Characterization of Zeolite as a Heterogeneous Catalyst Derived From Sungai Sayong Pottery Waste

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Catalyst is a substance that speed up the rate of reaction without itself being worn out at the end of the reaction. Most of Conventional catalysts do not seem relevant anymore due to economical constrains, not environmental friendly, and waste disposal issue of raw materials and the treatment applied. Synthesis of Sungai Sayong pottery waste into zeolite to be used in industrial as catalyst, would give some add value to these ceramic industries such as a proper waste management and a cheaper alternative to existing commercialized catalyst. The purpose of this study is to prepare ZSM-5 zeolite acting as catalyst derived from Sungai Sayong pottery waste and to characterize physically and chemically of synthesized zeolite. This study start with preparation of raw material from Sungai Sayong pottery waste into powder by crushing, grinding and sieving of the waste. After that, the pottery waste was treated with different ratios of 1M Hydrochloric acid and 1M Hydrogen peroxide. The treated and untreated samples were then characterized by using analytical equipment that are Thermogravimetric Analyzer (TGA), X-ray Fluorescene, BET method and Temperature Programmed Reduction Analysis. The results obtained shows that (TGA) of sample 1, sample 3, sample 4 and sample 5 have the similar trend with the commercialized zeolite. Meanwhile, by comparing the amount of Al_2O_3 and SiO_2 in commercialized zeolite with sample produced, the percentage of SiO_2 in samples produced is higher than Al_2O_3 in contrary with commercialized zeolite. The SiO_2/Al_2O_3 ratio for commercialized zeolite is 0.91 and the closest ratio value is 1.05 by 500 µm pottery waste. However, BET surface area shows that all the samples prepared has higher surface area than commercialized zeolite and the highest surface area is from sample 1 that is 66.4731 m^2/g. On the other hand, sample 1 and sample 4 has the nearest pore diameter to commercialized zeolite that are 67.751 Å and 63.268 Å . TPR analysis shows that the highest temperature of reduction of sample produced is about 800℃ starting from 100℃ to 740℃ for commercialized zeolite. Unsieved pottery waste and sample 5 share same maximum temperature for reduction that is 800℃ but at different temperature of reduction that are 100℃ to 560℃ for unsieved pottery waste and 40℃ to 240℃ for sample 5. As conclusion, zeolite derived from Sungai Sayong pottery waste has similarity with the commercialized zeolite in term of temperature profile, elemental content, surface area, pore volume and pore diameter which may affect the efficiency of the catalyst produced.

Keywords— *zeolite, pottery waste, metakaolinization, zeolitization*

I. Introduction

Zeolites is a crystalline microporous aluminosilicate materials which has been widely used in industrial field [1]. As the characteristics of zeolites are microporous, highly selectivity due to their crystallization structure and solid acid properties which are suitable to be used as ion exchangers, adsorbents and catalysts [2]. There are two types of zeolite which are natural zeolite and hierarchical zeolites but hierarchical zeolites are more beneficial than natural zeolites as hierarchical zeolites have been proven to function beyond limitation of natural zeolites such as low activity to large substrates with different chemical reactions, low mass transfer issue and catalyst deactivation [3].

Synthesis of hierarchical zeolite could be done from raw materials instead of metals such as clay minerals, municipal sludge waste, activated carbon which is cheaper, environmental friendly and highly availability. Most the methods of hierarchical zeolites synthesizes are focussing on the formation of micropores or mesopores as it could assist in fast mass transfer and to fulfil the characteristics of zeolite as heterogeneous catalyst. In addition, synthesizing of zeolites commonly involves two basic steps : metakaolinization is the process of converting chemically stable kaolin into a very reactive shapeless material, metakaolin and zeolitization is where the calcined kaolin is treated hydrothermally with sodium hydroxide solution [4].

Zeolites from kaolinite were using economical naturals resources compare to conventional pure sodium aluminate and sodium silicate [5] . Sungai Sayong clay has been classified as kaolinite based on previous study .For the time being, the usage of natural clay from Sungai Sayong is still limited for pottery works only but there is study prove that natural clay from Sungai Sayong is suitable materials for biocatalyst immobilization [6]. 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. Modification of zeolites will contribute to enhance the catalytic reaction as there is improvement in the accessibility to the active site and mass transport issue by additional of mesoporosity or microporosity compare to the conventional zeolites [3].

Waste management of the pottery waste is one of the problem faced by the manufacturers as those waste cannot be recycled or reformed into another new pottery products. Mismanagement of the waste may lead to the pollution of water or soil as there is usage of sodium silicate during slip preparation process. Usually, pottery wastes are being disposed just like other solid wastes, which end up decomposed in the landfill. During production process, “Labu Sayong” was fired in gas kiln at temperature of 850℃ for 10 hours [8]. Meanwhile, in synthesizing of zeolites, metakaolinization process at temperatures between 550℃ to 900℃ is necessary to reactivate the kaolin [9]. 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. Hence, neglecting of metakaolinization process and proceeding to zeolitization process during synthesizing of zeolite is recommended. The present study aimed of determining the characteristics of treated and untreated of Sungai Sayong pottery waste as zeolite using different analytical equipments such as thermogravimetric analyzer and X-ray Fluorescene.

II. METHODOLOGY

A. *Materials*

Pottery waste sample that was collected from pottery barn in Sungai Sayong was crushed, ground and sieved through 500 µm and 355 µm mesh of particle. Sample from 500 µm mesh of pottery waste particle then sorted into 5 samples with 5.0 grams weight of each sample before being treated with 1M Hydrogen peroxide and 1 M Hydrochloric acid. Other 3 samples were prepared from unsieved pottery waste, 500 µm and 355 µm mesh of pottery waste particle were kept untreated as control.

B. *Synthesis of catalyst*

5 samples were prepared with 5.0 grams of each sample were weighed by using electronic weighing balance. The sample was then added to 100 mL of 1M Hydrochloric acid and 1M Hydrogen peroxide solution and stirred for 30 minutes. Ratios of Hydrochloric acid to Hydrogen peroxide are as in the table below :

Table 1 : Ratio of Hydrochloric acid to Hydrogen peroxide solution

Sample	Hydrochloric acid (%)	Hydrogen peroxide (%)
1	0	100
2	100	0
3	25	75
4	75	25
5	50	50

The samples were then filtered and dried in drying oven for 24 hours at 80 °C.

C. *Analytical equipment*

Mettler Toledo TGA/DSC 1 Star system was used to determine the thermogravimetric analysis of clay samples at range temperature of 25°C to 1097°C at 10°C/min. X-ray Fluorescene (Model PW-2400) used to determine elemental composition of the samples. Surface Area Analyzer (Micromeritics Chemisorb 2750, USA used to determine surface area by using BET method and TPDRO 1100 SERIES to determine Temperature Programmed Reduction (TPR) of the samples.

III. RESULTS AND DISCUSSION

A. *Thermogravimetric analysis*

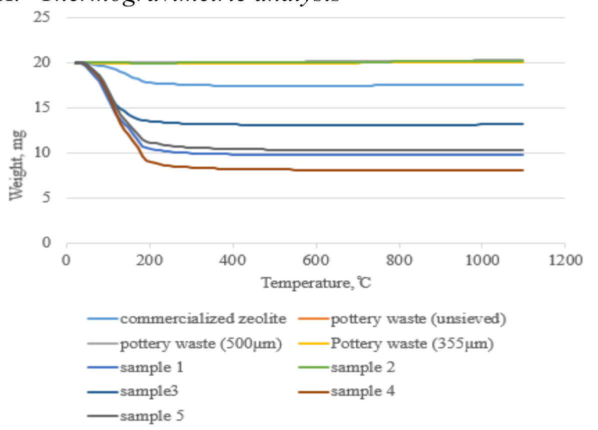

Fig 1 : Thermogravimetric analysis of samples

Based from Figure 1, themogravimetric analysis curves of unsieved pottery waste, 500-µm mesh of pottery waste, 355-µm mesh of pottery waste and sample 2 shared the same trends as the weight of the samples increased with temperature. These four samples have similarity, as they did not undergo hydrochloric acid treatment after metakaolinization process hence 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 [10].

Volatile matter in the catalyst will determine the internal structure and shape of the particles [11]. Based from the table above, the highest percentage content of volatile matter is in sample 4, 17.63% while the lowest one is in pottery waste (355µm) that is 0.19%. By comparing volatile matter content in commercialized zeolite which is 5.89%, the nearest value of volatile matter is in sample 3, 5.26%.

The objective of finding ash content in the sample to detect the presence of organic material in the sample. The highest ash content is produced by sample unsieved pottery waste about 60.82 x 10^{-3} mg which is quite similar to ash content of commercialized zeolite while the lowest ash content produced by sample 1 that is 589.37 x 10^{-6} mg. Organic material in the sample should be removed during calcination process depends on the temperature of calcination

B. *X-ray fluorescene*

The parameters that been considered by using XRF are Al_2O_3 and SiO_2 as the presence of those elements in chemical composition of zeolite. Table 4.2.1 shows the existence of Al_2O_3 and SiO_2 in all the samples produced as raw material used that is kaolinite is also an aluminosilicates mineral. By comparing the SiO_2/Al_2O_3 ratio of commercialized zeolite that is 0.91 with other samples, pottery waste (500µm) has the nearest SiO_2/Al_2O_3 ratio that is 1.05 followed by pottery waste (355µm) with SiO_2/Al_2O_3 ratio of 1.06 sharing the same value of ratio with sample 4.

Table 2 : Elemental component of treated and untreated sample of Sungai Sayong pottery waste

Elemental Content (%)			**SiO_2/ Al_2O_3 ratio**
Sample	**Al_2O_3**	**SiO_2**	
Commercialized zeolite	52.481	42.519	0.91
Pottery waste (unsieved)	47.891	52.181	1.09
Pottery waste (≥500um)	48.667	51.333	1.05

Pottery waste (500um≥-355um)	48.650	51.350	1.06
Sample 1(0% H_2O_2, 100%HCl)	47.329	52.671	1.11
Sample 2(100% H_2O_2, 0%HCl)	46.279	53.721	1.16
Sample 3(75% H_2O_2, 25%HCl)	43.180	56.820	1.32
Sample 4 (25% H_2O_2, 75%HCl)	48.569	51.431	1.06
Sample 5 (50% H_2O_2, 50%HCl)	48.339	51.661	1.07

The value of SiO_2 is higher than Al_2O_3 for all the samples produced which is in contrary to the value of SiO_2 and Al_2O_3 of commercialized zeolite. This may due to sodium silicate that has been added to the Sungai Sayong clay during the production process of pottery as to increase the plasticity of the ceramic product might become one of the contributions of high percentage of SiO_2 compared to Al_2O_3. Acid treatment may increase SiO_4 groups as all the exchangeable ions is replaced with H ions before Al and other cations in both tetrahedral and octahedral sites are leached out [6].

C. BET method

Table 3 : BET surface area

Sample	BET surface area (m^2/g)
Commercialized zeolite	1.0251
Pottery waste (unsieved)	18.6414
Pottery waste (500µm)	20.1827
Pottery waste (355µm)	20.3561
Sample 1 (0% H_2O_2, 100% HCl)	66.4731
Sample 2 (100% H_2O_2, 0% HCl)	22.7650
Sample 3 (75% H_2O_2, 25% HCl)	71.7087
Sample 4 (25% H_2O_2, 75% HCl)	79.1382
Sample 5 (50% H_2O_2, 50% HCl)	73.1711

Based on the table above, the highest surface area is sample 4, followed by sample 5 and sample 3 that are 79.1382 m^2/g, 73.711 m^2/g and 71.7087 m^2/g. While, unsieved surface area has the lowest surface area than other samples that is 18.6414 m^2/g. Based on the comparison, the results obtained from treated and untreated Sungai Sayong pottery waste is always higher than commercialized zeolite, which act as a reference for the samples. 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

Table 4 : Pore volume and diameter of samples

Sample	Pore volume (cm^3/g)	Pore diameter (Å)
Commercialized zeolite	0.00169	65.906
Pottery waste (unsieved)	0.1249	243.429
Pottery waste (500µm)	0.1370	239.845
Pottery waste (355µm)	0.1327	236.310
Sample 1 (0% H_2O_2, 100% HCl)	0.1126	67.751
Sample 2 (100% H_2O_2, 0% HCl)	0.1332	215.881
Sample 3 (75% H_2O_2, 25% HCl)	0.0961	53.628
Sample 4 (25% H_2O_2, 75% HCl)	0.1252	63.268
Sample 5 (50% H_2O_2, 50% HCl)	0.0983	53.761

Based on table above, 500 µm of pottery waste has the highest pore diameter while sample 5 has the lowest pore diameter. As standard size of mesopores is in between 2 nm to 50 nm, all the samples produced can be categorized as mesopores. Mesopores is favourable in synthesizing of active catalyst as by deriving of mesopores, highly accessible active sites could be achieved [1]. By comparing pore diameter of commercialized zeolite with other samples, sample 1 and sample 4 have the nearest pore diameter that are 67.751 Å and 63.268 Å respectively. Futhermore, one of the factor of mesopores generated is due to lower Al_2O_3 elements in zeolite framework due to extraction of Al framework during treatment and calcination process [12]. This is because formation of pores happened during treatment process by using Hydrochloric acid and calcination process.

D. Temperature-programmed reduction

Table 5 : Temperature-programmed reduction of the samples

Sample	Temperature of reduction	Maximum peak
Commercialized zeolite	100℃-740℃ 720℃-200℃	800℃ 740℃
Pottery waste (unsieved)	100℃-560℃ 600℃-260℃	800℃ 660℃
Pottery waste (500µm)	360℃-320℃	800℃
Pottery waste (355µm)	200℃-420℃ 460℃-300℃	580℃ 720℃
Sample 1(0% H_2O_2, 100%HCl)	100℃-500℃ 720℃-200℃	720℃ 580℃
Sample 2(100% H_2O_2, 0%HCl)	100℃-380℃ 400℃-200℃	580℃ 760℃
Sample 3(75% H_2O_2, 25%HCl)	160℃-100℃	760℃
Sample 4 (25% H_2O_2, 75%HCl)	120℃-640℃ 660℃-460℃	700℃ 760℃
Sample 5 (50% H_2O_2, 50%HCl)	40℃-240℃	800℃

Based on Table 5 above, commercialized zeolite consist of two maximum peaks that are 800℃ and 740℃. By comparing with other samples, only 500 µm of pottery waste, sample 3 and sample 5 have one maximum peak which are at 800℃, 760℃ and 800℃ respectively. Samples which form multiple peaks, might due to presence of other metals in the samples instead of zeolite, hence different reduction temperature happened depending on activation temperature of the material in the sample. The highest maximum peak is at 800℃ from commercialized zeolite, unsieved pottery waste and sample 5 indicates that those samples have higher difficulty in reduction compare to other samples that have lower maximum peak. This is due to more heat or energy is required to activate the samples before high rate of reaction of the process could be achieved.

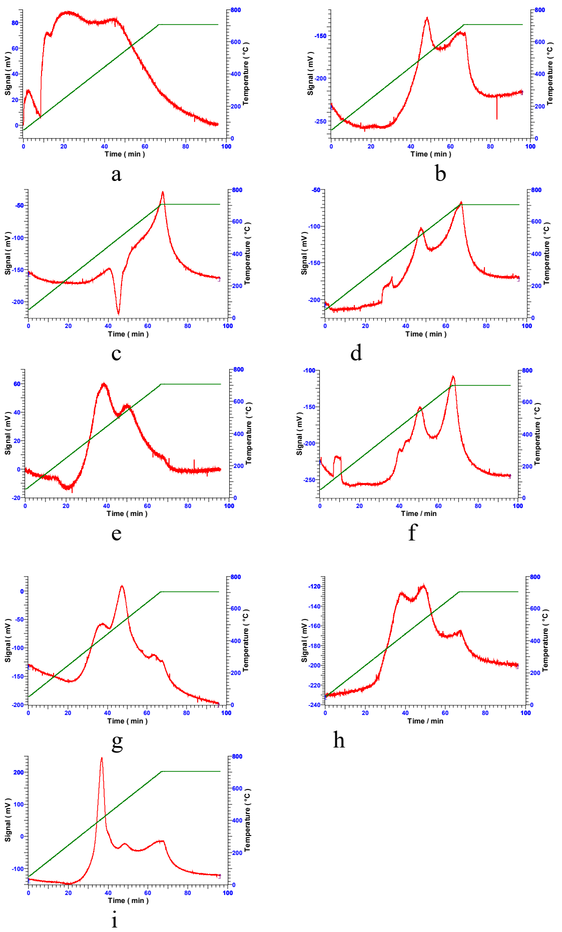

Fig 2 : a)TPR profile of commercialized zeolite b)TPR profile of unsieved pottery waste c)TPR profile of 500µm of pottery waste d)TPR profile of 355µm pottery waste e)TPR profile of sample 1 f) TPR profile of sample 2 g)TPR profile of sample 3 h)TPR profile of sample 4 i) TPR profile of sample 5

IV. Conclusion

As conclusion, zeolite derived from Sungai Sayong pottery waste has similarity with the commercialized zeolite in term of temperature profile, elemental content, surface area, pore volume and pore diameter which may affect the efficiency of the catalyst produced.

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References

[1] Luo, W., Yang, X., Wang, Z., Huang, W., Chen, J., Jiang, W., Zhao, D. (2017). Synthesis of ZSM-5 aggregates made of zeolite nanocrystals through a simple solvent-free method. *Microporous and Mesoporous Materials, 243*, 112-118. doi:10.1016/j.micromeso.2017.01.040

[2] Mohiuddin, E., Isa, Y. M., Mdleleni, M. M., & Key, D. (2017). Effect of kaolin chemical reactivity on the formation of ZSM-5 and its physicochemical properties.

[3] Feliczak-Guzik, A. (2017). Hierarchical zeolites: Synthesis and catalytic properties. *Microporous and Mesoporous Materials*. doi:10.1016/j.micromeso.2017.09.030

[4] Rocha, J., Klinowski, J., Adams, J.M., 1991. Synthesis of zeolite Na-A from metakaolinite revisited. J. Chem. Soc. Faraday Trans. 87, 3091–3097

[5] Johnson, E. B. G., & Arshad, S. E. (2014). Hydrothermally synthesized zeolites based on kaolinite: A review. *Applied Clay Science, 97-98*, 215-221. doi:10.1016/j.clay.2014.06.005

[6] Edama, N. A., Sulaiman, A., Ku Hamid, K. H., Muhd Rodhi, M. N., Musa, M., & Abd Rahim, S. N. (2013). Preparation and Characterization of Sg. Sayong Clay Material for Biocatalyst Immobilization. *Materials Science Forum, 737*, 145-152. doi:10.4028/www.scientific.net/MSF.737.145

[7] A. Saat, Z. Hamzah and Z. A. Bakar, XRF determination of major elemental contents of clay samples from North-West Peninsular Malaysia, Journal of Nuclear and Related Technologies 6 (2009) 230-236

[8] Haron, H. and Abd Mutalib, N. (2014). The Innovation of Labu Sayong Manufacturing Technology: A Technical Analysis. *Jurnal Teknologi*, 69(1).

[9] Kovo, A. (2012). Effect Of Temperature On The Synthesis Of Zeolite X From Ahoko Nigerian Kaolin Using Novel Metakaolinization Technique. Chemical Engineering Communications, 199(6), pp.786-797

[10] Esposito, S., Marocco, A., Dell'Agli, G., De Gennaro, B. and Pansini, M. (2015). Relationships between the water content of zeolites and their cation population. *Microporous and Mesoporous Materials*, 202, pp.36-43.

[11] Valentim, B., Białecka, B., Gonçalves, P., Guedes, A., Guimarães, R., Cruceru, M., Całus-Moszko, J., Popescu, L., Predeanu, G. and Santos, A. (2018). Undifferentiated Inorganics in Coal Fly Ash and Bottom Ash: Calcispheres, Magnesiacalcispheres, and Magnesiaspheres. *Minerals*, 8(4), p.140.

[12] Awadallah, A., El-Desouki, D., Aboul-Gheit, N., Ibrahim, A. and Aboul-Gheit, A. (2016). Effect of crystalline structure and pore geometry of silica based supported materials on the catalytic behavior of metallic nickel particles during methane decomposition to COx-free hydrogen and carbon nanomaterials. *International Journal of Hydrogen Energy*, 41(38), pp.16890-16902.