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Fabrication Material Zeolite Modified by Fe with Treatment and Without High Energy Milling on Zeolite Materials

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Abstract. Natural zeolite in Indonesia are generally found in bulk form and many impurities. The purpose of this research was obtaining iron modified zeolite with and without High Energy Milling treatment on zeolite material. Zeolite material was done by milling using a High Energy Milling and modifications were done by soaking in a solution of iron (Fe). Natural zeolites was sifted and then milling by HEM, activation and Fe modification. Characterization of iron modified zeolites were done using SEM-EDX, BET and XRD. SEM analysis showed that the surface morphology of ZmA-Fe was elliptical agglomerated and ZA-Fe was elliptical. EDX showed that the percentage of Fe atom increased in ZmA-Fe and ZA-Fe against natural zeolite respectively by 566.67% and 333.33%. BET analysis of the ZmA-Fe to ZA-Fe showed the specific surface area decreased difference of 15%, the pore volume increased difference of 13.44%, and the average pore size increased difference of 30.48%. XRD analysis as well as provided information about crystallinity ZmA-Fe and ZA-Fe did not differ significantly from the natural zeolite. Based on the analysis results indicated that the Fe which has been modified into the zeolite with and without treatment by High Energy Milling on a zeolite material.

Key words: natural zeolite, *High Energy Milling*, iron

Introduction

Zeolite is porous and hydrated alumina-silicate minerals that contain alkali and alkaline earth metals. Result by volcano product, founded bulk form and many impurities (Armbruster, 2001). Many treatment for increase the activities of zeolite such as milling force, dehydration, dealumination, calcination, metal impregnation and ion exchange (Hamdan, 1992). Activity of zeolite increase by milling force, activation, and modification on this research. Size of zeolite getting smaller is better for further application. Efficient time for getting the smaller size used modern instrument likes High Energy Milling (HEM). According Charkhi, et al., (2010) about optimized experimental design for natural clinoptilolite ball milling to produce nano powder showed that larger than 1 mm particle size of clinoptilolite powder may mechanically be reduced into the size range of less than 100 nm to 30 μm . Ayoup, et al., (2009) on their research showed size of zeolite materials after milling is 47,6 nm dan 41,8 nm. HEM is one of the grinding tool that produces a material

with a smaller surface morphology size to be able to achieve nanometer size with a relatively faster or more efficient.

Chemical activation could be done by adding hydrochloric acid (HCl). HCl 4 M treatment can eliminate impurities such as oxide metals without damaging the structure (Setyawan and Handoko 2003) and increase the crystallinity (Pardoyo 2009). Besides, activation also could used high thermal or calcination to vaporize water trapped in the pores of the zeolite crystal (Khairinal, 2000). Modification natural zeolite by means of metal impregnation such iron (Fe) can be expected to increase the adsorption capacity of natural zeolite. According Kragović, dkk., (2013), their research showed Fe-oxides was also active sorbents and play an important role in the reactions behavior of many ions. The aim this research was fabrication Fe-modified zeolite materials with and without treatment by High Energy Milling on zeolite material.

Method

Preparation and Activation

Washing natural zeolite from Bayat, Klaten and dried then comminution with 230 mesh sieve. Partly passes 230 mesh sieve zeolite milled by HEM for 4 h on 600 rpm.

Each zeolites treated with HCl 4M for 24 h. Then calcined 500°C for 3h to produce activation zeolite (ZA) and milling activation zeolite (ZmA).

Iron Modification

The system was prepared by mixing 50 g of each ZA and ZmA, 100 mL of freshly prepared $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution in a 250 mL pyrex glass and heated at 70 °C for 6 h. After the appropriate period the product of reaction was removed from pyrex glass, washed (until free of Cl^- ions) and finally dried. The product were activation zeolite-Fe (ZA-Fe) and milling activation zeolite-Fe (ZmA-Fe).

Characterization

Results of the study were characterized by SEM-EDX to determine the surface morphology and elemental composition. BET was used to identify knowing the specific surface area, total pore volume and average pore diameter. XRD was to determine the crystallinity.

Result and Discussion

Decrease the size of zeolite from bulk level becomes a material with a smaller size due to the crushing activity. HEM was used as a milling tool in this study aims to acquire smaller sized zeolite powder which was expected to reach nanometer size. The used of these tools produced smaller grain in a shorter time. The process of milling for 4 h with 600 rpm rotation meant that the zeolite in the milling material having a smaller surface morphology size and also uniform.

Time and rotation which were too high could produce a material with a smaller size, but did not rule out the possibility of the occurrence of agglomeration of the milling material.

Activation of zeolite using an acid such as HCl 4 M intended to dissolve impurities metal oxides. Activation using 4 M HCl enough to damage the zeolite framework, where in the charge balancing cations will be dissolved and replaced by H^+ from HCl. Calcination on 500°C is optimum activation process to evaporate the water trapped in pores. This was confirmed by Gustian and Suharto (2005) on the activation of zeolite used in a decrease in the salinity of the water. Setiadi dan Pertiwi (2007) declared that calcination on 500 °C not damage the structure zeolite until 50%.

Mixed each ZA and ZmA on iron solution, stirrer and heated on 70 °C for 6 h, homogeneous mixture as well as over the amount of Fe attached to each zeolite. The Products of modification by iron were activation zeolite-Fe (ZA-Fe) and milling activation zeolite-Fe (ZmA-Fe). The reaction of modification by Fe supposes to be figure 1 (Sazama, 2012).

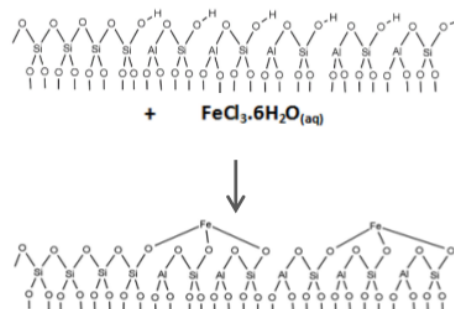


Figure 1. Modified iron with zeolite

Figure 2 showed that surface of Z consists of a rod shape with non-uniform surface morphology size, cause the grinding process was prevalent so that the surface morphology size distribution of the zeolite be varied. Form of ZmA-Fe was elliptical seen agglomeration and ZA-Fe seen elliptical.

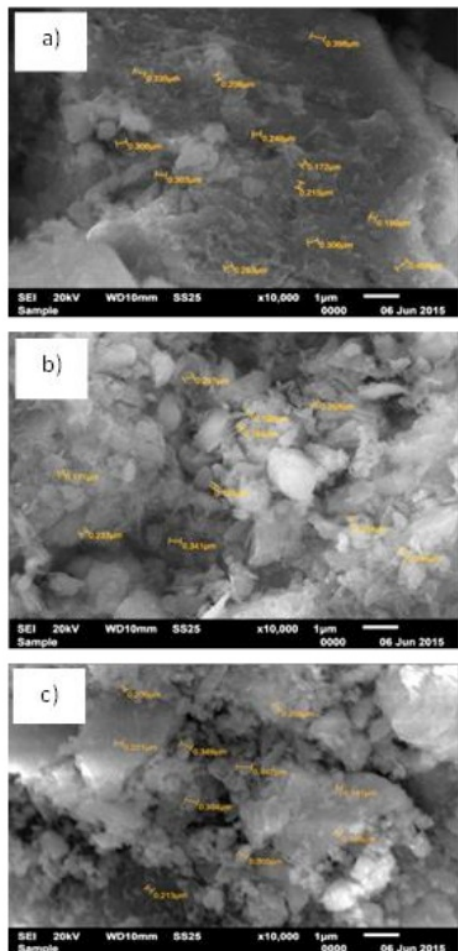


Figure 2. SEM result of: a) Z, b) ZA-Fe,
c) ZmA-Fe

Table 3 showed that ZmA-Fe containing more Fe atom than Z and ZA-Fe. The existence of Fe treatment was suspected sticking on the surface of zeolite caused decreasing contact area between zeolite surface and nitrogen gases in ZmA-Fe compared with ZA-Fe. Appropriate with BET method principle that inert gases adsorption of N_2 on the surface of solids. Shown on table 2, ZA-Fe 1,9-fold increased in surface area from Z while ZmA-Fe was 1,6-fold from Z with difference surface area for ZA-Fe was greater than ZmA-Fe about 15%. More agglomeration in zeolite was one of porous material that enable greater number of porous diameter caused merge of porous caused by grain agglomeration.

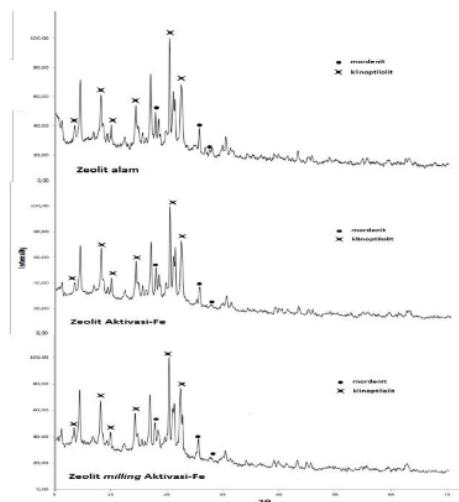
Table 2: BET analysis

| Sample | Specific surface area (m^2/g) | Total pore volume (mL/g) | Average pore size (Å) |
|-------------------------------|-----------------------------------|--------------------------|-----------------------|
| Natural zeolite | 33,997 | 0,097 | 1,146 |
| Activation zeolite-Fe | 99,994 | 0,139 | 5,557 |
| Milling activation zeolite-Fe | 86,909 | 0,158 | 7,263 |

Table 3: EDX analysis

| | Natural zeolite | | ZA-Fe | | ZmA-Fe | |
|--------|-----------------|----------|-----------|----------|-----------|----------|
| | Atoms (%) | Mass (%) | Atoms (%) | Mass (%) | Atoms (%) | Mass (%) |
| O | 62,80 | 60,86 | 62,48 | 56,75 | 60,01 | 52,13 |
| Al | 2,06 | 3,36 | 4,74 | 7,27 | 2,76 | 4,05 |
| Si | 8,85 | 15,06 | 10,19 | 16,25 | 19,56 | 29,82 |
| Fe | 0,09 | 0,32 | 0,39 | 1,23 | 0,60 | 1,82 |
| others | 26,2 | 20,4 | 22,2 | 18,5 | 17,07 | 12,18 |
| Total | 100 | 100 | 100 | 100 | 100 | 100 |

Table 3 showed that increased Al atoms on ZA-Fe, its presumed impurities Al form metal oxide from washing. Diffractogram XRD analysis results matched with JCPDS (Joint Committee on Powder Diffraction Standard), the peak intensity observed that there were high peaks at $2\theta = 13,46^\circ$; $25,64^\circ$; $26,1^\circ$; $27,64^\circ$, which indicated the type major mineral in the zeolite was mordenite. Other mineral content was clinoptilolite with smaller amounts. Diffractogram of each zeolite indicated that crystallinity ZmA-Fe and ZA-Fe after suffering activation of acid and thermal treatment and modification with Fe, did not differ significantly from the natural zeolite. This suggested that the natural zeolite Bayat, Klaten had a fairly high stability.



Gambar 4. Difraktogram XRD Zeolit

Conclusion

Based on the study and discussion, the conclusions were the use of High Energy Milling (HEM) as a more efficient means of grinding to obtain zeolites with a smaller size. The modification Fe on ZA and ZmA produced ZA-Fe and ZmA-Fe with the highest Fe on the ZmA-Fe.

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