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STUDY OF ZEOLITE PHASE MADE FROM RICE HUSK ASH AND SIDRAP CLAY

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 the 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 $AlCl_3$. The addition of $AlCl_3$, an alkaline solution of NaOH and H_2O 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 $AlCl_3$, an alkaline solution of NaOH and H_2O was used for 20.5 grams and variations of rice husk ash from 2.5 grams and 6.5 grams. Then the mixture was then put into an autoclave with a temperature of 100°C for 3 hours. The basic material used in the manufacture of zeolite is carried out by X-ray Fluorescence (XRF) characterization to determine the constituent elements of basic material, which showed the content of SiO_2 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 were determined by using Scanning Electron Microscopy (SEM).

Keyword: Autoclave; Clay; Rice Husk Ash; Zeolite

1. Introduction

Zeolite is a silica-alumina crystal that 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. Besides, 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 [4,5]. Zeolite which is synthesized by hydrothermal method generally uses silica, alumina, and metal cations as precursors in the presence of an organic template [6]. 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 [7].

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 (SiO_2) content in rice husk ash are 94-96% [7]. Rice husk ash has been widely applied as a source of silica [8]. The high content of silica in rice husk ash, so it has the potential to be used as a material for making silica-based materials such as silica gel [9] and zeolite [10]. One way to increase the ability of silica to adsorb is modify the silica surface by adding certain materials. Materials added has properties that can bind to one or more metal ions so as to increase adsorption [11].

Clay minerals are layered silicates. The mineral crystalline structure is composed of SiO_4 tetrahedron layers. There is usually a hydroxyl ion (OH–) in the center of the 6-girded SiO_4 tetrahedron. Clay minerals, consisting mainly of aluminum and/

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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 [12].

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°C [8]. 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 [13]. Azizi and Yousefpour (2010) synthesized zeolite NaA and analcime using rice husk ash using the hydrothermal method [14].

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 the 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 were 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°C 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°C.

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. Washing with HCl will help increase the SiO_2 content in the reaction mixture. In acid treatment, the iron oxide present in rice husk ash will dissolve so that its presence can be removed. In addition, at the time of washing, the rice husk ash was dealuminated (low Al content), thus increasing the Si / Al ratio [15]. The soaking product was washed with aquadest several times until the remaining HCl solution was lost and dehydroxylated at 850°C 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 H_2O and mixed 2.5 grams of $AlCl_3$.

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 Al^{3+} ions in the zeolite framework, but they are also needed for zeolite synthesis under hydrothermal conditions [16].

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°C.

TABLE 1

Chemical compositions for zeolite production

Sample Identity	Mass of raw material (gram)			
	$NaOH+H_2O$	$AlCl_3$	RHA	Clay
$A_{31}AlCl_3$100°C	20,5	2,5	5	25
$A_{32}AlCl_3$100°C	20,5	2,5	6,5	25
B_{31} 100°C	25,5	—	5	25
B_{32} 100°C	25,5	—	6,5	25

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).

TABLE 2

Results of XRF Characterization

Element	Clays (wt%)	RHA (wt%)
Al_2O_3	18,00	—
SiO_2	45,80	93,40
K_2O	0,78	4,53
CaO	0,29	1,34
TiO_2	2,19	—
V_2O_5	0,13	—
Cr_2O_3	0,11	—
MnO	0,085	0,466
Fe_2O_3	32,71	0,13
NiO	0,030	—
CuO	0,12	0,071
ZnO	0,029	0,054
ZrO_2	0,11	—

From the table above, it can be seen that the SiO_2 content in each of the basic ingredients is very high, namely 45.80 wt% clay and 93.40 wt% rice husk ash.

Characterization of *X-Ray Diffraction*(XRD)

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

It can be seen that the XRD results in Fig. 1A showing the diffractogram of dehydroxylated clay at 750°C. The content that is dominated by Quartz and is followed by other elements such as

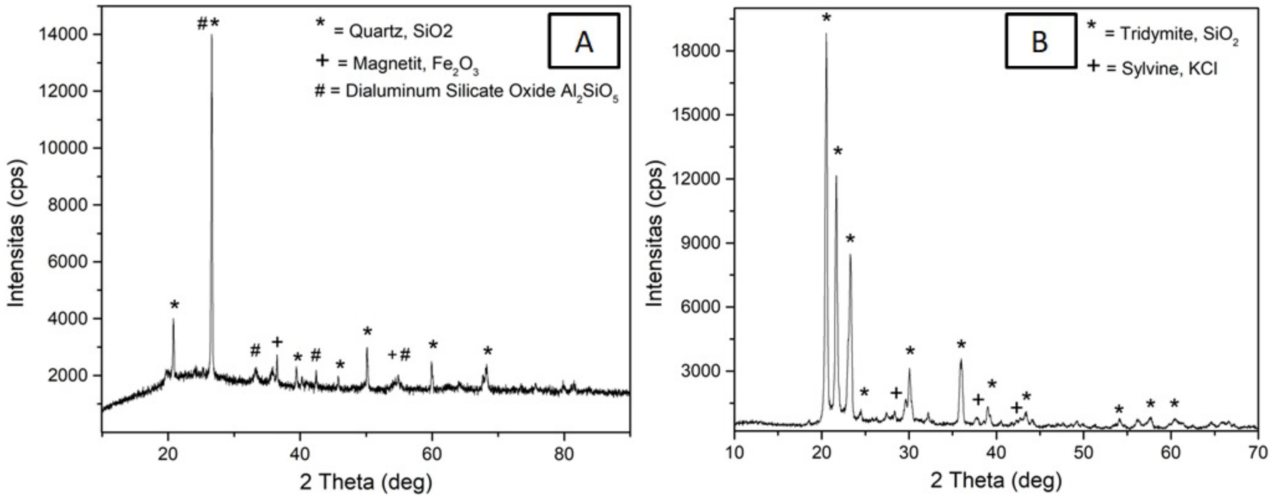

Fig. 1. Results of Characterization of X-Ray Diffraction (XRD) A) Clay Base Material and B) Rice Husk Ash

Magnetite and Dialuminum Silicate Oxide. The highest intensity is at 26,613° (2θ) which is identified as Quartz.

Meanwhile, rice husk ash that had been dehydroxylated at 850°C was characterized using XRD in Fig. 1B. It shows that the SiO_2 diffractogram pattern of rice husk ash is crystalline, with the highest intensity at the peak of 23.2810° (2θ) owned by Tridymite.

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

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

TABEL 4

XRD Qualitative Analysis Data

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

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 [17]. Thus, rice husk ash is used as a source of SiO_2 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 Fig. 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 $AlCl_3$.

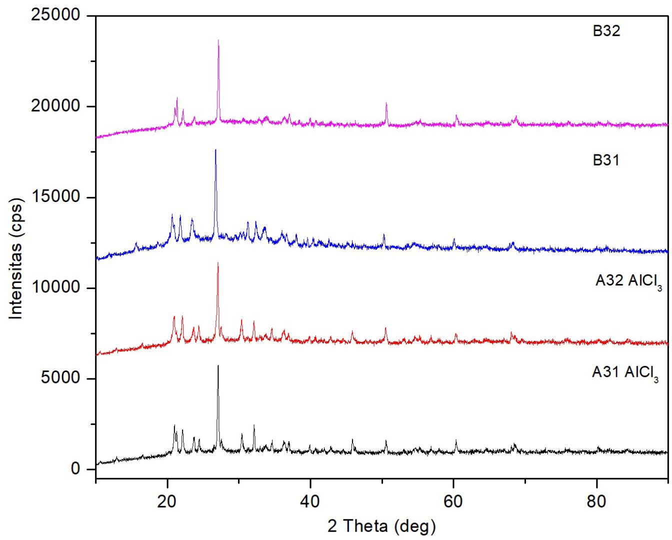

Fig. 2. The results of the X-Ray Diffraction (XRD) characterization of zeolite samples

TABLE 5

XRD Qualitative Analysis Data

Phase Name	A_{31} $AlCl_3$ 100°C (wt%)	$A_{32}AlCl_3$ 100°C (wt%)	B_{31} 100°C (wt%)	B_{32} 100°C (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

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. Fig. 3 shows the XRD pattern in each sample.

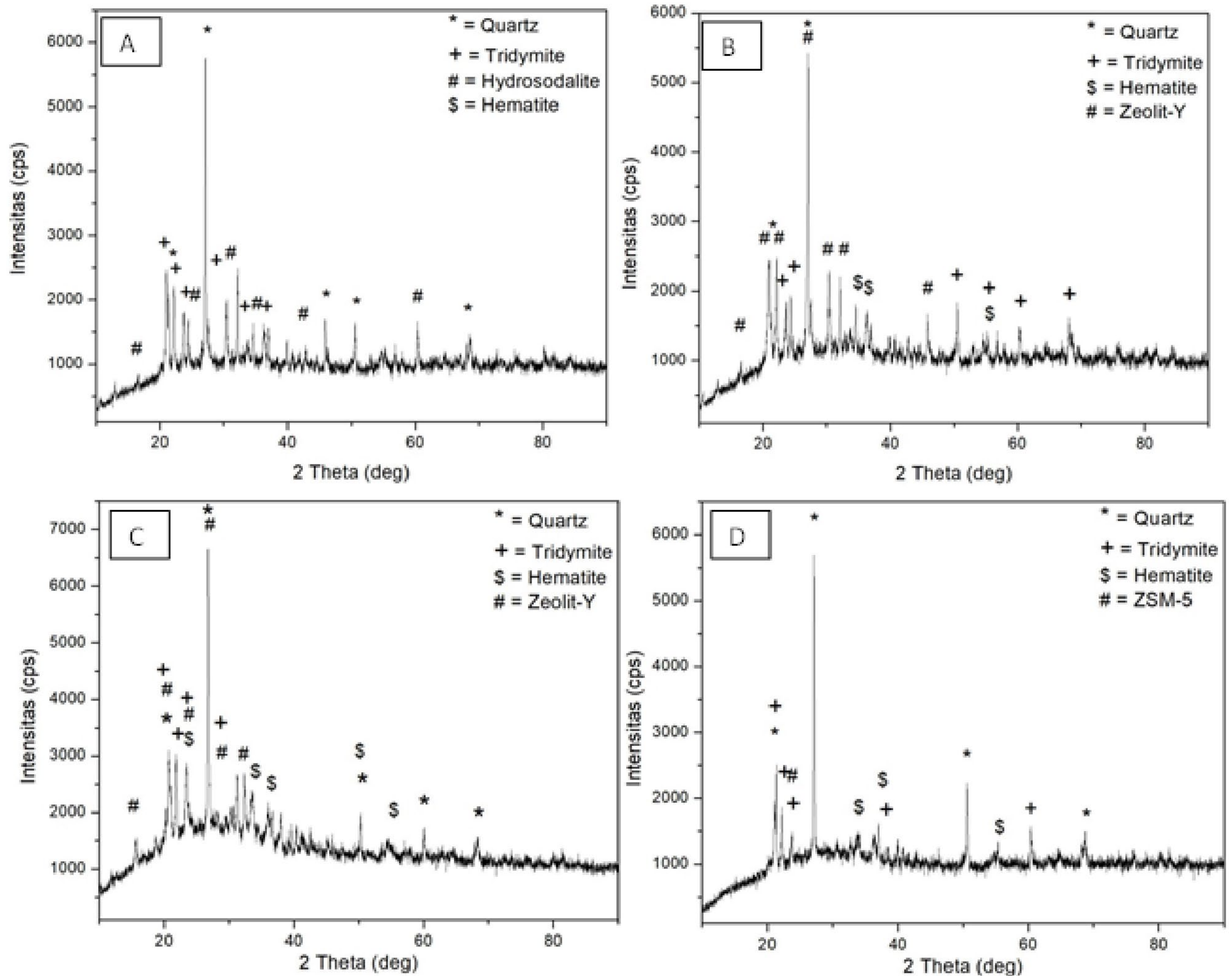

Fig. 3. Characterization Results of X-Ray Diffraction (XRD) A) A31 $AlCl_3$, B) A32 $AlCl_3$, C) B31, and D) B32

Fig. 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 [18]. 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 [19].

In contrast to research conducted by Arnelli, et al. 2017 zeolite synthesis carried out at hydrothermal temperatures of 150°C gave results in the form of a different diffractogram than the zeolite diffractogram that was synthesized at hydrothermal temperatures of 50°C and 100°C. At 50°C and 100°C zeolite-A was obtained and at 150°C Zeolite-Y was obtained [20].

In general, ZSM-5 synthesis is carried out hydrothermally at temperatures above 100°C, 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°C. 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°C although there was still a small amount of zeolite contained, namely 0.5% [21].

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 Fig. 4.

It can be seen that the sidrap clay morphology with a magnification of 10.00 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. 5 shows the morphology of zeolite A and B samples at 100°C having a uniform size on the addition of $AlCl_3$ compared

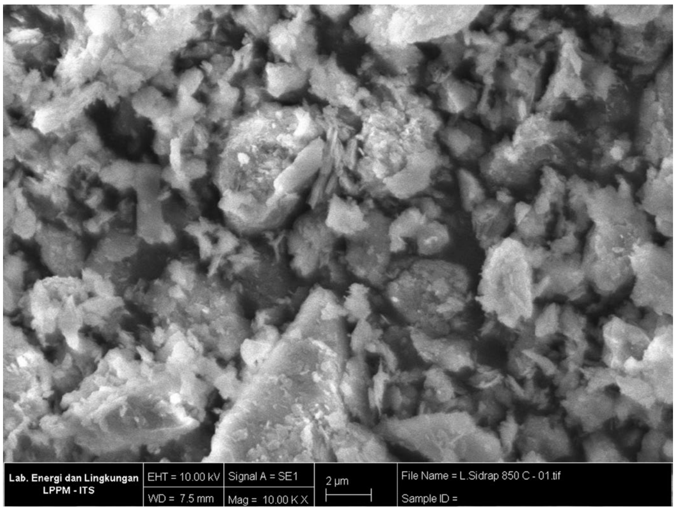

Fig. 4. Results of Characterization Scanning Electron Microscopy (SEM) Clay Base Material with magnification of 10.00 KX

to zeolite without $AlCl_3$. Whereas zeolite without the addition of $AlCl_3$ in Figs 5 C and D, the grain size of the zeolite varies widely. It can be seen that the addition of $AlCl_3$ greatly affects the size shape of the zeolite sample produced.

4. Summary

Zeolite has been successfully synthesized in powder form from clay and rice husk ash by hydrothermal method using a variety of chemical composition and rice husk ash. Zeolite is a good B3 absorbent material with abundant raw materials and easy synthesis procedures. The hydrothermal zeolite diffractogram pattern of XRD test results in each crystal sample was identified with different types of zeolite formed, namely Zeolite-Y, ZSM-5, and Hydrosodalite. This is due to the varying conditions of the material and alkaline composition. Based on the results of characterization by Scanning Electron Microscopy (SEM) morphological images 5 C and D, it can be seen that the addition of $AlCl_3$ greatly affects the size shape of the zeolite sample given.

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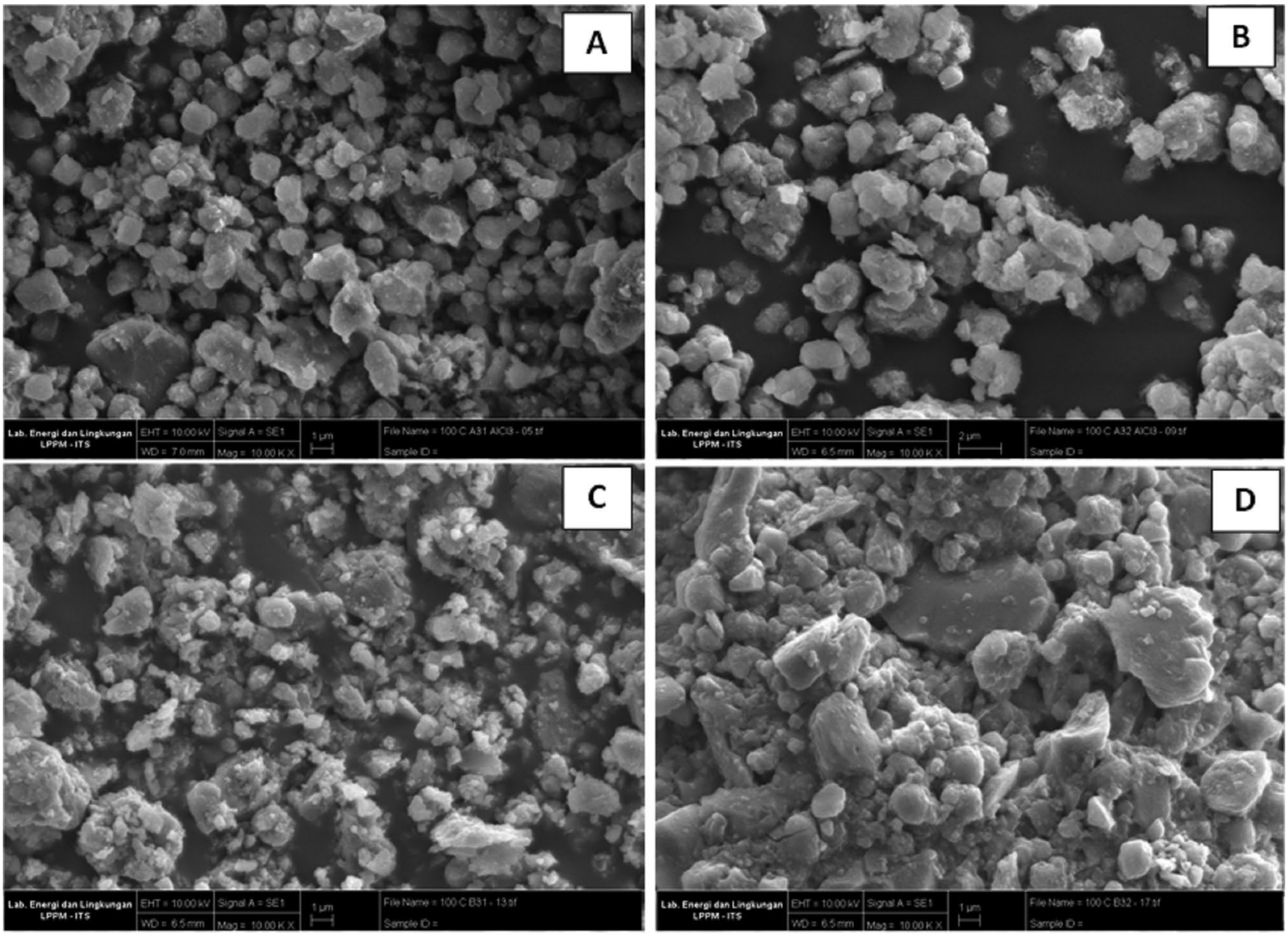

Fig. 5. Scanning Electron Microscopy (SEM) Characterization Results of Zeolite with magnification of 10.00 KX A) A31 $AlCl_3$, B) A32 $AlCl_3$, C) B31, and D) B32

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