The Effect of Aging and Crystallization Time on the Synthesis and Characteristics of Zeolite-Y from Malang-Quartzite Silica

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Abstract. The purpose of this study is to determine the effect of aging and crystallization time on the synthesis and characteristics of zeolite-Y. The raw material of silica used was obtained from the silica extraction of Malang quartzite by leaching and sol-gel methods. The extracted silica was analyzed using XRF and XRD. Synthesis of zeolite-Y was carried out using hydrothermal method by mixing NaOH, Al(OH)₃, SiO₂, and H₂O according to the molar ratio of the elements in zeolite-Y. The aging process was carried out with time variations of 12, 24, 48 hours and the crystallization process were carried out with time variations of 6, 9, 12 hours at a temperature of 150 °C. The synthesized zeolite-Y was analyzed using XRF, XRD, FTIR, and SEM. The results showed that quartzite silica could be extracted by leaching and sol-gel methods with a yield of 99.1 wt%. The optimum condition of synthesis zeolite-Y was obtained at the aging time of 12 hours and the crystallization time of 12 hours.

1. Introduction
In general, researchers obtain silica from the extraction of other natural materials such as perlite stones [1], diatomite [2], shale rock [3], and bentonite [4]. However, to the best of our knowledge, research on the use of quartzite as a precursor of zeolite catalysts has not been reported yet. In this work, Malang quartzite stone will be used as the source of silica as the precursor of the zeolite-Y catalyst.

Silica or silicon dioxide (SiO₂) is an abundant compound in nature. Generally, the source of silica that has been widely used in industry is quartz sand or silica sand. Other sources of silica can also be found in rice husk ash which contains 86.9% of silica [5] or Lapindo mud (Indonesia) with contains 53.03% of silica [6]. The other compounds in silica sand are Al₂O₃, Fe₂O₃, CaO, TiO₂, V₂O₅, Cr₂O₃, MnO, CuO, SrO, and ZrO₂. XRF results in the preliminary test of this work show that silica content in Malang quartzite is 75.7%. The result also shows that silica is the most abundant element in Malang quartzite compared to other compounds. Based on the XRF results, Malang quartzite rocks have the potential as the source of silica for further development.

Zeolite is an alumina-silica crystal with a three-dimensional porous structure [2]. Zeolites are divided into natural and synthetic zeolites. Natural zeolite has been widely used; thus the number is decreasing. Generally, natural zeolites are used for fertilizer and water purification, while synthetic zeolites are widely used in the industry. However, in Indonesia, synthetic zeolites have not been widely produced, and most zeolites in Indonesia are generally imported. Synthetic zeolites are widely used for chemical processes in the chemical industry such as catalysts [7], ion exchangers [8], [9], and adsorbents in waste treatment [5]. High-purity, high-quality synthetic zeolites are needed in the industry. The raw material for making zeolites is silica and aluminium. One of the potential sources of silica is quartzite. Zeolites
can be synthesized with different crystal structures, fixed pore sizes, Si/Al ratio frameworks and acid centres that can be adjusted to gain the targeted catalytic properties.

Previous study showed that zeolite-Y was successfully synthesized using Pluronic P123 block copolymer as a template reported [10] using diatomite from Bolivian as silica base material [2], and using perlite glass as basic ingredient of silica [1]. In this research, silica extracted from quartzite was used as a base material. Quartzite silica stone is extracted by leaching and sol-gel methods. In this study, the synthesis of zeolite-Y using silica extracted from Malang quartzite stone is discussed. The purpose of this study was to determine the effect of aging and crystallization time on the characteristics of the synthesized zeolite-Y.

2. Method

2.1. Materials
SiO$_2$ was obtained from quartzite stones (Malang, East Java). HCl (analytical grade) and NaOH (analytical grade) were purchased from Merck. Al(OH)$_3$ was purchased from Sigma-Aldrich. All chemicals were used without further purification.

2.2. Synthesis of Zeolite-Y
Silica were obtained from the extraction of Malang quartzite stone by mixing 22.5 grams of its powder with 30 grams of NaOH in a hotplate until the mixture become completely melted and well mixed to get sodium silicate. The sodium silicate then was dissolved in 150 mL DI water before being filtered. The resulting filtrate then were titrated with HCl p.a before being filtered again to get the residual precipitate. The as-obtained residual precipitate was dried at 100°C for 12 hours to obtain silica. The impurity of as-obtained amorphous silica was observed to be as high as 99.1%. Synthesis of zeolite-Y was carried out using a procedure that has been reported [11] with a NaOH:Al(OH)$_3$:SiO$_2$:H$_2$O molar ratio of 58:58:134:384. The synthesis was carried out by dissolving 2 grams of SiO$_2$ in 40 mL NaOH 2 N, stirred for 30 minutes until it fully dissolved to obtain sodium silicate. Sodium aluminate was prepared by dissolving 2 grams of Al(OH)$_3$ in 60 mL of 7 M NaOH followed by refluxing the mixture until it completely dissolved. Sodium silicate and sodium aluminate were then mixed together for 30 minutes. The mixture then stands for aging for 12, 24, and 48 hours at RT before transferred into a hydrothermal Teflon bottle equipped with a stainless-steel autoclave for the crystallization process. The crystallization was performed at 150 °C for 12, 9, and 6 hours. After the aging and crystallization completed, the mixture was filtered off, and the residual precipitate was washed with DI-water. The precipitate was then dried for 24 hours at 80 °C to form zeolite-Y.

2.3. Characterisation of Zeolite-Y
In order to obtain the as-synthesized zeolite-Y phase information, the samples were characterized with X-ray Diffraction (XRD, PANalytical Brand, type X’pert-Pro) using Cu-Kα under 40 kV and 35 mA, the 2θ range was set between 10° to 90°. The microstructures and morphologies of the samples were observed using scanning electron microscopy (SEM, FEI Brand, type inspect S50) at 20 kV with magnification 10000x, and 50000x. X-ray Fluorescence were recorded on a MiniPal (PANalytical type MiniPal 4) to observed the Si and Al atoms and its atomic weight ratio. FTIR analysis were carried out on an IR spectrophotometer (Shimadzu Brand, type IR-prestige 21), with scanning range between 4000-400 cm$^{-1}$, using KBr pellet method.

3. Results and Discussion

3.1. Synthesis and Characterization of Zeolite-Y
The silica was reacted with sodium alumina for the synthesis of zeolite-Y. The XRD results showed that zeolite-Y has been formed, as proven by comparing the diffraction pattern of synthesized zeolite-Y with
that of a standard zeolite-Y [12]. The diffraction pattern for the synthesized zeolite-Y is presented in Figure 1.

![Diffractogram of as-synthesized zeolite-Y.](image)

**Figure 1.** Diffractogram of as-synthesized zeolite-Y.

The synthesis of zeolite-Y was carried out at 150 °C with a variation of aging time and crystallization time. Crystallization and aging time are the factors that influenced the formation of zeolite-Y. Comparison of 2θ and d-spacing between zeolite-Y in various aging time and crystallization time are shown in Table 1.

| Zeolite-Y standard | Z-12-12 (ta = 12; tc = 12) | Z-24-12 (ta = 24; tc = 12) | Z-48-12 (ta = 48; tc = 12) | Z-48-9 (ta = 48; tc = 9) | Z-48-6 (ta = 48; tc = 6) |
|--------------------|-----------------------------|-----------------------------|-----------------------------|---------------------------|---------------------------|
| 2θ (°)             | d-spacing (Å)               | 2θ (°)                      | d-spacing (Å)               | 2θ (°)                    | d-spacing (Å)             |
| 14.61              | 6.064                       | 14.15                       | 6.259                       | 14.29                     | 6.199                     | 14.25                     | 6.215                     | 14.33                     | 6.182                     | 14.22                     | 6.228                     |
| 20.71              | 4.288                       | 20.06                       | 4.427                       | 20.15                     | 4.408                     | 20.09                     | 4.420                     | 20.24                     | 4.387                     | 20.04                     | 4.431                     |
| 24.06              | 3.699                       | 24.62                       | 3.616                       | 24.70                     | 3.604                     | 24.65                     | 3.611                     | 24.53                     | 3.630                     | 24.57                     | 3.623                     |
| 31.95              | 2.801                       | 31.95                       | 2.802                       | 31.99                     | 2.798                     | 31.93                     | 2.802                     | 31.78                     | 2.816                     | 31.82                     | 2.813                     |
| 35.29              | 2.543                       | 35.09                       | 2.558                       | 35.11                     | 2.556                     | 35.05                     | 2.560                     | 35.28                     | 2.544                     | 34.91                     | 2.570                     |
| 37.82              | 2.379                       | 38.00                       | 2.368                       | 38.01                     | 2.367                     | 37.95                     | 2.371                     | 38.20                     | 2.356                     | 37.80                     | 2.380                     |
| 41.28              | 2.187                       | 40.73                       | 2.215                       | -                         | -                         | -                         | 40.91                     | 2.206                     | -                         | -                         | -                         |
| 43.51              | 2.080                       | 43.32                       | 2.089                       | 43.31                     | 2.089                     | 43.25                     | 2.092                     | 43.51                     | 2.080                     | 43.05                     | 2.101                     |
| 44.84              | 2.021                       | 45.80                       | 1.981                       | 45.78                     | 1.982                     | 45.69                     | 1.986                     | -                         | -                         | -                         | -                         |
| 48.03              | 1.894                       | 48.18                       | 1.889                       | 48.13                     | 1.891                     | 48.06                     | 1.893                     | 48.40                     | 1.881                     | 47.86                     | 1.901                     |

*ta = aging time (hours); tc = crystallization time (hours)*

From Table 1, there is no peak observed at 2θ of 41.28° for the aging times of 24 hours (tc = 12), 48 hours (tc = 12), 48 hours (tc = 6). Meanwhile, in the aging time of 12 hours a peak at 2θ of 40.73° was observed or shifted 0.54° from the standard angle. In the tc of 9-hour, there is a peak at 2θ of 40.90° or shifted 0.38° from the standard. Moreover, at 2θ of 44.84°, there was no peak observed in of 9 hours and 6 hours, whereas in the 12 hours crystallization time there was a peak at 2θ of 45.68°, which shifted 0.84° from the standard. This result indicated that the number of peaks displayed by the 2 hours aging time are greater than that of the 24 or 48 hours. There are also more peaks exhibited by the 12- and 9-hours crystallization times compared to that of 6 hours crystallization time.
Figure 2. Zeolite-Y diffractograms at various aging and crystallization times.

Figure 2 shows that the peaks in zeolite-Y with a variation of aging time of 12 hours and crystallization time of 12 hours has the highest intensity compared to others. It means that although zeolites-Y successfully made at all 5 different conditions, the optimum results was obtained when the synthesis of zeolite-Y was done at 12 hours aging time and 12 hours crystallization time.

XRF analysis conducted on zeolite-Y samples aims to determine the relative concentration levels of the elements in the synthesized zeolite. Thus, the Si/Al molar ratio of the zeolite can be identified. The Si/Al molar ratio of zeolite-Y was in range of 2.045 to 2.087. Complete data of the Si/Al molar ratio is presented in Table 2.

| Zeolite-Y | Time  | Element composition (%) | Moles     | Molar ratio of Si/Al |
|-----------|-------|-------------------------|-----------|----------------------|
|           | Aging (hours) | Crystallization (hours) | Si | Al | Si | Al | Si/Al |
| Z-12-12   | 12    | 12                      | 66.9 | 31.1 | 2.389 | 1.152 | 2.073 |
| Z-24-12   | 24    | 12                      | 65.5 | 30.9 | 2.339 | 1.144 | 2.045 |
| Z-48-12   | 48    | 12                      | 66.8 | 31.1 | 2.385 | 1.152 | 2.071 |
| Z-48-9    | 48    | 9                       | 65.0 | 30.3 | 2.321 | 1.122 | 2.068 |
| Z-48-6    | 48    | 6                       | 67.1 | 31.0 | 2.396 | 1.148 | 2.087 |

The reported molar ratio of Si/Al of zeolite-Y was in the range of 1.5 to 3 [13]. The synthesized zeolite-Y in this work has the largest Si/Al molar ratio of 2.087 (48 hours aging time and 6 hours crystallization time) and the smallest Si/Al molar ratio of 2.045 (24 hours aging and 12 hours crystallization time). Based on this XRF data, which is in the expected range of Si/Al, it can be stated that zeolite-Y was formed in all five variations of aging time and crystallization time.
Characterization of the synthesized zeolite-Y using FTIR aims for support the successful synthesis through the analysis of functional groups contained in the product. The FTIR spectra of zeolite-Y in five variations of aging and crystallization time are presented in Figure 3 and the interpretation is presented in Table 3.

Table 3. The Interpretation of FTIR spectra of the synthesized zeolite-Y at various aging and crystallization time.

| Wave numbers (cm\(^{-1}\)) | Ref. (cm\(^{-1}\)) | Z-12-12 (ta = 12; tc = 12) | Z-24-12 (ta = 24; tc = 12) | Z-48-12 (ta = 48; tc = 12) | Z-48-9 (ta = 48; tc = 9) | Z-48-6 (ta = 48; tc = 6) | Interpretation |
|-----------------------------|-------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|----------------|
| 500 - 418                   | 450               | 418.55                      | 447.49                      | 447.49                      | 418.55                      | -                           | Buckling vibration T-O (Si-O or Al-O) |
| 650 - 500                   | 574               | 501.49                      | 609.51                      | 561.29                      | 567.07                      | 549.61                      | Double ring               |
| 820 - 650                   | 722               | 744.52                      | 736.81                      | 740.67                      | 719.45                      | 719.45                      | Symmetric stretching vibrations O-Si-O and O-Al-O |
| 1250 - 950                  | 1025              | 1103.86                     | 1141.43                     | 1149.57                     | 1053.13                     | -                           | Asymmetric stretching vibrations Si-O-Si/Al-O-Al |
| 1655 -1610                  | 1646              | 1614.42                     | 1693.55                     | 1645.28                     | 1631.78                     | 1614.42                     | Buckling vibration Si-OH/Al-OH |
| 2400-2300                   | 2375              | 2380.16                     | 2378.23                     | 2347.37                     | 2380.16                     | 2380.16                     | Buckling vibration Si-H    |
| 3200-3600                   | 3459              | 3271.27                     | 8,53468.01                  | 3444.87                     | 3444.87                     | 3442.94                     | Bonding O-H                |

\(ta = \text{aging time (hours)}; \; tc = \text{crystallization time (hours)}\)

The IR spectra of synthesized zeolite-Y shows some wave numbers of functional group indicating the formation of zeolite-Y. For instance, the IR spectra of zeolite-Y with aging time for 12 hours and crystallization time of 12 hours shows a peak at wave number of 1103.86 cm\(^{-1}\) that corresponds to asymmetric stretching vibrations of Si-O-Si/Al-O-Al, a peak at wave number of 744.52 cm\(^{-1}\) that
corresponds to symmetrical stretching vibrations of O-Si-O-Al-O, and a peak at wave number of 418.55 cm$^{-1}$ that corresponds to Si-O-Si or Al-O-Al vibration. However, the peaks spectra of zeolite-Y produced at aging time of 12 hours and crystallization time of 12 hours was higher. This data indicated that the obtained zeolite-Y under these conditions was more successful. SEM analysis for the synthesized zeolite-Y were presented in Figure 4, Figure 5, and Figure 6.

**Figure 4.** SEM zeolite-Y with 12 hours aging time and 12 hours crystallization time with (a) 10.000x and (b) 50.000x magnification.

**Figure 5.** SEM zeolite-Y with 24 hours aging time and 12 hours crystallization time with (a) magnification of 10.000x and (b) 50.000x magnifications.

**Figure 6.** SEM zeolite-Y with 48 hours aging time and 12 hours crystallization time with (a) magnification of 10.000x and (b) 50.000x magnifications.
Based on the SEM data in Figure 4, Figure 5, and Figure 6, it was known that the diameter of the crystal unit is 1.2 micrometres with octahedral shape. It was in line with the characteristics of zeolite-Y reported by previous researchers [1], [14] where the crystalline form of zeolite-Y is octahedral.

4. Conclusions
Zeolite-Y has been successfully synthesized using a hydrothermal method in variations of aging time between 12 to 48 hours and crystallization time of 6 to 12 hours. The optimal synthesis conditions of zeolite-Y were 12 hours aging time and 12 hours crystallization time with mole ratio Si/Al of 2.073. The FTIR spectra shows asymmetric stretching vibrations of Si-O-Si/Al-O-Al at wave number of 1103.86 cm\(^{-1}\). Symmetrical stretching vibrations of O-Si-O/O-Al-O appeared at wave number of 744.52 cm\(^{-1}\) and the bonding vibrations of Si-O-Si/Al-O-Al was appeared at wave number of 418.55 cm\(^{-1}\). The SEM data shows that the produced zeolite-Y has an octahedral crystalline structure which also supports that the synthesis of zeolite-Y is successful.

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