

Effect of Heating Method on Zeolite Synthesis

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Abstract: A study on the effect of oven and reflux heating on zeolite synthesis was carried out. Heating is part of the zeolite crystallization process, which is carried out for 1, 3, 5, and 7 days at a temperature of 110 °C. The synthesized zeolite was characterized using XRD and FTIR. Based on the analysis results obtained, the composition of zeolite consists of gibbsite, quartz, and faujasite. Gibbsite peaks appear at $2\theta = 18.29, 20.32, \text{ and } 37.6$; faujasite at $2\theta = 20.22, 26.84, \text{ and } 37.61$; meanwhile quartz at $2\theta = 26.72, 37.63, \text{ and } 44.18$. Based on the functional groups of the resulting product, the zeolite phase is formed on heating using an oven or reflux.

Keywords—zeolite, faujasite, gibbsite, quartz, oven heating, reflux heating.

1. INTRODUCTION

Zeolite is one of the natural resources that are very useful for the chemical industry in Indonesia. At this time, the use of zeolite minerals is increasing, from use in small industries to large-scale industries. In developed countries such as the United States, zeolite has been used in industry. Both natural zeolite and synthetic zeolite have high economic value. If the zeolite mineral is further processed, it can be utilized optimally. The use of zeolite minerals, in general, is as a CO₂ adsorbent [1], amoxicillin elimination [2], ecological field [3], hydrocracking catalyst [4], [5].

Natural zeolites are generally found mixed with metal oxides and other minerals. In addition, the continuous exploration of natural zeolite will reduce the deposit. Therefore, synthetic zeolite is developed. Synthetic zeolite is made through a synthesis process with the desired function and engineered in such a way as to get the desired character.

Many types of research on zeolite synthesis have been carried out. The hydrothermal method is the most commonly used in the synthesis of zeolite and has been carried out by many researchers such as Zhang et al. [6], Luo et al. [7], Jin et al. [8], and Sriatun et al. [9]. Madhu et al. have synthesized Linde-type zeolite (LTA) by hydrothermal method at 100 °C for 12 hours. The molar ratio was 3.165 Na₂O: Al₂O₃:1.926 SiO₂:1.28 H₂O [10]. Other methods in the synthesis of zeolites are microwave-hydrothermal such as carried out by Stafin et al. [11] and Oliveira et al. [12] and heating by microwave [13], [14]. Meanwhile, the synthesis of LTA, FAU, MFI, and BEA zeolites by reflux method under atmospheric pressure has been carried out by Sun et al. This method has reduced the risk of high pressure when using the autoclave, so this method is considered safer [15]. However, the reflux method is still rarely used. Therefore, in this study, the effect on the character of the synthesized zeolite was studied.

The character of the synthesized zeolite is also influenced by the source of the precursors, namely silica and alumina. Some researchers use natural renewable sources as a source of

silica, such as rice husk ash [16], fly ash [17], [18], [19], or sodium silicate [20], [21].

Ozdemir and Piskin have carried out a hydrothermal synthesis of zeolite X from different sources of silica and alumina. The first sample uses silica sources, namely sodium metasilicate pentahydrate (Na₂SiO₃·5H₂O) and alumina (Al₂O₃), the second sample is sodium metasilicate pentahydrate (Na₂SiO₃·5H₂O) and sodium aluminate (NaAlO₂), the third sample is sodium silicate (Na₂SiO₃) and sodium aluminate (NaAlO₂) carried out by the autoclave method at a temperature of 100 °C for 4 hours. The zeolite X crystals formed were influenced by the sources of Si and Al used. This can be seen in the diffractogram similarities of sodium metasilicate pentahydrate (Na₂SiO₃·5H₂O) and alumina (Al₂O₃), and sodium metasilicate pentahydrate (Na₂SiO₃·5H₂O) and sodium aluminate (NaAlO₂) with standard zeolite X diffractogram [22]. Pimraksa et al. have synthesized zeolite from fly ash, rice husk ash, and bottom ash as silica material by comparing the hydrothermal method using an autoclave carried out at a temperature of 130 °C, a pressure of 1.14 atm for 4 hours, while at reflux, it was carried out at a temperature of 130 °C. 100 °C for 24 and 48 hours. The results of the synthesis of zeolite with silica as a source of fly ash (FA) produced sodalite, bottom ash (BA) produced phillipsite-K, and rice husk ash (RHA) produced zeolite P1. The highest value of cation exchange capacity is sodalite [23]. Sriatun et al. have synthesized zeolite using sugarcane bagasse ash as a source of silica [24], [25].

Based on this background, the determination of an effective method for synthesizing zeolites using sodium silicate and sodium aluminate under oven heating and reflux with time variations for 1, 3, 5, and 7 days were studied. Heating in the oven is a process of transferring heat and water vapor simultaneously, which requires energy to evaporate the water content that is transferred from the surface of the material. Meanwhile, reflux heating uses a constant temperature so that the steam produced is condensed back into the container.

2. METHODOLOGY

2.1 Materials

Sodium hydroxide (Merck), distilled water (H₂O), Hydrochloric acid (Merck), Aluminium hydroxide (Merck), and Sodium silicate (Sigma Aldrich).

2.2 Equipment

Glassware, Teflon container, Whatman 42 filter paper, analytical balance (Ohaus), oven, magnetic stirrer, hot plate, X-Ray Diffractometer (XRD), Fourier Transform Infrared Spectroscopy (FTIR).

2.3. Synthesis Procedure

5.6 g of sodium hydroxide (NaOH) was dissolved in 58 mL of distilled water. The sodium hydroxide solution was added to 2.04 g of Al(OH)₃ and stirred for 30 minutes. Moreover, sodium silicate was added. The Si/Al ratio used was 50. The mixture was stirred at room temperature for 12 hours to form a gel, the pH > 11 of the mixture was adjusted, then heated using reflux at a temperature of 110 °C for 1, 3, 5, and 7 days. The solid product obtained was filtered and washed with distilled water to a neutral pH, then dried in an oven for 2 hours at a temperature of 100 °C to obtain a crystalline solid product. The synthesis products were coded S-R1, S-R3, S-R5, and S-R7.

The difference in product crystallinity is compared to zeolite, synthesized with the shortest (1 day) and most prolonged time (7 days) using an oven, and coded as Z-OV1 and Z-OV7. The product was characterized by Fourier Transform Infra-Red Spectroscopy (FT-IR) and X-Ray Diffraction (XRD).

3. RESULTS AND DISCUSSION

Zeolite polymers can be obtained by reaction between sodium aluminate and sodium silicate. The formation of zeolite polymer began via the formation of silica-alumina gel and was influenced by pH conditions. The different levels of basicity of different compounds will be found. The aluminate compound associated with the formation of the silica-alumina polymer is Al(OH)₄⁻, which can be found at pH > 9. The system's pH is 11-12 because this condition was related to the presence of Si₄O₈(OH)₄⁴⁻ and Al(OH)₄⁻. These species interact to form a silica-alumina polymer to affect the rate of nucleation and crystal growth.

During the heating process, crystal growth occurs. The amorphous gel will undergo a rearrangement in the structure to form a crystal nucleus embryo. In this state, there is an equilibrium between the crystalline core embryo, the remaining amorphous gel, and the supersaturated solution. The process is in a metastable state. If the residual amorphous gel dissolves again, crystal growth will occur from the core embryo until the remaining amorphous gel is used up and crystals are formed in a stable state [26].

In this study, the hydrothermal process used reflux heating at a temperature of 110 C for 1, 3, 5, and 7 days. As a comparison, heating was also carried out using the oven for only one day and seven days. The variation time of crystallization was carried out to determine the effect of time on the crystallinity of the synthetic zeolite product. Using an oven was carried out to release water molecules in the gel to form a crystalline solid. However, the water molecules were not completely evaporated. In the synthesis process using reflux, the aim is that the results obtained are more optimal because no compounds are lost, namely in the presence of condensed water vapor through the condenser so that the water vapor returns to the container, which takes place continuously.

3.1 CHARACTERIZATION USING X-RAY DIFFRACTION (XRD)

Based on Fig. 1 and Fig. 2, the peaks of the zeolite diffractogram from heating with an oven and reflux are gibbsite, quartz, and faujasite. Due to the tendency of decreasing crystallinity when the heating time in reflux is getting longer, the synthesis of zeolite using an oven was only carried out at the shortest time (Z-OV1) and the longest time (Z-OV7). In the Z-OV1 and S-R1 diffractograms, the intensity decreased, the intensity of Z-OV1 was smaller than that of S-R1. This is due to the influence of the heating method used in zeolite synthesis. In the diffractogram, Z-OV7 and S-R7 decreased crystallinity. The decrease in crystallinity causes the presence of new peaks, and this happens because when it reaches a specific heating time, the structure tends to be stable. This is in accordance with West [27], which states that the structure of a solid is a function of time and temperature. A solid will be more stable at a specific time and temperature, and when it passes through a specific phase, the stability can change.

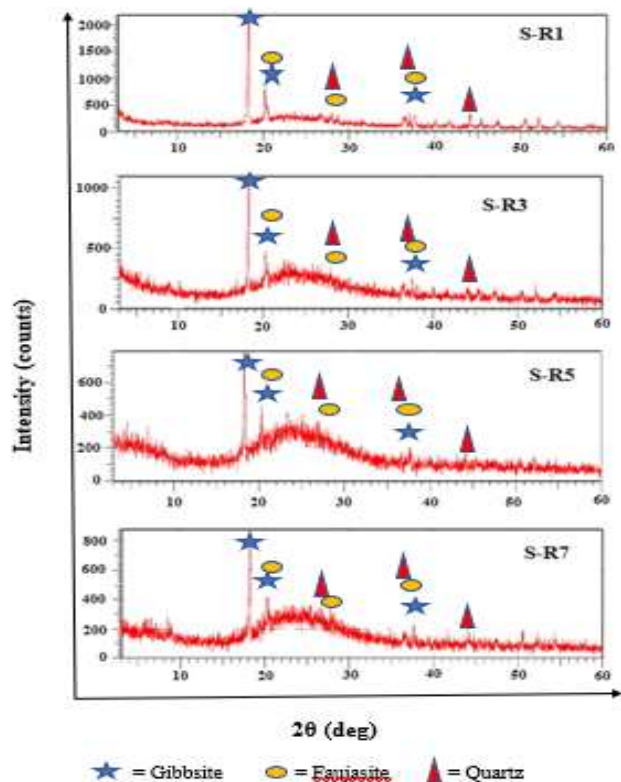


Fig 1: XRD diffractogram pattern of synthesized zeolite using reflux

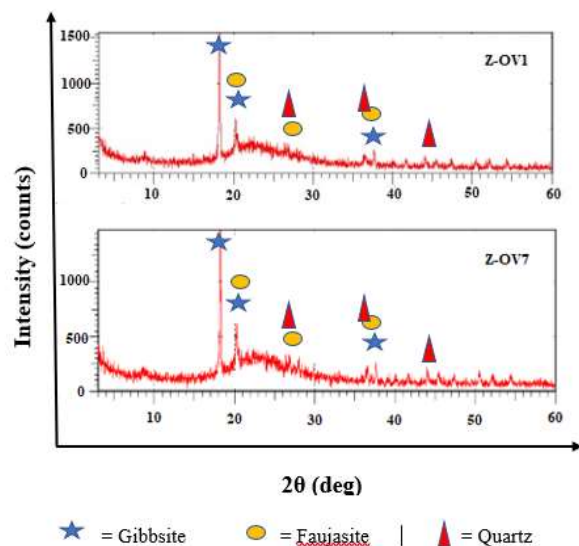


Fig. 2: XRD diffractogram pattern of synthesized zeolite using an oven

A diffractogram with a clear separation pattern, high intensity, and sharp peaks have good crystallinity. Based on Fig.1 and 2, the results of the diffractogram of the zeolite synthesized by heating with an oven and reflux, seen from the value of 2θ there is a difference in peak intensity that can be

observed at $2\theta = 18.2^\circ; 20.2^\circ; 37.6$, which indicates the type of mineral that is most abundantly contained in the synthesized zeolite is gibbsite. Other mineral content is quartz and faujasite in lesser amounts. This is confirmed by calculating the value of the relative mineral composition of Z OV1, Z-OV7, S-R1, S-R3, S-R5, and S-R7 in **Table 1**. The mineral gibbsite is more dominant than quartz and faujasite. The structure of the gibbsite has similarities to the structure of the micas. The basic structure forms stacked sheets of linked octahedra. Meanwhile, the faujasite consists of sodalite cages connected through hexagonal prisms. The quartz mineral has a framework of SiO_4 tetrahedra, with each oxygen being shared between two tetrahedra, giving an overall chemical formula of SiO_2 .

Table 1: Relative percentage of zeolite products

Sample code	Mineral type	Relative composition (%)
Z-OV1	Gibbsite	77.04
	Faujasite	15.37
	Quartz	7.59
Z-OV7	Gibbsite	65.66
	Faujasite	24.85
	Quartz	9.48
S-R1	Gibbsite	78.83
	Faujasite	14.33
	Quartz	6.83
S-R3	Gibbsite	75.6
	Faujasite	16.7
	Quartz	7.72
S-R5	Gibbsite	72.5
	Faujasite	15.0
	Quartz	12.7
S-R7	Gibbsite	72.56
	Faujasite	14.61
	Quartz	12.83

3.2 CHARACTERIZATION USING FOURIER TRANSFORM INFRARED

Fig. 3 and Fig. 4 show the FTIR spectra of zeolite from reflux and oven heating. The absorption region between $500 - 420 \text{ cm}^{-1}$ correlated with the functional group of T-O (Si-O or Al-O) bending vibration wavenumbers on S-R7 (462.92 cm^{-1}) and Z-OV7 (470.63 cm^{-1}). An absorption between $820-650 \text{ cm}^{-1}$ is a stretching vibration of symmetry O-Si-O or O-Al-O. The Z-OV7 and S-R7 have absorptions of 802.39 and 794.67 cm^{-1} , respectively. This stretching vibration indicates the composition of the Si-Al bond in the zeolite framework [28].

The decrease in absorption also occurs at wavenumbers between $500-420 \text{ cm}^{-1}$. Elaiopoulos et al. suggested that the main structural unit is the internal vibration associated with the TO_4 tetrahedral [29]. The spectra in question are in the $950-1250 \text{ cm}^{-1}$. The wavenumber shows an asymmetrical stretching vibration internal and external network. The

absorption bands were Z-OV7 at 1087.85 cm^{-1} and S-R7 at 1064.71 cm^{-1} . This wavenumber identified that the absorption band Z-OV7 had a smaller intensity than S-R7 due to heating. The longer the heating time, the better the synthesized zeolite formed by high intensity [30].

In ZOV-1 and Z-OV7, there are wavenumbers of 3448.72 cm^{-1} , respectively, and on S-R1 and S-R7 of 3525.88 cm^{-1} , respectively, indicating the presence of -OH stretching bonds. This group provides information that the presence of water (hydrate) is owned by zeolite crystals [30]. The absorption band between 1600-3700 cm^{-1} indicates the presence of water. In the IR spectra produced by the synthesized zeolite for Z-OV1, Z-OV7, and S-R1, there was absorption from 1635.64 cm^{-1} while S-R7 from 1651.07. The absorption band in the area around 1645-1650 cm^{-1} shows water's -OH bending vibration [31]. The absorption band of 420-300 cm^{-1} indicated pore opening [28]. The absorption for Z-OV1 and S-R1 were at 354.90 cm^{-1} and 347.19 cm^{-1} , while Z-OV7 and S-R7 were at 354.90 cm^{-1} .

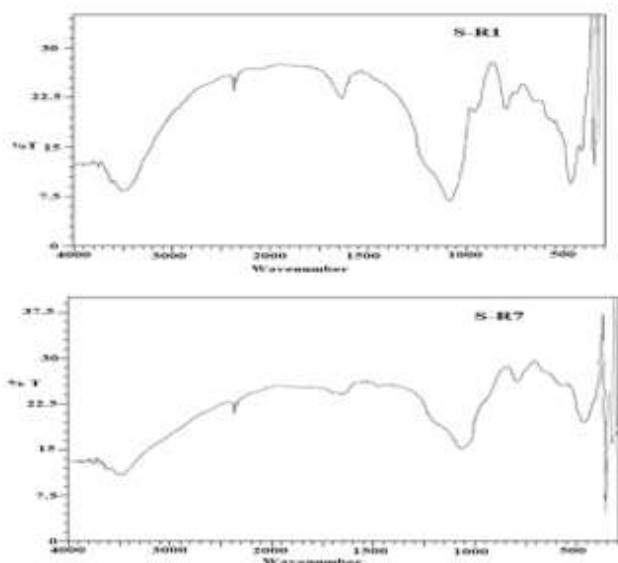


Fig. 3: FTIR spectra of zeolite products using reflux

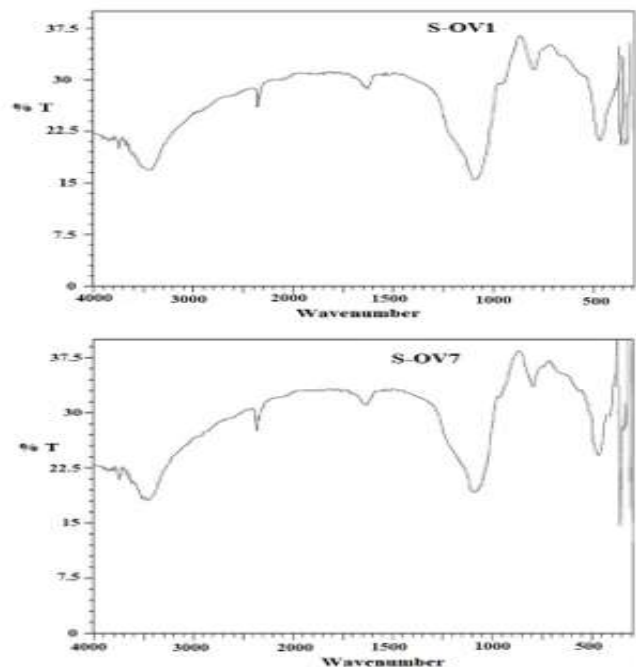


Fig. 4: FTIR spectra of zeolite products using an oven

4. CONCLUSION

From the results and discussions that have been carried out, it can be concluded that this research has obtained zeolite in the form of faujasite and other mixtures, namely gibbsite and quartz. The best crystallinity was obtained by heating using reflux or oven for one day. Meanwhile, the highest faujasite composition was 16.7% at reflux three days 24.85 % at oven heating.

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