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Hydrothermal Synthesis of Zeolite A Using Natural Kaolin from KG. Gading Bongawan Sabah

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Abstract: Zeolite A was successfully synthesized from natural kaolin procured from KG. Gading, Bongawan Sabah. The raw kaolin was treated with sodium hexametaphosphate to remove the impurities exist in the natural kaolin. The kaolin clay undergoes metakaolinization at 800°C for 5 h transforming it into highly disordered and amorphous. The raw kaolin and metakaolin were characterized under XRF, XRD and SEM. Reaction mixture for zeolite A was obtained by mixing metakaolin and sodium hydroxide without additional silica. The reaction mixture was stirred for 30 min before hydrothermally synthesised at 100°C for 8 h. Optimum condition for the zeolite A synthesis was studied by preparing reaction mixture with varying molarity. The formation of zeolite A and sodalite was strongly influenced by the molarity of the NaOH used in the reaction mixture.

Key words: Kaolin, zeolite A, hydrothermally, metakaolinization

INTRODUCTION

Zeolites are porous crystalline aluminosilicate, which have a highly regular and open structure formed by a three-dimensional network of SiO_4 and AlO_4 tetrahedra. The tetrahedra are linked together by oxygen bridges to give cages connected by pore openings of defined size. The pore sizes range from approximately 0.3-1 nm (Szostak, 1998). Zeolite also known as molecular sieves with unique pore and channel systems in the molecular size range. These features are the basis of their important contribution in ion exchange, separation and catalysis (Kessler, 1996; Meier *et al*., 1996). Zeolite A is one of the synthetic molecular sieves that has various applications in adsorption, separation, catalysis and detergents and desiccants (Dyer, 2007). Recent study by Loiola *et al.* (2012) shows that kaolin based LTA type zeolite give better performance compared to the commercial zeolite as water as water softener. Where a reduction of the water hardness in 1 L of solution requires 1 g of the kaolin based LTA zeolite compared to 4 g of commercial zeolite is necessary for 95% hardness reduction of the same solution.

Usually, zeolites are conventionally synthesized from aqueous basic aluminosilicate precursor gels under hydrothermal conditions at elevated temperatures in autoclave (Chandrasekhar, 2001; Breck, 1974). Basic aluminosilicate precursor gels preferably prepared from pure solutions of sodium silicate and sodium aluminate. The use of kaolin to produce zeolites is lead by the fact that it provides a cheaper and easy means of silica and alumina source (Kovo and Holmes, 2010). Utilizing the local kaolin from Sabah also enable the exploitation of the large sources of clay mineral deposit, consisting mainly of kaolinite in area of Sabah, which have been reported with an estimated value of 12.9 million tonnes (mt) (Malaysian Delegation, 2008). A lot of researchers have worked on the synthesis of zeolites from different sources of kaolin around the world (Bosch *et al*., 1983; Costa *et al*., 1988; Basaldella *et al*., 1993; Chandrasekhar and Pramada, 2001; Covarrubias *et al*., 2006; Reyes *et al*., 2010; Kovo and Holmes, 2010; Zwingmann *et al*., 2011; Kovo, 2012). However, no such report has been carried out on the utilization of Sabah kaolin for the purpose of zeolite synthesis.

In the present study, Sabah natural kaolin was utilized to synthesise zeolite A using hydrothermal synthesis technique. The optimum condition to synthesis zeolite A in terms of alkalinity without any additional silica to the reaction mixture was studied.

MATERIALS AND METHODS

Metakaolinization: Ten kilogram sample of kaolin clay was procured from KG. Gading Bongawan Sabah (coordinate 53, 65' 8"N, 115, 57'32"E). Sedimentation of the raw clay was done by stirring a mixture of 1 L distilled water with 500 g raw clay and deflocculant for 10 min.

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The 2.5 wt (%) of sodium hexametaphosphate (>65% w/w P_2O_5, Systerm) was used as deflocculant during the sedimentation process. The mixture of raw clay and sodium hexametaphosphate was stirred and let to settle down before the supernatant was separated. Supernatant then dried at 100°C overnight and labelled as treated clay. The treated clay then undergoes metakaolinization process at 800°C. The chemical composition and structural analysis of the raw kaolin and metakaolin were performed with under X-Ray Fluorescence (XRF), X-Ray Diffractometer (XRD) and Scanning Electronic Microscope (SEM).

Synthesis of zeolite A: The hydrothermal synthesis of zeolite A was carried out by modifying the method from Youssef *et al.* (2008). One gram of metakaolin (MK) was mixed with 20 mL NaOH solution prepared from NaOH pellet (>99% w/w, Merck KGaA) to get the reaction mixture. Metakaolin was slowly added to the NaOH solution and a thorough mixing was done to get uniformity. Reaction mixture with different amount of NaOH (0.02, 0.04, 0.05, 0.06, 0.08 and 0.1 moles) prepared by adjusting the amount of NaOH in each sample to study the optimum alkalinity required to synthesis zeolite A. The reaction mixture was kept in the 250 mL Teflon bottle and capped tightly. This mixture was shook for 30 min using orbital shaker to get homogenous solution. The Teflon bottles was not filled more than 50% to avoid spillage. Samples were crystallized in the oven for 8 h at 100°C. All samples were filtered then washed with 1 L of distilled water. Sample was dried overnight in the oven at 80°C. The resulting zeolites were characterized under XRD and SEM.

Characterization technique: Rigaku x-ray spectrometer model RIX 3000 was used to analyse the composition of raw kaolin and metakaolin. The powder X-Ray Diffraction (XRD) pattern were obtained using a Philip Expert Pro x-ray diffractometer model (Cu $K\alpha = 1.54056$, 30 mA, 40 kV). The data collection was carried out in the 2θ range of 5-70°, with a step size of 0.02°. The SEM images were taken under Scanning Electron Microscopy (EVO MA10 XVP) at voltage range of 10-30 kV.

RESULTS AND DISCUSSION

Metakaolinization of Bongawan kaolin: Figure 1a shows the x-ray diffractograms of raw kaolin and metakaolin. The raw kaolin contain quartz as major impurities with their main peaks at $2\theta = 21°$, 26.6°, 36.5°, etc. Meanwhile, the kaolinite peaks is detected at $2\theta = 12.5°$, 25° and 46°. The existence of SiO_2 and Al_2O_3 in the raw kaolin as the silica and alumina source was confirmed by the XRF analysis (Table 1), with their SiO_2/Al_2O_3 molar ratio is 3.2. Figure 2a shows the SEM images of raw kaolin contain the kaolinite mineral in stacking form as pointed by the arrow. The

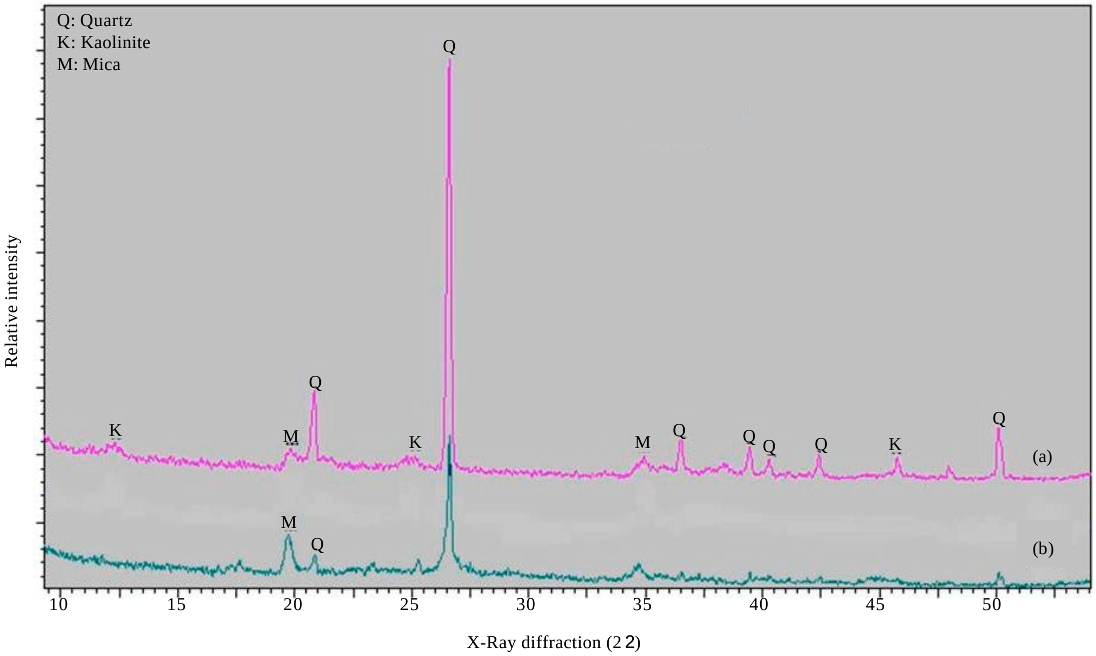

Fig. 1(a-b): X-ray diffractograms of (a) Raw kaolin and (b) Metakaolin

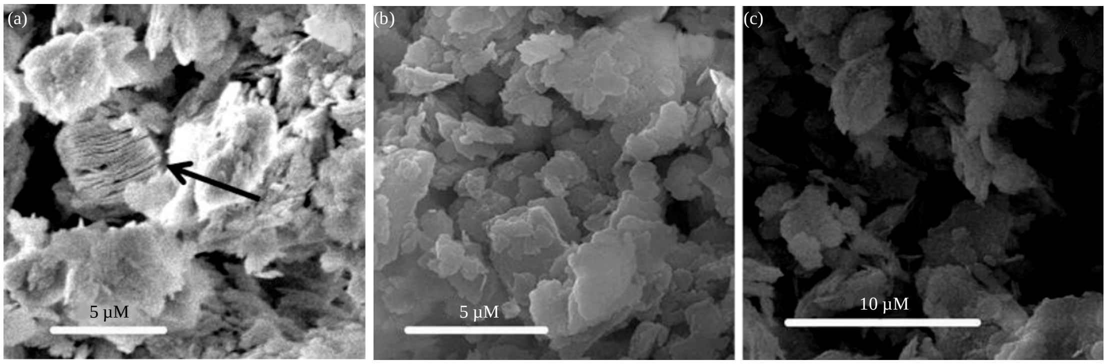

Fig. 2(a-c): SEM images of (a) Raw kaolin, (b) Treated kaolin and (c) Metakaolin

Table 1: Chemical composition of raw kaolin

Chemical content (weight %)	Raw kaolin	Metakaolin
MgO	1.3980	1.6810
Al_2O_3	27.9992	33.1583
SiO_2	63.5007	55.6057
K_2O	3.4497	4.4366
TiO_2	0.8025	0.8127
Fe_2O_3	2.6079	3.6711

positive and negative charges exist in the raw kaolin caused the kaolinite particles attracted to each other and form large aggregates or flocs. Figure 2a also shows that most of the kaolinite mineral are covered by impurities or quartz as indicated by the XRD analysis. After the treatment with sodium hexamethaphosphate, the kaolinite (Fig. 2b) is no longer in stacking nor covered by impurities. Apart from the usual pseudo-hexagonal shape, the treated kaolinite flakes shows rough edges. The image corroborates the fact that the soluble dispersing agent (sodium hexametaphosphate) ionizes to produce cations that are attracted to the negative charges on the clay particle so that each kaolinite plate or stack has a similar charge and thus they repel each other (Murray, 2007). The settling process during the sedimentation allowed the coarse grit particles to settle to the bottom of the beaker. Minerals such as mica, which is flake shaped, does not settle as rapidly as the quartz and heavy minerals (Murray, 2007). As the settling was removed and the supernatant was taken, kaolinite is separated from the major impurities exist in the raw kaolin. The x-ray diffractogram of metakaolin shows reduce in peaks intensity of quartz and the lost of kaolinite peaks. This indicates that the kaolin already transformed to metakaolin. The metakaolinization of kaolin at 800°C leads to the breakdown of the kaolinite crystal lattice structure and become highly disordered and amorphous (Said-Mansour *et al*., 2011). Figure 2c affirmed the transformation of kaolin to metakaolin since the kaolinites flakes and stacking are no longer exists.

The XRF analysis of metakaolin shows decreasing in SiO_2 percentage while increasing in Al_2O_3 percentage. The decrease in SiO_2 is in conjunction with the removal of the quartz impurities during the sedimentation of raw clay.

Synthesis of zeolite A: The reaction mixtures based on the molar ratio of 5 NaOH:0.450 MK:111.11 H_2O were prepared. Samples with different amount of NaOH = 0.02, 0.04, 0.05, 0.06, 0.08 and 0.1 moles) were obtained by adjusting the amount of NaOH added in the reaction mixture. All samples were crystallized at 100°C for 8 h. Figure 3 shows the x-ray diffractograms of samples when different moles of NaOH solution are used in the reaction mixture. When 0.02 moles of NaOH was used in the reaction mixture, there are no zeolite peak detected (Fig. 3a), indicating the sample still contained a large amount of amorphous gel. Reaction mixture with 0.04 and 0.05 moles of NaOH (Fig. 3b, c) shows the existence of zeolite A. The existence of sodalite was detected when the 0.06 moles of NaOH was used (Fig. 3d). This shows that larger amount of NaOH promotes the crystallization of sodalite. When 0.08 moles of NaOH was used, the sodalite peaks intensified. In this study, sodalite exists as the co-product of the synthesis when 0.06 and 0.08 moles of NaOH were used in the reaction mixture. Sodalite was the major product of the synthesis when 0.1 moles was used in the reaction mixture.

Figure 4 shows the SEM images of samples obtained when we used different moles of NaOH in the reaction mixture. Figure 4a shows there are no cubic shape crystal with 100 face. Only amorphous gel of silica and metakaolin were observed. This is in agreement with the result obtained by the XRD analysis as shown in Fig. 3a. Good crystallinity of zeolite A with perfect cubic crystals and sharp edges observed in Fig. 4b, c is in harmony with the peaks that shown in the x-ray diffractograms (Fig. 3b and c). This shows that 0.04 and 0.05 moles of

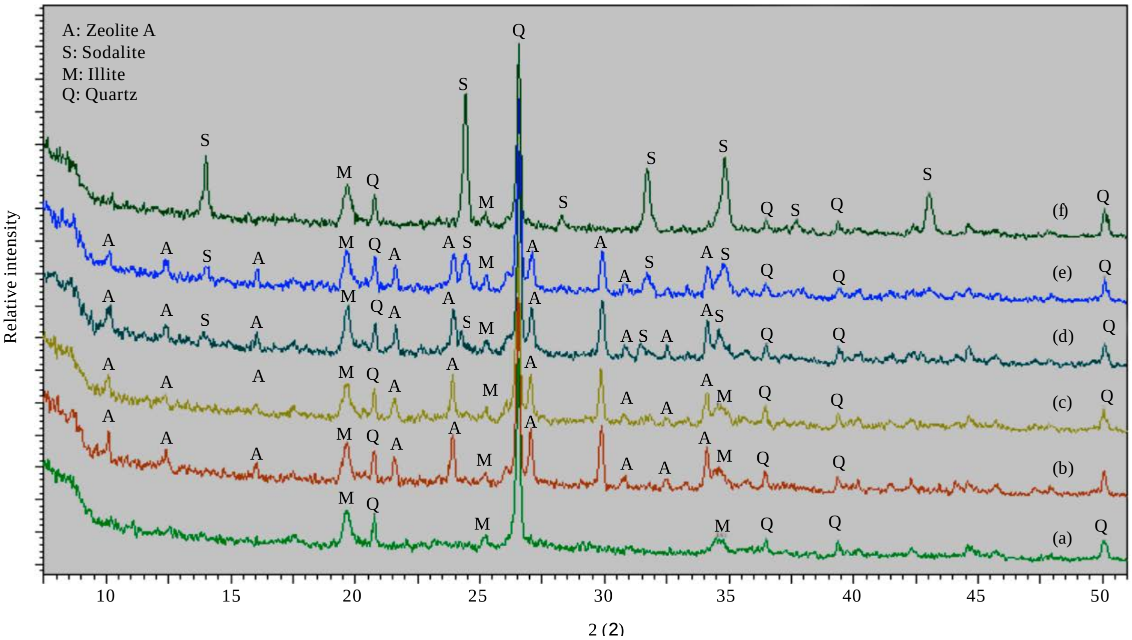

Fig. 3(a-f): X-ray diffractograms of zeolite A samples synthesised with different moles of NaOH in their reaction mixture, (a) 0.02, (b) 0.04, (c) 0.05, (d) 0.06, (e) 0.08 and (f) 0.1 moles

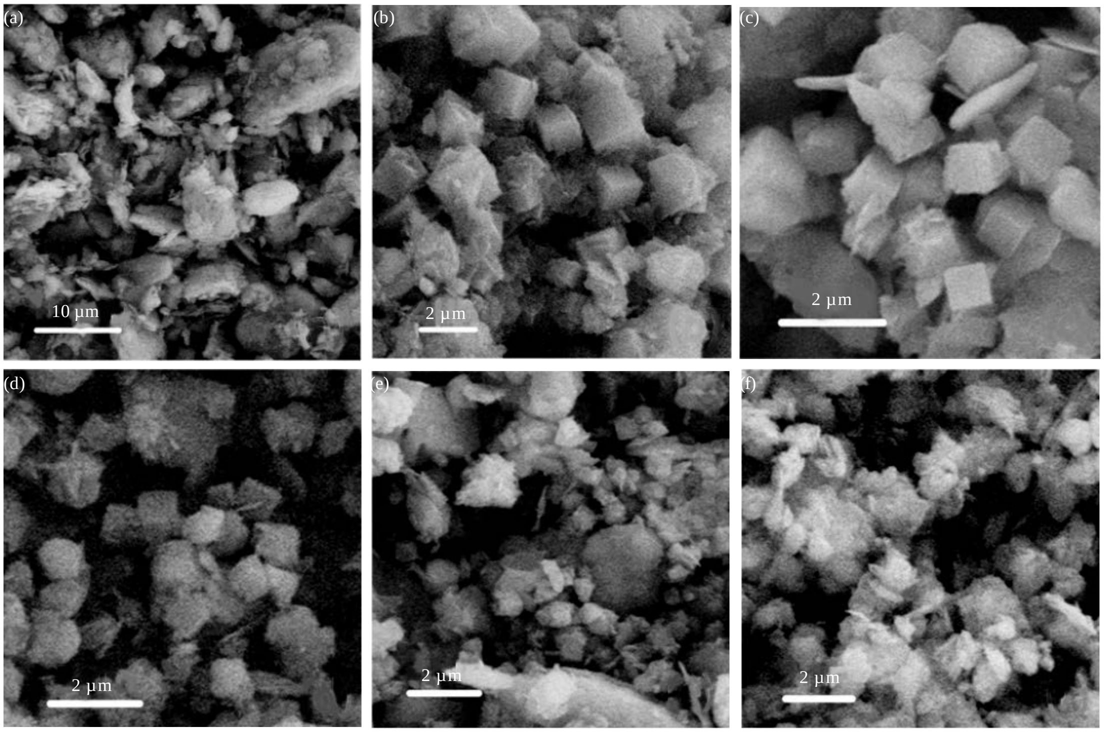

Fig. 4(a-f): SEM images of zeolite A samples synthesised with different moles of NaOH in their reaction mixture, (a) 0.02, (b) 0.04, (c) 0.05, (d) 0.06, (e) 0.08 and (f) 0.1 moles

NaOH are suitable for the zeolite A synthesis. The SEM image has shown the existence of other crystal together with zeolite A in (Fig. 4d, e) which is in agreement with the existence of sodalite as shown in the XRD analysis (Fig. 3d, e). The non-existence of cubic shape crystal in Fig. 4f is supported by the XRD analysis (Fig. 3f), where there are no zeolite A peaks observed except the dominant sodalite phase.

When the Si/Al ratio in the reaction mixture is equal, the final product depends on the concentration of hydroxyl ion in the reaction mixture Breck (1974). In our study, the Si/Al ratio of the metakaolin that we used is 1.5. There is no additional silica or alumina source was added into the reaction mixture of zeolite. This explained the different product that we obtained when using different NaOH concentration in the reaction mixture. Increase in OH^- ion strongly accelerates the crystallization of zeolite. By controlling the number moles of NaOH in the reaction mixture, we could control the process and rate of the crystallization. According to Grujic *et al.* (1989), the transformation rate of zeolite A to sodalite increased strongly with increasing NaOH concentration. The reaction was a solution-mediated process in which the zeolite A dissolved and the sodalite product nucleated heterogeneously without intermediate phases. The growth of the sodalite crystals (by surface addition of monomeric silicate and aluminate ions) was the rate-limiting step of the conversion (Subotic *et al.*, 1985; Subotic and Sekovanic, 1986).

Concentrated solution of NaOH in the reaction mixture (>10%) transforms zeolite A to hydroxysodalite (Breck, 1974). Transformation of zeolite A into sodalite occurred by dissolution of zeolite A in the caustic media. Formation of the primary sodalite is from the supersaturated solution of aluminate and silicate anions caused by the dissolution of zeolites in the hot alkaline media. The nucleation of sodalite occurred in the supersaturated solution. While, the microcrystals growth is due to a surface reaction of monomeric aluminate and silicate anions that depends on the supersaturation (Subotic and Sekovanic, 1986). The solubility of zeolite in the system increased with increasing concentration of hydroxyl ion. Similar result was reported by a study where zeolite A at lower alkalinity but sodalite at higher alkalinity (3.99 M) was obtained.

CONCLUSION

Sedimentation of raw clay has removed impurities from the natural clay by using sodium hexametaphosphate as dispersant agent. Metakaolin was obtained when the kaolin was heated at 800°C that turn it to amorphous state. Zeolite A does not formed when synthesised in lower concentration of NaOH. 0.05 moles of NaOH was found to be ideal for the synthesis of zeolite A without producing any co-product. Sodalite was found to be the major product at increasing NaOH concentration without any intermediate phases. NaOH molarity of the reaction mixture was found to be crucial in order to determine the type of zeolite will be produced when there is no additional silica was used.

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