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Transformation of Indonesian Natural Zeolite into Analcime Phase under Hydrothermal Condition

W W Lestari,^{1*} D N Hasanah,¹ R Putra,^{1,2} R R Mukti,³ K D Nugrahaningtyas¹

¹Research Group of Porous Materials for Sustainability, Chemistry Department, Faculty of Mathematics and Natural Sciences, Sebelas Maret University, Jl. Ir. Sutami No. 36A, Kentingan, Jebres Surakarta, 57126, Indonesia.

²Master of Chemistry Program, Graduate School, Sebelas Maret University, Jl. Ir. Sutami No. 36A, Kentingan, Jebres Surakarta, 57126, Indonesia.

³The Division of Inorganic Physical Chemistry, Faculty of Mathematics and Natural Sciences, Institute Technology Bandung, Jl. Ganesha No.10 Bandung, 40132, Indonesia.

*Corresponding Author. Email: witri@mipa.uns.ac.id

Abstract. Natural zeolite is abundantly available in Indonesia and well distributed especially in the volcano area like Java, Sumatera, and Sulawesi. So far, natural zeolite from Klaten, Central Java is one of the most interesting zeolites has been widely studied. This research aims to know the effect of seed-assisted synthesis under a hydrothermal condition at 120 °C for 24 hours of Klaten's zeolite toward the structural change and phase transformation of the original structure. According to XRD and XRF analysis, seed-assisted synthesis through the addition of aluminosilicate mother solution has transformed Klaten's zeolite which contains (mordenite and clinoptilolite) into analcime type with decreasing Si/Al ratio from 4.51 into 1.38. Morphological analysis using SEM showed the shape changes from irregular into spherical looks like takraw ball in the range of 0.3 to 0.7 micrometer. Based on FTIR data, structure of TO₄ site (T = Si or Al) was observed in the range of 300-1300 cm⁻¹ and the occupancy of Brønsted acid site as OH stretching band from silanol groups was detected at 3440-3650 cm⁻¹. Nitrogen adsorption-desorption analysis confirmed that transformation Klaten's zeolite into analcime type has decreased the surface area from 55.41 to 22.89 m²/g and showed inhomogeneous pore distribution which can be classified as micro-mesoporous aluminosilicate materials.

1. Introduction

Natural zeolites in Indonesia are spread out over several large islands, especially those with volcanic areas, such as Java, Sumatera and Sulawesi with the main phase content of mordenite (ca. 60-70%) and the rest are clinoptilolites and amorphous quartz [1–4]. Zeolite is divided into hundreds of topology types [5], one type of zeolite topology, mordenite, that is often used as a catalyst in the industrial world [6]. It can be used as a catalyst in cracking reaction, isomerization [6] and combinations of hydrogenation cracking reaction [2,3]. Natural zeolite from Klaten, Central Java contain mordenite and clinoptilolite with Si/Al ratio of 4.96 [7]. However, the existence of clinoptilolite and other impurities obtained in Klaten's natural zeolite need to be purified such as through dealumination or acid activation.



Another way to an obtained pure phase of zeolite might be carried out by phase transformation or through seed-assisted synthesis.

The activation process could be conducted via physically and chemically treatments [8]. The physical activation process is carried out by heating (calcination) to evaporate water trapped in zeolite pores so that the amount of pore and its specific surface area increases. Chemical activation can be proceed by employing hydrochloric acid, sulfuric acid, hydro-fluoride acid, and nitric acid solution to purify the pore surface, remove the impurities and re-arrange the exchangeable atoms [9]. Additionally, activation can also be performed by ammonium chloride or ammonium nitrate addition as an advanced process after catalytic treatments aimed for cation exchange [10]. These activation processes can improve purity and crystallinity of mordenite. However, based on Material Safety Data Sheet (MSDS) [11] strong acids like HF and HCl are corrosive, so better when it is avoided.

Another method possibly be used to improve the purity of mordenite is the seed-assisted synthesis. This method is more effective and environmentally friendly. The process of transformation of natural materials through hydrothermal synthesis by employing natural minerals as seed in the aluminosilicate parent solution was conducted by Mukti *et al.* [12]. This hydrothermal seed-assisted synthesis method has proven to transform natural minerals instead of zeolite into mordenite-type zeolite with high crystallinity [12]. This method was also successfully performed by Mignoni *et al.* [13] which transforms kaolin material into mordenite.

Transformation of natural mineral, like kaoline zeolite into a specific phase of zeolite currently become an interest. This transformation has spurred many researchers towards improving the quality of natural zeolites, synthesizing novel zeolites, and employing them in new applications. Analcime is a type of zeolite which abundantly available in nature. In a recent report, Sandoval *et al.* [14] synthesized of zeotype ANA framework by a hydrothermal reaction using natural clinker as starting material. Other type of ANA was also synthesized by Atta *et al.* [15] using a hydrothermal technique using rice husk ash and meta-kaolin as sources of silica and alumina with optimal condition sodium hydroxide ($\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 2.6$) after aging for 3 days and reaction time of 24 h at temperature of 180 °C. A successful synthesis of analcime was also reported by Hsiao *et al.* [16] under microwave-assisted hydrothermal route with commercial mica powders, composed of sericite and pyrophyllite, were treated by Na_2SiO_3 as the mineralizer. Herein, we report for the first time the transformation of natural zeolite (NZ) from Klaten into analcime phase via seed-assisted synthesis under the hydrothermal condition.

2. Experimental Section

2.1. Materials

NZ was obtained from Katen, Central Java (particle size 170/240 mesh), Tetraethylorthosilicate (TEOS, 99%), Aluminium Hydroxide [$\text{Al}(\text{OH})_3$] (98%), Natrium Hydroxide (NaOH, 99%) were provided from Merck, Germany and aquadest (Bratachem, Indonesia). All reagents were used as purchased without any further purification.

2.2. Preparation of Mother Solution and Hydrothermal Reaction

The mother solution was prepared according to modified literature procedure published by Kim *et al.* [17]. NaOH (1.52 g, 38 mmol) was dissolved in 3.2 mL aquadest. Into this solution $\text{Al}(\text{OH})_3$ (0.57 g, 7.3 mmol), aquadest (25.78 mL) and TEOS (3.93 g, 18.89 mmol) were carefully added. The mixture was then stirred for 30 minutes. The obtained mother solution was called as Z-1 (without seed-assisted). As variation, all reagent was measured in the same composition, but the addition of TEOS was modified (5 g, 24 mmol) then the sample was called as Z-2 and Z-3. In each Z-2 and Z-3 were added 1.62 g Klaten's natural zeolite (NZ) as seed.

Sample Z-1 and Z-2 were placed into an autoclave (50 mL) and continued with reaction under a hydrothermal condition at temperature 170 °C for 24 h in an Oven Memmert UN30. The obtained gels were filtered and washed with aquadest until a white precipitate was detected, then dried at room

temperature for 24 h and continued with drying at 120 °C for 6 h. The variation of hydrothermal reaction was also conducted at 120 °C for 24 h according to the procedure reported by Azizi *et al.* [18] dried at room temperature for 24 h and continued heated at 80 °C for 10 h. The obtained sample was notified as Z-3.

2.3. Materials Characterization

XRD diffractograms were obtained from Rigaku miniflex 600 dan X-ray Diffraction Philip type X'Pert MPD using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) to confirm the expected structure, phase purity and the crystallinity of the obtained materials. Elemental composition and Si/Al ratio of the materials were recorded using X-ray Fluorescence Spectrometry BRUKER S2 Ranger. Morphological analysis was observed using Scanning Electron Microscopy (SEM) FEI type Inspect S50. To determine the surface area, porosity dan pore size distribution analysis were conducted in liquid N₂ at 77.3 K using an Autosorb-iQ (Quantachrome Co., USA). FTIR analysis using Shimadzu IR Prestige-21 using the KBr technique in the range 4000–400 cm⁻¹ were performed to assign the functional groups found in the materials.

3. Results and Discussion

3.1. Materials characterization

X-Ray diffractogram of Z-1, Z-2 and Z-3 are presented in Figure 1. Seed-assisted synthesis of Z-2 and Z-3 resulted dominant diffraction peaks in high suitability with characteristic for analcime phase (ANA) at $2\theta = 15.79^\circ$ (211), 25.93° (400) and 30.51° (322) with parameter structure of symmetry of space group P-1 ANA, crystal system: triclinic, lattice parameter: $a = 13.1605$, $b = 13.0149$, and $c = 13.0335 \text{ \AA}$, angle between axis: $\alpha = 90.178^\circ$ $\beta = 86.849^\circ$ $\gamma = 88.601^\circ$ according to ICSD #156598. Affording to the database of zeolite structures (IZA) [19] the framework of ANA having a $19.2 \text{ T/1000 \AA}^3$ density greater than the MOR with a density of $17 \text{ T/1000 \AA}^3$, so that the zeolite structure changes from the MOR topology to ANA is acceptable. Moreover, the excessive presence of aluminum causes the distance adjacent so as to increase the density of the framework [3]. In contrast, hydrothermal synthesis (with the same parameter condition) but without the addition of natural zeolite as a seed (Z-1) showed unidentified phase as shown in XRD analysis (Figure 1).

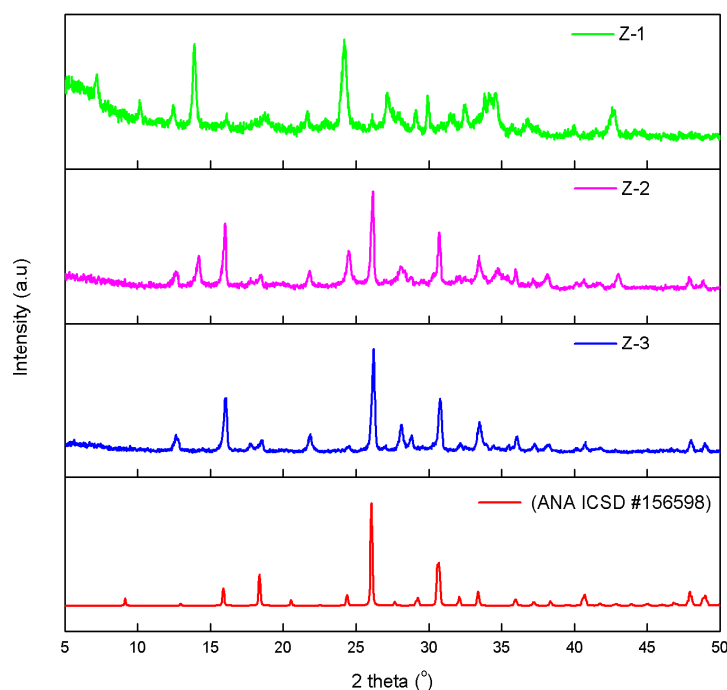


Figure 1. Diffractogram of Z-1, Z-2 and Z-3 in comparison with analcime standard pattern

Metal oxide contents and Si/Al ratio of NZ, Z-2 and Z-3 were observed using XRF spectroscopy and listed in Table 1. NZ itself has Si/Al ratio of about 4.51, it was transformed into Z-3 (in analcime phase) with Si/Al ratio 1.38, while Z-2 has Si/Al ratio 1.11.

Tabel 1. Metal oxides content and Si/Al ratio of NZ transformed into Z-2 and Z-3

Element	Concentration		
	NZ	Z-2	Z-3
SiO ₂	71.43%	38.01%	45.80%
Al ₂ O ₃	12.84%	30.20%	22.88%
CaO	5.53%	2.45%	4.57%
Fe ₂ O ₃	4.34%	1.30%	2.28%
MgO	1.82%	-	-
K ₂ O	1.64%	0.36%	0.81%
MnO	0.07%	0.03%	0.04%
	Si/Al = 4.51	Si/Al = 1.11	Si/Al = 1.38

The surface morphological analysis using SEM shows that NZ has a totally different image from Z-1 and Z-3 after hydrothermal treatment (Figure 2). NZ has bigger size and irregular shape, while Z-1 appear as cleaner plaque or looks like a rectangular thin sheet, Z-3 present as a spherical-looks like a takraw ball in the range of 0.3 to 0.7 micrometer with a unflat surface.

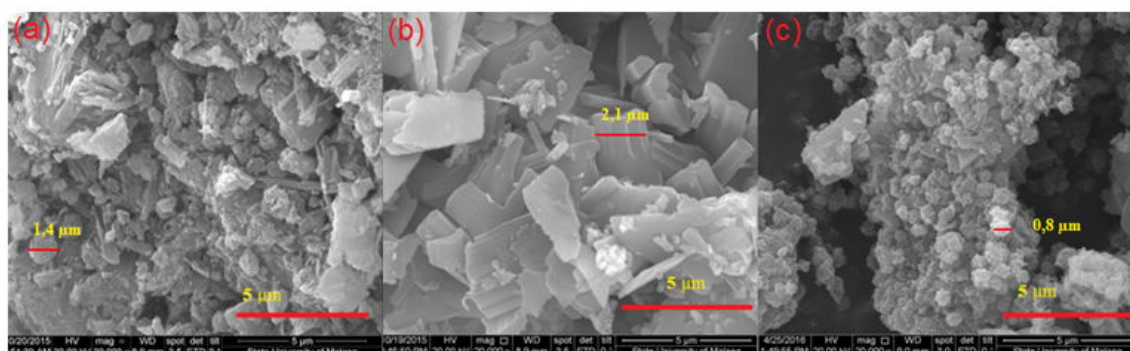


Figure 2. SEM image of NZ (a), Z-1 (b) and Z-3 (c) at magnification of 20,000x

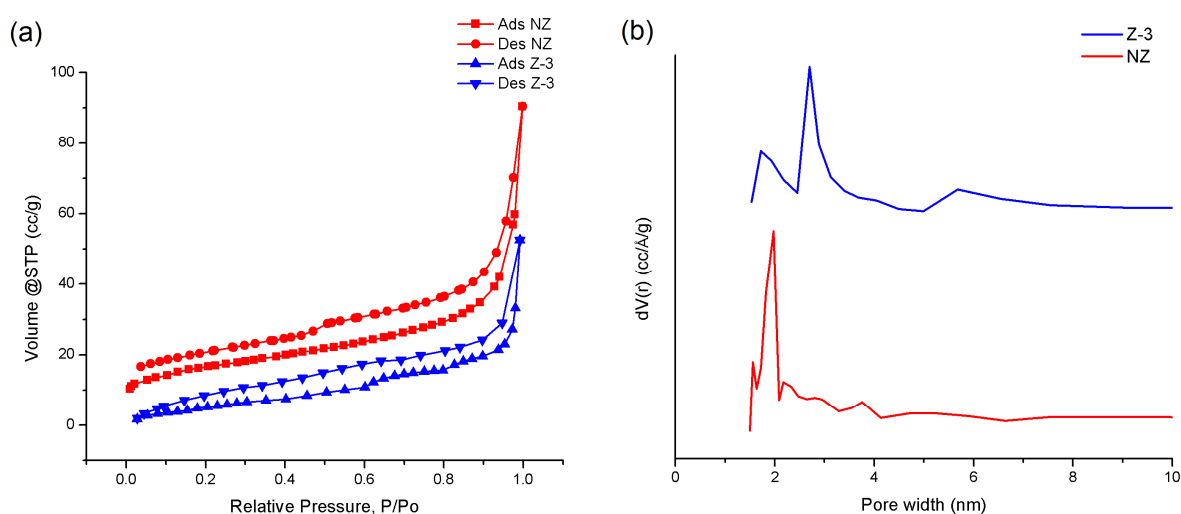


Figure 3. Nitrogen adsorption-desorption isotherm (a) and pore size distributions (b)

NZ exhibited type I adsorption isotherm typical of microporous materials with H4 type hysteresis loop and synthesized ANA phase (Z-3) exhibited type IV adsorption isotherm typical of mesoporous materials (figure 3(a)). This data is confirmed from BJH desorption branch result as shown in figure 3 (b) and proved that the materials are classified as crystalline micro-mesoporous (2-50 nm) aluminosilicate materials. The transformation of NZ into ANA (Z-3) lead to decrease BET surface area and pore volume total up to 22.888 m²/g and 0.08134 cc/g as shown in Table 2.

Table 2. Surface area and porosity of NZ and Z-3

Materials	BET surface area (m ² /g)	Volume total pore (cc/g)	Average pore size (Å)
NZ	55.413	0.09249	33.3815
Z-3	22.888	0.08134	71.0794

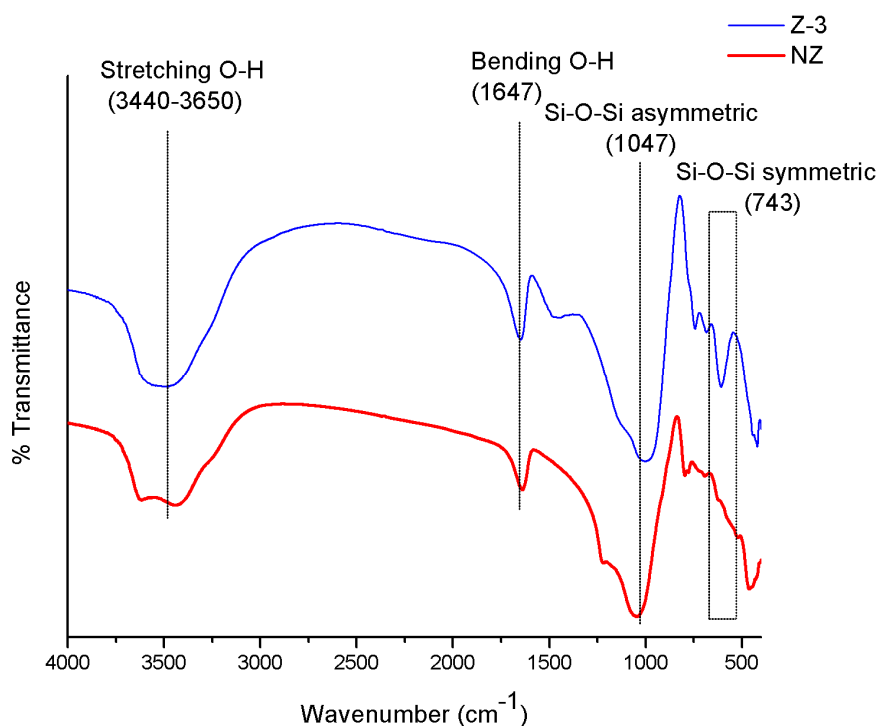


Figure 4. FTIR spectra of NZ and Z-3

There is no significant shift observed in FTIR spectra (Figure 4) of both materials, NZ and Z-3. The absorption spectra corresponding to the synthesized analcime obtained in this study are similar to previous results reported by Sandoval *et al.* and Atta *et al.* [14,15]. However, the present of absorption band at 743 cm⁻¹ which is characteristic of symmetric stretching of Si-O-Si for the Z-3 sample has appeared indicated that synthesizing analcime is in a good agreement with the aluminosilicate materials. Furthermore, these spectra indicated that transformation of NZ into ANA phase (Z-3) under hydrothermal condition does not affect the change of functional group in zeolitic structure, although the frameworks are changed as confirmed previously by XRD data (Figure 1). Peaks in the range of 300-1300 cm⁻¹ corresponded the frame vibration (T-O-T unit; where T is SiO₄ and AlO₄ tetrahedron) which is characteristic of aluminosilicate compounds such as zeolites. OH-groups as bridging unit (such as ≡Al(OH)Si≡ groups with Brønsted acidic character) give bands in the fundamental stretching region at

about 3440-3650 cm^{-1} (free bridging OH-groups) which are responsible for important catalytic properties of the hydrogen forms of zeolites. Furthermore, the fundamental vibrations of bending OH-groups are approximately observed at 1600 cm^{-1} . Detail absorption peak and its assignment are presented in Table 3.

Tabel 3. Interpretation of IR Spectra of NZ and Z-3

Interval Wavenumber (cm^{-1})	NZ (cm^{-1})	Z-3 (cm^{-1})	Interpretation of vibration types
3400-3700	3444.05	3498.06	Stretching O-H
1600-1850	1639.56	1647.28	Bending O-H
950-1250	1047.39	1002.06	Asymmetric Si-O-Si
750-820	796.64	743.59	External symmetric O-Si-O/Al-O-Al
650-720	692.47	683.79	Internal symmetric O-Si-O/Al-O-Al
420-500	461.01	441.72	Bending Si-O/Al-O
300-420	446.54	420.50	Pore opening

4. Conclusions and Outlook

Seed-assisted synthesis of NZ under a hydrothermal condition at 120 °C for 24 h was successfully transformed the NZ which contain MOR and HEU phase into ANA (Z-3). This phenomenon totally changes the Si/Al ratio of the obtained material up to 1.38 and the morphology turns from irregular shape into a spherical-looks like a takraw ball. Purification of NZ into MOR or transformation into other type of zeolite such as ZSM-5 would be an interesting further investigation by reducing the $\text{Al}(\text{OH})_3$ composition in mother solution or increasing the NaOH concentration. Moreover, further study about the application of the obtained ANA phase in this work for environmental or catalytic application is currently on progress in our group.

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