Synthesis and characterization of LTA zeolite from Kaolin Bangka

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Abstract. The synthesis of LTA zeolite from kaolin Bangka using hydrothermal method at low temperatures has been reported. Kaolin was converted into metakaolin by calcination process at a temperature of 750 °C for 2 hours then hydrothermal subsequently process at 60°C for 5 hours in a NaOH 3M solution. Characterization by using XRD provides information on changes from the crystalline to amorphous phase in the conversion of kaolin to metakaolin to complete and the formation of LTA zeolite after hydrothermal. SEM provides information on morphological changes that are typical for Kaolin, metakaolin and zeolite LTA. From these characterizations, it can be concluded that successfully synthesized LTA zeolite from Kaolin Bangka with high crystallinity using a simple method.

1. Introduction
The engineering of porous material including controlling porosity, pore size, surface area and solid surface content, is an important basis for the application of interest in the chemical and petrochemical industries. The engineering of porous material in clays is intended to change porosity, surface area [1], and surface content of solids, as well as thermal stability [2]. Various methods have been carried out in order to change the abundant, inexpensive and easily obtained clay material into more valuable new materials [3].

The acid treatment in clays can increase the role of clay as a catalyst for the reaction of organic compounds reported [4]. This increase is due to the role of surface layer charge in the catalytic activity of clay and the significant changes in surface load due to acid, treatment [5]. Despite an increase in catalytic activity due to acid activation, these activated clays are only able to work at low temperatures with relatively low efficiency. This is due to the collapse of the distance between the layers of clay due to the loss of water hydrate when heating at high temperatures, thereby changing the surface area and load of the clay catalyst.
Engineering to convert natural clay to zeolite has already begun. The transformation of layered silica as kaolin into sodalite with NaOH base treatment and hydrothermal temperature of 80°C. However, further research to alter the layered structure of silica alumina into a three-dimensional form, just started again in the early 2000s. This may be due to the limited application of pillared clay, so the effort to increase the use of coated material through pore engineering begins to transform the coating into a zeolite structure. The transformation of kaolinite and montmorillonite and Al₂O₃ pillared clay into sodalite by addition of NaOH followed by heating at 100°C [6]. By using solid-solid transformation, Geer et al. [2] succeeded in synthesis of sodalite from clay. The formation of sodalite in these reaction is due to the absence of molecules that direct the formation of zeolite structure, so the reaction leads to the most stable form of the zeolite base structure i.e. sodalite. To synthesize zeolite with a certain type, the commonly used hydrothermal method [7]. The use of hydrothermal method had shown success in changing the structure of silica into zeolite structure in base environment.

Changing the kaolin structure from Bangka to zeolite has not been reported. Since kaolin-structures are similar to magadiite structures, the use of hydrothermal methods using bases is expected to be able to convert kaolin from Bangka to zeolite. Changing this structure is based on the ability to self-arrange silica alumina molecules in the hydrothermal reactor in the optimum thermodynamic conditions for the formation of zeolite crystals. Conditioning of time and temperature of hydrothermal is the focus of the study to be carried out. The study of the duration of hydrothermal is used to explore information on the rate and mechanism of zeolite crystal formation. Characterization using SEM is expected to be able to provide information on the morphology of the synthesized zeolite. XRD spectroscopy was used for structural elucidation and determination of the crystallinity of the synthesized zeolite structure.

2. Methods
The synthesis method is using the metakaolin formation path followed by aging and hydrothermal reaction to produce zeolite A. Kaolin from Bangka heated at a temperature of 750 degrees Celsius for 3 hours in order to produce metakaolin. Then the metakaolin obtained was added by 3M NaOH solution, followed by aging process for 2 hours at 60°C and hydrothermal with various of crystallization time (3, 5, 7, 9 and 12) hours at 90°C. Furthermore, the neutralization process is carried out by washing using DM aqua to pH around 10-11, then washing with 10% HF aqueous solution until pH around 7. Then proceed with washing with DM again for ± 2-3 weeks to obtain pH 7-7. The synthesized zeolite filtered and dried at room temperature overnight, then dried in an oven at a temperature of around 70-80°C for two days.

3. Results and discussion
The first step in the synthesis of zeolite A is the thermal treatment of raw kaolin to obtain a more reactive phase, metakaolin. The raw material XRD pattern, shown in Figure 1 according to kaolinite, which has a layered structure with d₁₀₀ at 12.34 and d₂₀₀ 24.64 which is the characteristic peak of kaolinite. SEM micrographs (Figure 2) confirmed the hexagonal plate morphology of kaolinite crystals. After calcination process at 750°C for 3 hours, the XRD pattern showed significant expected changes compared to the initial kaolin pattern, which was characterized by loss of the kaolin diffraction peak, accompanied by the appearance of amorphous aluminosilicates. Metakaolin is the amorphous material and the highest diffraction peak corresponds to the presence of quartz (SiO₂), which is the crystalline phase, in metakaolin. Transition of kaolin to metakaolin occurs in the temperature range of 400-800 degrees Celsius due to the OH structure dehydroxylation process of kaolin and metakaolin formation [8] (Figure 2).
Figure 1. XRD diffractogram of kaolin and metakaolin.

Figure 2. SEM photomicrograph of Kaolin from Bangka and its metakaolin after calcination process.

3.1. Effect of crystallization time
Base concentration is one of the most important parameters that controls the crystallization of zeolites. Increased alkalinity causes an increase in the rate of crystallization through nucleation and crystal growth. This is a consequence of the greater concentration of reactive silicates, aluminate and aluminosilicate species caused by the rapid increase in solubility of amorphous aluminosilicate precursors. In addition, with increasing alkalinity, particle size usually decreases, resulting in a narrow distribution of particle sizes due to increased nucleation rate and increased polymerization rate between polysilicate and aluminate anions. In this study researchers used a base concentration of 3M tested to produce zeolite A in converting metakaolin to zeolite A supported by SEM data which showed the uniformity of A. zeolite morphology.

Figure 3. XRD diffraction and SEM micrograph of as synthesized zeolite A from kaolin.
The successful synthesis of zeolite A shown in Figure 3 provides information about obtaining the right conditions in terms of the number of bases needed and the time of curing and crystallization. To evaluate the effect of crystallization time on crystallinity and cubic zeolite A, variations in crystallization time were carried out. Tests are carried out for crystallization times of 3, 5, 7 and 9 hours. In the initial stage of the reaction, the rate of formation of zeolite is slow so the crystallinity of the reaction product is not too high. In the first hour, the reaction product showed high results almost the same as the best reaction time crystallinity 5 hours after it was calculated using the rietveld method using two software namely Match and High score plus. The synthesized zeolite A composition was quantified (Table 1) which showed that the reaction product from the reaction time of hydrothermal 5 had the highest crystallinity, this was possible because the conversion of relatively high amounts of amorphous aluminosilicate gel compared with crystallites from other samples. All samples showed crystallites in the presence of amorphous aluminosilicate gel indicated by the high baseline in the XRD diffractogram for samples examined.

![Figure 4. XRD diffractogram of Zeolite A in various crystallization time.](image)

| Time of crystallization (hours) | Match! (chi^) | Highscore plus (GOF) |
|--------------------------------|--------------|---------------------|
| 3                              | 8.3          | 5.93                |
| 5                              | 7.2          | 4.82                |
| 7                              | 8.3          | 5.69                |
| 9                              | 8.4          | 6.03                |

Rietveld refinement is done to find out to minimize the difference between the pattern of the experimental results and the database pattern hypothesized to be the same as the experimental pattern and the calculated pattern (instrument parameters). The rietveld refinement achievement parameter is one of the minimum errors expressed by index R (least square) such as goodness of fit (GOF) or chi^2. In order to find minimum value of refinement, we employ Match! and High score plus software, where the minimum chi^2 and GOF are found in the 5 hour of crystallization time. This is show that optimum
time of crystallization of amorphous phase into zeolite A is at 5 hours of crystallization. If the sample diffraction has a large GOF value, it indicates do not have a good of fitness with the value of reference peak, the XRD diffraction pattern is less than standard diffraction.

4. Conclusion
Zeolite A from bangka kaolin has been successfully synthesized from kaolin Bangka d through the gel formation method of the amorph metakaolin phase in an alkaline aqueous solution. The optimum time for zeolite crystal formation is 5 hours.

References
[1] S Aguado, G Bergeret, C Daniel and D Farrusseng 2012 Absolute Molecular Sieve Separation of Ethylene / Ethane Mixtures J. Am. Chem. Soc. 20–22
[2] H Greer, P S Wheatley, S E Ashbrook, R E Morris, and W Zhou 2009 Early stage reversed crystal growth of zeolite A and its phase transformation to sodalite J. Am. Chem. Soc. 131 49 17986–17992
[3] M D Oleksiak, J A Soltis, M T Conato, R L Penn and J D Rimer 2016 Nucleation of FAU and LTA Zeolites from Heterogeneous Aluminosilicate Precursors Chem. Mater. 28 14 4906–4916
[4] B Bananezhad, M R Islami, E Ghonchepour, H Mostafavi, A M Tikdari and H R Rafiei 2019 Bentonite clay as an efficient substrate for the synthesis of the super stable and recoverable magnetic nanocomposite of palladium (Fe 3 O 4 /Bentonite-Pd) Polyhedron 162 192–200
[5] O S N Sum, J Feng, X Hu, and P L Yue 2004 Pillared laponite clay-based Fe nanocomposites as heterogeneous catalysts for photo-Fenton degradation of acid black Chem. Eng. Sci. 59 22–23 5269–5275
[6] D C Lin, X W Xu, F Zuo and Y C Long 2004 Crystallization of JBW, CAN, SOD and ABW type zeolite from transformation of meta-kaolin Microporous Mesoporous Mater. 70 1–3 63–70
[7] Y Ji, B Zhang, W Zhang, B Zhao, H Li, D Wang and Y Li 2017 High-efficient synthesis of zeolite LTA via a wet-gel crystallization route Chem. Res. Chinese Univ. 33 4 520–524
[8] D Novembre, B di Sabatino, D Gimeno and C Pace 2011 Synthesis and characterization of Na-X, Na-A and Na-P zeolites and hydroxysodalite from metakaolinite Clay Miner. 46 03 339–354