Synthesis of Zeolite Na-A from Local Kaolin for Bioethanol Purification

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Abstract

Background/Objectives: Malaysia has abundant resources of kaolin. Currently, the kaolin industries are not able to attract large companies to mining due to lower price. An alternative method to increase the price of the local kaolin is by converting it to the zeolite. The zeolite of the type Na-A can be used to dehydrate ethanol water mixture during production of bioethanol. In this study, mesoporous silica Na-A zeolite was synthesized from local clay which obtained from Perak. **Methods/Statistical Analysis:** The raw kaolin was pretreated by using sodium metaphosphate to remove impurities and activated at 800°C for 5 hours. By using the hydrothermal method, zeolite Na-A was synthesized by using NaOH as the activator. The mesoporous materials obtained were characterized by Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) analysis. **Findings:** The prepared materials showed a superior ability to adsorb water (H₂O) from azeotropic water-ethanol mixture. From the water adsorption test, the average H₂O adsorption capacity was 70 mg H₂O/g adsorbent. This value was almost twice the adsorption capacity of commercial zeolite 3A. Zeolite Na-A was the main product with quartz presences as minor impurities which was confirmed by XRD, FTIR and SEM analysis. **Applications/Improvements:** The local kaolin can be used to synthesize the zeolite Na-A by using a hydrothermal reaction method. This new application may increase the value of local kaolin.

Keywords: Bioethanol, Ethanol Purification, Kaolin, Mesoporous Material, Molecular Sieve, Zeolite Na-A

1. Introduction

Kaolin is a white colored substance which is also known as China Clay. Its fine particles size and color are the physical properties which differentiate kaolin from other industrial clay base mineral. In kaolin, mineral such as feldspar decomposed to form a hydrous aluminum silicate or mineral kaolinite. This mineral kaolinite is the main component of kaolin¹. The kaolin mining activities throughout the world has been started since colonial time in Georgia and South Carolina in The United States of America.

There are many applications of kaolin. The paper industry is the primary user of kaolin². In paper making industries, kaolin is used to improve the appearance of paper by applying the kaolin as paper coating. This step

improves the paper brightness, smoothness and gloss. Kaolin also has been used as a filler to reduce the paper production cost and the use of tree-based resources. The excellent characteristic in color, gloss and hardness of kaolin make it valuable substance for ceramic ware and other tableware manufacturing. Kaolin also has been used in many industries including paint, rubber, cable insulation, specialty film and fertilizers. The demands for kaolin is expected to increase due to more new uses of kaolin are being discovered.

Malaysia has large amount deposit of kaolin. Kaolin deposit can be found in states of Perak, Johor, Kelantan, Selangor, Pahang and Sarawak. Approximately 112 million tons total of kaolin reserve has been discovered throughout Malaysia³. There are 17 active kaolin mining

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company operated since 1980's. Most of these companies are located in Perak. The main uses of Malaysia kaolin are in paper making industries, ceramic manufacturing, paint, rubber, plastic and chemical product industries.

The price of raw kaolin is RM2000 per tons as July 2015. The price of kaolin can be increased if it can be converted to high value industrial product. Producing such product requires financial and technologies input. In return, it may increase the value of kaolin. One of the promising products of kaolin is mesoporous material such as zeolite. There are many researchers studied the synthesis of zeolite from kaolin globally⁴⁻⁶. In Malaysia, only a few researchers have studied the possibility to convert local kaolin to zeolite⁷.

The high content of Al and Si in kaolin makes it possible to produce zeolite⁸. Zeolite is porous and crystalline aluminosilicates. Covalent oxide of Al and Si form porous structure with interconnected channel or cages. The zeolite frameworks are negatively charged and balanced by exchangeable cation. The general chemical formula for zeolite is $M^{k+} x/k [Al_x Si_y O_{2(x+y)}] z H_2O$ (where M^{k+} is the exchangeable cation). The special characteristic of zeolite is the ability to exchange cation for different application (cation affects the pore size of zeolite) and the ability to adsorb small molecule through internal pore volume⁹.

Zeolite or also known as molecular sieve has been utilized for numerous industrial and household applications. The specific application depends on zeolite types. Zeolite the type of Na-A has attracted many researchers' attention due to ability to adsorb water molecules. The Na-A zeolite has high demand in the industrial market, especially for process stream dehydration. In bioethanol industry, an alternative renewable fuel of Na-A zeolite is used to dehydrate the ethanol water mixture (>99.3 % wt) in order to be used in vehicles¹⁰.

In the present work, local kaolin was converted to the zeolite Na-A by using hydrothermal method where NaOH as the activator. The synthesized materials were then tested for removing water from the azeotrope ethanol water mixture, and compared its performance with the commercial-grade molecular sieve. Ethanol and biodiesel are two potential and promising alternative fuels for internal combustion engines. Ethanol can be used with biodiesel fuel to extend the availability of diesel¹¹. The zeolite Na-A can be used to dehydrate bioethanol, and indirectly the new non traditional application of kaolin which may increase the value of local kaolin.

2. Methodology

2.1 Kaolin Pretreatment

Raw kaolin was bought from Kaolin Malaysia Sdn. Bhd. with the specification as shown in Table 1. In pretreatment process, unwanted component in raw kaolin was removed by sedimentation. Sodium metaphosphate was used as a deflocculant agent during the process. About 2.5 wt% sodium metaphosphate was added into the mixture of 1 L distilled water and 500 g raw kaolin. The mixture was thoroughly stirred by using IKA Stirrer at 500 rpm for 30 minutes. The mixture was left to settle down. The supernatant was taken out, then dried at 105°C overnight.

Table 1. Physical and chemical properties of S300 kaolin from Kaolin (Malaysia)

Physical Properties	
Moisture content	< 1.5%
pH (30% solid)	3.5-6.0
100 mesh residue	<10.0%
60 mesh residue	<0.5%
Chemical Properties	
Aluminium (Al ₂ O ₃)	7.0-12.0%
Silica (SiO ₂)	80-90%
Iron (Fe ₂ O ₃)	<2.0%
Potassium (K ₂ O)	<2.0%
Magnesium (MgO)	<0.5%
Loss on ignition @ 1025°C	2.0-6.0%

2.2 Metakaolinization

Metakaolinization of pretreated kaolin was made by heating at 800°C for 5 hours. The metakaolin was kept in desiccators for future use.

2.3 Synthesis of Zeolite

The zeolite was synthesized by hydrothermal reaction method. One gram of metakaolin was reacted with 13.3 ml 2.5M NaOH. The mixture was homogeneously mixed by using Buchi rotary evaporator at 100 rpm. Water bath was used to control the reaction temperature at 70°C. After 2 hours of reaction, the mixture was transferred into a 250 ml Teflon bottle and kept in an incubator at 60°C overnight for crystallization process. Then, the mixture was filtered and washed with distilled water until pH 7 to ensure the complete removal of unreacted NaOH. The product was dried in oven at 105°C for 12 hours and ready for characterization and further testing.

2.4 Performance Tests

The ability of the synthesized zeolite to adsorb water was tested by a batch experiment. The azeotrope ethanol-water mixture was prepared. The zeolite was dried at 220°C for 2 hours to remove adsorbed water. For water adsorption test, 1 ml of the azeotrope ethanol water mixture was added to 0.3g zeolite in 1.5 ml vial. After 1 hour, the water content of the resultant ethanol water mixture was determined by using Karl Fisher Titrator. The zeolite adsorption capacity was calculated by using Equation (1): Zeolite adsorption capacity =

$$\frac{(C_{initial} - C_{final}) \times m_{ethanol}}{100 \times m_{zeolite}} \tag{1}$$

Where $C_{initial}$ is the initial concentration of water in azeotrope ethanol, C_{final} is the final concentration of water in azeotrope ethanol, $m_{ethanol}$ is the mass of azeotrope ethanol and $m_{zeolite}$ is the mass of zeolite.

2.5 Characterization

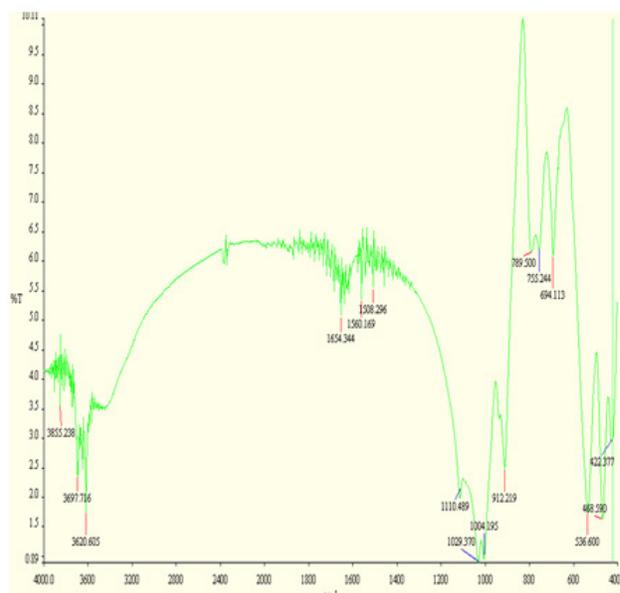
In order to study the physical and chemical changes during the overall conversion process, selected samples were analyzed by using Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) machines.

3. Results and Discussion

3.1 FTIR Evaluation

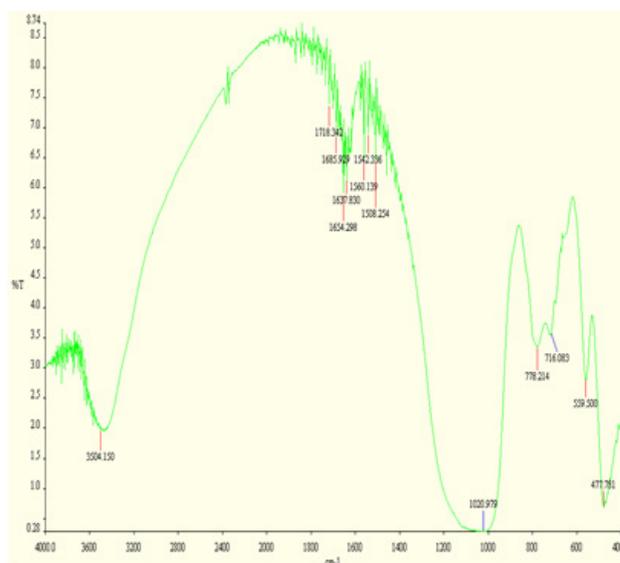
From the FTIR spectra (Figure 1.), the transformation of kaolin to metakaolin and then to zeolite A can be clearly observed in the region 1400-400 cm^{-1} . The effect of a pretreatment process followed by conversion of kaolin to metakaoline can be observed by the disappearance of several bands¹². Metakaolin FTIR spectrum Figure 1(c) shows a broad intense asymmetric band at 1026 cm^{-1} . Desertion of bands at 912 and 920 cm^{-1} indicated the loss of Al-OH unit, while changing in Si-O stretching band and the disappearance of the Si-O-Al band at 789 and 760 cm^{-1} are consistent with distortion of tetrahedral and octahedral layers. The features bands for zeolite framework at 557 cm^{-1} was due to the external vibration of double four rings, about 1001 cm^{-1} for the internal vibration of (Si,Al)-O asymmetric stretching, almost 671 cm^{-1} for the internal vibration of (Si, Al)-O symmetric

stretching and 467 cm^{-1} for the internal vibration of (Si, Al)-O bending can be observed from the FTIR spectrum of synthesized zeolite¹³. In addition, the FTIR spectrum for synthesized zeolite was comparable with the FTIR spectrum for commercial zeolite Figure 1(d).



(a)

Figure 1. FTIR spectrum of. (a) Raw kaolin. (b) Metakaolin. (c) Synthesized zeolite. (d) Commercial zeolite.



(b)

Figure 1. FTIR spectrum of. (a) Raw kaolin. (b) Metakaolin. (c) Synthesized zeolite. (d) Commercial zeolite.

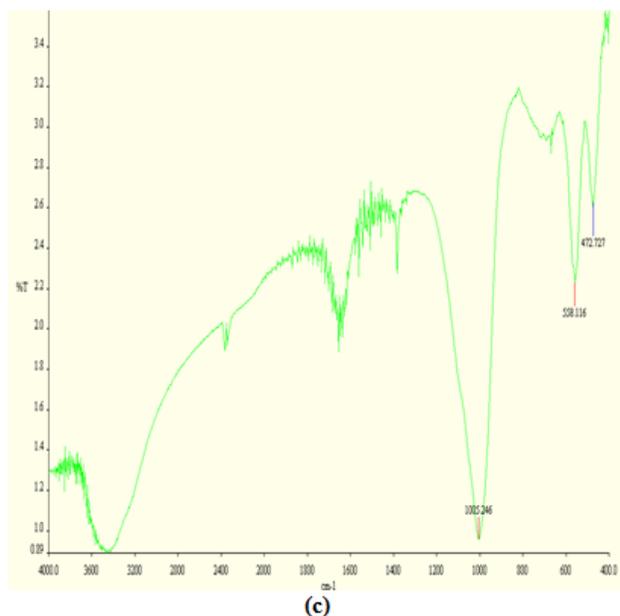


Figure 1. FTIR spectrum of. (a) Raw kaolin. (b) Metakaolin. (c) Synthesized zeolite. (d) Commercial zeolite.

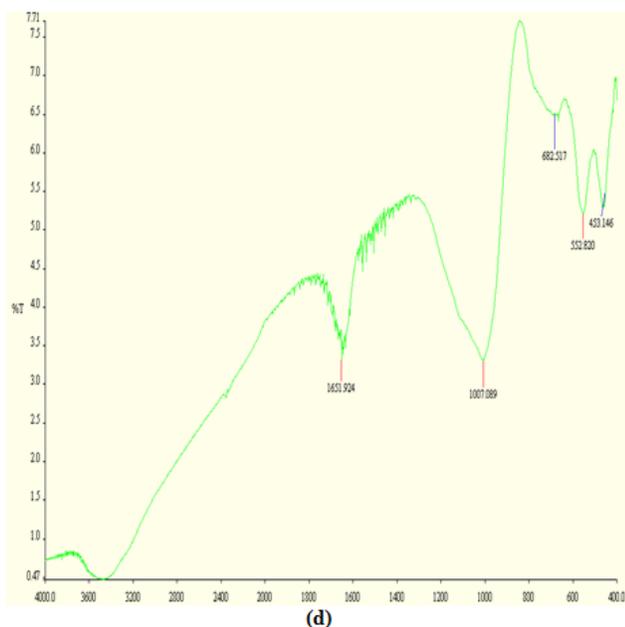


Figure 1. FTIR spectrum of. (a) Raw kaolin. (b) Metakaolin. (c) Synthesized zeolite. (d) Commercial zeolite.

3.2 XRD Analysis

Figure 2 shows the x-ray diffractogram of raw kaolin and metakaolin. The peaks at $2\theta=21^\circ$, 26.6° , 36.5° , etc. are showing the quartz are the main component in raw kaolin. The kaolinite peaks were detected at $2\theta=12.5^\circ$, 25° and 46° . The results agree with the analysis, which reported by¹⁴. The XRD pattern of metakaolin in Figure 2(b) showed

that the intensity of the quartz has reduced significantly. This result showed, the settling process of kaolin with sodium metaphosphate has removed the quartz. During this process, the coarse particles including quartz were settled to the bottom¹⁵. This process enables kaolinites to be separated from the major impurities exist in the raw kaolin. The metakaolinization of kaolin by heating the raw kaolin for 5 hours at 800°C has resembled all the kaolinite peaks, except for the peaks due to admixed impurities. Thermal treatment of kaolin causes the kaolinite crystal lattice to collapse and form highly disordered and amorphous structure. The only crystalline phase in metakaolin was quartz because quartz was not affected by the thermal treatment during calcination. The activation of kaolin produces structural changes of this mineral, promoting its reactivity for synthesizing zeolitic materials.

Figure 3 illustrates the X-ray powder diagrams of reaction products which were obtained from the reaction of metakaolin with 2.5 M NaOH solution at 60°C for 16 hours and the commercial zeolite A sample (Methrom 62811000) for comparison. The most important changes observed in the XRD patterns were the appearance of the characteristic peaks of zeolite Na-A. The synthesized products matched the characteristic peaks of zeolite Na-A at 2θ values of 12.6° , 16.2° , 21.6° , 24° , 26.2° , 27.2° , 30° , 30.9° , 32.6° and 34.3° ¹⁶. The results indicated that the synthesized zeolite products contained zeolite A as the major constituent phase, whereas Hydroxysodalite (HS) and quartz were found as minor phases (Figure 3(b)).

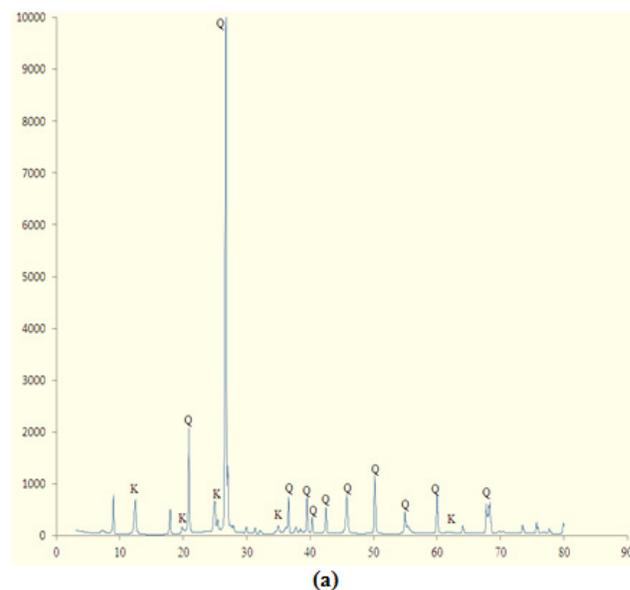


Figure 2. X-ray diffractogram of. (a) Raw kaolin. (b) Metakaolin.

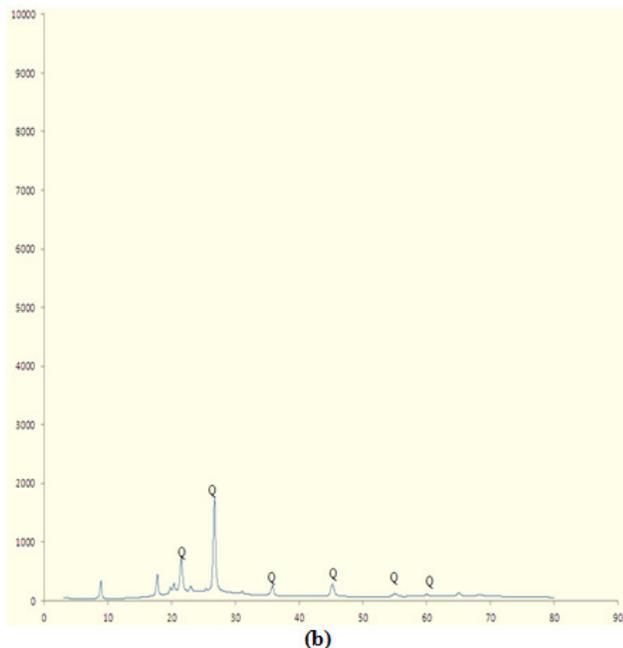


Figure 2. X-ray diffractogram of. (a) Raw kaolin. (b) Metakaolin.

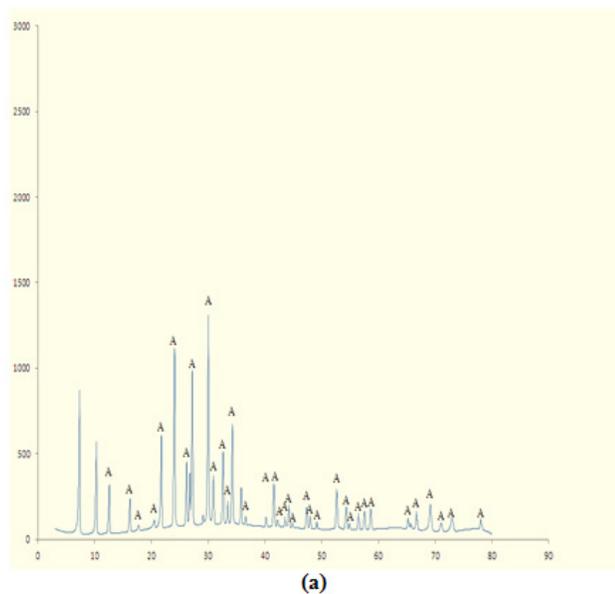


Figure 3. X-ray diffractogram of. (a) Reaction products which were obtained from the reaction of metakaolin with 2.5 M NaOH solution at 60oC for 16hours. (b) The commercial zeolite A.

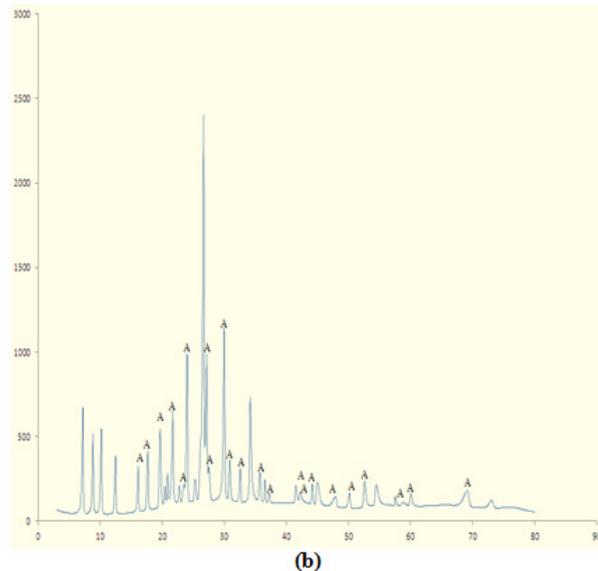


Figure 3. X-ray diffractogram of. (a) Reaction products which were obtained from the reaction of metakaolin with 2.5 M NaOH solution at 60oC for 16hours. (b) The commercial zeolite A.

3.3 SEM Analysis

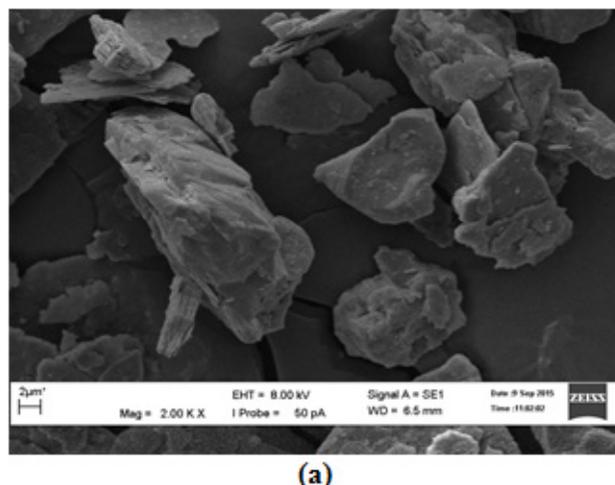
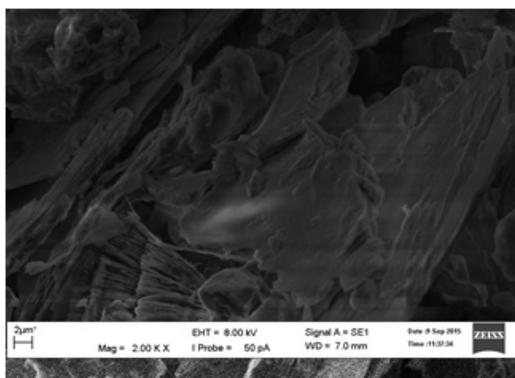


Figure 4. SEM micrographs showing the occurrence of zeolite A and associated phases obtained by hydrothermal synthesis. (a) hexagonal platy crystals of untreated kaolin. (b) metakaolin. (c) verywell developed cubes of zeolite A and relicts of metakaolin.

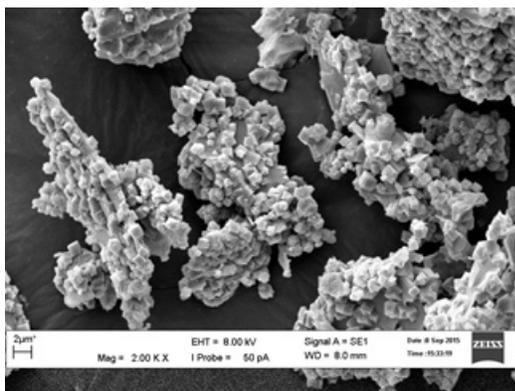
SEM micrographs (Figure 4.) show the occurrences of the zeolitic products obtained after hydrothermal treatment

of metakaolin with 2.5 M NaOH solution. It revealing a marked change in the morphology of the original surface of the starting materials. The kaolinite can be recognized by its platy morphology and hexagonal outlines (Figure 4(a)). Figure 4(c) represents the zeolite A formation obtained after activation of metakaolin at 60°C for 16 hours. According to the experimental results of this work, the observed morphologies are similar to those reported in previous studies. The data obtained by SEM agreed with the mineralogical composition of the zeolite products, which was supported by XRD analysis results (Figure 3). SEM image (Figure 4c) shows very well developed cubes of zeolite Na-A where co-exist with metakaolin debris.



(b)

Figure 4. SEM micrographs showing the occurrence of zeolite A and associated phases obtained by hydrothermal synthesis. (a) hexagonal platy crystals of untreated kaolin. (b) metakaolin. (c) very well developed cubes of zeolite A and relicts of metakaolin.



(c)

Figure 4. SEM micrographs showing the occurrence of zeolite A and associated phases obtained by hydrothermal synthesis. (a) hexagonal platy crystals of untreated kaolin. (b) metakaolin. (c) very well developed cubes of zeolite A and relicts of metakaolin.

3.3 Water Adsorption

The ability of synthesized zeolite Na-A to adsorb water was proven from the adsorption experiment. The experiment confirmed that, the synthesized zeolite Na-A was able to adsorb water from the azeotrope ethanol water mixture. The maximum water adsorption capacity was 100 mg of water for one gram adsorbent used. The results were in agreement with the other studies which using kaolin for zeolite synthesis⁴⁻⁶. The synthesized zeolite Na-A water adsorption capacity was found better than commercial zeolite. The water adsorption capacity for commercial zeolite was 40 mg of water per gram adsorbent.

4. Conclusion

The data gathered from the FTIR, XRD and SEM analysis showed that the zeolite Na-A can be synthesized by using local kaolin. High crystalline phases present in the synthesized zeolite were shown by the high intensity of the peak observed in the XRD pattern. SEM showed the synthesized zeolite has a cubic crystalline system. By using FTIR, the material changing during conversion process was observed. The synthesized products were found to contain quartz phases as impurities coming from the natural kaolin samples.

The result from water adsorption experiment clearly showed that the performance of synthesized zeolite was superior than commercial zeolite. It can be concluded that local kaolin can be used as cheap raw material for production of zeolitic material, especially zeolite Na-A and may increase the value of local kaolin.

5. References

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