

## Optimization of Pretreatment and Hydrothermal Process of Na-X Zeolite from Kaolin and Metakaolin

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### Abstract

Synthesis of Na-X zeolite was conducted from kaolin and metakaolin. Synthesis varied in its pretreatment method and hydrothermal conditions. The pretreatment methods used were: conventional alkaline, alkaline fusion and conventional fluoride. Hydrothermal conditions for the experiments were gradual temperature 40 °C (6h), 60 °C (6h), 80 °C (12h), and constant temperature 80 °C for 24 h, 100 °C for 24 and 100 °C for 48 h. Synthesized products were characterized by X-Ray Diffraction (XRD), Fourier Transform InfraRed (FTIR), Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX), and N<sub>2</sub> Isotherm Adsorption/Desorption method. The result showed that pre-treatment by conventional fluoride could not produce Na-X zeolite, synthesis by conventional alkaline and alkaline fusion with hydrothermal at 100 °C (48h), 100 °C (24 h), and gradual temperature produce Na-X zeolite with Na-P1 or Na-A zeolite as impurities, while synthesis from metakaolin by conventional alkaline with hydrothermal at 80 °C for 24 hours produced pure Na-X zeolite. Na-X zeolite and Na-P1 zeolite with hierarchical pores were synthesized through alkali fusion with hydrothermal at 100 °C for 24 hours.

**Keyword:** NaX zeolite, kaolin, conventional alkaline, conventional fluoride, hydrothermal.

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### 1. INTRODUCTION

Zeolite X is included in Faujasite (FAU) type zeolite with low silica content (1-1.5). Zeolite X with Na<sup>+</sup> ion cations content called as Na-X zeolite with chemical compositions written as Na<sub>86</sub>Al<sub>86</sub>Si<sub>106</sub>O<sub>384</sub>·wH<sub>2</sub>O (w~260). Na-X zeolite has some superiority due to its great number of acid sites and great cations exchange capacity. Na-X zeolite has high aluminum content, resulting in more cations (generally H<sup>+</sup>) needed to compensate the charge of AlO<sub>4</sub><sup>-</sup> tetrahedral. In zeolite Na-X, H<sup>+</sup> is strong Bronsted acid. Therefore Na-X zeolite classified as acid catalyst. Due to its great number of acid sites and great cations exchange capacity, Na-X zeolite generally used as an adsorbent, catalyst, and ion exchanger.

Some previous researches have been successfully synthesized Na-X zeolite from various starting materials. Rios, et al. (2009, 2012) synthesized zeolite from kaolin by conventional alkaline and alkaline fusion as a

pretreatment method. Synthesized product identified as impure Na-X zeolite with a trace of Na-A and Na-P1 zeolite. Caballero, et al. (2007) synthesized X zeolite from dealuminated kaolin with sulfuric acid in high temperature. Ozdemir and Pişkin (2013) successfully synthesized pure Na-X zeolite from sodium aluminate (NaAl<sub>2</sub>O<sub>2</sub>), sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>), and sodium metasilicate pentahydrate (Na<sub>2</sub>SiO<sub>3</sub>·5H<sub>2</sub>O) as silica and alumina sources. The utilization of chemical reagent as silica and alumina sources in zeolite synthesis has some disadvantages: relatively expensive, relatively difficult to get (some chemical reagents need a long order time), potentially non-ecofriendly, etc. Natural mineral is one of the alternative green solution and suitable silica and alumina sources in zeolite synthesis.

In this research, Kaolin was used to synthesis Na-X zeolite. Three different pretreatment methods, namely conventional alkaline, alkaline fusion, and conventional

fluoride were applied. Silica addition was done to achieve the suitable mole ratio of Si/Al for Na-X zeolite synthesis. Moreover, to obtain the optimum condition for synthesis, the hydrothermal processes were carried out in different conditions. Kaolin as silica and alumina sources is an unreactive material. Therefore, as a comparison, syntheses were done by two different routes, from kaolin and metakaolin as starting material. Metakaolin is an active form of kaolin, the result of thermal activation (calcination) of kaolin. Syntheses from metakaolin were done in similar conditions with the syntheses from kaolin routes. But, to obtain the suitable Si/Al ratio in Na-X zeolite synthesis were done by dealumination process (reduction alumina content using strong acids). The utilization of kaolin as a raw material in zeolite synthesis is expected to increase kaolin's economic value. Synthesized Na-X zeolite is expected to be used as a catalyst and produced in large scale.

## 2. MATERIALS AND METHODS

### Materials

The materials in this research were Bangka Belitung kaolin, sodium hydroxide (NaOH, Merck,  $\geq 99\%$ ), colloidal silica (LUDOX<sup>®</sup> 40 wt.% SiO<sub>2</sub> in H<sub>2</sub>O, Aldrich), hydrochloric acid (HCl, Merck, 37%), sodium fluoride (NaF, Merck,  $\geq 99\%$ ) and distilled water. In this research, two different synthesis routes were used to obtain the best condition in Na-X zeolite synthesis. The first synthesis route used kaolin as starting material, while the second route used metakaolin. Both synthesis routes were done with variations in the stage of Si/Al mole ratio adjustment, pre-treatment and hydrothermal conditions.

### Metakaolinization and Dealumination

In the first synthesis routes, Na-X zeolite was synthesized directly from kaolin, while in the second synthesis routes, Na-X zeolite was synthesized from metakaolin. Metakaolin was obtained from calcination of kaolin in a furnace at 650 °C for 8 hours. In order to obtain a suitable mole ratio of Si/Al, metakaolin was refluxed with HCl 2 M (1/5 b/v) at 80 °C for 2 hours for dealumination process. Afterwards, the collected solids washed with distilled water until neutral pH, then dried in an oven at 80 °C for 24 hours.

### Preparation Method

Pretreatment was done by three different methods, namely conventional alkaline, alkaline fusion, and conventional fluoride methods. The conventional alkaline method started with 4 grams kaolin, mixed with NaOH solution made from 2 grams NaOH and 36.8 ml distilled water in a plastic beaker. Then the mixture stirred with magnetic stirrer for 1 hour. Alkaline fusion method was done by mixing 4 grams kaolin and 2 grams NaOH powders in porcelain Teflon crucible, then heated at 600 °C for 1 hour. The result of the fusion process then cooled down in room temperature, then ground. Afterwards, 50 ml distilled water added, and stirred for 1 hour with magnetic stirrer. The conventional alkaline method was done with the mixture of 2 grams NaF and 36.8 mL distilled water, then added 4 grams kaolin, and stirred for 1 hour with magnetic stirrer. Metakaolin preparations were done using the same method with mole ratio of materials 1SiO<sub>2</sub>: 0.3 Al<sub>2</sub>O<sub>3</sub>: 1 NaOH: 30 H<sub>2</sub>O and 1SiO<sub>2</sub>: 0.3 Al<sub>2</sub>O<sub>3</sub>: 1 NaF: 30 H<sub>2</sub>O.

### Na-X Zeolite Synthesis

Synthesis process was done with pre-treated kaolin, mixed with 16.2 ml distilled water, and mixed for 1 hour. After that 1.6 ml colloidal silica added to the mixture, and stirred for 1 hour. The addition of colloidal silica was done to obtain the mole ratio of mixture composition: 1SiO<sub>2</sub>:0.3Al<sub>2</sub>O<sub>3</sub>:1NaOH:30 H<sub>2</sub>O. Afterwards, the mixture stirred continuously for 15 hours for the aging process. For the hydrothermal process, the mixture moved to polypropylene bottle, sealed, and then heated in an oven at gradual temperatures: 40 °C for 6 hours, 60 °C for 6 hours, and 80 °C for 12 hours. After hydrothermal, the mixture then washed with distilled water by centrifugation until neutral pH, the solids were collected and dried in an oven at 60 °C for 24 hours. The product of this synthesis route noted as K-CA1. The similar synthesis route was done with different hydrothermal conditions: temperature 100 °C for 24 and 48 hours for sample K-CA24, K-CA48, K-AF24, K-AF48, K-CF24 and K-CF48, but sample K-AF24 and K-AF48 used mol ratio of the materials mixture: 1.75SiO<sub>2</sub>: 0.3 Al<sub>2</sub>O<sub>3</sub>:1NaOH:30H<sub>2</sub>O. CA used as the code for a sample that synthesized by alkaline fusion, AF for alkaline fusion, while CF for conventional fluoride.

Syntheses from dealuminated metakaolin was done by similar routes. Pre-treated dealuminated metakaolin were mixed with distilled water based on mole ratio of materials:  $1\text{SiO}_2$ :  $0.3\text{Al}_2\text{O}_3$ :  $1\text{NaOH}$ :  $30\text{H}_2\text{O}$  and  $1\text{SiO}_2$ :  $0.3\text{Al}_2\text{O}_3$ :  $1\text{NaF}$ :  $30\text{H}_2\text{O}$ , then stirred continuously for 15 hours. Afterwards, the mixture moved to polypropylene bottle, sealed, and heated in an oven at gradual temperatures:  $40$ - $60$ - $80\text{ }^\circ\text{C}$  respectively for  $6$ - $6$ - $12$  hours for hydrothermal process. The product then washed and separated by centrifugation; the collected solids were dried in an oven at  $60\text{ }^\circ\text{C}$  for 24 hours. These synthesis routes produce sample noted as M-CA1, M-AF1 and M-CF1. Sample M-CA24 was synthesized using the same method but it was prepared with constant temperature at  $80\text{ }^\circ\text{C}$  for 24 hours.

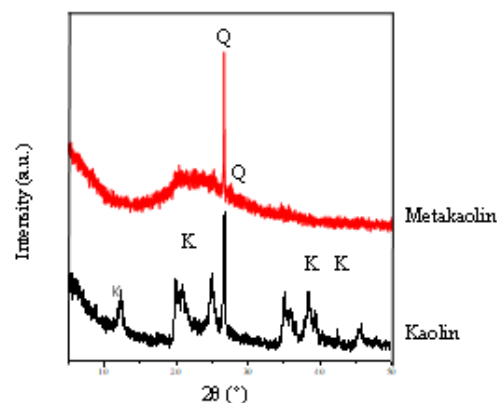
### Characterization Method

Characterization of synthesized samples was done with XRF Philips Analytical Minipal 4 to identified Bangka Belitung kaolin composition. Characterization with XRD was done to analyze type and crystallinity of synthesized samples. Samples were analyzed with Philips X'pert MPD-1 instrument with Cu-K $\alpha$  ( $\lambda=1,5405\text{ \AA}$ ) radiation at  $2\theta$  between  $5$ - $50^\circ$ ,  $30\text{ mA}$ ,  $40\text{ kV}$ . FTIR spectrophotometry measured at mid-IR range:  $4000$ - $400\text{ cm}^{-1}$  by DRIFTS preparation technique and Shimadzu IR Tracer-100 instrument. Surface morphology and composition of synthesized samples were analyzed by SEM-EDX, with Carl Zeiss Evo MA 10 instrument. While porosity characteristic was analyzed by  $\text{N}_2$  isotherm adsorption/desorption with Physisorption Analyzer Micromeritics ASAP 2020 V4.02.

### 3. RESULTS AND DISCUSSION

In this research, Na-X zeolite was synthesized from Bangka Belitung kaolin as raw material. Synthesis routes divided into two main routes, based on the type of starting materials: from kaolin and from dealuminated metakaolin. The optimum condition of Na-X zeolite obtained from variation in pre-treatment and hydrothermal condition. Metakaolin as starting material was obtained from calcination at temperature  $650\text{ }^\circ\text{C}$  for 8 hours. During the calcination, dehydroxylation was happened, caused the loss of water molecules from kaolin, which lead to rearrangement of kaolin structure, octahedral of  $\text{AlO}_6$  transformed to more reactive structure

(Lenarda *et al.*, 2007). Fig 1 showed the diffractogram of kaolin and metakaolin. The kaolin's diffractogram showed the characteristic of kaolinite peaks (ICDD No. 14-0164) at  $2\theta$  around  $12.31^\circ$  and  $24.64^\circ$ , while the characteristic of quartz peak (ICDD No. 33-1161) showed at  $2\theta$  around  $26.6^\circ$  (Ayele *et al.*, 2016). After the calcination process, crystalline phase of kaolin transformed into a more reactive amorphous phase of metakaolin.



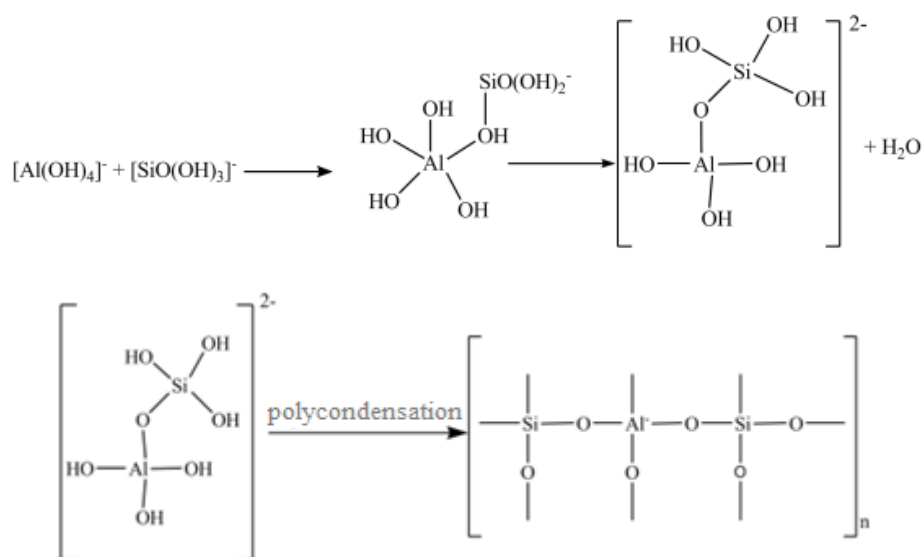
**Figure 1.** Diffractogram of kaolin and metakaolin (K: kaolinite, Q: quartz)

Dealumination process was carried out with a mixture of HCl 2 M and metakaolin in ratio 1:5 (Pan *et al.*, 2014). During the dealumination process alumina extracted from the metakaolin's framework, so the mole ratio of Si/Al increased (Mohiuddin *et al.*, 2016). The results of XRF analysis were summarized in Table 1. The result showed that dealumination process successfully increased the mole ratio of Si/Al, from 1.76 to 2.00.

During the conventional alkaline pre-treatment process, kaolin was activated by NaOH. Hydroxide ion ( $\text{OH}^-$ ) from NaOH stimulate the hydrolysis of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  to form free species of silicate  $[\text{SiO}(\text{OH})_3]^-$  and aluminate  $2[\text{Al}(\text{OH})_4]^-$ . Species  $2[\text{Al}(\text{OH})_4]^-$  and  $[\text{SiO}(\text{OH})_3]^-$  is the primary unit of zeolite framework. The activation process during alkaline fusion was happened by dry reaction between NaOH with mineral phase of the starting material, and NaOH acted as an activator. Pre-treatment by conventional fluoride were similar with a conventional alkaline method. NaF included as basic inorganic salt, in this process NaF acted as an activator, ion  $\text{F}^-$  also contributed in the formation of zeolite structure, leads to the formation of bigger crystal with fewer defects (Reyes dan William, 2013).

**Table 1.** XRF analysis of kaolin and dealuminated metakaolin

	% Mass						Si/Al mole ratio
	Si	Al	Ti	Fe	Ca	K	
Kaolin	58	31.6	1.9	4.49	0.65	1.2	1.76
Dealuminated metakaolin	61.4	29.4	1.97	4.08	0.6	1	2.00



**Figure 2.** The formation of zeolite framework unit during aging and hydrothermal process (Tanaka and Fujii, 2009).

In this research, aging process was carried out by continuous stirring for 15 hours, this process leads to more effective kaolin dissolution and increase the gel homogeneity (Tanaka and Fujii, 2009). The result of aging process is white colloidal gel. In this stage, free species of silicate and aluminate reacted and formed primary amorphous phase from hydrated alumina silicate gel by condensation reaction which depicted in Fig 2.

Hydrothermal processes were carried out in various conditions. In this hydrothermal process, Na-X zeolite crystals were started to form. The diffractogram of sample K-CA1 were depicted in Fig 3. The diffractogram showed diffraction pattern in the form of hump with irregular intensity. The characteristic of quartz peak showed at  $2\theta$  around  $26.28^\circ$ . This result indicates that the crystalline Na-X zeolite not formed yet, and the product is an amorphous phase of aluminosilicate (Bates *et al.*, 2006). The different result was obtained from sample M-CA1. The diffractogram of M-CA1 showed the characteristic peak of Na-X

zeolite at  $2\theta$  around  $6.06^\circ$ ,  $9.85^\circ$ ,  $11.60^\circ$ ,  $15.32^\circ$ ,  $18.30^\circ$ ,  $19.94^\circ$ ,  $23.17^\circ$ ,  $26.54^\circ$ ,  $29.09^\circ$ ,  $30.16^\circ$ ,  $31.88^\circ$  and  $33.46^\circ$ , but with the trace of Na-A zeolite.

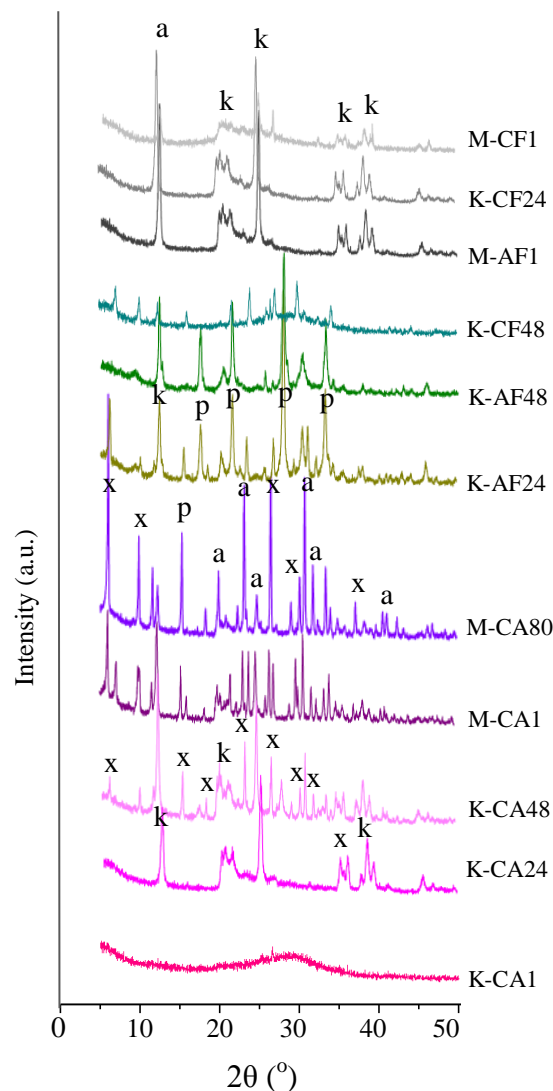
Based on the synthesis routes of K-CA1 samples which unsuccessfully synthesized Na-X zeolite, sample K-CA24 and K-CA48 synthesized with different hydrothermal conditions to obtained better result. M-CA24 also synthesized in different hydrothermal conditions to obtained pure Na-X zeolite. Diffractograms pattern of K-CA24 showed the characteristic of kaolinite at  $2\theta$  around  $12.39$ ,  $21.35$ ,  $25.03$ ,  $35.03$ ,  $38.54$ , and  $45.5^\circ$ . These indicate that zeolite not formed yet in the reaction time 24 hours. Different result obtained from sample M-CA24. The diffractogram pattern showed the characteristic of pure Na-X zeolite at  $2\theta$  about  $6.01^\circ$ ,  $9.88^\circ$ ,  $11.62^\circ$ ,  $12.23^\circ$ ,  $15.31^\circ$ ,  $18.25^\circ$ ,  $19.95^\circ$ ,  $23.19^\circ$ ,  $26.54^\circ$ ,  $29.05^\circ$ ,  $30.15^\circ$ ,  $30.80^\circ$ ,  $31.84^\circ$  and  $33.41^\circ$ . While in the same synthesis route with kaolin as starting material produce Na-X zeolite in sample K-CA48. The diffractogram

showed the characteristic of Na-X zeolite peaks at 6.12, 10.0, 11.7, 12.2, 15.4, 18.4, 23.3, 26.6, 30.3, 30.9, 31.9, 33.6, 37.3, 40.7<sup>o</sup>, but with the trace of kaolinite peak at 21.35, 35.03, and 45.5<sup>o</sup>.

The next synthesis was carried out by alkaline fusion method with the optimum hydrothermal conditions based on the previous results. Diffractogram of sample K-AF24 showed the characteristic peaks of Na-X zeolite at 6.22, 10.05, 12.2, 15.52, 18.47, 20.23, 22.57, 23.41, 25.74, 26.8, 29.49, 30.45, 31.22, and 32.14<sup>o</sup> with some Na-P1 zeolite peak at 12.45, 17.77, 21.72, 27.86, 30.81, and 46.16<sup>o</sup>. Sample K-AF48 diffractogram dominated by the characteristic of Na-P1 zeolite peaks at 12.45, 17.77, 21.67, 28.14, 30.83, 33.39, 35.65, 38.08, 44.16, 46.16<sup>o</sup>, and some Na-X zeolite peaks at 20.53, and 25.49<sup>o</sup>. While the diffractogram of M-AF1 sample showed some Na-X zeolite peaks at 2 $\theta$  around 26.57<sup>o</sup> and 30.87<sup>o</sup>, and many Na-A zeolite characteristic peaks at 2 $\theta$  about 10.10<sup>o</sup>, 12.39<sup>o</sup>, 16.05<sup>o</sup>, 21.65<sup>o</sup>, 23.98<sup>o</sup>, 27.10<sup>o</sup>, 29.90<sup>o</sup> and 34.15<sup>o</sup>. The synthesis routes with conventional fluoride pre-treatment (sample K-CF24, K-CF48, and M-CF1) showed similar diffractograms pattern. The peaks at 2 $\theta$  around 12.4, 25.07, and 38.9<sup>o</sup> are the characteristic peaks of kaolinite. This result indicates that fluoride medium is not good enough to activate kaolin/dealuminated metakaolin, so the zeolite formation did not occur.

The FTIR spectra of the products are depicted in Fig 4. A sharp band at 914 cm<sup>-1</sup> with a shoulder band at 937 cm<sup>-1</sup> is the vibration of Al-O band, while the vibration of Si-O-Al band appears as a wideband at 538, medium bands at 752 and 788 cm<sup>-1</sup>. M-CA1 showed spectra with bands at 468, 542, 673, 696, 752, 1006, 1112 cm<sup>-1</sup>. The band at 468 cm<sup>-1</sup> is indicated as the vibration of T-O-T ((T=Si or Al) band (Chen *et al.*, (2012), the band at 538 is indicate as six-ring(D6R), the sub-unit of zeolite framework which appears at around 543 cm<sup>-1</sup>, while bands at 673, 696, and 752 cm<sup>-1</sup> indicated as the characteristic bands of Na-X zeolite which usually appears around 650-750 cm<sup>-1</sup> (Flanigen, 2010). All samples showed the presence of zeolite crystalline phase, which indicated by the D6R bands at about 572 and 599cm<sup>-1</sup>. Spectra K-CA48 showed bending vibration of internal tetrahedral TO<sub>4</sub> bands at 432.05 and 468 cm<sup>-1</sup>. Symmetric stretching of TO external tetrahedral TO<sub>4</sub> appears at 736 cm<sup>-1</sup>, while

asymmetric stretching of Si-O internal tetrahedral TO<sub>4</sub> appears as wideband at around 1100 cm<sup>-1</sup>. The bands of asymmetric stretching of external tetrahedral TO<sub>4</sub> appears at around 1112 cm<sup>-1</sup>. FTIR spectra of M-CA24 showed the bending vibration of T-O-T appears at around 457 cm<sup>-1</sup>, the D6R band appears at 555 cm<sup>-1</sup>, while the characteristic of Na-X zeolite bands appears at 694 and 752 cm<sup>-1</sup>.



**Figure 3.** XRD Pattern of Samples (a=Na-A, p=Na-P1, x=Na-X, k = kaolin)

Spectra of sample M-CF1 showed bands at 569, 682, 856, and 995 cm<sup>-1</sup>. The band at 682 cm<sup>-1</sup> is identified as symmetric stretching, while asymmetric stretching appears at 995 cm<sup>-1</sup>. The D6R band appears at 569 cm<sup>-1</sup>. Sample K-AF24 spectra showed bands at 426 cm<sup>-1</sup> which indicated as bending vibration of internal tetrahedral TO<sub>4</sub>. The D6R bands appear at 611 and 590 cm<sup>-1</sup>. Symmetric stretching of TO external tetrahedral TO<sub>4</sub> appears at 740.67 cm<sup>-1</sup>, while asymmetric

stretching of Si-O internal tetrahedral  $TO_4$  appears as wideband at around  $1100\text{ cm}^{-1}$ . M-CF1 showed the vibration of asymmetric stretching bands at  $914$  and  $1033\text{ cm}^{-1}$ , vibration of symmetric stretching appears at  $696\text{ cm}^{-1}$ , and bending vibration appears at  $468\text{ cm}^{-1}$ . K-KF24 showed similar spectra with sample K-KA24, there are sharp bands at  $468$ ,  $694$ , and  $1112$ , and also the wider band at  $1029\text{ cm}^{-1}$ . A sharp band at  $914$  with a shoulder band at  $937\text{ cm}^{-1}$  is a vibration of Al-O while vibration of Si-O-Al appears as wide band at  $538$ , medium band at  $752$  and  $788\text{ cm}^{-1}$ . These spectra are identical with the spectra of kaolin.

Surface morphology, crystal form, and composition analysis by SEM-EDX were done to sample M-CA1, K-CA48, K-AF24, and M-CA24 which confirmed contain Na-X zeolite. Micrograph of M-CA1, K-CA48, K-AF24, and M-CA24 is depicted in Fig 5. The result of SEM-EDX sample M-CA1 in Fig 5 (A) showed that zeolite has octahedral and cubic form. The octahedral crystal is the crystal of Na-X zeolite (Belviso *et al.*, 2013), while the cubic crystal is the crystal of Na-A zeolite (Ayele *et al.*, 2016). The SEM image of K-AF24 (B) showed well defined octahedral crystal of Na-X zeolite, the cotton ball form is the crystal of Na-P1 zeolite. SEM image of K-CA48 (C) also showed the existence of Na-X zeolite octahedral crystals, Na-P1 zeolite cotton ball crystals, and irregular sheets which is the trace of unreacted kaolin. M-CA24 showed well defined octahedral crystal of Na-X zeolite.

The results of EDX analysis were summarized in Table 3. The result showed the composition of Si, Al, O, and Na atoms in synthesized samples. Based on the result, the Si/Al mole ratio of M-CA1 is 1.11, M-CA24 is 1.37, while K-CA48 is 1.13, and K-AF24 is 1.67. This result is suitable with the Si/Al mole ratio of Na-X zeolite about  $1.00 - 1.50$  (Tanaka and Fuji, 2009). Sample K-AF24 has a mole ratio of Si/Al more than 1.5 because besides from Na-X zeolite, the sample is also contained Na-P1 zeolite which has a higher Si/Al mole ratio.

The surface area, volume, and pore size distribution of synthesized Na-X zeolite were analyzed by  $N_2$  isothermic adsorption/desorption. The analyzed samples were the samples with the best result: M-CA1, K-AF24 and M-CA80. The result of the analysis is depicted in Fig. 6, the graphic showed the typical isotherm graphic of type I because

there is sharp adsorption increased at low relative pressure. From the collected and analyzed data, the BET surface area is  $361.2194\text{ m}^2/\text{g}$ , with total volume of  $0.1877\text{ cm}^3/\text{g}$ , and average pore diameter is  $2.0787\text{ nm}$ . Based on analysis by BJH method, pore size is about  $4.9\text{ nm}$ , while pore size distribution analyzed by Horvath-Kawazoe (HK) is  $0.594\text{ nm}$ . K-AF24 have BET surface area is  $195.5949\text{ m}^2/\text{g}$ . The graphic is identical with isotherm graphic type IV because there is hysteresis at relative pressure  $0.8-1.0$  which indicate the existence of mesopores (Sing, 1984).

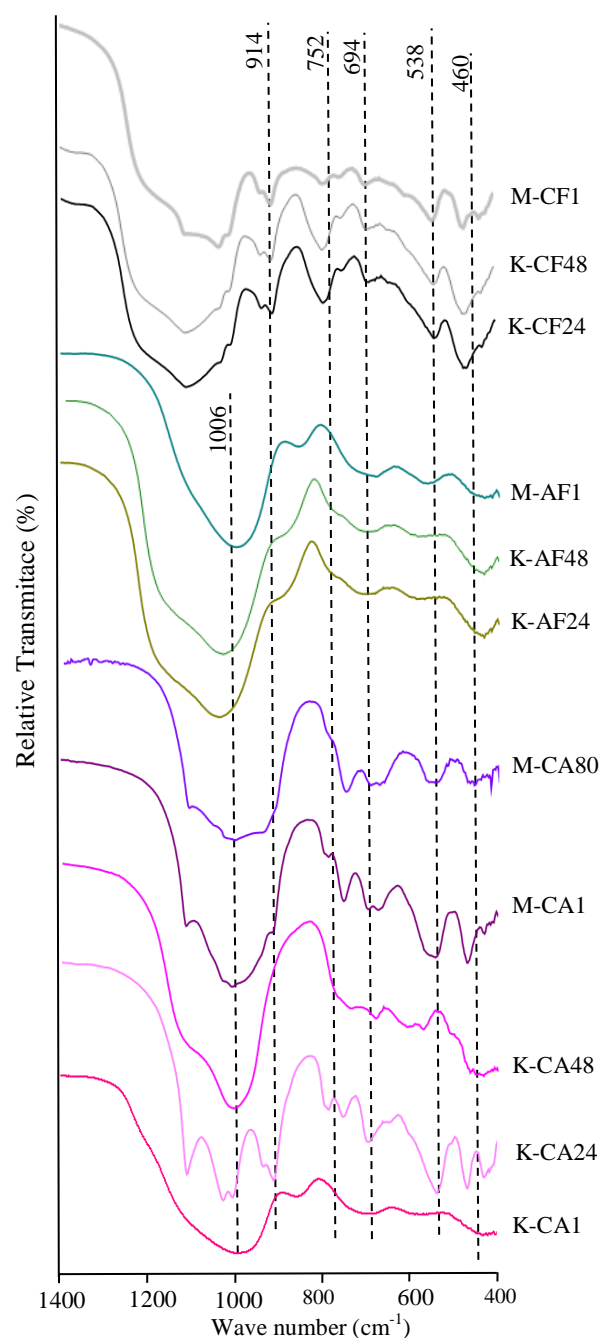
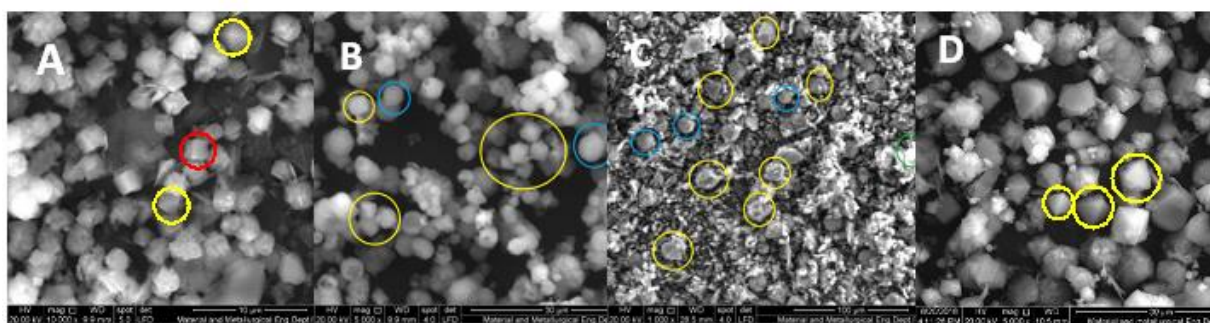


Figure 4. FTIR spectra of samples

**Table 2.** Table variation of zeolite synthesis routes and the product

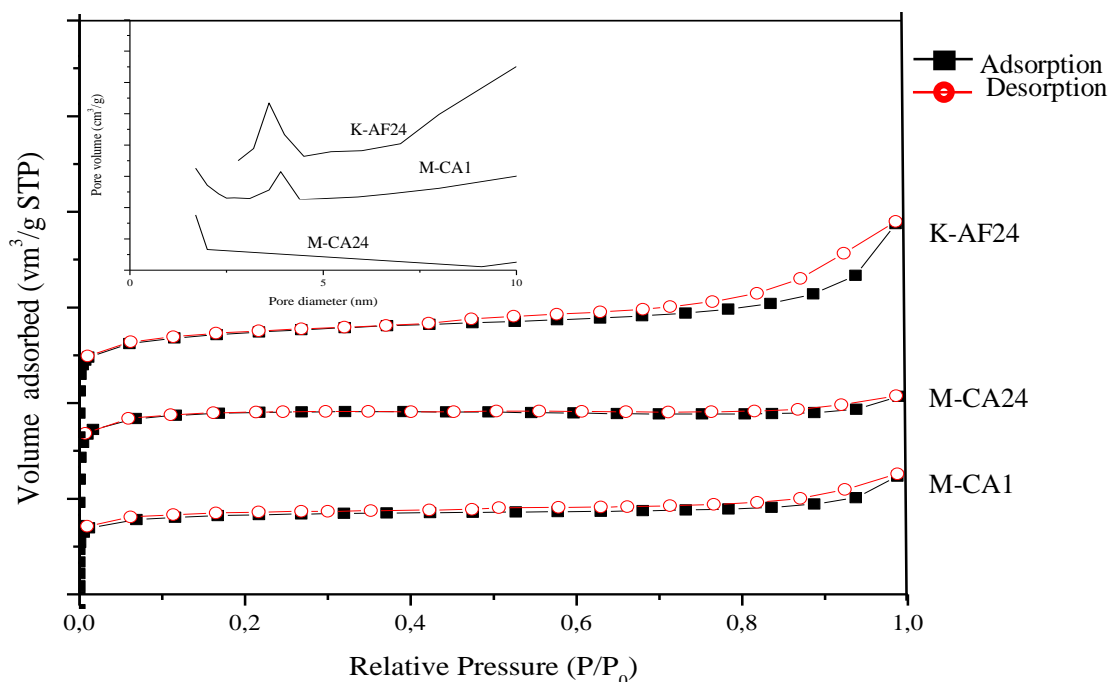
Starting Material	Pretreatment	Hydrothermal				Result
		40°(6h)- 60°(6h)- 80°(12h)	100°(24h)	100°(48h)	80°(24h)	
Kaolin	Conventional alkaline	K-CA1	K-CA24	K-CA48		Amorphous Kaolin Na-X + Na-P1 + kaolin
	Alkaline fusion		K-AF24	K-AF48		Na-X + Na-P1 Na-P1
	Conventional fluoride		K-CF24	K-CF48		Kaolin Kaolin
	Conventional alkaline	M-CA1			M-CA24	Na-X + Na-A Na-X
	Alkaline fusion	M-AF1				Na-X + Na-A
Metakaolin	Conventional fluoride	M-CF1				Kaolin

**Figure 5.** SEM images of A) M-CA1, B) K-AF24, C) K-CA48, D) M-CA24 (yellow: Na-X zeolite , Red: Na-A zeolite, Blue: Na-P1zeolite)**Table 3.** The result of EDX analysis

Sample	% Mass				Si/Al ratio
	Si	Al	O	Na	
M-CA1	27.61	23.92	41.72	06.76	1.11
K-CA48	25.96	31.47	47.12	02.63	1.13
K-AF24	20.17	11.12	44.62	09.29	1.67
M-CA24	29.01	20.50	37.04	13.45	1.37

**Table 4.** The result of N<sub>2</sub> isotherm adsorption/desorption analysis

Sample	Si/Al Ratio	S <sub>BET</sub> (m <sup>2</sup> /g)	S <sub>external</sub> (m <sup>2</sup> /g)	V <sub>micropore</sub> (cm <sup>3</sup> /g)	V <sub>total</sub> (cm <sup>3</sup> /g)	D <sub>BJH</sub> (nm)	D <sub>HK</sub> (nm)
K-AF24	1.67	195.5949	27.0469	0.0849	0.1321	3.6	0.619
M-CA1	1.11	185.5938	10.8674	0.0887	0.1061	3.9	0.763
M-CA24	1.37	361.2194	10.7968	0.1777	0.1877	4.9	0.594



**Figure 6.** N<sub>2</sub> isotherm adsorption/desorption and pore distribution curves

Further analysis was done by HK method. The result of the data analysis showed that micropore diameter is 0.619 nm with volume 0.0630 cm<sup>3</sup>/g. Pore distribution value analyzed by BJH is 3.4–3.8 nm, average diameter of 3.6 nm with volume 0.0401 cm<sup>3</sup>/g. Sample M-CA1 is also showed the characteristic of isotherm graphic type 1, which is the characteristic curve of micropore materials (Condon, 2006). This result is supported by the mathematic analysis shown in Table 4. The BET surface area is 185.5938 m<sup>2</sup>/g, with total volume 0.106049 cm<sup>3</sup>/g and average pore diameter 2.28561 nm, analyzed by BET. While based on BJH analysis, pore size distribution is about 3.9 nm. Horvath-Kawazoe (HK) analysis showed the micropore diameter is 0.7638 nm.

#### 4. CONCLUSION

Based on the result of this research, it can be concluded that calcination (thermal activation) process give great impact in the Na-X zeolite crystallization. Synthesis directly from kaolin with hydrothermal conditions: 40°C(6h)-60°C(6h)-80°C(12h) were produce amorphous phase of aluminosilicate, while in the same synthesis routes with metakaolin as starting material were successfully produced Na-X zeolite although with Na-A zeolite as a mixture. Synthesis with kaolin as starting material need higher hydrothermal temperature (100 °C) to produce Na-X zeolite. Pre-

treatment by conventional fluoride couldn't produce Na-X zeolite. The optimum condition for pure Na-X zeolite synthesis is from metakaolin, by conventional alkaline pre-treatment method, and hydrothermal conditions: 80 °C for 24 hours (M-CA24).

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