Synthesis and Characterization of Zeolite NaY from kaolin Bangka Belitung with variation of synthesis composition and crystallization time

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Abstract. Synthesis NaY zeolite using natural kaolin (Si/Al ratio~1) as an alternative source for silica and alumina is still challenging. The aims of this study is to find out an effective and environment friendly route to synthesis NaY zeolite from different source of silica and alumina. Pre-treatment kaolin like purification and fragmentation were conducted in order to reducing major impurity in kaolin such as quartz. Activation kaolin by Sub-Molten Salt System (SMS) using NaOH was employed because structure of Si-O and Al-O are inert and inactive. The kaolin was produced then used to synthesis NaY zeolite through hydrothermal method with a seeding technique using the mole ratio of (seed gel (5% of Al): 10,67Na₂O: Al₂O₃: 10SiO₂: 180H₂O) [1]. In order to find out optimum condition, the variation of crystallization time was performed. By the various characterization technique, the experimental result reported that NaY zeolite has the structure with mesoporous pore 3.6 nm and Si/Al ratio 3.8.

Keywords: fragmentation, kaolin, sub-molten salt system, NaY zeolite

1. Introduction

Kaolin is a natural mineral that mainly composed of kaolinite (Si / Al = 1) with the chemical composition Al₂Si₂O₅(OH)₄ but also contains some impurities such as quartz, illites, smectites, and feldspars [2]. It belongs to phyllosilicate group with layer tetrahedral adn octahedral structure [3]. In this study, kaolin was utilized as an alternative source of silica and alumina for zeolite synthesis, with expectation of providing a more affordable source of silica and alumina for zeolite synthesis.

Zeolite is a microporous alumina silicate material (pore size < 2nm) with different types of pore shapes and structure. One of the as-synthesized zeolites is NaY zeolite belonging to the faujasite class, with a Si/Al ratio of 2-4 and main frame of two 6 rings that bound through a sodalite cage with an average pore diameter of 7.4 Å [3]. Sunardi, et al reported the treatment of kaolin powder with alkaline salt at 500-950°C to convert kaoline to metakaolin, the more reactive form, before being used as Al-Si source [4]. However this process was shown ineffective, as some part of unreacted kaolin became impurities during synthesis. In 2014, Yue et.al reported the fragmentation of natural aluminosilicate minerals structure through sub-molten salt system and use it as precursor for synthesis of ZSM-5[5].

In this work, the attempt to synthesized NaY zeolite using fragmented kaolin as Si and Al source was reported. In order to reach the desired Si amount, suspension of colloidal silica (LUDOX 40) was also added. Several characterization techniques were applied to the as-synthesized materials, and show that the synthesis was successful to produce mesoporous NaY.
2. Materials and methods

2.1. General

Bangka Belitung natural kaolin, colloidal silica -LUDOX 40 (Sigma Aldrich), NaOH (pellet, 99%, Merck), CH<sub>3</sub>COOH (glacial, Merck), CH<sub>3</sub>COONa.3H<sub>2</sub>O (Merck), H<sub>2</sub>O<sub>2</sub> (30%, Merck), Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>.2H<sub>2</sub>O (Merck), NaHCO<sub>3</sub> (Merck), deionized water.

2.2. Modification of Natural Kaolin

Modification of Bangka Belitung natural kaolin consisted of physical activation, purification and fragmentation. Natural kaolin was polished using a grinder and filtered with a sieve. Activation of natural kaolin was performed by washing the kaolin with deionized water (1:3 w/v) under stirring for 3 h. The solid phase then was dried at 300ºC for 1 h. The purification process was conducted following Ming and Dixon, 1987. The activated natural kaolin was treated with 1 M NaOAc buffered to pH 5, 30% H<sub>2</sub>O<sub>2</sub>, and dithionite-citrate-bicarbonate. After purification, fragmentation was done by sub-molten salt system (SMS) [6] technique using strong base (NaOH) with 2: 1 ratio in 250ºC. Characterization of natural zeolite was done using XRD, FTIR, and SEM-EDX [7].

2.3. Synthesis of NaY Zeolite

The synthesis of NaY zeolite refers to the method of Ginter et al [1] with the ratio of the mole ratio (Seed gel: Na<sub>2</sub>O: Al<sub>2</sub>O<sub>3</sub>: SiO<sub>2</sub>: H<sub>2</sub>O = (5% Al): 10,67: 1: 10: 180). Fragmented kaolin was used as Al and Si source and certain amount of colloidal silica (LUDOX 40) was an additional Si source. The crystalization was carried out in polypropylene bottle at 100 ºC for 16 and 24 hours. Extensive characterization techniques such as XRD, FTIR, SEM-EDX, surface area analyzer were carried out on kaolin, fragmented kaolin and the as-synthesized zeolites. The cation exchange capacity of raw kaolin and as-synthesized NaY were also conducted.

3. Results and discussion

Characterization of Pre-treated Kaolin

The synthesis process of zeolite NaY begins with activation and purification to remove impurities on the raw material of the synthesis of zeolite.

![Figure 1. Spectra FTIR kaolin pre-treated Bangka Belitung](image-url)
Figure 1 shows the comparison between FTIR spectra of raw, activation and purification kaolin. The peaks around 1105-1117 cm\(^{-1}\) indicate the purity difference since it belongs to quartz that shifts from 1115 cm\(^{-1}\) to 1108 cm\(^{-1}\) [4]. It confirmed that purified kaolin has smaller absorption in that area than the others, estimated quartz in kaolin reduced.

From Figure 2a, it is found that there are significant differences between raw kaolin and kaolin after fragmentation such as fragmented kaolin has peak at wavenumber 1646 cm\(^{-1}\), while in the raw kaolin it does not appear.

The XRD pattern from Figure 2b shows comparison of raw diffraction patterns of kaolin [7] and kaolin after fragmentation, in which there is a peak shift at 13.90 ° and 24.86 °. As well as the disappearance of some kaolin peaks in the two theta of 12.34 °, 19.87 °, 35.6 °, and 38.4 °. So that it can be concluded that the process of fragmentation or submolten salt system (SMS) successfully done because it has destroyed kaolin framework.

**Figure 2.** a. FTIR spectra of kaolin fragmentation b. XRD pattern raw kaolin and kaolin fragmentation

**Zeolites NaY Characterization**

Figure 3 illustrates the FTIR spectra of two synthesis variations (NaY 2116 and NaY 2124) indicate a double six ring absorption or a secondary builder 4 and 6 external linkage rings with a faujasite structure (FAU). Peaks at 3750-3500 cm\(^{-1}\) shows the presence of hydroxyl groups (-OH) in the silanol group (Si-OH). The absorption band at 1500-1700 cm\(^{-1}\) belongs to H-O-H bending vibration of water molecules and also there is a peak of Si-O / Al-O asymmetry vibration at 1250-950 cm\(^{-1}\) wavenumber which is the typical peak of the silica alumina compound. The results from FTIR spectra confirm that synthesis of zeolites NaY has been successful.
Figure 3. FTIR Spectra comparison zeolite NaY synthesis with commercial NaY (Sigma Aldrich)

Figure 4 shows that characterization of as-synthesized NaY zeolite with XRD instrument, which was carried out to find out crystallinity and prove that the zeolite formed is NaY zeolite. For that reason, the comparison of NaY diffraction, resulted from synthesis, and standard NaY zeolite from IZA-online was carried out. Differences in diffraction pattern are possible because there are still some impurities such as Fe$^{2+}$, Ca$^{2+}$, K$^+$ and Mg$^+$ ions in the fragmented kaolin, the source used in this synthesis. However, it can be seen that on the addition of NaOH 2:1 during fragmentation in NaY2124 resulted in the formation of pattern of resemblance with more NaY zeolite compared to the 2:1 fragmentation of NaY2116. This indicates that 24 hour crystallization (of NaY2124) has given more NaY crystals compared to 16 hour crystallization.

Figure 4. Summary of the comparison XRD patterns of as-synthesized NaY zeolites
After matching the patterns of the zeolite peaks with those from IZA-online, as shown in Figure 4, it is found that the Sodalite octahydrate type is closest to as-synthesized zeolites. The impurities of zeolite P (Sodalite) are often found in NaY synthesis [8]. The peaks that have similarities with those in NaY zeolites are with 20 of 14.42°, 24.74°, 35.26°, and 43.52°. This resemblance indicates that the as-synthesized zeolite NaY is formed over the dominant sodalite framework. Characterization using EDX was also carried out to find out the Si/Al ratio contained in the zeolites. Supporting the XRD data, the most closely related to the Si/Al ratio of zeolite NaY is the as-synthesised zeolite with code NaY2124, with Si/Al ratio of 3.8, while the Si/A; ratio of NaY2116 is 4.68.

In Figure 5, some images of the as-synthesized zeolites NaY2116 and NaY2124 are displayed. Rugged morphology on the crystalline shapes may indicate the effect of mesoporosity on the zeolite. Further characterized using BET surface area analysis (summarized in Table 1) shows that the NaY2124 has lower surface area than the NaY2116, and its pore size is smaller, although the average size is within mesopore range. The time of crystallization affects the formation of crystals. It was observed at higher magnification (10,000x) of the two as-synthesized zeolites showed that at 24 hours of crystallization (Figure 5D) the NaY zeolite crystal habit is better developed, compared to that of the NaY zeolite synthesized for 16 hours (Figure 5C). It can be seen from their morphology that the crystals were intergrown and built through growing phases derived from the larger crystals.

![Figure 5. SEM Imaging of NaY zeolite synthesized](image)

| Samples   | Surface area (S\text{BET}) (m\textsuperscript{2} g\textsuperscript{-1}) | Average Pore Radius (nm) |
|-----------|---------------------------------------------------------------|--------------------------|
| NaY2116   | 990.4                                                        | 5.012                    |
| NaY2124   | 162.3                                                        | 3.601                    |

TABEL 1. Textural Parameters of Zeolites
4. Conclusions

The as-synthesized zeolite that closely similar to NaY zeolite is NaY2124 with 2:1 fragmentation composition and a 24 hours crystallization time. This is evidenced by the XRD results addressing some typical zeolite NaY peaks and the Si/Al ratio of 3.8. The zeolite is mesoporous with an average pore of 3.601 nm.

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References

[1] D M Ginter, A T Bell and C J Radke 1992 Synthesis of Microporous Material Molecular Sieve vol 1 ed M L Occelli and H E Robson (New York: Van Nostrand Reinhold)
[2] Murray H H et al 1993 Kaolin Genesis and Utilization Ed Boulder CO (The Clay Minerals Society)
[3] Cundy C S and Cox P A 2005 The Hydrothermal Synthesis of Zeolites: Precursors, Intermediates and Reaction Mechanism. (Microporous and Mesoporous Materials) vol 82 pp 1–78
[4] Sunardi, Arryanto Y and Sutarno 2009 Adsorption Gibberelic Acid Onto Natural Kaolin From Tatakian, South Kalimantan vol 9(3) (Indonesia : Indonesian Journal of Chemistry) pp 373-379
[5] Yue, Y Liu, Haiyan,Yuan, et al 2014 From Natural Aluminosilicate minerals to hierarchical ZSM-5 Zeolite: A Nanoscaledepolimerization-reorganization approach. (Journal of Catalyst: 319), pp 200-210
[6] Zhang Y, LI Zuo-Hu and et al 2005 Sub-Molten Salt Environmentally Benign Technology (China )
[7] Ekosse G E 2005 Fourier Transform Infrared Spectrophotometry and X-ray Powder Diffractometry as Complementary Technique in Characterizing Clay Size Fraction of Kaolin vol 9 (2) (Nigeria : University of Port Harcourt) pp 43-48
[8] Wang L, Zhang Z, Yin C, et al 2010 Hierarchical Mesoporous Zeolits with Controllable Mesoporosity Templated from Cationic Polymers. Microporous and Mesoporous Materials, vol 131(1–3) (Amsterdam: Elseiver) pp 58–67