Hydrothermal synthesis of zeolite A utilizing commercial bentonite clay as the Si/Al source

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ABSTRACT Formation of zeolites from bentonite clay has not been largely explored since most research on zeolite formation from clay is currently more focused on kaolinite clay. In this study, zeolite A was synthesized via hydrothermal technique using commercial bentonite clay. To activate the bentonite clay, it underwent thermochemical treatment for 24 hours at $98 \pm 2\,^{\circ}C$ in the presence of concentrated hydrochloric acid. Reaction mixture of zeolite A was obtained by mixing the activated bentonite clay with sodium hydroxide and sodium aluminate. The reaction mixtures were prepared at various silica to alumina ratio (1.0, 1.25, 1.5, 1.75 and 2.0) and molarity of sodium hydroxide (1.5M, 2.0M, 2.5M, 3.0M and 3.5M). All of the reaction mixtures underwent aging for 30 minutes and crystallized for 8 hours at $100\,^{\circ}C$. The effect of silica to alumina ratio and molarity of sodium hydroxide was examined using XRD and SEM. The optimum silica to alumina ratio and molarity of NaOH for the synthesis was found to be 1.5 and 2.5M respectively.

INTRODUCTION

Zeolite A, or Linde Type A (LTA) is a synthetic zeolite with low silica to alumina ratio (Si/Al). Zeolite A was known as a material which gives high adsorption capacity and high cation exchange capacity which gives various applications such as in drying agents, air purifiers and used in detergents. This is because, the alumina tetrahedral in the framework gives unbalanced negative charge to the structure of zeolite, and this charge is compensated by an exchangeable cation (Na^+ or K^+) Demirci *et al.*, 2014). To synthesis zeolite A, sodium metasilicate, Ludox, sodium aluminate and aluminium hydroxide are often used as silica and alumina sources. However, due to the expensive cost of chemical sources, many researchers are going for alternative resources by using natural minerals and waste, which was found to be more cost efficient. Zeolite formation from clay is one of the most explored areas among these alternative resources. Kaolinite clay, for instance is one of the natural minerals that most commonly used as Si and Al sources. Numerous researches have been done on exploitation of kaolinite clay as raw material for zeolite synthesis (Costa *et al.*, 1988; Alberti *et al.*, 1994; Chandrasekar, 1996; Sanhueza *et al.*, 1999; Rios *et al.*, 2007; Mostafa *et al.*, 2011; Melo *et al.*, 2012; Johnson & Arshad, 2014). Unfortunately, there are still relatively small numbers of research on utilizing bentonite clay as Si and Al sources for zeolite synthesis.

Bentonite is a natural clay composed mainly of montmorillonite. It belongs to the smectite group of clay which is structurally composed of octahedral alumina sheet sandwiched in between two tetrahedral silica sheets (Faghihian & Godazandeha, 2009). Man *et al.*, 2000 reported bentonite clay resources can be found in the southeast coast areas of Sabah; Segama (5.3 million tonnes), Sepagaya (1.9 million tonnes), Mansuli (1.5 million tonnes) and Andrassy (3.6 million tonnes). Moreover, due to its high porosity and high cation exchange capacity properties, there are growing interests on utilizing bentonite clay in a wide range of applications. There was not much research done on utilizing bentonite as aluminosilicate source to synthesis zeolite, considering their abundance in Sabah and also the composition which is rich in SiO_2 and Al_2O_3, making bentonite as a promising

starting material to develop tetrosilicates of zeolite. Previously, there were reports on zeolitization of bentonite clay (Ismail *et al.*, 2013; Qian *et al.*, 2014); however, due to the inactive structure of Si-O and Al-O in bentonite clay, it needs to be activated by thermochemical treatment where the benonite clay was reacted with either alkaline or acidic solution in elevated temperature (Faghihian & Godazandeha, 2009; Ma *et al.*, 2010; Ismail *et al.*, 2013).

There are studies on the effect of Si to Al ratio in synthesizing zeolite A from bentonite clay done by Ma *et al.*, 2010 and Ismail *et al.*, 2013 with different outcomes. Ma *et al.* obtained zeolite A with Si/Al at 1.5 using natural bentonite while Ismail *et al.* obtained zeolite A with Si/Al at 4.0 using commercial bentonite. The different outcomes are may be due to the different sources of bentonite clay and the synthesis condition itself, where Ma *et al.* used alkali fusion for bentonite activation while Ismail *et al.* used direct alkali hydrothermal approach. Therefore, this study aimed to investigate the thermochemical treatment of bentonite clay which was subsequently used as raw material for the synthesis of zeolite A. In addition, this study discussed the optimum Si/Al ratio in commercial bentonite clay and optimum alkalinity in synthesizing zeolite A.

MATERIALS AND METHODS

Materials

The bentonite clay powder used in this research was acquired from SIBELCO Australia. Table 1 shows the chemical composition of the commercial bentonite. Sodium aluminate ($NaAlO_2$), technical grade (13404), and sodium hydroxide (NaOH), with $\geq$ 97.00% purity for the synthesis of zeolite A were obtained from Sigma-Aldrich. Hydrochloric acid (HCl), used for activation of bentonite clay was obtained from Sigma-Aldrich.

Table 1. Chemical Composition of Commercial Bentonite

Wavelength (cm^{-1})	SiO$_2$	Al$_2$O$_3$	MgO	Fe$_2$O$_3$	CaO	K$_2$O	Na$_2$O
3500-3200	63.6	14.6	2.0	2.8	0.3	0.5	1.3

Synthesis and Characterization of Zeolite A

The method to activate bentonite was modified from Zhansheng *et al.*, 2006 and Oboh *et al.*, 1987, where inert bentonite was thermally transformed into an active phase at 98 ± 2 °C for 24 hours with the presence of concentrated HCl. By using method from Rios *et al.*, 2007 and Ma *et al.*, 2010, zeolite A was synthesized using activated bentonite as silica and alumina source, with addition of NaOH and $NaAlO_2$ as an extra alumina source. Throughout this research, formulation of zeolite A used was 2.5Na$_2$O: Al$_2$O$_3$: 1.5SiO$_2$: 166H$_2$O. Reaction mixture of zeolite A was prepared by adding 1g of activated bentonite into NaOH solution. The mixture was shaken to get a homogenous mixture. $NaAlO_2$ was added into the homogenous mixture and underwent ageing process for 30 minutes and then crystallized at 100°C for 8 hours. The synthesis was done in two sets where the first set of synthesis, silica to alumina ratio in the reaction mixtures were manipulated at 1.0, 1.25, 1.5, 1.75, and 2.0 with 2.5M of NaOH solution. Another set of synthesis was done by varying the concentration of NaOH at 1.5M, 2.0M, 2.5M, 3.0M, and 3.5M with silica to alumina ratio of the reaction mixtures was maintained at 1.5. All of the products obtained were filtered and dried in the oven at 80°C. Structural characterization of the products was obtained using X-ray diffraction (XRD) Philip Expert Pro X-Ray diffractometer model DY1496 (CuKα = 1.54056, 30 mA, 40kV). The morphology and size of the crystallites was examined using Scanning Electron Microscopy (SEM, Carl Zeiss MA10).

RESULTS AND DISCUSSION

Acid Activation of Bentonite

The X-ray diffraction pattern of commercial bentonite on Figure 1(a) indicates that it contains montmorillonite, quartz and feldspar and in good agreement with the standard JCPDS (card no.01-088-0891) During the acid treatment of bentonite clay, -OH groups at octahedral sheets were protonated resulting of dehydroxylation of the clay framework. Dehydroxylation led to the decomposition of octahedral sheet inside the clay framework in which, the Al^{3+}, Fe^{3+} and Mg^{2+} were leached out leaving the amorphous silica and unaltered layer in the clay product (Krupskaya *et al.*, 2017; Komadel & Madejova, 2013).
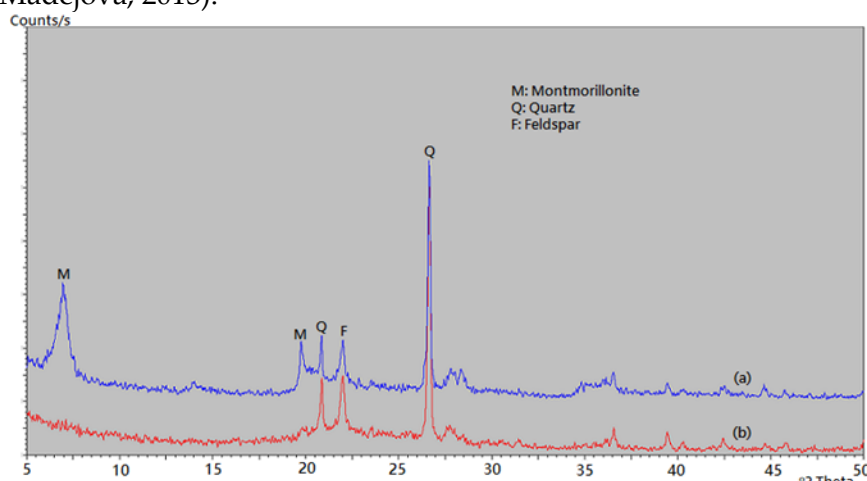

Figure 1. XRD diffractograms of (a) bentonite (b) acid activated bentonite

Effect of Silica to Alumina Ratio

The hydrothermal conditions for the synthesis of zeolite A were maintained at 100 °C for 8 h. To investigate the optimum Si/Al ratio for zeolite A formation from bentonite, zeolite A was synthesized at various Si/Al ratio, i.e 1.0, 1.25, 1.50, 1.75 and 2.0 by adjusting the amount of sodium aluminate, while the alkalinity of reaction mixture was kept constant at 2.5M of NaOH.
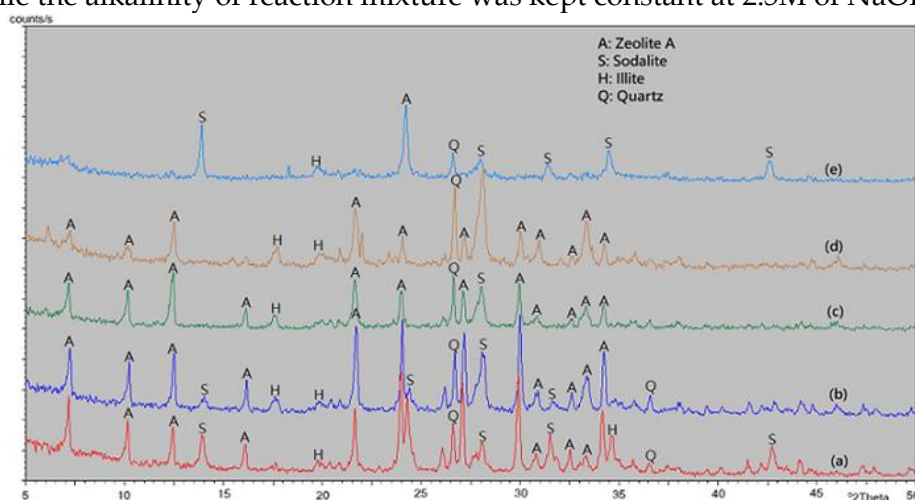

Figure 2. XRD diffractograms of Zeolite A samples with different silica to alumina ratio in their reaction mixture, (a) 1.0 (b) 1.25 (c) 1.5 (d) 1.75 (e) 2.0

Figure 2 shows the XRD patterns for zeolite A (in good agreement of JCPDS sample synthesized with different Si/Al ratio in their reaction mixture. Based on the XRD patterns (agreement with the standard JCPDS (card no. 39-0222), it shows that the optimum Si/Al ratio to synthesis zeolite A was 1.5, where zeolite A was found to be a major product with the least amount of sodalite peak. When the Si/Al ratio exceeded 1.5, sodalite peak intensified, while the zeolite A peak intensity decreased at

1.75 (Figure 2d). Subsequently, as Si/Al ratio increased at 2.0, it leads to the formation of sodalite as a major product. In contrast, when the Si/Al was kept below 1.5, there was a comparable amount of zeolite A peaks that co-exist with intensified sodalite peaks at both samples for 1.0 and 1.25 Si/Al ratio.

Figure 3a and 3b shows the SEM image of the zeolite A samples synthesized with Si/Al at 1.0 and 1.25 respectively. It shows that the cubic crystal shape of zeolite A co-exist with the spherical agglomerates of sodalite [. While the Figure 3c gives perfect cubic shape crystals, Figure 3d and 3e in contrary shows that the cubic shape crystals of zeolite A are hardly can be seen. This is due to the formation of sodalite as the Si/Al increased. It is in agreement with the result shown by XRD pattern on Figure 2.
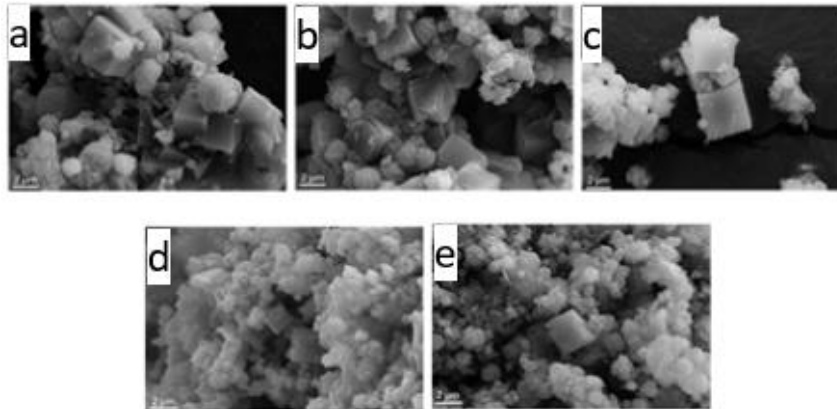

Figure 3. SEM images of Zeolite A samples with different silica to alumina ratio in their reaction mixture (a) 1.0 (b) 1.25 (c) 1.5 (d) 1.75 (e) 2.0

Effect of the Alkalinity of Reaction Mixture

To investigate the optimum condition in alkalinity for the zeolite A synthesis, the reaction mixture of samples were prepared by adjusting the molarity of NaOH used i.e 1.5M, 2.0M, 2.5M, 3.0M and 3.5M. Optimization is crucial since the alkalinity of reaction mixture will affect the degree of crystallization of the medium and nucleation rate of the reactant (Ma *et al.*, 2010). Figure 4 shows the XRD patterns of zeolite A samples (JCPDS card no. 39-0222) synthesized at various alkalinity conditions. These XRD patterns show that the NaOH concentration at 2.5M was found to be the most optimum alkalinity condition where major product of zeolite A existed with the least peak of sodalite. Although increasing the NaOH concentration at 3.0M and 3.5M promoted the increasing of zeolite A phase, the sodalite phase was also rapidly increased. In contrast, decreasing the NaOH concentration at 1.5M and 2.0M caused de-creased crystallinity of zeolite A, while promoting the intensified co-existence of sodalite.
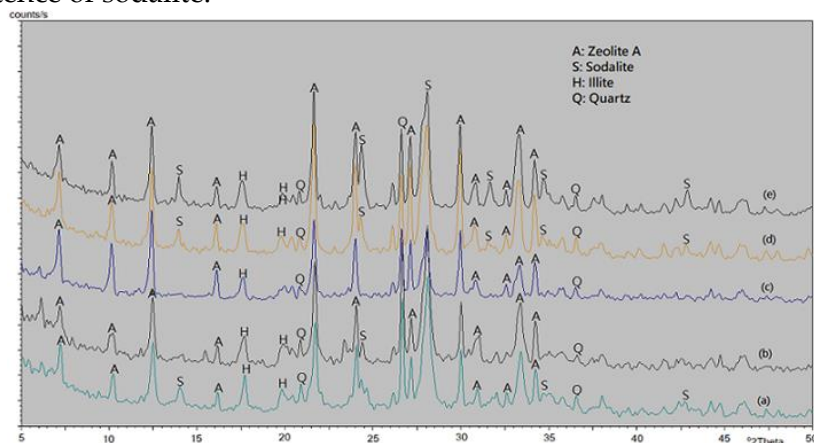

Figure 4. XRD diffractograms of Zeolite A samples with different concentration of NaOH in their reaction mixture, (a) 1.5M (b) 2.0M (c) 2.5M (d) 3.0M (e) 3.5M

Figure 5a shows the co-existence of poor cubic shape crystals and sodalite as opposed to Figure 5b which displayed a significant cubic shape, albeit also fiercely co-existing with sodalite. Meanwhile, a perfect cubic shape crystal of zeolite A can be seen clearly on Figure 5c. However, as the alkalinity of reaction mixture was increased to 3.0M (Figure 5d) and 3.5M (Figure 5e), the formation of cotton ball like sodalite also increased rapidly. Suffice to say, although increasing alkalinity may accelerate the crystallization process, uncontrolled moles of OH- in the reaction mixture may led to the formation of sodalite (Grujic et al., 1989).
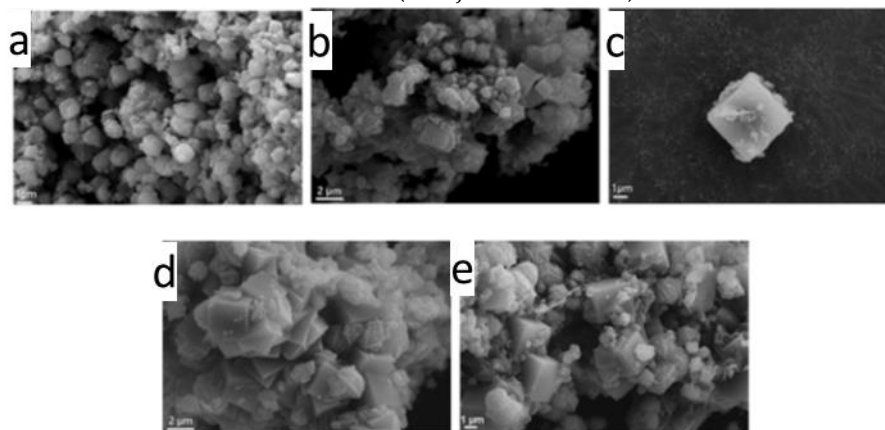

Figure 5. SEM images of Zeolite A samples with different concentration of NaOH in their reaction mixture, (a) 1.5M (b) 2.0M (c) 2.5M (d) 3.0M (e) 3.5M

CONCLUSIONS

The commercial bentonite clay was successfully activated by performing thermochemical treatment at 98 ± 2 °C last for 24 hours in the presence of concentrated HCl. While, zeolite A crystal was successfully synthesized from the activated commercial bentonite clay through hydrothermal technique. The optimum Si/Al ratio for zeolite A synthesis was found to be 1.5. High Si/Al ratio caused the formation of sodalite as a major product, whereas low Si/Al ratio led to the co-existence of zeolite A and sodalite. Optimum alkalinity condition was found to be on 2.5M of NaOH where zeolite A with least trace of sodalite was obtained. Increasing the NaOH concentration intensified the sodalite products while lowering NaOH concentration led to the formation of imperfect zeolite A crystals.

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