Effects of Chemical & Physical Pretreatment to Natural Zeolite Catalyst from Pottery Waste

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Natural zeolite catalyst from pottery waste would give some added value to pottery industries such as a proper waste management and a cheaper alternative to existing commercialized catalyst. The purpose of this work is to study catalytic properties of pottery waste via physical and chemical treatments and to characterize the catalytic properties of treated pottery waste. Sungai Sayong pottery waste was turned into powder by crushing, grinding and sieving. Then, it was pre-treated by physical and chemical means of hot water, autoclave, 1M of HCl, 1M Acetic Acid, Hexane and Propanol. The treated and untreated samples were then characterized by using analytical equipment which are Thermogravimetric Analysis (TGA), X-ray Diffractometer (XRD), BET method, CHNS Elemental Analyzer and Fourier-Transform Infrared Spectrometer (FTIR). The results obtained shows that (TGA) each sample have the similar trend of weight loss and temperature stability with the commercialized zeolite. By using elemental analyzer, the amount of organic content for each sample can be seen whereby weak acid sample has the highest content of carbon of 53.8908% while the next highest sample only contains 5.6220% carbon From the analysis of XRD, when being cross-referenced with components of Kaolin which are Si, Al, Mg, Fe, Ti, O_2 showed positive presence of each elements and resembles XRD data of ZSM-5 but with a little lower intensity. BET surface area shows that sample 4,5 and 7 has a positive increment from the pretreatment done as their surface area increases to 30.4137 m^2/g, 29.2670 m^2/g and 20.6381 m^2/g compared to sample 1 (untreated sample) which is 19.0779 m^2/g. FTIR was done to see presence of functional groups which are mostly Al and Si derivatives according to Kaolinite Clay and also ZSM-5. As conclusion, zeolite derived from Sungai Sayong pottery waste has similarity with the commercialized zeolite in term of weight loss, elemental content and functional groups. Strong acid pre-treatment showcased the best results when being characterized compared to the other pretreatments.

Keywords— Clay, Zeolite, Catalyst, ZSM-5, Pretreatment

I. Introduction

Clay industry to create handcrafted potteries called 'Labu Sayong' produces a large amount of pottery waste which are not suitable to be used in the industry anymore. These pottery wastes are being disregarded, sometimes not in a proper manner and this could lead to serious problems of pollution such as produce settling ponds and create undesirable structures of land. According to the statement of Haron et al, Sayong is not only famous of its active clay industry but also known to produce best quality of potteries [1]. Based on several studies, Sayong clay consists of 27.7 % of Silicon (Si), 12.6 % of Aluminium (Al), 0.57 % of Iron (Fe), 0.08 % of Titanium (Ti) and 2.32% of Potassium (K)[2]. According to A. Saat et al (2009) Si/Al molar ratio of typical illite and kaolinite are remained steady at about 1.9. Hence, Sungai Sayong clay can be classified as low silica zeolite grade since the Si/Al molar ratio is less than 2.

Clays have the potential to be used in other applications such as the synthesis of zeolite catalysts as it has similar properties. The usage of natural clay having content of aluminosilicate minerals as catalysts have even been used since 1940s to increase aviation fuel production in a catalytic cracking process [4]. This would be a great way to repurpose the pottery waste and help solve clay waste management problems. Clay can be categorized according to its mineralogical composition into three main groups which are kaolinite, montmorillonite and illite as well as other 30 various types of pure clays within these three main categories. As clay possess high catalytic performance, discoveries have led us to a more comprehensive use of a less-polluting catalysts in the industry. Modification of natural zeolites will contribute to enhance them as there is improvement to increase catalytic potential of clay as catalyst [3].

Zeolites are a type of porous aluminosilicates that comes with crystal-like structure. Aluminosilicate is basically a term used to describe how Aluminum (III) ions replaces Silicon (IV) ions in its anionic silicate form as it has approximately the same size causing an alteration in the charge whereby the negative charge reduces for every Aluminium replacement [5]. Zeolites can be derived from natural resources and also by synthesis methods. Volcanic rocks have been identified to contain natural zeolites and have been mined globally for quite a long time to get zeolite for a lot of usage. On the other hand, there are also many synthetic zeolites that occurred by synthesis using the process of slow crystallization of silica-alumina gel in presence of alkalis and organic forms. It is expected that more crystal structure can be made theoretically and in the long run, practically [6]. As researchers are striving for a "greener" chemistry to achieve development in chemical industry but causing minimal impact on the environment, zeolite is very much preferred because of its values of having lack of toxicity, being non-corrosive, recovers easily and is able to be reused and repurpose.

Furthermore, it creates a cost-effective solution to industries which requires the usage of zeolite catalyst as the resource comes from waste. As the world evolves into a more modern and technological era, potential of clays as 'green' and cost-effective catalysts should be further enhanced for small scale and big scale chemical productions and reactions to ensure that we utilize this nature's wonder, transforming it from waste to wealth. If so as claimed that clay is as potential as it is said to be, we should expand the usage of its use for the beneficial and profitable of larger industries. Pretreatment should be done to the clay sample collected by chemical and physical means whereby catalytic properties of clay are being modified to vary its composition and structure and explore its potential similar to zeolite catalysts [7]. The effects of the pretreatment of the clay should be characterized and studied. Hence, it is a great way to utilize clay wastes from the pottery industry as a source of catalysts for the chemical industries, small scale or big scale to solve both problems of high cost catalysis requirement in chemical plants and waste or pollution problems.

II. METHODOLOGY

A. Materials

Pottery wastes was collected from the 'Labu Sayong' industry in Sungai Sayong with the assistance of workers there. As these pottery wastes were hard solid, they were crushed, grounded and sieved through 125 µm mesh. Particles of ≤125 µm are then weighed and sorted into 7 samples of 5.0 grams.

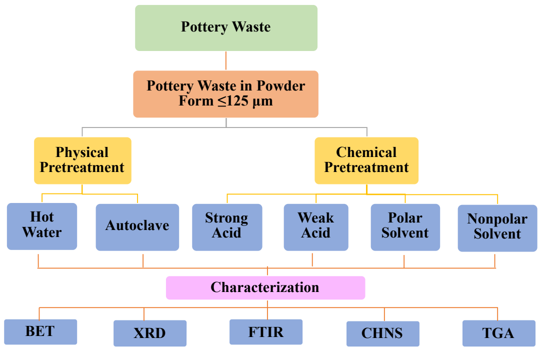

Figure 1: Simplified flowchart of study

B. Pretreatment of Samples

As can be seen in figure 1, pottery waste was pre-treated after it is in powder form using physical and chemical means. Physical pretreatments done were hot water and steam treatment while chemical pretreatments done were mixing with strong acid, weak acid, polar solvent and nonpolar solvent. The pretreatment details together with the apparatus and materials involved for each sample are as shown in table 1:

Table 1: Physical & Chemical Pretreatment of Samples

Sample	Type of Pretreatment	Pretreatment Details	Apparatus/ Materials
1		Untreated	
2	Physical	Hot Water	Hot Water
3	Physical	Steam Treatment	Autoclave
4	Chemical	Strong Acid	1M HCl
5	Chemical	Weak Acid	1M CH_3COOH
6	Chemical	Polar Solvent	1-Propanol
7	Chemical	Nonpolar Solvent	Hexane

For hot water process, as much as 5ml of boiling water (100 ºC) has been mixed with 5.0 grams of sample while for autoclave, sample undergoes steam treatment in an autoclave using temperature of 121ºC for 3 hours. As for all chemical pretreatment, 5ml of each chemical were mixed with 5.0 grams of each sample. All of the samples need to be evaluated in powder form hence need to be in dry condition. Samples which are still wet after a few days were then dried using a laboratory oven at 100 ºC for an hour.

C. Characterization

Several analyses were done to identify if the pretreatments were effective as part of making the clay samples better to be synthesized as clay catalysts as shown in flowchart in figure 1. Mettler Toledo TGA/DSC 1 Star system was used to determine the thermogravimetric analysis of samples at range temperature of 25°C to 1000°C at 10°C/min. X-ray Diffraction analysis was done using X'Pert Pro of Model DY2536 to determine phase and elemental composition of the samples. Surface Area Analyzer (Micromeritics Chemisorb 2750, USA were used to determine surface area by using BET method and Perkin Elmer (Model: Spectrum One) FTIR Spectrometer was used to identify functional groups present in samples. Lastly, Carbon, Nitrogen, Hydrogen and Sulphur determination in samples were done using a Thermo Finnigan EA112 Elemental Analyser.

III. RESULTS AND DISCUSSION

A. Functionality Analysis using FTIR

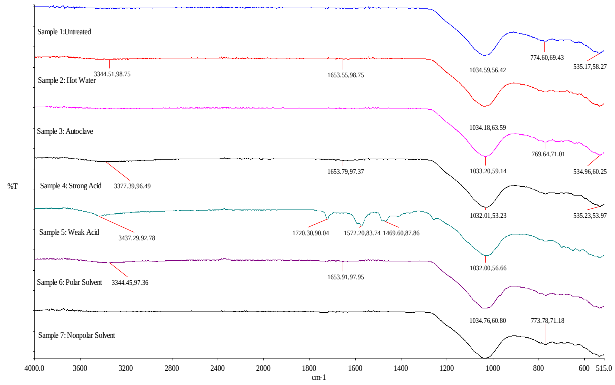

Figure 2: A compiled FTIR analysis of 7 samples

Table 2: Functional Groups available in all samples

Wavelength (cm^{-1})	Functional Groups
1032 - 1090	Silicate minerals
787-749	Kaolinite
555-501	Crystallization
1032-1009	Si-O
1200 - 950	Al-O-Si and Si-O-Si

References: [9[10][11][17]

Based on the compiled FTIR graph of all 7 samples in figure 2, it can be seen that the patterns are alike for every graph showing that the functional groups that present in each sample are the similar. The following table 2 shows what kind of elements are present at the wavelength of the visible peaks.

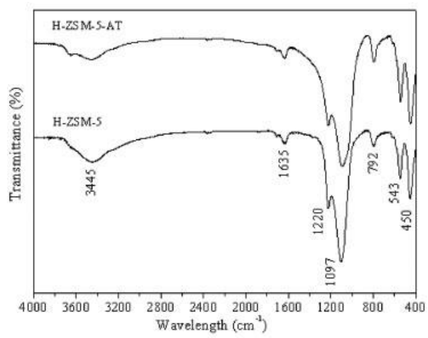

Figure 3: FTIR Data of catalyst ZSM-5 [13]

The functional groups present in the samples show that Si, Kaolinite and crystallization but what is more interesting is that most of the functional groups in the samples resembles in commercialized zeolite ZSM-5 as shown in figure 3. One of the most important identification in FTIR is at the broad absorption between 1200-950 cm-1 range, which shows formation of Al-O-Si and Si-O-Si bonds. These vibrational modes appear at frequencies near to Al-O-Al bonds, due to the similar mass of Al and Si atoms [17]. This is a significant finding from FTIR as zeolite is build based on its aluminosilicate bonds.

B. CHNS Elemental Analyser

Table 3: Area% of elements present based on chromatogram

Sample	Weight (mg)	C	H	N	S
Untreated	14.622	4.2522	28.4887	67.2579	0.0012
Hot Water	14.868	3.7001	19.3850	76.8902	0.0247
Autoclave	14.578	4.9858	26.0056	68.9799	0.0287
Strong Acid	14.762	3.4324	29.5566	67.0169	-
Weak Acid	14.498	53.8908	9.9951	36.1255	-
Polar Solvent	14.303	5.7016	28.1122	66.1820	0.0042
Nonpolar Solvent	13.627	5.6220	30.1616	64.2236	-

The concern with analysing the samples using a CHNS Elemental Analyzer is to see the content of organic elements after pretreatments have been done. Zeolites are inorganic material that appears similarly to activated-charcoal in possessing a highly microporous and mesoporous structure with the ability to adsorb volatile molecules [8]. Thus, pretreatments are expected to reduce the amount of organic matter presence in samples as they appear as contaminants rather than helpful elements. Based on the CHNS analysis shown in table 3, it can be seen that weak acid sample produces a very large amount of carbon as much as 53.8908% compared to the other samples which the second highest is only 5.6220%. This might be an indicator that Acetic Acid is not a suitable pretreatment method to be used. As clays are being added with lots of additives during the process of making pottery, those additives might influence content of organic elements in samples as well. These additives are unknown and should be known in order to know how to purify the catalysts by removing unwanted elements.

C. *Brunner Emmet Teller (BET) Method*

Table 4: BET Surface area of samples

Sample	BET Surface Area
1	19.0779 m^2/g
2	18.3576 m^2/g
3	16.4522 m^2/g
4	30.4137 m^2/g
5	29.2670 m^2/g
6	18.6559 m^2/g
7	20.6381 m^2/g
ZSM-5	297.4 m^2/g

Based on the table 4, the highest surface area is sample 4, followed by sample 5 and sample 7 that are 30.4137 m^2/g, 29.2670 m^2/g and 20.6381 m^2/g. While, hot water sample has the lowest surface area than other samples that is 18.3576 m^2/g. The higher the surface area, the higher the diffusion of reactant to the active sites. Porosity of catalyst is related with total surface area by which having high porosity in catalyst means high total surface area thus increase the accessibility to the active site by reactants and separation of catalyst from fluid reactants.

D. *X-Ray Diffraction (XRD)*

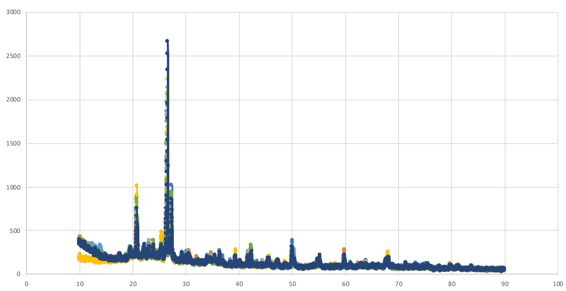

Figure 4: Compiled XRD Analysis Graph of 7 samples

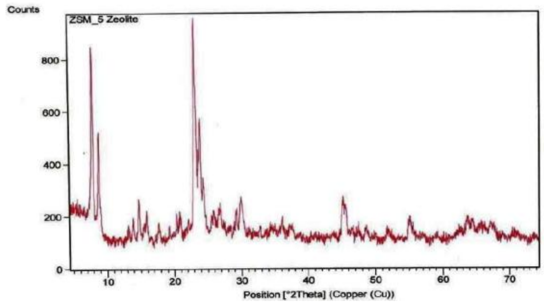

Figure 5: XRD graph for zeolite ZSM-5 [12]

From the analysis of XRD, when samples were being cross-referenced to components of Kaolin which are Si, Al, Mg, Fe, Ti, O_2, they showed positive presence of each elements and resulted in the data as shown in figure 4. When being compared with XRD data of ZSM-5 as in figure 5, the data are similar but with a little difference in intensity. XRD Analysis of all samples shows that they are in crystalline phase as shown in figure 6. The first prominent peak at 2θ = 12.34° is the distinctive XRD form of kaolin while the other peaks show presence of Silica, Aluminium, Magnesium and many more.

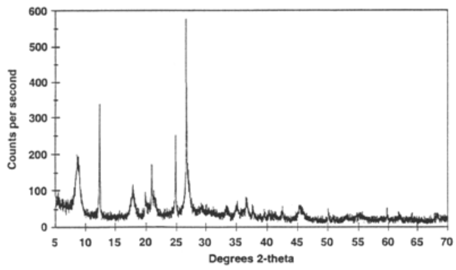

Figure 6: XRD showing Peak positions occur where the X-ray beam has been diffracted by the crystal lattice [15].

E. *Thermogravimetric Analysis (TGA)*

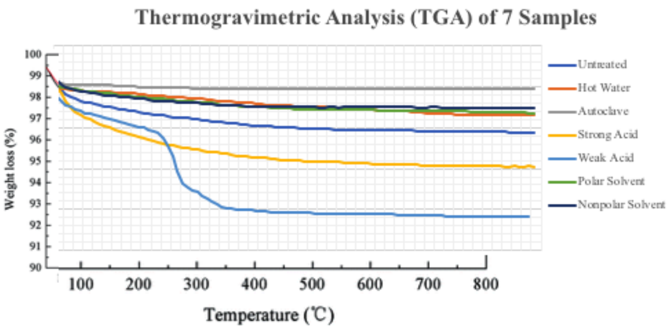

Figure 7: Thermogravimetric Analysis of 7 samples

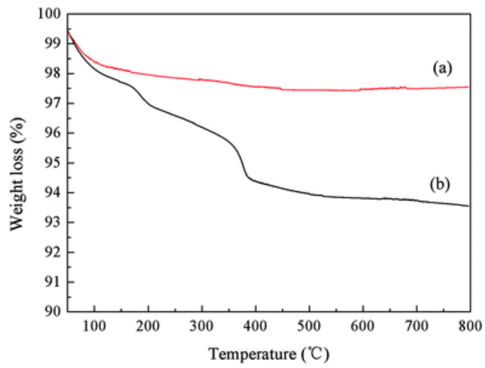

Figure 8: TGA profiles of the catalyst samples: (a) fresh Fe-ZSM-5 zeolite membrane catalyst, and (b) used Fe-ZSM-5 zeolite membrane catalyst, respectively [14].

Based on the compiled TGA data of all 7 samples and comparing it with ZMS-5 TGA profile, it can be seen that each sample have the similar trend of weight loss and temperature stability with the commercialized zeolite which mostly have majority weight loss at temperature between 200 ºC to 300ºC by comparing data in figure 7 and figure 8. The greatest weight loss at the particular temperature can be shown by the weak acid weight loss compared to the other samples. For the rest of the samples, only 2-5% weight loss was observed, and it is influenced by desorption of water, which was strongly combined in the aluminosilicates and the disintegration of a carbon-based composite such as Tetrapropylammonium hydroxide (TPAOH) and the transformation of hydroxide mixtures to oxide form [16] Four samples of non-polar solvent, autoclave, hot water and polar solvent showed very little weight loss might be because impurities are not extracted and cause weight gain during analysis. The higher the water content, the lower the number of alumina octahedral sheet and silica tetrahedral sheet per unit volume indicates that the quantity of water content depend on the catalyst structure [20].

During production process, “Labu Sayong” was fired in gas kiln at temperature of 850℃ for 10 hours [18]. Meanwhile, in synthesizing of zeolites, metakaolinization process at temperatures between 550℃ to 900℃ is necessary to reactivate the kaolin [19]. The temperature used during firing process is in the range of temperatures required during metakaolinization process and it can be assumed that kaolin in the pottery waste has been reactivated during firing process.

IV. Conclusion

As conclusion, natural zeolite catalysts derived from Sungai Sayong pottery waste has similarity with the commercialized zeolite in term of weight loss, temperature stability, elemental content and functional groups. From this study, it can be said that sample 4 (strong acid) portrays the best result for all of the analyses done especially for BET surface area, thermogravimetric analysis and also CHNS elemental analyser. With this information, a more detailed analysis could be done to test natural catalyst from clay with different types or concentration of strong acid or acid in general. The potential of clay or waste clay to become catalyst has been proven but needs to be further enhanced and improved to achieved full capacity and ability. The future to having cheaper alternative to industrial catalysts by utilizing natural resources can be seen as bright and waste management problems can be solved bits by bits by analysing the potential of trash becoming treasure such as biorefineries, biomass electricity generation or even recycling materials.

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