**Armayani Malek1, Musdalifa Mansur1, Reza Asra1, Muh Irwan1, Dhian Ramadhanty1, Subaer2, Mohd Mustafa Al Bakri Abdullah3, Ikmal Hakem Aziz3**

1Faculty of Sciences and Technology, Universitas Muhammadiyah Sidenreng Rappang, Jl. Angkatan 45 lt. Salo No. 1A Macarowalie Rappang 91651, Indonesia.

2Faculty of Mathematics and Natural Sciences, Universitas Negeri Makassar, Jl. Mallengkeri Raya Parang Tambung Kec Tamalate Kota Makassar 90224, Indonesia.

3Centre of Excellence Geopolymer and Green Technology (CEGeoGTech), Universiti Malaysia Perlish (UniMAP), Perlis, Malaysia.

**Study of Zeolite Phase Made from Rice Husk Ash and Sidrap Clay**

**Abstract**

Zeolite has been successfully synthesized from clay and rice husk ash in the form of powder by using the hydrothermal method with variations in chemical compositions of alkaline solution and the amount of rice husk ash. The clay raw material was obtained from Sidrap area of ​​South Sulawesi and rice husk ash is obtained from the burning pile of rice husks. Sidrap clay and rice husk ash were activated using an alkaline solution of NaOH, and varied rice husk ash and the addition of AlCl3. For the addition of AlCl3, an alkaline solution of NaOH and H2O was used in the amount of 25.5 grams and variations of rice husk ash were 2.5 grams and 6.5 grams. Meanwhile, without the addition of AlCl3, an alkaline solution of NaOH and H2O was used for 20.5 grams and variations of rice husk ash from 2.5 grams and 6.5 grams. Then the mixture were then put into an autoclave with a temperature of 100 ℃ for 3 hours. The chemical composition of raw material used in the manufacture of zeolite was measured by using XRF, which showed the content of SiO2 was 45.80 wt% in the clay and 93.40% in the rice husk ash. The crystalline structure of the zeolite formed was characterized by X-Ray Diffraction (XRD). It was found the resulting zeolite were identified as Zeolite-Y, Hydrosodalite, and ZSM-5. The microstructure properties of the resulting zeolite was determined by using Scanning Electron Microscopy (SEM).

**Keyword:** Autoclave, Clay, Rice Husk Ash, Zeolite

1. Introduction

Zeolite is a silica alumina crystal which has a three-dimensional skeleton structure with a cavity in it. The structure and framework of hollow zeolites make zeolites have many uses, including as absorbers, ion exchange, gas sensors, catalysts and molecular filters [1,2]. Besides being porous, zeolites also have a unique structure and shape. In addition, the strength of zeolite acid can also be controlled [3].

Zeolite is usually synthesized through salvo thermal or hydrothermal methods, under suitable conditions, such as reaction time and temperature, atomic source, mineralization agent, template and calcination temperature [4]. Zeolite which is synthesized by hydrothermal method generally uses silica, alumina, and metal cations as precursors in the presence of an organic template [5]. Silica is used as a reactant can be obtained from various sources, it is generally available commercially in either a solution, gel, solid, colloid, or a derivative, organic compounds, for example tetraethylortosilicate [6].

About 20% of the weight of rice is rice husk, and varies from 13 to 29% of the composition of the husk is husk ash which is generated every time the husks are burned. The most common values of silica (SiO2) content in rice husk ash are 94–96% [6]. The high content of silica in rice husk ash, make it suitable for manufacturing of zeolite-based materials [7].

Clay minerals are layered silicates. The mineral crystalline structure is composed of SiO4 tetrahedron layers. There is usually a hydroxyl ion (OH-) in the center of the 6-girded SiO4 tetrahedron. Clay minerals, consisting mainly of aluminum and/or iron and magnesium silicates. Some of them also contain alkaline or alkaline earth as their basic component. Clay minerals are very small (less than 2 microns in size) and are electrochemically active particles visible only by electron microscopy [8].

The synthesis of zeolite has been widely studied before, such as in Pattaraporn Lohsoontorn and Paisan Konglachuichay (2006) who succeeded in synthesizing zeolite from pearlite and rice husk ash using hydrothermal processes at temperatures of 140 and 170 ℃ [9]. Fuadi et al. (2012) succeeded in synthesizing zeolite from rice husk ash through a microwave process by varying temperature and time [1]. Mohammed et al. (2015) obtained zeolite Y in the form of sodium (NaY) synthesized using a silica source from rice husk ash [10]. Azizi and Yousefpour (2010) synthesized zeolite NaA and analcime using rice husk ash using the hydrothermal method [11].

In this research, zeolite synthesis will be carried out using the hydrothermal method by utilizing the waste of rice husk ash and clay which is widely found in Sidrap area of South Sulawesi where, in rice husk ash and clay, it contains silica which can be used as a zeolite material.

**2. Experiment**

The clays used as the basic material for zeolite was taken from Sidrap Regency, South Sulawesi. The clay is cleaned of impurities and soaked with aquadest to separate large clumps of clay particles. The resulting clay bath was filtered and then dried in the oven at 100 ℃ for 2 hours. The dry clay is crushed to obtain a smaller particle size and then sieved with a 200 mesh sieve. The result of the sieve was then dehydroxylated for 4 hours at a temperature of 750 ℃.

Rice husk ash used as a zeolite-making mixture comes from Sidrap Regency, South Sulawesi. The rice husk ash taken from the rice mill is first soaked in a solution of 0.1 mol of HCl for 4 hours. The HCl solution is intended to release impurity minerals that adhere to rice husks. The soaking product was washed with aquadest several times until the remaining HCl solution was lost and dehydroxylated at 850 ℃ for 4 hours.

The method used in the manufacture of zeolite is the hydrothermal method using an autoclave. Clay and rice husk ash was activated using a solution of NaOH and H2O and mixed 2.5 grams of AlCl3.

The addition of NaOH functions as an alkaline condition during the synthesis of zeolite Na-Y, and also to form a soluble sodium alumina salt so that it can be converted into zeolite. Na+ cations from NaOH are used to stabilize the charge of Al3+ ions in the zeolite framework, but they are also needed for zeolite synthesis under hydrothermal conditions [12].

After everything is mixed then it is poured into a cylinder mold and put into an autoclave and heated in an oven for 3 hours at 100 ℃.

<Tab. 1>

**3. Results and Discussion**

**X-ray Fluorescence (XRF) Results**

XRF analysis is carried out to determine the constituent elements of the raw material with the interaction of X-rays. The results of characterization (XRF) of the mineralogy of clay and rice husk ash is shown in table 2. The calculation of the oxide molar ratio of the starting material for synthesis was based on the results of X-ray fluorescence spectrometers (XRF).

<Tab. 2>

From the table above, it can be seen that the SiO2 content in each of the basic ingredients is very high, namely 45.80 wt% clay and 93.40 wt% rice husk ash.

**Characterizationof *X-Ray Diffraction*(XRD)**

XRD characterization was carried out to identify the phase, lattice parameter, and degree of crystallinity present in each sample.

<Fig. 1>

It can be seen that the XRD results in Figure 1A showing the diffractogram of dehydroxylated clay at 750 ℃. The content that is dominated by Quartz and is followed by other elements such as Magnetite and Dialuminum Silicate Oxide. The highest intensity is at 26,613o (2θ) which is identified as Quartz.

Meanwhile, rice husk ash that had been dehydroxylated at 850 ℃ was characterized using XRD in Figure 1B. It shows that the SiO2 diffractogram pattern of rice husk ash is crystalline, with the highest intensity at the peak of 23.2810 (2θ) owned by Tridymite.

<Tab. 3>

From the data in Table 3, it can be seen that the dominant phase formed in sidrap clay is the Quartz

<Tab. 4>

And from the percentage of table 4. XRD data shows that the dominant phase formed in rice husk ash is the Tridymite, syn phase of 99.5 wt% and there is a KCl (Sylvine) impurity of 0.5 wt%. Compounds containing potassium are one of the main impurities in rice husks, which greatly disturbs the isolation process of pure silica from rice husks [13]. Thus, rice husk ash is used as a source of SiO2 in the synthesis of Zeolite Y.

After going through the hydrothermal process, the results of the XRD diffractogram pile from mixing the basic ingredients of clay and rice husk ash can be seen in Figure 2. There is a difference in the diffractograms of each zeolite formed which indicates a difference in zeolite type as a result of the alkaline composition as the activator, rice husk ash content, and the amount of AlCl3.

<Fig. 2>

<Fig. 3>

<Tab. 5>

The hydrothermal zeolite diffractogram pattern of XRD test results in each sample was in the form of crystals with the identification of different types of zeolite formed, namely Zeolite-Y, ZSM-5 and Hydrosodalite. This is due to the varying conditions of the composition of the material and alkali as summarized in Table 5. Figure 3 shows the XRD pattern in each sample.

Figure 3A shows the zeolite types Hydrosodalite, B Zeolite Y, C Zeolite Y and D Zeolite type ZSM-5 with each containing a hematite phase in the sample according to table 5. Due to the clay content there is a hematite phase which is difficult to remove even though it has been synthesized. The impurity of zeolite formed or not forming zeolite with one particular type of zeolite mineral is due to the less optimal orientation of the crystal formation in the zeolite mineral. This is due to the formation of different zeolite frameworks according to the time required and the Si / AL ratio [14]. As well as the concentration of NaOH in taking silica from rice husk ash greatly affects how much silica is in the zeolite synthesis process so it will also affect the results of the zeolite formed [15].

In contrast to research conducted by Arnelli, et al. 2017 zeolite synthesis carried out at hydrothermal temperatures of 150 ℃ gave results in the form of a different diffractogram than the zeolite diffractogram that was synthesized at hydrothermal temperatures of 50 ℃ and 100 ℃. At 50 ℃ and 100 ℃ zeolite-A was obtained and at 150 ℃ Zeolite-Y was obtained [16].

In general, ZSM-5 synthesis is carried out hydrothermally at temperatures above 100 ℃, either with or without an organic template, from various types of silica sources. In Prasetyoko, et al. (2012) the results showed that the ZSM-5 phase began to form at 12 hours of hydrothermal crystallization at a temperature of 175 ℃. The maximum crystallinity and purity were achieved at 24 hours crystallization time. Meanwhile, in this study, zeolite ZSM-5 was formed at a temperature of 100 ℃ although there was still a small amount of zeolite contained, namely 0.5% [17].

**Characterization of *Scanning Electron Microscopy* (SEM)**

Characterization by Scanning Electron Microscopy (SEM) was performed to identify the surface morphology of the zeolite crystals formed. The results of the characterization of the basic material for sidrap clay are presented in Figure 4.

It can be seen that the sidrap clay morphology with a magnification of 10,000 kx shows grains of varying sizes and flat shapes. The relatively non-uniform white scale of the SEM image indicates the chemical composition of the material with the same atomic number, namely Fe.

<Fig. 4>

<Fig. 5>

Figure 5 shows the morphology of zeolite A and B samples at 100 ℃ having a uniform size on the addition of AlCl3 compared to zeolite without AlCl3. Whereas zeolite without the addition of AlCl3 in Figures 5 C and D, the grain size of the zeolite varies widely. It can be seen that the addition of AlCl3 greatly affects the size shape of the zeolite sample produced.

4. Conclusions

Zeolite has been successfully synthesized in the form of a powder which is synthesized from clay and rice husk ash by hydrothermal method using variations in chemical composition and rice husk ash. Zeolites formed at temperature of 100 ℃ for 3 hours are Zeolite-Y, Hydrosodalite, and ZSM-5.

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CORESSPONDING AUTHOR:

Malek Armayani, Faculty of Sciences and Technology, Universitas Muhammadiyah Sidenreng Rappang, Jl. Angkatan 45 lt. Salo No. 1A Macarowalie Rappang 91651, Indonesia.

e-mail: [armayanim@gmail.com](mailto:armayanim@gmail.com)

FIGURE CAPTIONS:

**Figure 1.** Results of Characterization of X-Ray Diffraction (XRD) A) Clay Base Material and B) Rice Husk Ash

**Figure 2.** The results of the X-Ray Diffraction (XRD) characterization of zeolite samples

**Figure 3.** Characterization Results of X-Ray Diffraction (XRD) A) A31 AlCl3, B) A32 AlCl3, C) B31, and D) B32

**Figure 4.** Results of Characterization Scanning Electron Microscopy (SEM) Clay Base Material with magnification of 10,000 kx

**Figure 5.** Scanning Electron Microscopy (SEM) Characterization Results of Zeolite with magnification of 10,000 kx A) A31 AlCl3, B) A32 AlCl3, C) B31, and D) B32

TABLES

**Table 1.**Chemical compositions for zeolite production

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Sample Identity** | **Mass of raw material (gram)** | | | |
| **NaOH+H2O** | **AlCl3** | **RHA** | **Clay** |
| **A31AlCl3100 ℃** | 20,5 | 2,5 | 5 | 25 |
| **A32AlCl3100 ℃** | 20,5 | 2,5 | 6,5 | 25 |
| **B31 100 ℃** | 25,5 | - | 5 | 25 |
| **B32 100 ℃** | 25,5 | - | 6,5 | 25 |

**Table 2.**Results of XRF Characterization

|  |  |  |
| --- | --- | --- |
| **Element** | **Clays (wt%)** | **RHA (wt%)** |
| **Al2O3** | 18,00 | - |
| **SiO2** | 45,80 | 93,40 |
| **K2O** | 0,78 | 4,53 |
| **CaO** | 0,29 | 1,34 |
| **TiO2** | 2,19 | - |
| **V2O5** | 0,13 | - |
| **Cr2O3** | 0,11 | - |
| **MnO** | 0,085 | 0,466 |
| **Fe2O3** | 32,71 | 0,13 |
| **NiO** | 0,030 | - |
| **CuO** | 0,12 | 0,071 |
| **ZnO** | 0,029 | 0,054 |
| **ZrO2** | 0,11 | - |

**Table 3**. XRD Qualitative Analysis Data of Clay Basics

|  |  |
| --- | --- |
| **Phase Name** | **Content (wt%)** |
| **Dialuminum Silicate Oxide, Sillimanite, High** | 2,6 |
| **Magnetite, syn** | 5,9 |
| **Quartz low, syn** | 92 |

**Tabel 4**. XRD Qualitative Analysis Data

|  |  |
| --- | --- |
| **Phase Name** | **Content (wt%)** |
| **Tridymite, syn** | 99,5 |
| **Sylvine** | 0,5 |

**Table 5**. XRD Qualitative Analysis Data

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Phase Name** | **A31 AlCl3 100 ℃ (wt%)** | **A32AlCl3 100 ℃ (wt%)** | **B31 100 ℃**  **(wt%)** | **B32 100 ℃**  **(wt%)** |
| **Tridymite, syn** | 38 | 29 | 4,5 | 35 |
| **quartz low HP, syn** | 48 | 50 | 58 | 62 |
| **Zeolite Y, (Na)** | - | 1.4 | 28 | - |
| **Iron diiron(III) oxide, magnetite low** | 1.3 | 19 | 9.6 | 3 |
| **Hydrosodalite, Sodalite** | 13 | - | - | - |
| **ZSM-5, dodecasilicon oxide hydrate** | - | - | - | 0.5 |