Effect of Temperature Synthesis on Structural Behaviours of NaY Zeolite Using Local Sand as A Silica Source

Sumari Sumari, Fauziatul Fajaroh, Yahmin, Ni’matus sholihah, Aman Santoso, Agus Budianto
1 Chemistry Department, Faculty of Mathematics and Science, State University of Malang, Jl. Semarang No.5 Malang 65145, Indonesia
2 Chemical Engineering Department, Faculty of Technology, Surabaya Institute of Adhi Tama Technology, Jalan Arief Rachman Hakim No. 100 Surabaya 60117, Indonesia

*Corresponding author’s email: sumari.fmipa@um.ac.id

Abstract. The purpose of this study was to synthesize NaY zeolite by utilizing local sand as a source of silica which was carried out at various crystallization temperatures. The synthesis of NaY zeolite is carried out using silica resulted from the purification of local sand while NaOH and Al2O3 are pure analysis (pa) quality. Crystallization temperature was carried out at various temperatures of 80, 100, and 150 °C. The synthesis results were characterized by physical properties, XRF, FTIR, XRD, SEM, surface area. NaY zeolite was successfully synthesized supported by FTIR data by the presence of functional groups such as Si–O, O–Al–O, Si–OH, and O–H from Si–OH, and SEM data which showed the formation of cube-shaped crystals. The formation of NaY zeolite is also strengthened by the appearance of peaks with a sharp intensity from XRD diffractogram that this zeolite is NaY and as well as data molar ratio of Si/Al is in the range of 2.027 to 2.045 respectively at various crystallization temperature. The crystallization temperature of 80 °C produces NaY zeolite better than that of crystallization temperatures of 100 and 150 °C. The synthesized NaY zeolites using local sand have a good surface area that is 658 m²/g. The crystallization temperature affects the success of NaY zeolite synthesis.

Keywords: Temperature synthesis, crystallization, NaY zeolite, silica.

1. Introduction
Zeolite is a three-dimensional open crystalline aluminosilicate micropore material composed of [SiO4]4− and [AlO4]3− tetrahedral and connected by four oxygen atoms to form an open three-dimensional framework containing canals and cavities, inside which are filled by metal ions, generally are alkali or alkaline earth metals and water molecules that can move freely [1,2]. The research on NaY zeolite NaY zeolite research is being promoted because it is widely used in industrial field such as Cr3+, Ni2+, Zn2+, Cu2+, and Cd2+ by adsorption on wastewater from the electroplating process and water purification [3,4]. Based on these facts, it can be said that zeolite Y plays a role in reducing environmental impacts, especially wastewater.
According to previous work [5][5], Zeolite Y belongs to Faujasite type (FAU) zeolite [6] which has a Si/Al ratio > 1.5 and is widely used as an FCC (Fluid Catalytic Cracking) because it has high thermal stability, acidity, and crystallinity [7]. The diameter of the zeolite Y particles is known to be around 50 –125 μm [8]. There are several forms of zeolite Y based on their cations exchange such as NaY zeolite and CaY zeolite. NaY zeolite is a three-dimensional porous compound with an exchange cation in the form of Na⁺ ion [9].

Synthetic NaY zeolite has been widely produced in the industry today, but this zeolite is expensive because it is commonly synthesized using an organic template as a driving agent [10]. There are several previous studies related to the synthesis of NaY zeolite, but they used raw materials of pure substances [5]. Therefore, it is necessary to look for other alternatives in the synthesis of NaY zeolite by using the cheaper materials. Silica is known to be one of the main components of zeolite in addition to the element of Aluminum. The small amount of silica determines the type of zeolite to be obtained. A high silica content has an impact on the high Si/Al ratio. The increase in the Si/Al ratio can improve the crystallinity and acidity of zeolite so that it has a better catalytic performance [9]. Therefore, the selection of natural silica sources needs to be considered because the higher the silica content used, the higher the quality of the zeolite catalyst can be synthesized.

The synthesis of NaY zeolite from natural silica sources has been reported. Bolivian diatomite rocks were used for the synthesis of NaY zeolite because they contain high silica. However, the study has several weaknesses such as the diatomite rocks used still contain impurities. In addition, in terms of the quality of zeolite products zeolite of P is formed due to heating of NaY zeolite at higher temperatures [11]. The bagasse ash is also used as a source of natural silica for the synthesis of NaY zeolite by the sol-gel method [12]. However, the synthesis of non-template Y Zeolite has the disadvantage that is still found P zeolite impurity. Another factor that also influences the purity of zeolite is the crystallization temperature. The zeolite of P is generally formed after the formation of NaY zeolite at a higher temperature [13]. In addition, the effort that can be done to overcome the presence of zeolite P impurities is to use natural sources with higher silica content [8]. Therefore, synthesis of NaY zeolite is carried out by utilizing silica produced from local sand and it is conducted at various temperatures to find the effect of temperature on the purity of NaY zeolite.

2. Methods

The materials used in this study were silica purified from local sand, HCl solution (pa, Merck), NaOH solution (pa, Merck), Al₂O₃ (Sigma-Aldrich), solid H₂C₂O₄ pa (Sigma-Aldrich), pp indicators, universal pH indicators (Merck), methylene blue (Sigma-Aldrich), and demineralized water.

2.1 Synthesis of NaY zeolite

The free template in synthesis of NaY zeolite used a procedure that has been reported by Belaabed [1]. NaY zeolite was synthesized with a molar composition of 58 NaOH: 58 Al(OH)₃:134 H₂O. The synthesis was started by weighing 2.0237 g of SiO₂ according to its molars composition, then dissolved in 40.5 mL of 2 N NaOH (aq) and stirred for 30 minutes until obtaining a homogeneous solution of sodium silicate. Sodium aluminate is made by weighing 2.262 g of Al(OH)₃, and dissolved in 58 mL of 7 N NaOH then refluxed until dissolved. Sodium silicate and sodium aluminate were mixed and homogenized for 30 minutes with a magnetic stirrer. The mixture obtained was then left to stand for 24 hours at room temperature. Then the mixture was put in a reactor temperature of 100 °C for 12 hours. Then filtered and the residue was washed with demineralized water. The residue was then dried for 24 hours at 80 °C to form NaY zeolite. The procedure was repeated at various crystallization temperature in the reactor temperature of 80 and 150 °C.

2.2 Characterizations

The synthesis results which were suspected of NaY zeolite were characterized through physical properties, elemental composition using the XRF (MiniPal 4), functional groups using FTIR (Shimadzu IR-prestige 21), zeolite structures using XRD (PANanalytical), surface morphology using SEM (FEI
Brand, type inspect S50), and determination of surface area by the methylene blue adsorption method using a visible spectrophotometer (spectronic-20, Genesys™) at a wavelength of 660 nm.

3 Results and Discussion

3.1 Characterization of NaY zeolite

The temperature of crystallization is one of the factors that influence the formation of NaY zeolite. This is because the NaY zeolite is formed at certain crystallization temperatures. If the heating is over the crystallization temperature of NaY then P zeolite will be formed as an impurity [14]. To find out the parameters of the success of the synthesis of NaY zeolite, one of them is conducting FTIR analysis of synthesized NaY zeolite. From the characterization using FTIR instruments can be known that there is a typical functional group present in NaY zeolite. The following is the result of the FTIR analysis for synthesized NaY zeolite in the variation of crystallization temperature as shown in Figure 1.

![FTIR analysis of NaY zeolite at various crystallization temperatures of 150, 100, and 80 °C](image)

Based on Figure 2, NaY zeolite at the crystallization temperatures of 150, 100, and 80 °C is known to have wavenumber absorption from a typical functional group of zeolite, i.e. at a wave number of 400 cm\(^{-1}\) indicating Si-O bending vibration of Si-O-Si, at 600 cm\(^{-1}\) wavenumber that indicates stretching vibration Si-O of Si-O-Si, at wavenumber of 700 cm\(^{-1}\) which indicates stretching vibration Si-O asymmetry of O-Si-O, at wavenumber of 1000 cm\(^{-1}\) which indicates O-Al-O asymmetry stretch vibration, at wave number 1600 cm\(^{-1}\) which indicates Si-OH bending vibration, and at wavenumber 3400 cm\(^{-1}\) which indicates OH stretch vibration from Si-OH [15]. Therefore, based on the functional group analysis it can be said that the synthesized zeolite is NaY for all variation of the crystallization temperatures of 150, 100, and 80 °C.

The parameter of the success on the synthesis of NaY zeolite was also carried out by conducting SEM characterization. SEM analysis aimed to determine the morphology and shape of the crystal. The results of SEM analysis on synthesized NaY zeolite samples are shown in Figure 3. Based on the results of SEM analysis, it can be seen that zeolite formed at the crystallization temperature of 150 °C appear granules with a cuboid-shaped surface that shows the formation of NaY zeolite. Crystal cube itself was a morphological form of Faujasite zeolite, specifically NaY zeolite [16]. However, the cube shape in NaY zeolite synthesized at the crystallization temperature of 150 °C has not revealed a single cube
shape. This is because at higher temperatures NaY zeolite would transform to another form so that the cube shape of NaY zeolite changes slightly to another zeolite [17]. The morphology of this zeolite was similar to NaY zeolite that has been synthesized by Ferchiche et al. [8]. Therefore, it can be said that NaY zeolite was successfully synthesized at the crystallization temperature of 150 °C. Then NaY zeolite synthesized at the crystallization temperature of 100 °C and 80 °C are shown in Figures 3 (b) and (c). These data show that more perfect NaY zeolite has been formed than that of crystallization temperature of 150 °C. In addition, at the crystallization temperature of 80 °C, the number of cube shape obtained was more than that of the 100 °C and 150 °C crystallization temperature.

Figure 2. NaY zeolite Morphology synthesized at crystallization temperatures of (a) 150 °C, (b) 100 °C, and (c) 80 °C

The success of the NaY zeolite synthesis can also be strengthened by the XRD characterization. This XRD analysis aims to determine crystallinity and the relative amount of NaY zeolite formed. The success of synthesizing NaY zeolite was carried out by matching the data 2θ and d-spacing of synthesized zeolite with 2θ and d-spacing data NaY zeolite reference on the JCPDS (Joint Committee for Powder Diffraction Standard). The following diffractogram is the result of XRD analysis of NaY zeolite types at several crystallization temperature variations as shown in Figure 4. The suitability of diffractogram peaks of synthesized NaY zeolite with 2θ data and d-spacing reference. The data 2θ of synthesized zeolite that similar to 2θ NaY reference data is shown by the Y alphabet.
Figure 3. Diffractogram of NaY zeolite in variations of crystallization temperatures of 150, 100, and 80 °C

There is a match of the 2θ and the spacing data of the synthesized NaY zeolite samples with the NaY zeolite reference data on JCPDS among others are 10.31; 12.10; 14.61; 19.01; 21.67; 21.98; 24.06; 27.52; 28.26; 30.16; 31.95; 33.03; 33.66; 34.69; 37.82; 46.61; 48.03, [18], [19]. It can be seen that NaY zeolite obtained at a crystallization temperature of 80 °C gives the most peaks of NaY zeolite compared with crystallization temperature of 150 and 100 °C. These data show that the formation of NaY zeolite by using silica from local sand optimally can occur at the temperature of 80 °C. While the smaller amount of NaY zeolite formed at the crystallization temperature of 100 °C and 150 °C. It is due to NaY zeolite being transformed into another zeolite namely zeolite of P. This type of zeolite is generally formed at higher temperatures [13,14].

The zeolite ratio of the Faujasite group especially NaY zeolite can be determined by calculating the Si/Al molar ratio from the XRF analysis data. It is known that NaY zeolite has a Si/Al ratio of more than 1.5 [7]. The following data are the results of the XRF analysis of synthesized zeolite at various crystallization temperature as shown in Table 1. Based on the XRF data in Table 1, it can be calculated the molar ratio of Si/Al in each type of NaY zeolite synthesized respectively as shown in Table 2.

| Table 1. Data of NaY zeolite analysis at several crystallization temperatures |
|-----------------------------|-----------------|-----------------|-----------------|
| **Element**                | **NaY zeolite-150 °C** | **NaY zeolite-100 °C** | **NaY zeolite-80 °C** |
| Al                         | 30.0            | 28.9            | 29.2            |
| Si                         | 63.0            | 61.3            | 61.9            |
| P                          | 2.0             | 1.90            | 2.10            |
| Ca                         | 2.1             | 5.76            | 5.10            |
| Sc                         | 0.03            |                |                |
| Cr                         | 0.17            | 0.17            | 0.16            |
| Fe                         | 0.62            | 1.36            | 1.14            |
| Ni                         | 0.08            | 0.06            | 0.05            |
| Cu                         | 0.21            | 0.20            | 0.21            |
| Zr                         | 1.80            |                |                |
| Mn                         | -               | 0.09            |                |
| Yb                         | -               | 0.20            | 0.20            |
Table 2. Molar ratio Si/Al of synthesized NaY zeolite at various crystallization temperatures

| Zeolite type       | Molar ratio Si/Al |
|--------------------|-------------------|
| NaY zeolite-150 °C | 2.027             |
| NaY zeolite-100 °C | 2.045             |
| NaY zeolite-80 °C  | 2.044             |

All types of synthesized NaY zeolites (Table 2) show that all three NaY zeolites which crystallization temperature carried out at 150, 100, and 80 °C have an almost equal molar ratio Si/Al of two. This shows that the variation in crystallization temperature does not have a large effect on the molar ratio Si/Al NaY zeolite. The Si/Al ratio is more influenced by the amount of reagent used [8]. According to the Si/Al ratio value shows that the synthesized zeolite is NaY zeolite. It is known that the Si/Al ratio for NaY zeolite is Si/Al 1.5-3 [20]. Therefore, this XRF analysis also strengthened the success of the NaY zeolite synthesis which varied the crystallization temperature. The surface area of NaY zeolite is determined by using adsorption of methylene blue method. The following data are the surface area of synthesized NaY zeolite at various crystallization temperatures of 150, 100, and 80 °C as shown in Table 3.

Table 3. Surface area of synthesized NaY zeolite at various crystallization temperatures

| Type of zeolite       | Surface area (m²/g) |
|-----------------------|---------------------|
| NaY zeolite-150 °C    | 638                 |
| NaY zeolite-100 °C    | 650                 |
| NaY zeolite-80 °C     | 658                 |

4 Conclusion

NaY zeolite synthesized from using local sand as a silica source has physical properties such as solid, smooth texture, and white color. NaY zeolite was successfully synthesized supported by FTIR data by the presence of functional groups such as Si-O, O-Al-O, Si-OH, and O-H from Si-OH, and SEM data which showed the formation of cube-shaped crystals. The formation of NaY zeolite is also strengthened by the appearance of peaks with sharp intensity from the XRD diffractogram that this zeolite is NaY and as well as data molar ratio of Si/Al is in the range of 2.027 to 2.045 respectively at various crystallization temperatures. The crystallization temperature has an effect on the results of producing of NaY zeolite. The crystallization temperature of 80 °C produces NaY zeolite better than that of crystallization temperature of 100 °C and 150 °C. The surface area of synthesized NaY zeolite using local sand is 658 m²/g approaching the surface area of NaY zeolite synthesized from pure analysis materials.

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