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Effect of Sulfuric Acid Treatment and Calcination on Natural Zeolites of Indonesia

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An activation of natural zeolite of Wonosari, Gunung Kidul, Indonesia has been done. Activation was applied by refluxing the zeolite in variation of the sulfuric acid concentration and calcination time. Calcination was applied using microwave of 2.45 GHz. Determination of acidity was applied by measuring the amount of adsorbed ammonia and pyridine. Morphological, functional groups and crystallinity characterizations were analyzed using SEM, TEM, FTIR and XRD. Porosity of the zeolite was analyzed using porosimetry method. The results showed that the greater of the concentration of sulfuric acid and calcination time was, the greater the amount of ammonia and pyridine adsorbed as well as the surface area. FTIR spectra and XRD patterns showed no fundamental changes in the structure of the natural zeolite, SEM, and TEM images were showing an increase in space or field. Optimization was obtained at a concentration of 2 M of sulfuric acid and calcination time of 20 min, respectively each amounted to 0,8941 mmol/g of ammonia and 0,0375 mmol/g of pyridine with 251.00870 m^2/g for surface area, 0.19129 m^3/g of pore volume and 3.04829 nm of pore diameter.

Keywords: Natural zeolite, Activation.

INTRODUCTION

Aluminosilicate-based catalysts such as zeolite and montmorillonite are known as a group of heterogeneous catalysts that are growing so rapidly. Some examples of catalysts are often used are modernite, clinoptilolite and saponite as a solid support as well as catalysts made with nanotechnology [1,2]. Aluminosilicate is a typical solid with porous structure that solvates easily adsorbent and environmental friendly. Catalysis process occurs in pores with a very good reaction efficiency [3].

In general, activation of aluminosilicates is applied by using the traditional method and microwave ovens. A number of studies have shown that use of microwave ovens produces activated aluminosilicate with quite good time and energy efficiency [4,5].

Aluminosilicate activation is influenced by many variables including pH, type of acid and the temperature and time of calcination preparation of zeolite A, pillared saponite and clinoptilonite using a microwave oven has worked at a frequency of 2.45 GHz with 0.5 M sulfuric acid for 20 min and low heating radiation [6]. Thermalization of zeolite A [7], ion exchange to clinoptilonite [8], conversion of coal fly ash to zeolite [9], zeolite acidity [10-12] were also reported.

The main objective of this research is to obtain aluminosilicate material along with the empirical relation of physical and chemical character especially thermal stability through several synthesis parameters. The results of this research will benefit the development of silica alumina-based catalyst material that possess characteristic to play key role in sustaining the development of the chemical industry.

EXPERIMENTAL

Preparation apparatus for the manufacture of active natural zeolite requires analytical balance, agate mortar and pestle, 200 mesh sieve, magnetic stirrer, pH meter, LG microwaves oven, thermometer, reflux apparatus and a set of glassware. Analytical instruments included X-ray diffractometer (XRD) of Shimadzu X-6000, surface area analyzer (SAA) of Tristar, Fourier transform-infrared (FTIR), scanning electron microscope (SEM) and Transmision Electron Microscope (TEM).

The reagents used in this research included bayah natural zeolite obtained from PT Zeolite Klaten, sulfuric acid (Merck), ethanol (Merck), acetic acid (Merck), and distilled water.

Preparation of active natural zeolite catalyst: 50 g of 100 mesh-fine zeolite refluxed in 0.5 M H_2SO_4 solution at 60 °C for 6 h, then filtered, washed with distilled water until pH 7 (neutral). The result after activation was dry zeolite, then sieved back in 100 mesh sieve. The activation of zeolite used the same procedure described above with concentrations of 1, 1.5 and 2 M H_2SO_4.

The acidity of the catalyst was carried out with ammonia gas adsorption. At first, zeolite was heated in the oven for 3 h at 110 °C and then cooled in a desiccator. After allowing zeolite to cool, weighed 0.5 g of zeolite in the crucible and placed in a desiccator along with 5 mL of NH_4OH in a glass beaker, vacummed and allowed to stand for 4, 8, 16 and 24 h. Removed and cooled crucible and weighed again. Calculated weight of adsorbed ammonia. In addition using adsorption of ammonia gas, acidity of catalyst was also performed with pyridine gas. The porosity determined with surface area analyzer.

Calcination was carried out in steps as follows: Optimized zeolite resulted with the treatment of acid activation, calcined with a 2.45 GHz LG microwave oven, with calcination time of 5; 10; 15; 20 and 25 min, respectively and then characterized.

Characterization: Characterization of calcined zeolite was carried out as the same step in the activation of zeolite using acidification, which was the test of catalyst's acidity using ammonia and pyridine.

RESULTS AND DISCUSSION

Fig. 1 showed the longer adsorption time as the amount of adsorbed ammonia increased. The increase due to the occurrence of ammonia adsorption arrangement on the surface of the zeolite particles, while the increasing concentrations of sulfuric acid activator causes pore open more and clean, then increases the adsorption. Optimization would occur at concentration of 1 M of sulfuric acid adsorption time of 24 h.

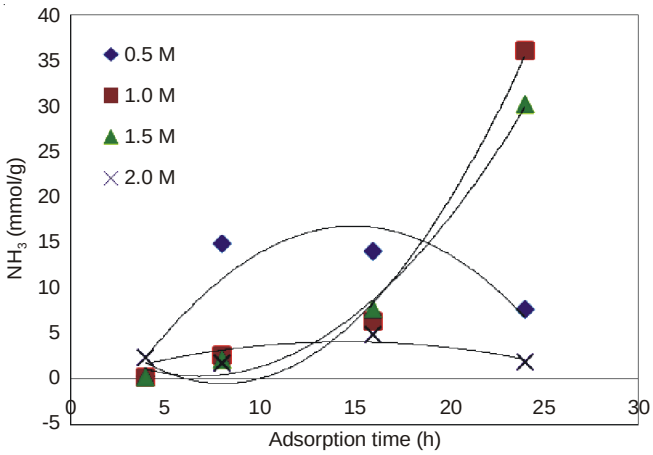

Fig. 1. Ammonia adsorption *versus* time using acid-activated natural zeolite

Fig. 2 showed that the longer adsorption time, the ability of zeolite in adsorbing pyridine and the maximum adsorption occurred at 16 h. This was caused by rearrangement of adsorbate. While the more increased the concentration of sulfuric acid, the higher the adsorption capacity was. The enhancement of pyridine adsorption took place with excellent results, the higher the concentration of sulfuric acid, the more adsorption occurred, optimization occurred at concentration of 2 M with treatment using sulfuric acid, while the optimization of ammonia adsorption occurred at 1 M. This situation occurred possibly because the size of the pore was large enough then the physical bonding could simply occur but not strong, while with large enough molecule, the physiccal bond was more powerful and efficient.

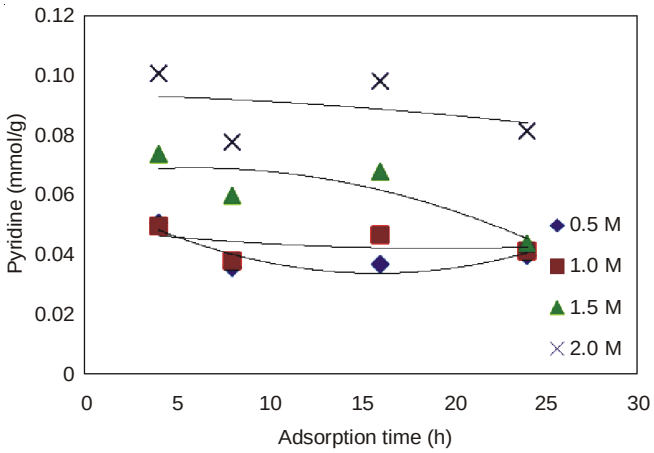

Fig. 2. Pyridine adsorption *versus* time using acid-activated natural zeolite

The other probability was to looking at the XRD pattern in Fig. 5 showed the presence of impurities such as clay, which of course has smaller pores and is capable of expanding to cover pores with smaller size. As the result, the pores were dominant on surface. The pore opened well after calcination where the tendency towards ammonia and pyridine adsorption produced the same pattern, this was due to the heating caused by microwave, caused impurities such as clay to be oxidized, then looking at Fig. 5, no longer shows the XRD pattern of the clay's peaks, caused the pore opened and was clean. It caused the amount of adsorbed substances increased.

The effect of calcination time with 2.45 GHz microwave oven shows that the increased amount of adsorbed ammonia and pyridine (Figs. 3 and 4). The longer the calcination time, it would increase the oxidation of impurities, resulting in the increased of number of active sites and would be optimum at 20 min. The adsorption would tend to decrease if the calcination time was more than 20 min, it might be due to pore damaged, then the surface area became smaller.

The XRD pattern (Fig. 5) shows that after activation process using sulfuric acid and then refluxed, continued with calcination, resulted in with no significant change to the structure of natural zeolite. This was shown by the absence of a shift and broadening peak. The emergence of the peak on the left side of the XRD pattern shown in Fig. 5, A and B indicate the presence of impurities such as clay, but after calcination, the XRD pattern in peak C, shows the loss of clay's

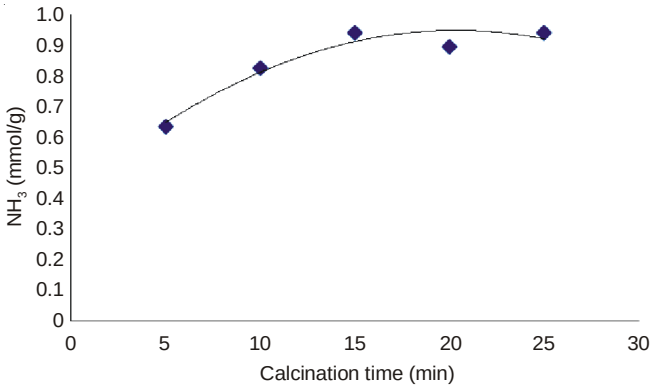

Fig. 3. Ammonia adsorption *versus* calcination time using acid-activated natural zeolite

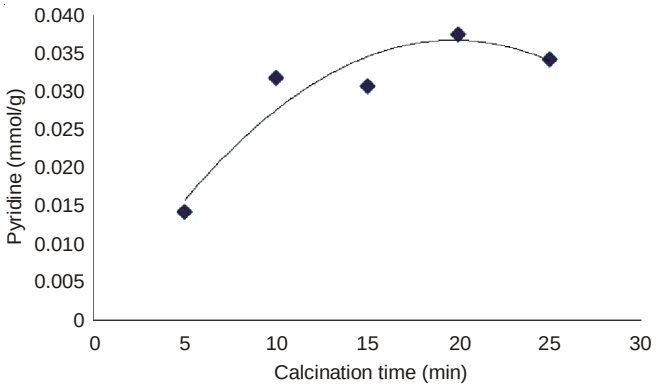

Fig. 4. Pyridine adsorption *versus* calcination time using acid-activated natural zeolite

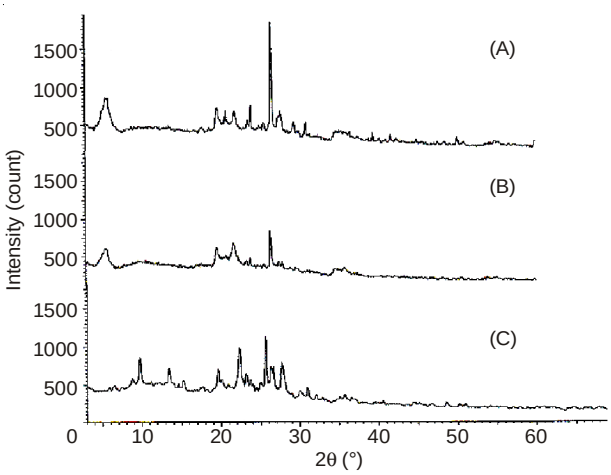

Fig. 5. XRD patterns of (A) natural zeolite (B) acid-activated natural zeolite (C) calcinated natural zeolite

peak and the peak of zeolite crystal is increasingly sharp. The relative amount of zeolite presented in Table-1, that shows the ratio between the intensity of natural zeolites, after reflux and calcination, it shows that the intensity of peaks was increased.

The natural zeolite both prior to treatment and after treatment, gave absorption peaks at wave number of 3626.17, 3445.72, 1651.07, 1049.28, 794.67 and 462.92 cm^{-1} that were the vibration patterns of functional groups, presented in Table-2.

Figs. 6-8 showed that the longer the time of calcination, the greater the oxidation of porous surface and will form a new surface, consequently caused larger pore volume and surface area of zeolite to form. This is in line with increasingly

TABLE-2
INTERPRETATION OF INFRARED SPECTRA

Wavenumber (cm^{-1})	Functional groups
3626.17	Stretching vibration OH of octahedral (AL-OH)
3445.72	Stretching vibration of the-OH Group of water
1651.07	Bending vibrations of the -OH group of water
1049.28	Asymmetric stretching vibration TO_4
794.67	Symmetric stretching vibration of tetrahedral TO_4 which is the external vibration
462.92	Bending vibrations of TO

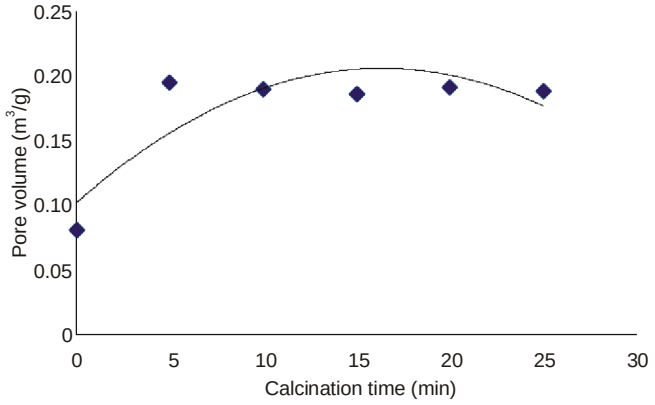

Fig. 6. Pore volume of activated natural zeolite with respect to time of calcination

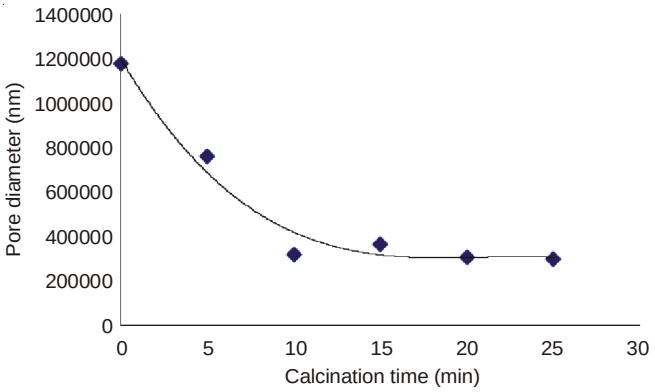

Fig. 7. Pore diameter of activated natural zeolite with respect to time of calcinations

TABLE-1
INTENSITY OF THE MAIN PEAKS OF DIFFRACTOGRAM

Mineral type	Natural zeolite			Reflux zeolite			Calcinations zeolite 20 min		
	2θ	D	Int	2θ	D	Int	2θ	D	Int
K	9.85	8.95	254	8.92	9.91	33	9.73	9.08	248
M	13.51	6.54	178	13.44	6.59	34	13.47	6.58	168
M	19.73	4.49	184	19.79	4.48	194	19.62	4.52	195
M	20.12	4.41	122	20.16	4.40	76	20.02	4.43	99
K	22.38	3.96	3.84	21.96	4.0	143	22.30	3.98	370
K	23.20	3.83	148	23.6	3.77	82	23.14	3.84	139
M	–	–	–	24.0	3.71	235	–	–	–
M	25.71	3.46	477	25.66	3.47	66	25.65	3.47	491
M	26.38	3.37	237	–	–	–	26.32	3.38	225
K	26.66	3.34	195	26.62	3.34	1036	26.58	3.35	229
M	27.85	3.20	240	27.98	3.19	100	27.68	3.21	279
M	–	–	–	–	–	–	30.89	2.89	112

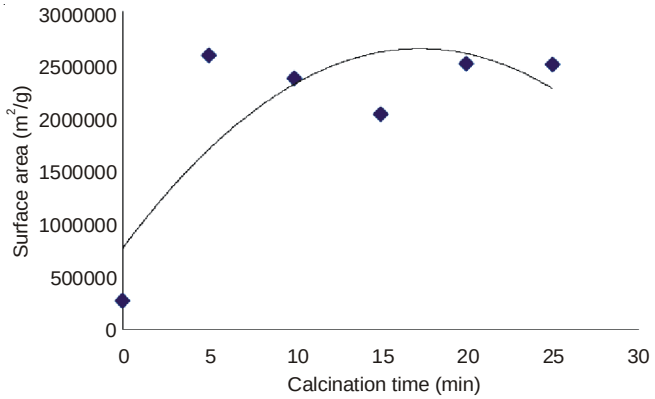

Fig. 8. Surface area of activated natural zeolite with respect to time of calcination

smaller pore diameter to form that indicate the increasing number of pores on the surface to form, meanwhile the analysis using SEM and TEM images (Figs. 9-12) show the performance of the surface with more gaps and more openings.

Fig. 9. SEM image of natural zeolite

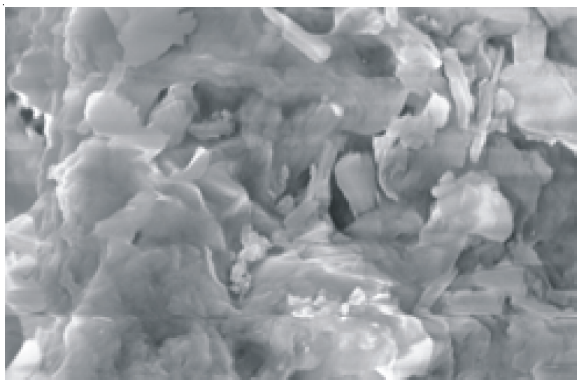

Fig. 10. SEM image of calcined zeolite with calcination time of 20 min

Conclusion

The greater the acid concentration and calcination time carried out, higher amount of ammonia and pyridine be adsorbed. Optimization occurred at concentration of 2 M of sulfuric acid and calcination time of 20 min, respectively adsorbed 0.8941 mmol/g of ammonia and 0.0375 mmol/g of pyridine with surface area of 251.00870 m^2/g, pore volume of 0.19129 m^3/g and pore diameter of 3.04829 nm.

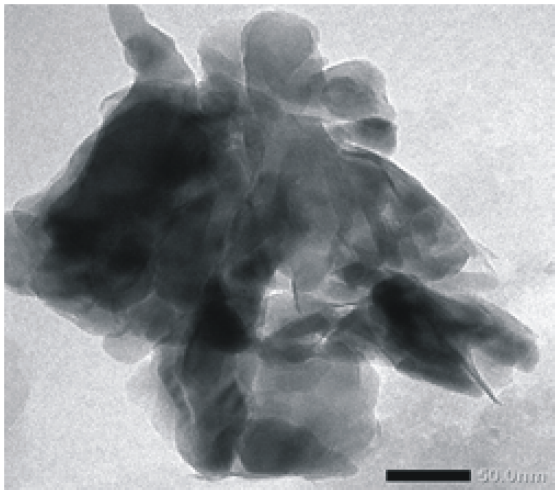

Fig. 11. TEM image of the natural zeolite

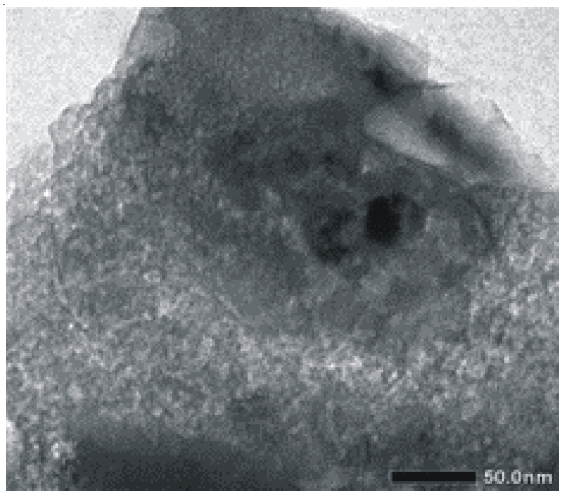

Fig. 12. TEM image of calcined zeolite with calcination time of 20 min

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