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Analysis of the Effect of Zeolite Size Variations on The Content of Chemical Compounds in Acid Activated Natural Zeolite

(Analisis Pengaruh Variasi Ukuran Zeolit Terhadap Kandungan Senyawa Kimia Zeolit Alam Teraktivasi Asam)

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Abstract
One of the zeolite producing areas in Indonesia is Sukabumi. Natural zeolite originating from Sukabumi is composed of three main types of minerals: mordenite, clinoptilolite, and quartz. Zeolite as a catalyst can be improved by carrying out physical and chemical activation processes. Physically the catalyst can be activated by reducing the size of the zeolite through the grinding and sieving method. This physical activation process can increase the surface area of the zeolite. In this study, variations in the size of zeolite 80 mesh and 100 mesh were carried out and chemically activated by the acid activation method through immersion of natural zeolite with HCl and HF, from this acid activation process it will increase the acidity of the zeolite. Measurement of functional groups and chemical compounds in activated zeolite using XRF and FTIR. The results of XRF analysis showed that the SiO_2 content in 80 mesh zeolite was 69.5% and in 100 mesh zeolite 82.1%, and the FTIR analysis showed the presence of the C-H alkene functional group at a wavelength of 675-995 cm^{-1}, ring C-H aromatic at a wavelength of 690-900 cm^{-1}, C-O alcohol/ether/carboxylic acid/ester at wavelength 1610-1680 cm^{-1}, functional group C=C alkene 1610-1680 cm^{-1}, the O-H functional group is carboxylic acid at a wavelength of 3500-3650 cm^{-1} and an alcohol monomer/phenol O-H functional group at a wavelength of 3590-3650 cm^{-1}.

Keywords: Zeolite, Activation, Acid, XRF, FTIR

Sari
Salah satu daerah penghasil zeolit di Indonesia adalah sukabumi. Zeolit alam yang berasal dari sukabumi tersusun dari tiga jenis mineral utama yakni mordenit, klinoptilolit dan kuarsa. Zeolit sebagai katalis dapat ditingkatkan kemampuannya dengan melakukan proses aktifasi fisik maupun kimiawi. Secara fisika katalis dapat diaktivasi dengan cara mereduksi ukuran zeolit melalui metode penggerusan dan pengayakan dari proses aktivasi secara fisika ini dapat meningkatkan luas permukaan dari zeolit. Pada penelitian ini dilakukan variasi ukuran zeolite 80 mesh dan 100 mesh dan diaktivasi secara kimia dilakukan dengan metode aktivasi asam melalui perendaman zeolit alam dengan HCl dan HF, dari proses aktivasi secara asam ini akan meningkatkan sifat keasaman dari zeolit. Pengukuran gugus fungsi dan kandungan senyawa kimia pada zeolite yang telah diaktivasi menggunakan XRF dan FTIR. Hasil analisis XRF menunjukkan kandungan SiO_2 pada zeolite ukuran 80 mesh sebesar 69,5% dan pada zeolite ukuran 100 mesh sebesar 82,1%, dan hasil analisis FTIR menunjukkan adanya gugus fungsi C-H alkena pada Panjang gelombang 675-995 cm^{-1}, C-H cincin aromatic pada Panjang gelombang 690-900 cm^{-1}. C-O alcohol/eter/asam karboksilat/ester pada Panjang gelombang 1610-1680 cm^{-1}, gugus fungsi C=C alkena 1610-1680 cm^{-1}. Gugus fungsi O-H asam karboksilat pada Panjang gelombang 3500-3650 cm^{-1} dan gugus fungsi O-H alcohol monomer/fenol pada Panjang gelombang 3590-3650 cm^{-1}.

Kata-kata kunci: Zeolit, Aktivasi, Asam, XRF, FTIR

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I. INTRODUCTION

Indonesia has a total zeolite deposit of 447,490,160 tons. The potential of zeolite in Indonesia is caused by the location of Indonesia's territory which is in a series of volcanoes which causes geologically Indonesia to have great potential to produce zeolites (Kusdarto, 2008)

Natural zeolites are alumina silicate mineral crystals containing cations such as Na, Ca, K, Mg and Fe (Ginting et al, 2007). These crystals structurally form a three-dimensional framework, are acidic and porous in molecular size.

In its application, zeolites can be used as ion exchange agents, adsorbents, molecular filters, and catalysts (Windarti and Ahmad, 2004). The pore structure of the zeolite is filled with exchangeable cations, so that the zeolite has the ability as an ion exchange agent. This can be done by placing the zeolite into a neutral base or salt solution, which causes the cations in the zeolite framework to be replaced by ions in the alkaline/salt solution in equivalent amounts. When the zeolite is brought into contact with an acid solution, the aluminum contained in the -frame.

The zeolite used in this study is a natural zeolite originating from Sukabumi which has not been activated so that there are still many impurities. Impurities in the zeolite will reduce the ability of the zeolite to adsorb because the surface is covered by impurities.

Zeolites can be activated because of their hollow 3-dimensional structure. Zeolite can be activated both physical and chemical properties. The physical properties of zeolite can be changed through a heating process to remove water content from the zeolite structure. While the chemical properties of zeolite can be changed by removing impurities from the surface of the zeolite by reacting the zeolite with acid.

Several researchers have previously activated zeolite with the addition of transition metals (Sibarani, 2012) using the addition of Ni-Cr/natural zeolite metal and showed research results in the form of increasing cracking activity and selectivity of zeolite. In addition (Kusuma et al, 2011) utilize natural zeolite in the process of making biodiesel from palm oil.

In this research, an initial study of zeolite activation test will be carried out by immersing zeolite with acid at various sizes of zeolite. After that, FTIR and XRF tests were carried out to see the effect of size variations on the content of chemical compounds in the zeolite.

The surface area and acidic properties of zeolite make zeolite easier to change on the surface. In order for the performance of the zeolite as expected, it is necessary to activate the zeolite to condition it according to its designation. Zeolite can be activated both physical and chemical properties. The physical properties of zeolite can be changed through a heating process to remove water content from the zeolite structure. While the chemical properties of zeolite can be changed by removing impurities from the surface of the zeolite by reacting the zeolite with acid (Buchori and Budiyono, 2003). Zeolite is reacted with acid compounds through an immersion process for a while until the impurities are gone and rinsed until a neutral test result is obtained, after the zeolite is neutral, then the activated zeolite is dried.

The empty space in the zeolite cavity causes zeolite to be used as a catalyst (Setiadi et al, 2008). In the process of using zeolite as a catalyst, the diffusion process occurs in an empty space on the surface (Setiadi and Pratiwi, 2007).

The effectiveness of zeolites has also been shown to be applicable to isomerization activities, addition of alkyl hydrocarbons and petroleum cracking processes (Ermawati et al, 2016).

The variables observed included the effect of differences in the size of the zeolite on the content of chemical compounds in the zeolite. The observed characteristics include wavelength shift, zeolite crystallinity, chemical composition and Si/Al ratio in the zeolite. Natural zeolite as the raw material used is sourced from Sukabumi and is raw, not yet activated. Data collection was carried out at the Chemical Laboratory, Faculty of Earth and Energy Technology, Trisakti University, Jakarta.

II. METHOD

The zeolite used is natural zeolite obtained from Sukabumi. Preparations were carried out to condition the zeolite to have a larger volume and surface area, as well as the expected acidity and Si/Al ratio. These activities include washing, filtering, drying and calcining.

The zeolite activation process is carried out by being activated by acid by adding HCl and HF as shown in Figure 1.

Figure 1. Research Procedure

2.1. Zeolite size reduction

Zeolite was ground and filtered on a filter measuring 80 mesh 100 mesh.


(a)


(b)

Figure 2. Zeolite Filter

2.2. Zeolite Immersion and Filtration

The washing was carried out using distilled water for 3 repetitions, then filtered for further drying at a temperature of 120 oC for 2 hours. A total of 100 grams of natural zeolite were immersed in 1% (w/v) HF solution for 30 minutes. After being washed with distilled water to a neutral pH, the zeolite was filtered and dried in the sun to dry.


(a)


(b)

Figure 3. Zeolite Immersion and Filtration

2.3. Zeolite Reflux

The zeolite was refluxed in 6 M HCl for 5 hours, at an operating temperature of 60 oC, with continuous stirring.

Figure 4. Zeolite Reflux

2.4. Zeolite Drying

After being filtered and washed with distilled water until the pH of the filtrate was neutral, the zeolite was dried in an oven at 130°C for 3 hours. After drying soaked in 1% HF solution for 30 minutes.

Washing and neutralization using distilled water was again carried out until the pH of the filtrate was neutral. Zeolite was dried in an oven at 130°C for 3 hours. Calcination was carried out in a furnace at a temperature of 450°C, in order to obtain Na-Z (natural sodium zeolite).

Zeolite heating is carried out to evaporate the water particles contained in the zeolite cavities. In the presence of heating, the water will evaporate and increase the catalytic ability of the zeolite.

The catalytic ability and increased surface area make the zeolite easier to react and adsorb other elements. In addition, heating can also cause the structure of the zeolite to be stronger with the evaporation of water and the chemical bonds in the zeolite are getting stronger.

Figure 5. Zeolite Drying

2.5. Zeolite characterization

The prepared zeolites were analyzed for characteristics to determine the content of chemical components using XRF (X-Ray Fluorescence), to determine functional groups using FTIR (Fourier-Transform Infrared Spectrometer).

III. RESULTS AND DISCUSSION

Zeolite activation process is carried out physically and chemically.

3.1 Physical Activation Process

The Physical Activation process is in the form of reducing the size of the zeolite by grinding and sifting with various sizes, in this case the size of 80 and 100 Mesh is used which serves to see how the effect of size on the zeolite activation process.

Zeolites are aluminasilicate crystals. The constituent components of zeolite consist of three components, namely cations as the first component that can be exchanged on its surface with other cations and if heated it will increase the proton donor ability of the zeolite which causes the zeolite's catalytic activity to increase, alumina silicate framework and water content. In addition, zeolite also has a microporous structure which causes a large zeolite surface area.

This causes the zeolite to have a place that can be used in the reaction process. Another characteristic of zeolite is its hydrophobic nature, which indicates that zeolite is difficult to dissolve in water due to the presence of high Si/Al content. The hydrophobicity causes the reactants to diffuse rapidly.

Physical activation serves to increase the surface area of natural zeolite by reducing its size. The larger the surface area of a zeolite, the more the catalytic reaction will increase because more reactants can enter the pores. In addition, physical activation can be done by heating the zeolite so that the water trapped in the pores of the zeolite can evaporate and cause the surface of the pores to increase.

3.1 Chemical Activation Process

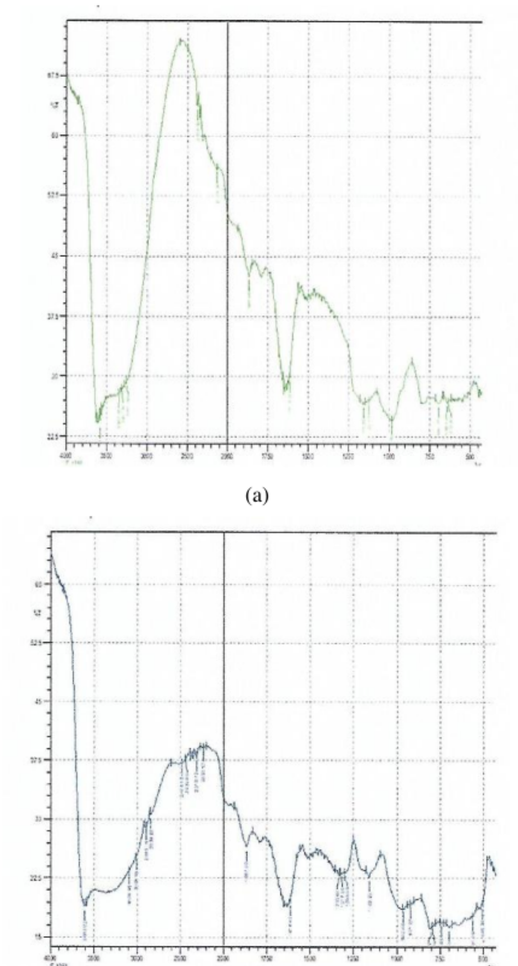
The chemical activation process is in the form of acid activation by immersing it with HCl and HF. Soaking with this acid serves to increase acidity, clean the surface of the pores, remove impurities and can also rearrange the position of the atoms that are exchanged and clean the zeolite from impurities which can increase the catalytic activity of the zeolite.

The acidity of a catalyst can be viewed from the understanding of acids and bases according to Bronsted and Lewis. Bronsted stated that the acidity of a catalyst is determined by the ability of the catalyst to form protons or proton donors, whereas according to Lewis, a compound or catalyst can act as an acid if it can accept a free pair of electrons from a base molecule. accepts a pair of electrons and binds them chemically to the catalyst surface. The addition of acidity to the catalyst aims to increase the catalytic activity of the catalyst. The increase in catalytic activity is influenced by the Si/Al ratio which increases with increasing acidity.

3.1 Zeolite Characterization

Zeolite characterization was carried out by analyzing the results of zeolite activation with XRF and FTIR

The FTIR test was carried out to see the functional groups contained in the sample. The movement of the graph peaks and the intensity of the graph on the FTIR show the difference in absorption in the sample. In this study, the samples were differentiated based on the sample size, namely 80 and 100 mesh.



(a)

(b)

Figure 6. Natural Zeolite 80 Mesh (a) and 100 Mesh (b) FTIR Test Results

From Figure 6, it is known that a peak appears at the wavelength of 675-995 cm^{-1} which indicates the presence of the C-H alkene functional group which usually appears at wavelengths of 3010-3095 and 675-995 cm^{-1}. Then a peak appears at a wavelength of 690-900 cm^{-1} which indicates the presence of an aromatic ring C-H functional group that appears at a wavelength of 3010-3100 and 690-900 cm^{-1}. Then a peak appears at a wavelength of 1050-1300 cm^{-1} which indicates the presence of a C-O alcohol/ether/carboxylic acid/ester functional group that appears at that wavelength. Then a peak appears at a wavelength of 1610-1680 cm^{-1} which indicates the presence of a C=C alkene functional group that appears at that wavelength. Then it appears at a wavelength of 3500-3650 cm^{-1} which indicates the presence of a monomeric carboxylic acid O-H functional group that appears at that wavelength. Then at a wavelength of 3590-3650 cm^{-1} which indicates the presence of the O-H alcohol monomer/phenol functional group which usually appears at that wavelength.

XRF test was performed on samples with a size of 80 mesh and 100 mesh. XRF tests were carried out on both samples in elemental and oxide forms. This is done to see how the percentages of elements at different sizes compare.

Table 1. Comparison of chemical element content between 80 mesh size zeolite and 100 mesh

No	Komponen	Kandungan Unsur Kimia Zeolit 80 Mesh (%)	Kandungan Zeolit 100 Mesh (%)
1	Al	9,1	0
2	Si	55,9	65,8
3	K	11,2	13,9
4	Ca	9,59	8,62
5	Fe	11,9	9,81

Different particle sizes cause the content of chemical elements in zeolite is also different. This is due to the difference in the surface area of the zeolite. There is a chemical element content that increases with increasing particle size and conversely there is an elemental content that decreases.

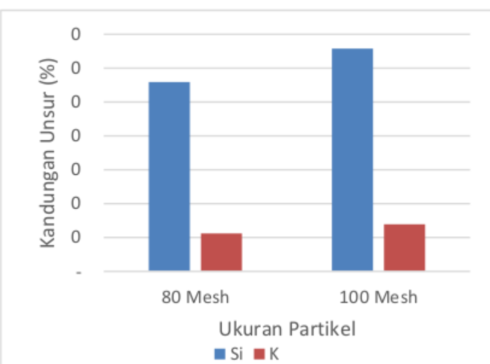


Figure 7. The content of chemical elements which increases with increasing size

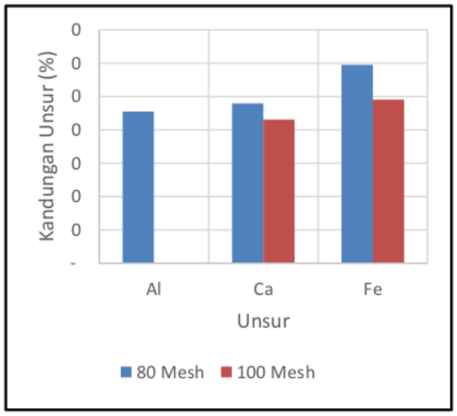


Figure 8. The content of chemical elements which decreases with increasing size

The content of Si and K elements increased with increasing sample size while the content of Al, Ca, and Fe elements decreased with increasing sample size. This is influenced by differences in the surface area of the sample so that it can increase the acquisition of elements, the smaller the size, the larger the surface area. While the elements that experience a decrease can be caused by the dissolved elements along with impurities.

Table 1. Comparison oxide compound content between 80 mesh size zeolite and 100 mesh

No	Komponen	Kandungan Senyawa Oksida 80 Mesh (%)	Kandungan Senyawa Oksida 100 Mesh (%)
1	Al_2O_3	11	0
2	SiO_2	69,5	82,1
3	K_2O	6,15	7,21
4	CaO	5,63	4,73
9	Fe_2O_3	6,42	5,01

In addition to analyzing the content of zeolite in elemental form, measurements of the content of bonded elements or elements in the form of oxides were also carried out. Oxide compounds are the occurrence of elemental bonds in the zeolite with oxygen. The same results were shown by XRF measurements of oxide compounds, namely differences in zeolite particle size resulted in differences in the content of oxide compounds.

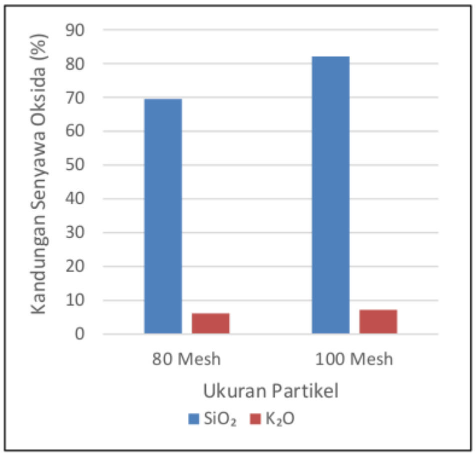


Figure 9. The content of oxide compound which increases with increasing size

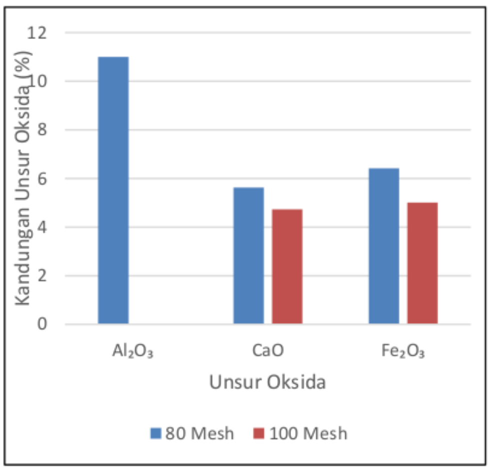


Figure 10. The content of oxide compound which decreases with increasing size

The results of measurements of compounds contained in zeolite in the form of oxides show the same results as the measurement of elements that have different content for the size of 80 mesh with 100 mesh. The content of SiO_2 and K_2O compounds increased in percentage while Al_2O_3, CaO and Fe_2O_3 compounds decreased.

IV. CONCLUSIONS

1. The FTIR analysis showed the presence of the C-H alkene functional group at a wavelength of 675-995 cm^{-1}, ring C-H aromatic at a wavelength of 690-900 cm^{-1}, C-O alcohol/ether/carboxylic acid/ester at wavelength 1610-1680 cm^{-1}, functional group C=C alkene 1610-1680 cm^{-1}, the O-H functional group is carboxylic acid at a wavelength of 3500-3650 cm^{-1} and an alcohol monomer/phenol O-H functional group at a wavelength of 3590-3650 cm^{-1}.
2. The content of chemical elements and oxide compounds in zeolite has a difference with the difference in size. Si and K elements increased with increasing sample size while the content of Al, Ca, and Fe elements decreased with decreasing sample size. For oxide compounds SiO_2 and K_2O elements increased with increasing sample size while the content of Al_2O_3, CaO, and Fe_2O_3 decreased with decreasing sample size.

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