Preparation of molecular sieve from natural pyrophyllite and characterization of its Al/Si ratio, crystal structure, and Porosity

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Abstract. Pyrophyllite is one abundant mineral in Indonesia which has not been optimally processed. Hence, this study further processed natural pyrophyllite to be an advanced material usable for industrial sector as a molecular sieve (MS). Natural pyrophyllite was chosen due to its ability to filter gas or liquid selectively. The MS made from natural pyrophyllite was prepared by using a simple method, in short time and with less cost via leaching process. NaOH was varied to 10 M (MS1), 15 M (MS2), and 20 M (MS3) of molarity. Such solution was subsequently dissolved in distilled water and followed by decantation and filtration processes to obtain the deposit. Eventually, the deposit was drained to form MS powders. The BET characterization showed that the respective surface areas of MS1, MS2, and MS3 are 0.350 m$^2$/g, 2.869 m$^2$/g, and 1.176 m$^2$/g with the pore sizes of 30 Å, 542 Å, and 550 Å, respectively. The XRF characterization results showed that the Al/Si ratio of MS10, MS15, and MS20 are 2.4, 2.2, and 2.3, respectively. Meanwhile, the XRD investigation pointed out that the primary phase of MS10 and MS15 samples was sodalite with cubic crystal system, quartz with hexagonal crystal system, and diaspore with orthorhombic crystal system, while the MS20 phase was pure in the form of sodalite phase. Moreover, the results of FTIR characterization showed that the synthesized MS has a functional group of Si-O-Si bending, Si-O-Al, Si-O, Si-O-Si normal to the plane stretching, inner surface Al-OH deformation, Si-O-Si siloxine, H-O-H, -OH, C-H stretching, and H-O-H bending water.

1. Introduction

Indonesia is a mineral-rich country since mineral stones are spread in almost all areas across the country. However, unfortunately, such plentiful minerals has not been optimally benefitted. Thus far, the minerals are not processed to be advanced materials yet. The advanced materials provide larger benefits, either for economic, scientific, or technological development. Therefore, a mineral processing to produce materials that are more advanced is highly necessary. One sample of rich mineral available in Indonesia which has big potential to be processed as the advanced material is pyrophyllite.
Chemically, pyrophyllite is aluminum silicate hydroxide synthesis with the formula of $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ and has similar characteristics with zeolite [1] or kaolinite [2] which has relatively high silica and alumina contents [3]. In general, pyrophyllite in Indonesia has been quarried conventionally and sold as raw material without any further processes. The findings of recent research performed by Fuad et al. states that Indonesian pyrophyllite contains relatively high silica and alumina contents of approximately 78% and 15.4% [4].

Technically, pyrophyllite is formed in advanced argillic alteration zone, such as kaolinite. Nonetheless, it can be formed at high temperature and acidic pH. Molecular sieve synthesis requires raw materials with high silica and alumina contents. Ugal, J.r. successfully synthesized type 4A molecular sieve ($\text{Na}_{12}(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}.27\text{H}_2\text{O}$) from kaolinite by refluxing at the temperature of 90 °C and with 1:5 comparison between kaolinite and sodium hydroxide [5]. A similar study was also conducted by Ivan Petrov who fabricated type A MS from zeolite via hydrothermal method at the temperature of 100 °C. Zeolite and kaolinite have comparable Al/Si content [6]. Unfortunately, however, there is not a report of molecular sieve synthesis from pyrophyllite. Thus, we proposed pyrophyllite utilization to form molecular sieve.

Molecular sieve synthesis has been executed in several methods, such as reflux [7] and hydrothermal [8] methods. Even though reflux method offers an advantage as being able of extracting rough-textured samples, this method has a weak point since it needs a great volume of solvent and some manipulations from the operator. In line with the hydrothermal method, although it requires a simple preparation, it requires highly costly equipment, and it is hard to control its stoichiometry [9, 10]. Thus, the development of molecular sieve method becomes essential to overcome the deficiencies of the two approaches. In this research, we propose pyrophyllite-based molecular sieve synthesis advancement through the means of simple leaching method and NaOH. Furthermore, the crystal structure, porosity, particle size and chemical bond of the synthesized molecular sieve would be observed to identify the success of the advancement.

2. Method
The sample of molecular sieve in this research was prepared by using NaOH leaching method. The first stage was to prepare the raw material by turning the pyrophyllite taken from Malang, Indonesia into powder. The powdered pyrophyllite was then refined by using filter paper with 200 mesh size. Then, the researchers performed a reaction between 40-grams pyrophyllite powder and 10M NaOH through a stirring process with a stirrer accompanied by heating at the temperature of 120 °C for 24 hours. After that, the material was dissolved in distilled water and decanted for 24 hours followed by the filtration process to obtain the deposit. The deposit was dried at the temperature of 250 °C for 21 hours. The same procedure was done to the other variations of NaOH molarity; i.e., 15 M and 20 M. The powdered sample obtained was then smoothened for the characterizations of X-Ray Fluorescence (XRF), X-Ray Diffractometry (XRD), Brunauer Emmett Teller (BET), and Fourier Transform Infra-Red (FTIR) Spectroscopy.

3. Results and discussion
Figure 1 presents the results of XRD characterization on the pyrophyllite. According to the findings of qualitative data analysis, pyrophyllite has corresponding peaks with the pyrophyllite phase, while the results of quantitative data analysis point out that pyrophyllite contains three elements, namely the pyrophyllite itself of as much as 48%, diaspore element of 12.9%, and 39.1% SiO$_2$-Quartz element. XRF characterization was conducted subsequently to ascertain the pyrophyllite contents. The results of XRF characterization of pyrophyllite and the synthesized MS sample are subsequently presented in Table 1 and Table 2.
Figure 1. X-ray Diffraction Pattern of Natural Pyrophyllite

Table 1. Results of XRF Characterization of Natural Pyrophyllite

| Elemental content | Al   | Si   | Ca   | Ti   | Other elements |
|-------------------|------|------|------|------|----------------|
| Percentage (%)    |      |      |      |      |                |
| Al                | 17.6 |      |      |      |                |
| Si                | 77.6 |      |      |      |                |
| Ca                | 0.96 |      |      |      |                |
| Ti                | 2.08 |      |      |      |                |
| Other elements    | 1.7  |      |      |      |                |

From the XRF characterization results, it is identified that the biggest pyrophyllite constituent is Si with the percentage of 77% and Al with the rate of 17.6%. The two elements are the main components with the highest concentration, while there are other minor elements, namely Ti, Ca, V, Cr, Fe, Ni, and Cu. Thus, pyrophyllite is a kind of mineral which contains high concentration of silica or quartz.

Table 2. Comparison of Pyrophyllite Concentration in MS10, MS15, and MS20

| Sample     | Al       | Si       | Ca       | Ti       | Other elements |
|------------|----------|----------|----------|----------|----------------|
| Pyrophyllite| 17.6     | 77.6     | 0.96     | 2.08     | 1.71           |
| MS10       | 23.9     | 56.5     | 1.8      | 12.9     | 4.95           |
| MS15       | 23.0     | 51.2     | 2.2      | 17.0     | 6.42           |
| MS20       | 21.0     | 48.0     | 2.8      | 18.4     | 9.78           |

Based on the results of XRF characterization presented in Table 2, it can be described that there was a declining concentration of silica which is represented by relatively significant Si element so that there is an increase of alumina (Al) level. The levels are suitable since it produced an almost similar ratio comparison between silica and alumina as shown in Table 3.

Table 3. Comparisons of Si/Al Ratio in MS10, MS15, and MS20

| Sample | Al  | Si   | Al : Si |
|--------|-----|------|---------|
| MS10   | 23.9| 56.5 | 1 : 2.4 |
| MS15   | 23.0| 51.2 | 1 : 2.2 |
| MS20   | 21.0| 48.0 | 1 : 2.3 |

According to Table 3, it can be concluded that Al/Si has an almost similar ratio comparisons between 1:2.2 and 1:2.4. In other words, the addition of greater NaOH concentration did not
significantly influence the A1/Si ratio in the sample. The highest ratio was found in MS1, i.e. 1:2.4, and the lowest ratio is found in MS2, namely 1: 2.2. Therefore, the A1/Si in this study is included in the S materials (Sodalite/SOD), namely the minerals contained in the zeolite structural classification since it is categorized as aluminosilicate mineral [11]. These research findings are also supported by a theory proposed by A. Derkowski which states that Si/A1 ratio of sodalite is 1: 1.21 [12].

Figure 2 reflects the results of X-ray diffraction patterns of the MS samples via NaOH leaching method with the variations of NaOH morality of 10 M, 15 M, and 20 M.

![Figure 2. X-Ray Diffraction Patterns of MS10, MS15, and MS20](image)

From the results of refinement analysis, the MS10 and MS15 samples have three phases, namely quartz phase with hexagonal crystal system, diaspora phase with orthorhombic crystal system, and sodalite phase with cubic crystal system, while there was one pure phase of sodalite found in MS20 sample. Detailed results of X-ray diffraction data analysis for all samples are demonstrated in Table 3.

| Sample | Compositions of Phase | Parameter | FoM | Lattice Parameter | % wt | V (Å³) |
|--------|-----------------------|-----------|-----|-------------------|------|--------|
|        |                       | Rp (%)    | Rwp (%) | Rexp (%) | a(Å) | b(Å) | c(Å) |      |
| MS10   | Sodalite              | 18.96     | 27.21 | 1.75  | 8.897 | 8.897 | 8.897 | 72.4 | 704.185 |
|        | Quartz                | 18.96     | 27.21 | 1.75  | 4.919 | 4.919 | 5.405 | 26.8 | 130.749 |
|        | Diaspore              | 18.96     | 27.21 | 1.75  | 4.402 | 9.432 | 2.847 | 0.80 | 118.195 |
| MS15   | Sodalite              | 10.11     | 13.14 | 0.28  | 8.870 | 8.870 | 8.870 | 94.7 | 697.770 |
|        | Quartz                | 10.11     | 13.14 | 0.28  | 4.906 | 4.906 | 5.423 | 5.30 | 130.536 |
|        | Diaspore              | 10.11     | 13.14 | 0.28  | 4.301 | 9.525 | 2.890 | 0.00 | 118.402 |
| MS20   | Sodalite              | 11.6      | 15.21 | 2.64  | 8.865 | 8.865 | 8.865 | 100  | 696.755 |

The data analysis findings of crystal structure in Table 3 display the formation of three phases which are quite similar with the cubic crystal model of sodalite phase from ICSD with the database code of 072059, p-43n space group number 218, quartz phase with hexagonal crystal model from ICSD with the database code of 027832, P3221 space group number 154, and diaspore phase with orthorhombic crystal model from ICSD with the database code of 066800, Pbnm space group number 62. Furthermore, the results of data analysis also demonstrate that the NaOH composition in the related parameter of crystal lattice in each sample has the tendency to be stable. Such stability has a consequence of having stable crystal volume. Hence, the variations of NaOH molarity do not affect the crystal volume in each sample.
All of the samples were characterized by using the BET technique to determine the physical properties of their pore size and surface area. Technically, the surface area was obtained through an N\textsubscript{2} adsorption test. This method utilized Quadrasorb SI analyzer complemented with QuadraWin software. The test results in the form of average pore size and surface area of MS10, MS15, and MS20 samples are presented in Table 5.

| Sample | Pore Diameter (Å) | Surface Area (m\textsuperscript{2}/g) |
|--------|------------------|-------------------------------------|
| MS10   | 30               | 0.350                               |
| MS15   | 542              | 2.869                               |
| MS20   | 550              | 1.176                               |

As reported in Table 5, MS10 sample has 30 Å pore diameter. Thus it is classified as mesoporous material. Additionally, the respective pore diameters of MS15 and MS20 samples are 542 Å and 550 Å, so that they are categorized as macroporous materials. This study shows that the higher the molarity concentration of NaOH, the larger or the more porous the pore diameter. Based on a theory proposed by Rosemane Szostak, BET method is used not only to identify the pore diameter but also to determine the surface area of the samples [13]. The surface area of MS10 was identified to be 0.350 m\textsuperscript{2}/g, while MS15 has an area of 2.869 m\textsuperscript{2}/g, and MS20 has a surface area of 1.176 m\textsuperscript{2}/g. The surface area of an adsorbent determines its adsorption ability. A large surface area leads to a high performance of adsorption. Thus, the variations of NaOH compositions have are highly potential to turn the samples into a molecular sieve.

The functional group formed in all samples with variations of NaOH molarity is characterized through the means of FTIR. This characterization identified a graphic of correlation between the transmittance and wave number as can be seen in Figure 3. The black curve shows the characterization result of MS10, the red curve displays the MS15 characterization result and the blue curve presents MS20 characterization result.

The IR Spectrum of MS10 on the wave number of 482.2 cm\textsuperscript{-1} shows the formation of Si-O-Si bond [14]. The Si-O-Al stretching bond [14] was formed at the wave number ranging from 540.07-665.44 cm\textsuperscript{-1}. Si-O quartz bond [14] was found at the wave number ranging from 696.3-798.53 cm\textsuperscript{-1}. There was inner surface Al-OH deformation bond [15] found at the wave number of 950.91 cm\textsuperscript{-1}. The wave number of 985.62 cm\textsuperscript{-1} showed Si-O planar stretching bond [15]. There was Si-O-Si siloxane bond [16] at the wave number ranging from 1047.35-1120.64 cm\textsuperscript{-1}. There was Si-O normal to the plane stretching bond [15] at the wave number of 1159.22 cm\textsuperscript{-1}. H-O-H bending bond can be found at the wave number of 1454.33 cm\textsuperscript{-1}. Aromatic nitrate bond [14] was found at the wave number of 1598.99 cm\textsuperscript{-1}. The wave number of 1687.71 cm\textsuperscript{-1} showed H-O-H bending water bond [14]. C-H stretching
bond[14] could be found at the wave number ranging from 2846.93-2945.3 cm\(^{-1}\) and OH silanol bond [16] also was found at the wave number ranging from 3527.8-3672.47 cm\(^{-1}\).

On MS15, the wave number ranging from 489.92-665.44 cm\(^{-1}\) exhibited the existence of Si-O-Si bond [14]. Si-O quartz bond [14] was identified at the wave number ranging from 702.09-713.66 cm\(^{-1}\). Si-OH silanol bond [16] was determined at the wave number ranging from 869.9-881.47 cm\(^{-1}\). Inner surface Al-OH deformation bond [15] was found at the wave number of 948.98 cm\(^{-1}\). Al-O as Si cage (TO4) bond[14] was found at the wave number of 1396.46 cm\(^{-1}\). The wave number ranging from 1415.75-1435.04 cm\(^{-1}\) showed H-O-H bending bond[15]. The wave number of 1633.71 cm\(^{-1}\) showed O-H (water molecule) bond [16]. –OH silanol bond [16] was found at the wave number ranging from 3269.93-3379.29 cm\(^{-1}\). Meanwhile, on the MS20, the wave number ranging from 430.13-665.44 cm\(^{-1}\) marked the formation of Si-O-Si bending bond [14]. The wave number of 709.8 cm\(^{-1}\) showed Si-O quartz bond [14]. Si-OH silanol bond [16] was found at the wave number of 866.04 cm\(^{-1}\). The wave number ranging from 958.62-979.84 cm\(^{-1}\) showed the inner surface Al-OH deformation bond [15]. The wave number ranging from 1413.82-1454.33 cm\(^{-1}\) showed H-O-H bending bond[15]. The wave number of 2978.09 cm\(^{-1}\) identified C-H stretching bond[14]. There was OH silanol bond [16] at the wave number ranging from 3010.88-3635.82 cm\(^{-1}\).

The results of the FITR characterization show that the MS10 produced a greater number of bonds than MS15 and MS20. However, as a consequence, there can be a higher level of impurity contained in the samples. Such results are in accord with the XRD data analysis results which state that MS10 has three phase contents. Hence, it is highly possible that there was a functional group of the impurity which was accidentally adsorbed by the ultraviolet ray during the FITR analysis.

4. Conclusion

The molecular sieve has been prepared from natural pyrophyllite via leaching route. The samples in the forms of MS1, MS2, and MS3 have respective Si/Al ratio of 2.4, 2.2, and 2.3. MS1 and MS2 were formed in sodalite phase with the cubic crystal structure, quartz phase with the hexagonal crystal structure, and diaspore phase with the orthorhombic crystal structure, while the MS3 was formed in one pure sodalite phase with cubic crystal phase. Moreover, the respective pore sizes of MS1, MS2, and MS3 are 30 Å, 542 Å, and 550 Å. Meanwhile, the results of FITR characterization showed that the MS10 had more bonds compared with MS15 and MS20 due to the existence of impurity.

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