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The Effect of Acid Treatment on The Characteristics of Modernite Zeolite

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ABSTRAK

Penelitian ini menyelidiki penggunaan perlakuan asam pada karakteristik mineral zeolit. Efek dari perlakuan zeolit dengan berbagai larutan asam, yaitu asam klorida (HCl) dan asam sulfat (H2SO4), diukur dengan menggunakan fluoresensi sinar-x (XRF), difraksi sinar-x (XRD), dan pemindaian mikroskop elektron (SEM). Hasil penelitian menunjukkan adanya peningkatan persentase SiO2 dan Al2O3 setelah aktivasi zeolit, serta penurunan jumlah pengotor. Fase kristal zeolit dilakukan dengan menggunakan analisis XRD, yang mengindikasikan jenis zeolit yang digunakan adalah modernite. Fase SiO2 dalam sampel adalah kuarsa, dan fase Al2O3 adalah korundum. Ukuran kristal rata-rata menurun setelah aktivasi, dari 14,23 nm menjadi 6,85 nm untuk HCl dan 5,42 nm untuk H2SO4. Selanjutnya, morfologi permukaan semua sampel zeolit memiliki bentuk permukaan yang tidak beraturan, dan ukuran permukaan partikel setelah aktivasi menunjukkan bentuk partikel yang lebih kecil. Hasil penelitian ini diharapkan dapat menjadi rekomendasi untuk penelitian lebih lanjut terkait pretreatment zeolit alam sebagai pendukung katalis.

Kata Kunci: Zeolit, Modernit, Asam

ABSTRACT

This work investigated the use of acid treatment on the characteristics of zeolite mineral. The effects of treating zeolite with various acid solutions hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) were measured using x-ray fluorescence (XRF), x-ray diffraction (XRD), and scanning electron microscope (SEM). The results showed an increase in the percentage of SiO_2 and Al_2O_3 after zeolite activation, and also a decrease in the amount of impurities. The crystalline phase of the zeolite was carried out using XRD analysis, indicating the type of zeolite used is modernite. The SiO_2 phase in the sample is quartz, and the Al_2O_3 phase is corundum. The average crystal size decreased after activation, from 14.23 nm to 6.85 nm for HCl and 5.42 nm for H_2SO_4. Furthermore, the surface morphology of all zeolite samples has a form of irregular spherical surface, and the surface size of the particles after activation shows a smaller particle shape. The results of this study are expected to

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become recommendations for further research related to natural zeolite pretreatment as a catalyst support.

Keywords: Zeolite, Modernite, Acid

INTRODUCTION

Zeolites are aluminosilicate minerals that are found naturally all over the world. Zeolite is widely used because it has high acidity, good thermal stability, and has a higher selectivity (Burris & Juenger, 2016). They have a large surface area due to the arrangement of their molecules; However, some of the active sites located in the pores are inaccessible due to the presence of some impurities that cover the surface of the zeolite pores (Velichkina et al., 2021). Zeolite is used as an adsorbent because it has an open pore structure with a large surface area that allows for higher absorption of molecules. Zeolite is one of the inorganic materials which has an active side on the surface. The active site of the zeolite is the –OH group. Therefore, zeolite could be used as an adsorbent or catalyst or catalyst support (Ahmad et al., 2020).

Therefore, much attention is paid to the preparation of zeolite-based porous materials, which have advantages over other porous materials. To improve the performance of zeolite, some researchers activate it first. Zeolite activation can be done physically and chemically (Heraldy et al., 2010). Physical activation is carried out by reducing grain size, sieving, and heating at high temperatures, where the function of the heating is to remove organic impurities, enlarge pores and expand the surface (Dewi Permatasari et al., 2019). The activation process with heat can be carried out at temperatures between 200-400 ºC for several hours (Al-Ani et al., 2019).

The chemical activation is carried out by an acidification process, which the aim is to remove inorganic impurities. This acidification process will cause the exchange of cations with H^+ ions (Amari et al., 2021). Chemical activation of natural zeolite was carried out with acid (HCl or H_2SO_4) and alkali (NaOH) compounds at various concentrations (Clay et al., 2022). Activation of natural zeolite which is carried out with acid aims to dissolve and remove adsorbed metal oxides which cover the surface of the zeolite so that it is more porous and the surface area of contact becomes larger, while the alkali treatment will result in the formation of silicate compounds so that the surface of the zeolite becomes more porous will turn out to be more negative (Philia et al., 2023).

The activation process of natural zeolite can increase the adsorption capacity. The increase in the value of the adsorption capacity of natural zeolite was due to the activation treatment which had cleaned the zeolite pore from water molecules and metal oxides which were considered as impurities. The empty pores formed on the surface of the zeolite can enlarge the active surface so that the adsorption capacity becomes greater (Li et al., 2020). The activation process can also change the type of cation, the ratio of Si/Al and the characteristics of the zeolite to suit the material to be absorbed. In this study, zeolite activation was carried out chemically using HCl and H_2SO_4 which aims to determine the

metal oxide content, crystalline phase, and morphology of natural zeolite before and after activation.

METHODS

Preparation of Zeolite

The natural zeolite sample is homogenized first, then dried in the sunlight to remove the water content. Then crushed and sieved using a 200 Mesh sieve. The samples used are those that pass the filter. The natural zeolite samples were then analyzed for the content of alumina silica and crystal phase using XRF and XRD. Illustration of zeolite preparation is shown in Figure 1.

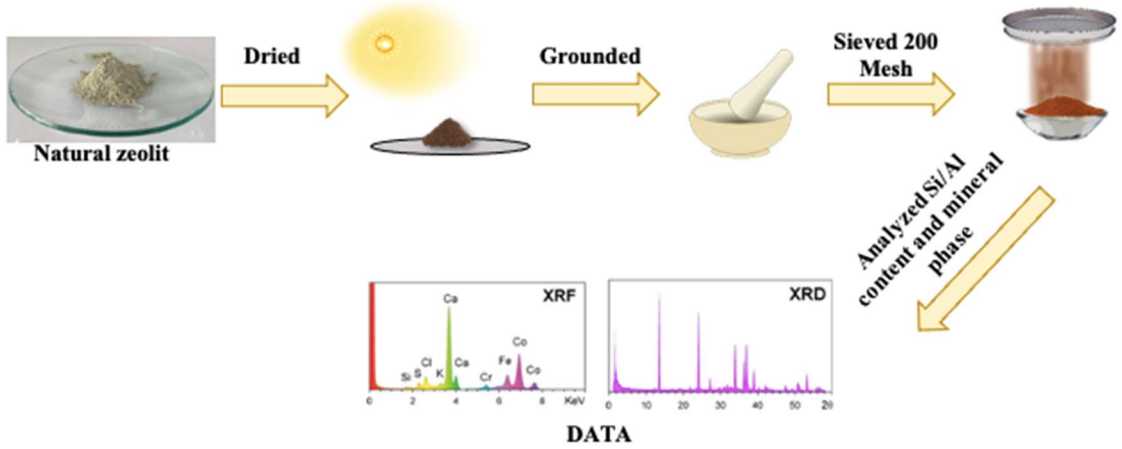

Figure 1. Illustration of zeolite preparation

Activation of Zeolite

100 g of natural zeolite that have been prepared is put into a beaker glass and 1000 mL of distilled water is added, while stirring with a magnetic stirrer for 3-4 hours. The natural zeolite is then filtered and heated at 50 ºC to a constant weight. Into 100 g of washed zeolite, 100 mL of 2 M HCl and H_2SO_4 was added and stirred for 14-16 hours using a magnetic stirrer. The zeolite was then washed with distilled water until clean and dried at 120 ºC until it reached a constant weight. The dried zeolite was crushed and sieved again until it passed a 200 Mesh sieve. The illustration of zeolite activation is shown in Figure 2.

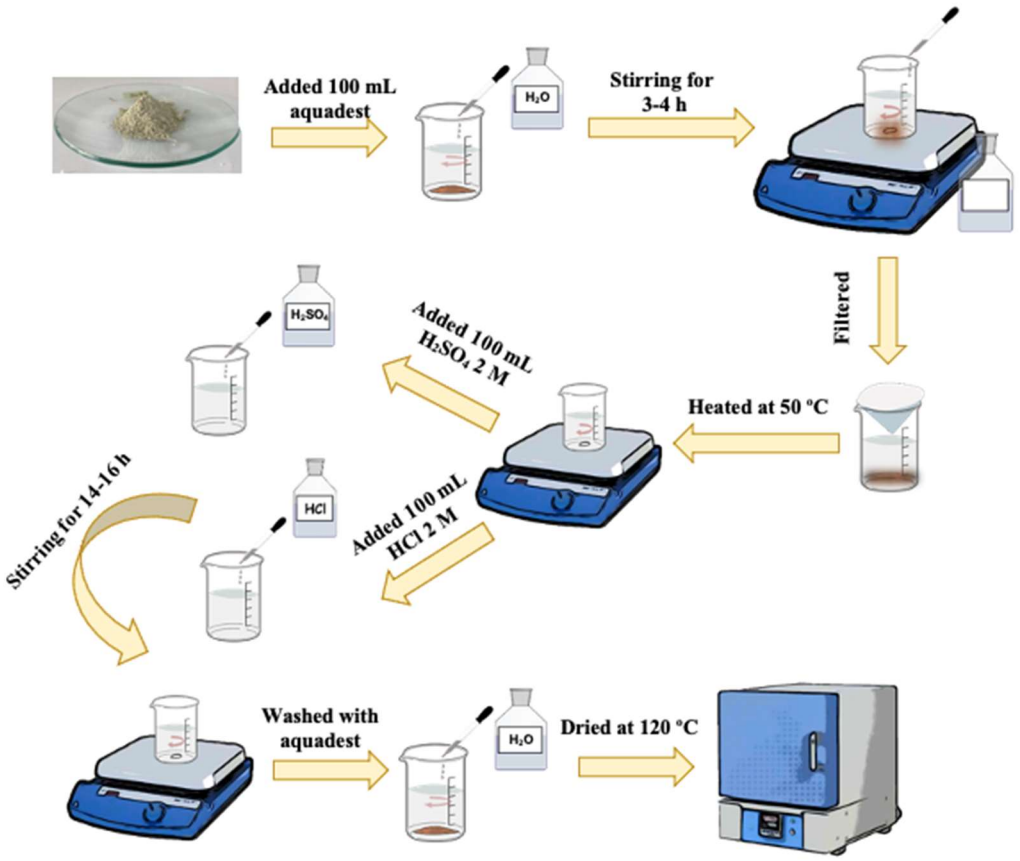

Figure 2. Illustration of zeolite activation

Characterization

The activated and pre-activated zeolite was then analyzed for its metal oxide content using Thermo Fisher Scientific's XRF with x-ray path: air, Eff. Stationer: 13.0 mm and Eff. Area : 132.7 mm^2, sample height : 3.77 mm with a mass of 500 mg. Furthermore, the crystalline phase of zeolite was evaluated using a powder X-Ray diffractometer (XRD, Shimadzu 7000) with CuKα radiation ($\bar{\lambda}$ = 1.5405 Å) operated at a scanning range of 20-80 configuration. The crystallite domain size was calculated using the Debye-Scherrer formula as shown in Equation (1).

$$D = \frac{0.9\,\lambda}{\beta\,cos} \qquad (1)$$

The surface morphology of zeolite was captured using the scanning electron microscope (SEM, JEOL JSM 6063LA) with operated at an accelerated voltage of 130 kV.

RESULTS AND DISCUSSION

Zeolite is a porous material that is often used in the synthesis of several advanced materials. The most superior character of zeolite is having a large surface area. However, this character can be further enhanced by removing the impurities contained in the zeolite. The treatment that can be done is by activating the zeolite material.

The activation process can remove existing impurities so as to increase the surface area and open pores. The activation carried out in this study was chemical activation using an acidic solution, namely HCl and H_2SO_4. After the zeolite is activated with acid, it is neutralized by washing with distilled water until the pH is neutral. This washing process removes the chlorine (Cl^-) and sulfate (SO_4^{2-}) anions present in the solution, which based on their properties, these anions dissolve easily in water (Zhou et al., 2021).

In the activation process, H^+ ions produced from the decomposition reaction of HCl and H_2SO_4 will break down the Al atomic bonds that are in the zeolite structure and also remove the balancing cations in natural zeolites (Na, Mg, Ca, Br). The H^+ ion will be attacked by oxygen atoms bound to Si and Al because the of the dissociation energy Al-O bond (116 kcal.mol^{-1}) is much lower than the Si-O bond dissociation energy (190 kcal.mol^{-1}), thus Al-O bonds are much easier to decompose than Si-O (Li et al., 2020). Meanwhile, the Cl^- and SO_4^{2-} anions from the decomposition of HCl and H_2SO_4 have a high electronegativity, making them easy to bond with large-valent cations such as Si^{4+} and Al^{3+}. However, these anions tend to bond with Al^{3+} because the electronegativity of the Al atom is lower than that of the Si atom. The mechanism reaction while activation process of zeolite using acid treatment shown in Figure 3.

XRF analysis

XRF analysis was carried out to determine the content of metal oxides in the zeolite before and after acid activation. Based on the results of the XRF analysis shown in Table 1, it can be seen that the main contents in natural zeolite are alumina (Al_2O_3) of 4.45% and silica (SiO_2) of 85.34%. The composition of Al_2O_3 and SiO_2 zeolite activated by HCl is 4.54% and 86.14%, while the zeolite activated by H_2SO_4 has 4.98% of Al_2O_3 and 85.87% of SiO_2.

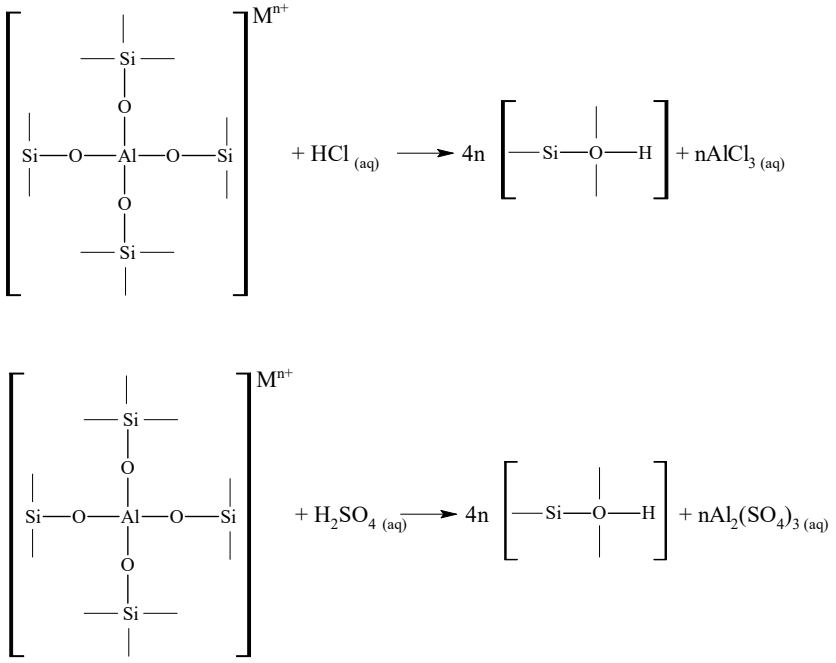

Figure 3. Mechanism reaction between zeolite and HCl and H_2SO_4

The activation process with HCl and H_2SO_4 can remove the impurities. This is indicated by the reduced of Fe_2O_3, TiO_2, SrO, MnO, ZnO, and ZrO_2. In acid activation treatment, an activating agent that causes dealumination of natural zeolite. It is difference with the activation by alkaline treatment, known as desilication process (Nasief et al., 2021). Dealumination is performed by selectively removing aluminum atoms from the zeolitic framework. It is caused defect through the hydrolysis of Si-O-Al bonds.

Table 1. Results of analysis of metal oxide content in zeolite samples before and after activation

Metal oxide	Before Activated (%)	After Activated HCl (%)	After Activated H_2SO_4 (%)
Al_2O_3	4.45	4.54	4.98
SiO_2	85.34	86.14	85.87
K_2O	3.93	3.79	3.53
CaO	2.15	1.95	1.89
Fe_2O_3	3.11	2.89	2.87
TiO_2	0.34	0.32	0.29
MnO	0.21	0.14	0.17
SrO	0.22	0.17	0.18
ZrO_2	0.04	0.02	0.02
ZnO	0.0175	0.0078	0.0145
Nb_2O_5	0.0091	0.0089	0.0082
Y_2O_3	0.1734	0.0143	0.1684
MoO_3	0,01	0.009	0.0089

The results in this research in line with the previous study which use the acid treatment (Side et al., n.d.) and alkaline activation treatment (Philia et al., 2023). Following the XRF data, both activator agents decreased the Si composition of the zeolite. In addition, the decrease in the percentage of metal oxide impurities in the zeolite and the increase in the Si/Al ratio indicated that HCl and H_2SO_4 were effectively used for the activation process.

XRD analysis

XRD analysis was carried out to determine the type of natural zeolite mineral used and the crystalline phase of SiO_2 and Al_2O_3 contained in the sample before and after acid activation. Figure 4 shows the XRD patterns of zeolite, it can be seen that the peak intensity of the activated zeolite phase is stronger than that of the catalyst without activation. This is because amorphous silicon is embedded in the zeolite framework during the acid activation process resulting in a more perfect zeolite crystal structure. This results agrees with the previous study which use zeolite-Y and activated using nitric acid (Le et al., 2019).

The diffractogram showed the distinct diffraction peaks at 22^o and 27.72^o. According to the diffraction peaks, it can be seen that the zeolite used is a zeolite with a mordenite phase with an orthorhombic crystal system according to JCPDS (Joint Committee for Powder

Diffraction Standard) Number 06-0239 using PCPDFWIN Software with lattice parameters a=18.05Å, b=20.40Å, c=7.502Å and angles α = 90°, β = 90°, γ = 90°.

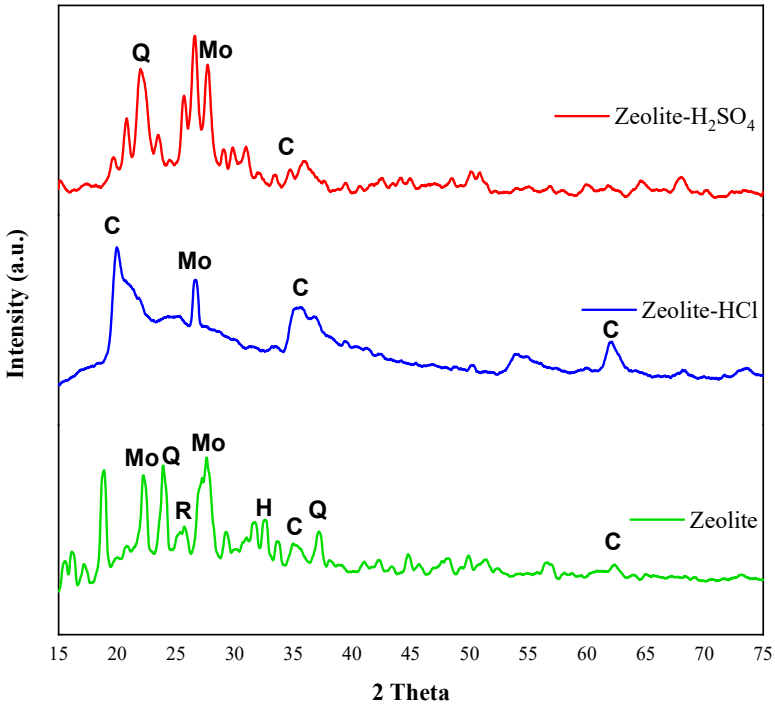

Figure 4. The XRD pattern of zeolite before and after activation (Mo = Modernite, Q = Quartz, C = Corundum, H = Hematite, R = Rutile)

In addition, the zeolite before activation also showed the appearance of a quartz phase which showed the crystalline phase of SiO_2 and corundum which was the crystalline phase of Al_2O_3. These two crystalline phases also appeared at the peak of HCl and H_2SO_4 activated zeolite. As for the zeolite before activation, the hematite peak appears which indicates the crystalline phase of Fe_2O_3 and rutile which indicates the crystalline phase of TiO_2. However, these two peaks did not appear in the acid activated zeolite samples. It shows that after acid treatment, it can reduce impurities found in zeolite such as Fe_2O_3 and TiO_2. In other words, the acid activation process facilitates the formation of active Al_2O_3 and increases the crystallinity of the zeolite which is advantageous for the synthesis of zeolite which will be applied as an adsorbent or catalyst.

On the other hand, hydrochloric acid and sulfuric acid, have a higher impact on zeolite crystallinity, from higher to lower impact respectively. It is known that adsorption is related to surface area and surface chemistry. It is expected that higher crystallinity decreases porosity and surface area, leading to surfaces with fewer defects, less energetic sites, and lower adsorption properties. The peak intensity decreased at 22.5˚possibly due to lamellar distortion causing partial decomposition of the structure while the shift was associated with a decrease in the interlayer area as metal was removed after acid leaching (Silva et al., 2019).

The average size of zeolite crystals before and after activation was calculated based on the Debye Scherrer equation (Equation 1) shown in Table 2. The results obtained showed that the average size of zeolite crystals decreased after acid treatment. The results obtained differ from the results of previous studies which showed no effect of acid treatment on crystal

size (Meng et al., 2021). This is presumably because in this study no physical activation was carried out beforehand.

Table 2. The average crystallite size of zeolite

Samples	Average of crystallite size (nm)
Zeolite	14.23
Zeolite-HCl	6.85
Zeolite-H_2SO_4	5.42

SEM analysis

The SEM analysis was carried out to determine the surface morphology of zeolite and activated zeolite. Figure 5 shows the morphology of samples, it can be seen that overall has a form of irregular spherical surface. In addition, all zeolite samples tend to have uneven particle sizes, there are still relatively large particles. Then the zeolite before activation in Figure 5(a) shows a larger particle surface shape compared to the surface of the activated zeolite particle in Figure 5(a)(b). It shows that acid activation has an effect on the particle surface size of the zeolite. With the acid treatment, the morphology showed a significant difference in particle size although it still showed an irregular bulb shape. The results obtained in this study are in line with the morphology of the zeolite produced in previous study which use physically activated (Pardoyo et al., 2020). In addition, Figure 5 also shows that the activation process is able to make zeolite into smaller particle sizes than without activation. It is supported by data from the calculation of the average crystallite size as shown in Table 2.

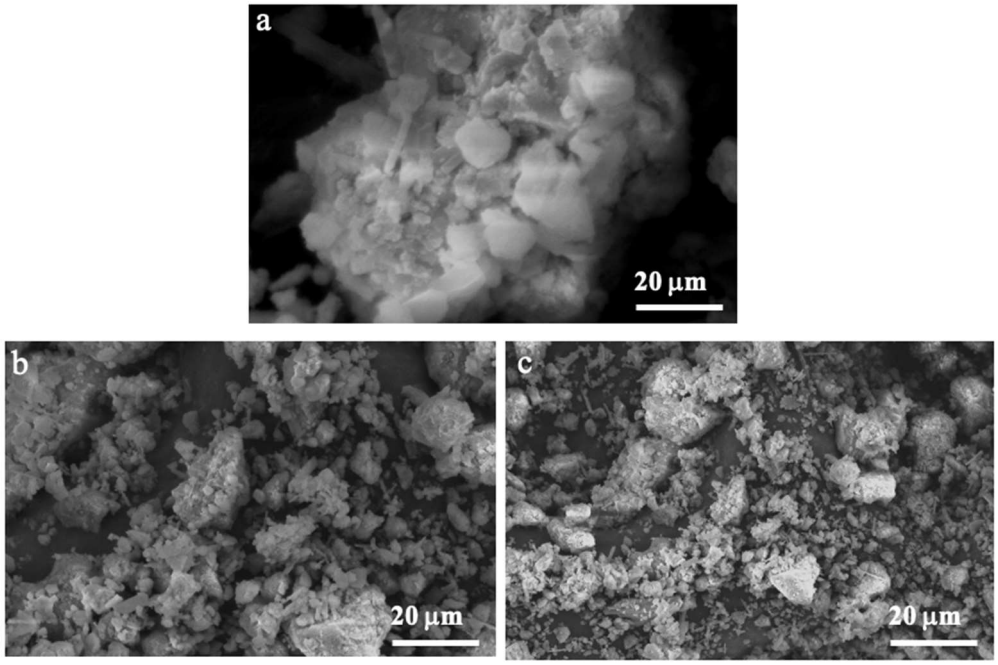

Figure 5. The morphology of (a) zeolite, (b) zeolite activated by HCl, (c) zeolite activated by H_2SO_4

CONCLUSION

Characterization of zeolite before and after activation using hydrochloric acid and sulfuric acid has been carried out in this study. Based on the results of the XRF analysis, it showed an increase in the percentage of SiO_2 and Al_2O_3 after zeolite activation, and also a decrease in the number of impurities. The crystalline phase of the zeolite was carried out using XRD analysis, indicating the type of zeolite used is modernite. The SiO_2 phase in the sample is quartz, and the Al_2O_3 phase is corundum. The average crystal size decreased after activation, from 14.23 nm to 6.85 nm (HCl) and 5.42 nm (H_2SO_4). Furthermore, the surface morphology of all zeolite samples has a form of irregular spherical surface, and the surface size of the particles after activation shows a smaller particle shape. Thus, the activation of zeolite using HCl acid and H_2SO_4 at a low concentration of 2 M can be recommended to produce superior zeolite characteristics for applications as adsorbents and catalyst supports.

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