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Synthesis of Zeolite Y from Lapindo Mud with the Comparative Variation of the Weight of NaOH/Mud and Molar SiO_2/Al_2O_3

Novita Andarini,[a], Rizky Prambudi,[a] Tanti Haryati,*[a] Suwardiyanto,[a] and Yudi Aris Sulistiyo[a]

Abstract: Lapindo mud is a waste that can be used as a zeolite formation material. Zeolite is a mineral there are silica and alumina. The zeolite synthesized was the zeolite Y. The synthesis of zeolite Y is carried out the melting method followed by hydrothermal process. The ratio of NaOH/sludge weight varied the weight of NaOH added to the sludge weight which was made constant, there were 1.1 gram of NaOH/1 gram of sludge; 1.3 gram of NaOH/1 gram of sludge; 1.5 gram of NaOH/1 gram of sludge; and 1.7 gram of NaOH/ 1 gram of sludge. The sludge was pretreated using HCl in the leaching process and NaOH for smelting. The melted sludge from the four variations was characterized using XRF. The results of characterization are used as the basis for determining the mass of SiO_2 and NaOH that need to be added in the synthesis. The melted sludge was added with water, SiO_2, and NaOH and cured for 48 hours at room temperature. The mixture that has been brooded is then filtered, the result of the filtering is the filtrate of sodium silicate and sodium aluminate solution. The filtrate was hydrothermal 100-105 °C for 24 hours. The resulting crystals were filtered and neutralized using aquademine. The resulting synthetic zeolite was white, then characterization was carried out using XRF and XRD. The characterization results on the variation of NaOH/sludge weight ratio could be seen from the XRF results. Zeolite Y varies the weight ratio of NaOH/sludge based on the character of the best zeolite produced at a weight ratio of NaOH/sludge 1.5.

Keywords: Mud Lapindo, The zeolite Y, hydrothermal process.

INTRODUCTION

Mud is an abundant material in nature. The Lapindo mud is a disaster where hot mud comes out of the earth due to a technical error in drilling by PT. Lapindo Tbk in 2006 in the Porong sub-district, Sidoarjo Regency, the average volume of mud that came out every day in 2006 recorded by BPLS (Sidoarjo Mud Management Agency) was 100,000 m^3/day. Based on the results of the characterization research on the Energy Dispersive X-ray Spectroscopy (EDX) test, it was shown that the highest content in the Lapindo mud is silica and alumina compounds so that it can be used as raw material for making zeolites. According to Jalil, et al. (2010), the compounds contained in the Lapindo mud are SiO_2 53.40%; Al_2O_3 23.80%; Na_2O 5.59%; Fe_2O_3 5.47%; Cl 2.89%; MgO 2.62%; CaO 2.40%; K_2O 1.63%; SO_3 1.24%. [1]

Zeolite is a gray mineral that is an alumosilicate crystal. Zeolite framework structure is only composed of polymers of inorganic compounds SiO_4 and AlO_4^- in a tetrahedral form with O atoms as the linker. This zeolite structure causes the zeolite to have pore channels with regular cavities. The regularity of the voids in this zeolite makes it easy for alkali and alkaline earth metal ions to fill the voids to balance the charge of Al cations. Zeolites have several uses, including as a catalyst, ion exchange, membranes and others. Natural zeolite has several shortcomings, including low crystallinity, thereby reducing its ability as an absorbent and catalyst, to overcome the weakness of natural zeolite, synthetic zeolite was developed [2].

Zeolite Y is a type of large porous zeolite. Zeolite Y is belongs to the type of faujasite. Faujasite can be synthesized using silica and alumina sources like other types of zeolite. The general formula for faujasite zeolite is $Na_j(AlO_2)_j(SiO_2)192_{-J})$. Zeolite Y is composed of chains of sodalite cages forming a 6-membered double ring with oxygen as a link then forming supercages with an average pore diameter of 7.4 while the inner cavity has a diameter of 12 which is surrounded by 10 solidtaes cages. Zeolite Y has a 3 axis structure with dimensions with pores that are perpendicular to each other and is built from construction units 4; 6 and 6-6 [3].

The synthesis method is often applied that is the hydrothermal method. The hydrothermal method is a synthesis method that involves heterogeneous chemical reactions with a solution medium at low temperature with a pressure of 1 atm in a closed system [4]. Hydrothermal is often termed as the reaction of hydrogen with an aqueous solvent under high pressure and at a controlled temperature and recrystallizing an insoluble material under ordinary conditions. The hydrothermal method itself has the basic principle of synthesizing the growth of a crystal in several reactions in a large number of water solvents using high pressure to dissolve the mineralizer and recrystallizing the material with the lowest solubility. The hydrothermal process itself uses a special vessel made of steel that is resistant to high temperatures and pressures called an autoclave [5]. The synthesis of zeolite Y was carried NaOH/Sludge in this study is to vary the weight of NaOH added to the weight of the mud which is kept constant.

METHODS

The equipments were glassware, mortar, and pestle, autoclave, oven, 100 mesh sieve, universal pH indicator, a set of reflux apparatus, magnetic stirrer, analytical balance of Ohauss Analytical Plus brand, Muffle furnace 1400 brand Barnsted Termoylne, XRF brand Bruker S2 Ranger, XRD brand Xpert MPD.

[a] N. Andarini, R. Prambudi, T. Haryati, Suwardiyanto, YA. Sulistiyo
Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Jember
*e-mail: tanti.fmipa@unej.ac.id

The materials used in this study included Lapindo mud from Sidoarjo, NaOH (Merck, 99%), HCl (Merck, 37%), SiO_2 (Merck), ordinary filter paper, and aquademin.

Sample Preparation

The Lapindo mud taken from Balongnongo Hamlet, Renokenongo Village, Porong District, Sidoarjo Regency, East Java. Mud was taken at 4 points from the source of the mudflow, namely the north, south, west, and east of the mudflow source. Each point is 2 km from the center of the burst. Lapindo mud as much as 800 grams was washed using aquademin 1:2 (weight/volume) then filtered to separate the mud from impurities. Filtering is done by decantation to separate the mud from the filtrate. The decanted sludge was dried using an oven for 24 hours at 100 ºC to remove the water content, then ground and sieved with a 100 mesh sieve which would then be characterized using XRF.

Leaching

Sludge was taken as much as 10 grams in reflux using a 100 mL 2 M HCl solution. Reflux was carried out at 90 ºC for 1 hour. The refluxed sludge was then washed with aquadamine until the pH of the washing filtrate was neutral and the solids were dried in an oven.

Alkaline Smelting

The leached lapindo mud was mixed with NaOH in a porcelain cup, with variations in the weight ratio of NaOH/lapindo mud = 1.1; 1.3; 1.5; and 1.7. The mixture was heated in a muffle furnace at 550 ºC for 2 hours. The mixture from the furnace is then cooled, ground and then 5 grams is taken for analysis by XRF. Based on the XRF results, the ratio of 1.5 is the best.

Hydrothermal Process

The autoclave containing the sample was placed in an oven at a temperature of 100 ºC-105 ºC for 24 hours. Furthermore, the hydrothermal zeolite was filtered and washed with aquademin until the pH of the washing filtrate was neutral. The filtered residue was dried in an oven at a temperature of 100 ºC until dry, then the resulting mass was weighed.

Zeolite Characterization

The zeolite from the synthesis was characterized by using X-Ray Difractometer (XRD) and X-Ray Fluorescence (XRF). The characterization used XRD to identify the crystal structure and purity of the synthesized zeolite, and XRF to determine the composition of the elements in the zeolite sample.

RESULTS AND DISCUSSION

Composition of the starting material or zeolite precursor Y

Zeolite Y synthesized from Lapindo mud has the main content of silica and alumina. The dried Lapindo mud was pulverized and then sieved using a 100 mesh sieve, the next step was the leaching process using HCl. The purpose of leaching is to reduce other metals that are not needed in the zeolite synthesis process. The desired metal content in this research process is Si and Al because these two elements are the main constituents of zeolite Y to be made, while metals whose presence is not desired in this study are Fe, K, Ca, Mo, and Ti metals. These metals can later interfere with the zeolite formation process. The initial samples of leached mud and sludge were analyzed using XRF to determine the effect or changes in composition that occurred. Based on the results of XRF analysis, most of the Lapindo mud content is shown in Figure 1.

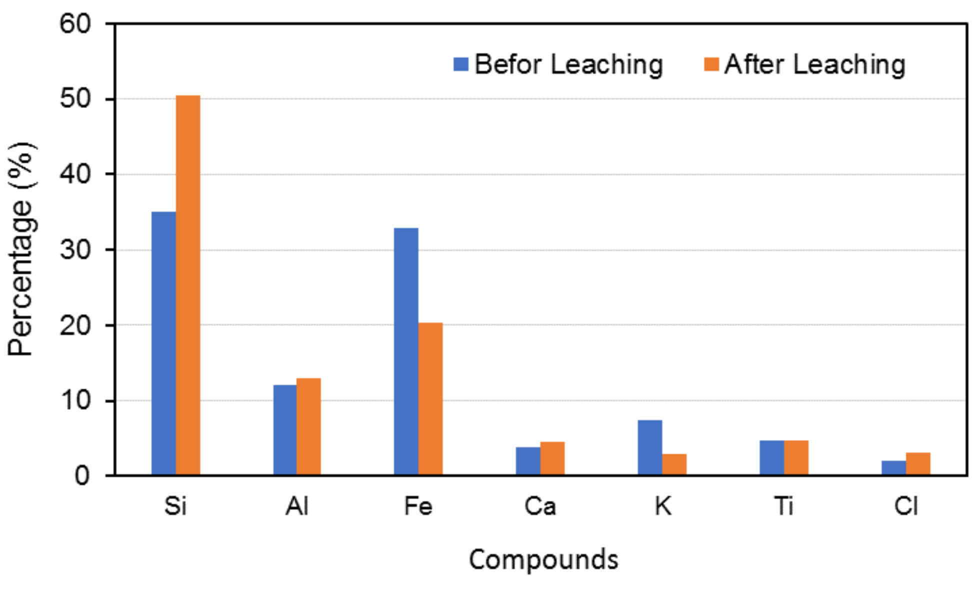

Figure 1. The composition of the sludge from the XRF analysis before and after the leaching process

Figure 1. Shows that there was a large increase in the percentage of Si and Al compounds after the leaching process, and also a decrease in the percentage of other elements. In general, this is due to the binding of Fe, Al, Ca, Ti, Fe, Ni, Cu, Zn, Re and V compounds by acid solvents so that these compounds dissolve in acid solvents. In contrast to the element Si which has a small solubility in acid solvents so that its content increases after the leaching process. In addition, there are several other factors that affect the leaching process, including the concentration of HCl, leaching time, temperature, and the ratio of HCl to sludge. Some of these factors have an effect that is directly proportional to the amount of metal oxides dissolved in the HCl solution. The dissolution reaction of metal oxides against HCl is shown in the following equation:

$$K_2O(s) + 2\,HCl(aq) \rightarrow 2\,KCl(aq) + H_2O(l)$$
$$Fe_2O_3(s) + 6\,HCl(aq) \rightarrow 2\,FeCl_3(aq) + 3\,H_2O(l)$$
$$CaO(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l)$$

The yellow color of the filtrate indicates ferrous metal dissolved in HCl solution. The physical properties of the sludge before the leaching process have a gray-black color, while the physical properties of the leached sludge that have been neutralized and dried are lighter gray than the initial sample before the leaching process. The alumina content should be lower than the initial content before leaching because the alumina compound (Al_2O_3) is an amphoteric compound that will react with acids or bases so that it dissolves in HCl solution. Alumina will react with HCl molecules to form aluminum chloride compounds ($AlCl_3$) which are soluble in water. The composition of alumina in Figure 1 increases due to the decrease in the percentage of other elements so that it affects the percentage of alumina in the percentage of concentration as much as 100%.

The next process is the melting process. The prepared sludge will be melted with NaOH. The purpose of smelting using NaOH is to activate the compound so that sodium silicate and sodium aluminate are dissolved in water. When the NaOH content is higher in the mixture during the smelting process, the more Na^+ ions will react with the alumina and silica contained in the mud so that the results of sodium silicate and sodium aluminate will be more and more. The reactions that occur during melting are:

$$NaOH + Al_2O_3.SiO_2 \rightarrow Na_2SiO_3 + NaAl(OH)_4$$

After the smelting process, the resulting sludge is then characterized using XRF. Based on the results of XRF analysis, the contents of the smelted samples can be seen in Figure 2.

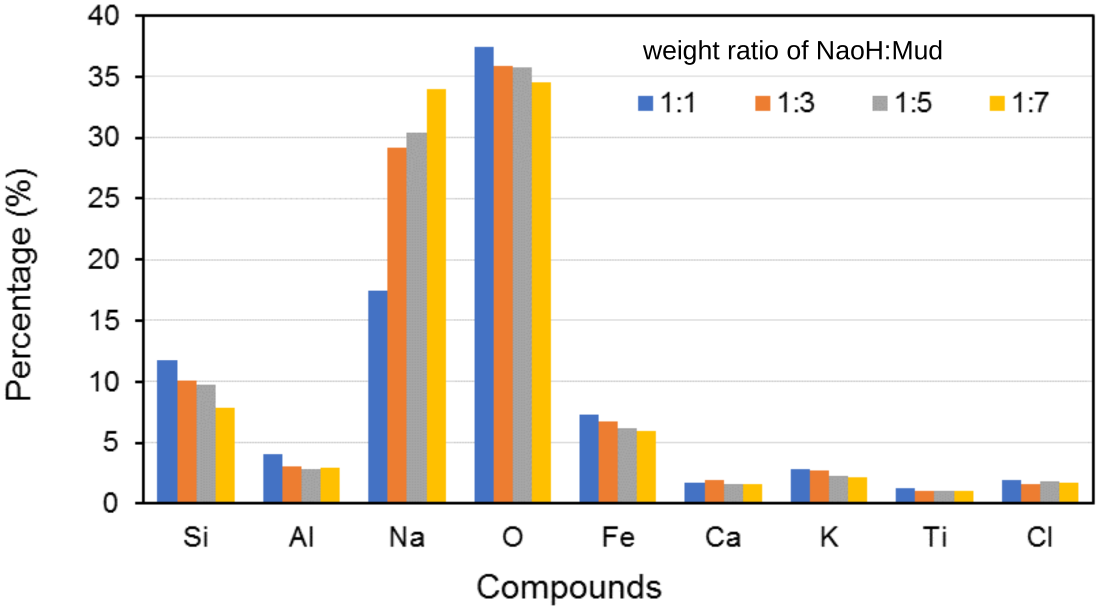

Figure 2. Composition of elements in the smelting sample at various weight ratios of NaOH/mud from XRF analysis

Based on Figure 2. Shows that the four smelted samples at various ratios of NaOH/mud weight ratio have some metal element content, but not all of these metal contents are used in the zeolite Y synthesis process. The metals needed in this study are Si, Al, Na and O, because these four elements are the main constituents of zeolite Y. Metals that are not needed in this study are Fe, Ca, K, Ti, and Cl, because these five elements are not involved in the process of making zeolite Y. Based on Figure 2. it can be seen that the higher the ratio of the content of metal elements needed the higher and also followed by a decrease in the content of metals that are not needed. The data obtained in the XRF analysis. The analysis data is used as an indicator to determine the mass of SiO_2 and NaOH that needs to be added.

The smelted mud mixture was added with water, SiO_2, and NaOH. Water is needed in a hydrothermal process in a certain amount, besides the purpose of adding water is to dissolve the sodium silicate and sodium aluminate contained in the mixture so that it can be separated from impurities through filtration. The mixture is then aged for 48 hours. The purpose of the aging process is to produce a more crystalline zeolite polymer. The aging mixture in the form of colloid is then filtered, the filtered filtrate is a solution of sodium silicate and aluminate. This is in accordance with the reaction equation.

$$SiO_2(s) + 2NaOH(aq) \rightarrow Na_2SiO_3\,(aq) + H_2O(aq)$$

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2NaAl(OH)_4(aq)$$

The resulting filtrate of sodium silicate and sodium aluminate solutions is slightly yellowish in color, not cloudy, the solution is slippery and slightly viscous. The filtrate is then hydrothermally using an autoclave and placed in an oven at a temperature of 100-105 °C for 24 hours. Hydrothermal is a heating process at a certain temperature with the balance of steam and water maintained. The resulting crystals are then filtered and neutralized using aquademin. The resulting synthetic zeolite is white.

The synthesis of zeolite Y in this study was carried out at alkaline pH because at that pH in solution polymerization of zeolite-forming ions will occur. The zeolite synthesis is influenced by the ions present in the mixture. At pH>6, $Al(OH)_4^-$ or AlO_2^- anions are formed, which are zeolite-forming anions derived from alumina. This will be different if the solution is in an acidic state, namely at pH 1 to 4 because the dominant Al compound is $[Al(H_2O)_6]^{3+}$.

The presence of these cations will inhibit the formation of the aluminosilicate framework of the zeolite. The zeolite framework is also affected by the presence of silicate anions. At pH>12, $Si(OH)_4^-$ ions will be formed, which is the main ion in the formation of the zeolite framework. The total reactions that occur during the synthesis are as follows:

$$2\ NaOH(aq) + Al_2O_3(s) \rightarrow 2\ NaAlO_2(aq) + H_2O(l)$$
$$2\ NaAlO_2(aq) + 4H_2O(l) \rightarrow 2\ NaAl(OH)_4(aq)$$
$$2\ NaOH(aq) + Al_2O_3(s) +\ 3H_2O(l) \rightarrow NaAl(OH)_4(aq)$$
$$Si(OC_2H_5)_5\ (aq) +\ 4\ H_2O(l) \rightarrow Si(OH)_4(aq) + 4C_2H_5OH(l)$$
$$NaOH(aq) + Al_2O_3(s) + Si\ (OC_2H_5)_4\ (aq) + 7\ H_2O(l) \rightarrow\ 2\ NaAl(OH)_4(aq) + Si(OH)_4(aq) +\ 4C_2H_5OH(l)$$
$$2NaAl(OH)_4(aq) + Si(OH)_4(aq) + 4C_2H_5OH(l) \rightarrow [Na_2(AlO_2)_2\ (SiO_2).\ 6H_2O]\ (gel)$$
$$[Na_2(AlO_2)_2\ (SiO_2).6H_2O](gel) \rightarrow Na\ [(AlO_2)_2\ (SiO_2).6H_2O]\ (crystal)$$

Y Zeolite Crystal Structure

The synthesized zeolite in this study was characterized by X-Ray Diffraction (XRD) to determine the purity and crystallinity of the zeolite Y produced by comparing the diffractogram of the zeolite sample analysis with standard zeolite Y The diffractogram of standard zeolite and zeolite Y samples is presented in Figure 3.

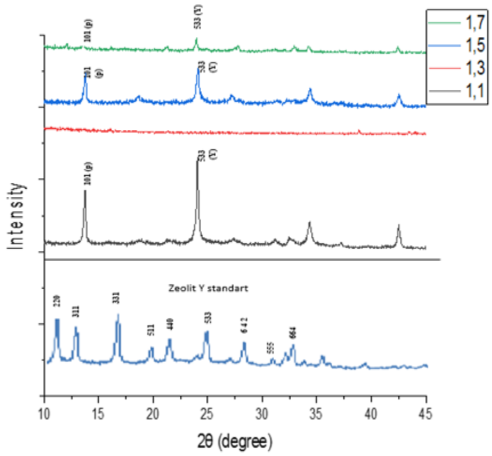

Figure 3. Standard Zeolite Y Diffractogram and Zeolite Y Diffractogram Synthesis Results Variation of NaOH/mud weight ratio

Based on Figure 3, the four samples of zeolite Y which were synthesized with variations in the weight ratio of NaOH/mud have diffractogram patterns that are not much different. The difference that is clearly visible in the diffractogram above is the ratio of 1.3 because it looks flat and there is no peak between 2θ 10˚-15˚ angles. The peak was produced by zeolite as a result of the synthesis of various weight ratios of NaOH/mud ratio 1.1; 1.5; and 1.7. The 2θ 10˚-15˚ angle is the main peak characteristic of the standard Y zeolite.

Based on Table 1, it can be seen that the zeolite Y produced from the four variations in this study was not pure, because the formation of the faujasite framework could undergo a metastable state. In general, the synthesis of zeolite Y from natural materials tends to produce a mixture of zeolite Y and zeolite P. It can be seen in Table 1. That zeolite P appears in the four variations in the weight ratio of NaOH/mud from an angle of 2θ. The cause of the mixture of zeolite Y and zeolite P is due to the influence of unnecessary metals found in the lapindo mud which is used as a source of silica and alumina. The higher the ratio of NaOH/mud weight, the less 2θ angle of zeolite P appears, this is because the increase in the weight ratio of NaOH/sludge is also followed by a decrease in cations. Because the higher the NaOH content, the higher the Si/Al ratio, the smaller the cation needed to neutralize it because the Al is getting less where Al is a negative charge carrier. The comparison of Si/Al content can be seen in the appendix. The reduced source of silica and alumina causes a slight 2θ peak typical of zeolite P found, namely the ratio by weight of NaOH/mud 1.5 and 1.7 has a higher degree of similarity with pure Y zeolite than the variation in the ratio of NaOH/mud 1.1 and 1.3 because fewer typical 2θ peaks of zeolite P were found.

Table 1. Results of qualitative analysis of zeolite Y products with standards in the Collection of Simulated XRD Powder Patterns for Zeolite

Weight Ratio of NaOH:Mud							
1:1		1:3		1:5		1:7	
2θ (º)	Intensity	2θ (º)	Intensity	2θ (º)	Intensity	2θ (º)	Intensity
-	-	-	-	-	-	12.06	27.82
13.74	72.1	-	-	13.82		13.64	53.7
15.91	39.93	16.04	55.9	-	-	16.26	7.04
21.28	4.27	-	-	-	-	-	-
24.06	100	-	-	24.11	100	23.93	100
27.37	4.66	-	-	27.25	22.27	27.84	41.75
31.18	5.11	-	-	31.4	5.97	31.21	13.56
34.34	27.52	-	-	34.4	43.82	34.24	44.9
-	-	38.38	100	-	-	-	-

The data from XRD analysis can also be used to determine the crystal size. The crystal size of the synthesized zeolite Y can be calculated using the Debye Schereer equation. The crystal size of the synthesized zeolite Y can be seen in Table 1. The crystal size of the synthesized zeolite Y is in the range of 19 nm - 735.40 nm. The small size of the crystal is related to the value of FWHM. FWHM is a parameter commonly used to calculate the width of the hill from a curve by determining the distance between 2 points that have a value of half of the maximum value of the curve. The smaller the FWHM value, the larger the crystal size. [9].

Table 2. Size of Synthesized Zeolite Y Crystals

Molar ratio SiO_2/ Al_2O_3	Angle 2θ	Crystal Size (nm)	average (nm)
7.35	6,84	10.29	37.27
	24.42	84.44	
	31.42	16.98	
8.35	12.38	59.67	42.17
	24.24	65.85	
	31.41	23.37	
9.35	12.26	40.05	47.57
	24.23	87.81	
	31.37	14.86	

Based on Table 2, the crystal size of zeolite Y synthesized by the molar variation of SiO_2/Al_2O_3 has an average crystal size from the smallest order to the largest, which is the NaOH/mud ratio of 1.5; NaOH/sludge ratio 1.7; the NaOH/sludge ratio is 1.3 and the NaOH/sludge ratio is 1.1. The smaller the crystal size, the more tightly and regularly the crystal structure results, causing a higher degree of crystallinity [10]. Thus, the best Y zeolite is 1.5 because the crystal size is small so that the crystallinity is high and the zeolite P impurity is also small.

CONCLUSION

Zeolite Y variations in the weight ratio of NaOH/mud based on the zeolite character produced the best at a weight ratio of 1.5 NaOH/mud because the crystal size is small so that the crystallinity is high and the zeolite P impurity is also small.

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