Production Of Santa Barbara Amorphous 15 (SBA-15) Using Extracted Silica From Fly Ash

Nor Adila Mohd Shah and Fazlena Hamzah

Faculty of Chemical Engineering, Universiti Teknologi Mara

***Abstract*— Fly ash is waste generated through combustion of coal from factories and thermal power plants. It is a type of waste that is available in abundant worldwide and may be reuse for other purposes. In this study, Santa Barbara Amorphous 15 (SBA-15) was synthesized from silica extracted from fly ash (FA). This is one of the method utilization of fly ash waste into a valuable product. Silicon dioxide or also known as silica, SiO_2 was extracted from FA via treatment with organic acid and alkali with addition of triblock copolymer surfactants of Pluronic 123 (P123) to produce SBA-15 as the end product. SBA-15 formed were characterized using X-ray fluorescence (XRF), X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Thermogravimetric analysis (TGA), Brunauer–Emmett–Teller (BET) analyzer and Field Emission Scanning Electron Microscopy (FESEM). The result from X-ray fluorescence (XRF) analysis indicated that fly ash contains 49.85% of silicate after treatment with acid. Fourier transform infrared (FTIR) data indicated the presence of siloxane and silanol groups which represent the silica group.**

Keywords—fly ash; utilization; SBA-15; silica

I. INTRODUCTION

Fly ash is the major residue formed during the incineration of coal. Fly ash is a type of coal remaining released by factories and thermal power plants. 43.4 million Metric tons of coal combustion fly ash were produced by the electric utilities in the United States in 1993. From this values, only about 22% of this amount was utilized by cement manufacturers mainly for cement and concrete products. The low level of ash consumption and application shows that fly ash is not completely utilized and the full potential of its application still needs to be discovered. Therefore, there is a constant need for finding new ways and usage of fly ash as such by extracting some of the components and using it as source for production of other new products. For a significant increase in ash exploitation, it is necessary to expand the range of useful products, derived from ash. [1]

Coal waste fly ashes contain mostly of alumina and silica mixture with smaller amounts of calcium, potassium, iron, and sodium. It was reported that fly ash can be altered via hydrothermal reaction into zeolites in alkali solutions, which is an effective method to yield new values from fly ash and reduce the environmental pollution problem caused by a stack of fly ash [2]. Silica in ash constitutes about 40-65% of the total mass, thus the likelihood of silica recovering and converting into a wide variety of pure chemical silicate products is higher. In terms of technical and economic features these perspective technologies shows a new discovery of ash utilization [3]

In Malaysia, there are six recognized coal fired electric power station. Coal fired electric power station is preferred as it is one of the cheapest way to produce electric comparing to the amount of power that it can produced. The development of power plants that use coal as their fuel source has created hundreds of millions of tons of ash every year. Formerly, they disposed the fly ash waste by burying it in landfills or returning it to strip mines, which is less environmentally friendly. Therefore, extensive studies and research had been made to find solution to this problem and one of the way is by reusing the waste for producing other valuable products. The main part of waste management is to prevent the production of waste through minimizing the waste made and also reusing the waste materials by recycling[4]. This paper are discussing the utilization of ash as silica source for formation of Santa Barbara Amorphous 15 (SBA-15).

II. METHODOLOGY

A. Materials

Sample of fly ash was taken from a cement manufacturer in Negeri Sembilan known as NS Cement. The fly ash was stored in a container and kept at room temperature. The materials used are Hydrochloric Acid (HCl), Sodium Hydroxide (NaOH), boric acid, distilled water and Pluronic P-123. All the chemical used are analytical grade.

B. Method

The SBA-15 was synthesized from silica extracted from the fly ash. There are 2 major steps involve in these SBA-15 synthesis which are the extraction of silicate from fly ash and the formation of SBA-15 from the extracted silicate.

In the preparation of fly ash extract, 5g of fly ash was stirred at 400 rpm with 50 ml of 1 M HCl for 2 hours at room temperature. The suspension formed was filtered using vacuum filter and the solid residue was washed with 20 ml of distilled water to remove other metal ion. The solid residue is then left dried overnight at 40ºC to ensure the sample is completely dried for further process.

Extraction of silicate from the fly ash, was conducted using alkali treatment process. 50 ml of NaOH was added into the dried fly ash. Then, the mixture were heated and stirred at 80ºC and 400rpm on a hot plate. It was stirred vigorously and continuously for 4 hours to produce sodium silicate solution. After 4 hours, the mixture was filtered by using vacuum filter. In this step, the filtrate silica supernatant is taken as source of silicate for SBA-15 formation meanwhile the residual of fly ash was discarded.

The mechanism of reaction is shown in equation 1.0 :

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_2 \quad (1.0)$$

In the formation of SBA-15 from the extracted silica supernatant, 5g of Pluronic 123 (P123) a triblock copolymer and 100 ml of 1 M HCl were stirred together at 400rpm at 35ºC for 1 hour. The pH of the mixture was maintained below pH 2 in order to achieve an isoelectric point for silica and to increase the condensation of the copolymer template and silica.

A homogenous, colorless solution was formed after an hour and 20 ml of the extracted silicate supernatant was added. The mixture is later transferred into a conical flask and stirred constantly at 150 rpm for 24 hours. The combination of the silicate and the mixtures of surfactant P-123 forming a P-123/SiO_2 composite. Then, the synthesis solution was aged for 24 hours at 100 ℃ in an oven. A yellowish solid products formed after aged for a day. The products were filtered and dried at room temperature for another 24 hours. Then, calcination process was performed at different temperature of 450ºC, 550ºC and 650ºC in order to remove the P123 as the final step [5]

C. Characterization

X-ray powder diffraction (XRD) was used to determine the crystalline structure of the synthesize SBA-15. Phillips PW 1830/40 was used to determine the samples structure, using Cu-Kα1 radiation with λ = 1.5406 Å, generator tension 40 kV, in the range 0.0-50° 2θ and at a rate of 1°/min. The Field Emission Scanning Electron Microscopy, FESEM analysis was used to observe the morphology of the SBA-15. FESEM images shows surface structure of the sample and its morphology.

Fly ash that undergoes acid treatment was analyzed using XRF in order to determine its composition. The sample was compressed into solid form by using a hand operated type compressor.[6] The sample was binded with some boric acid in order to maintain the solid form of ash. After that, the sample was inserted in a XRF sample holder and the analysis was conducted. The result of the chemical composition of each sample was displayed after 1 minute that gave the composition in wt %.

FTIR was used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas in the sample. The thermal stability of the SBA-15 synthesized was estimated by using Thermogravimetric Analysis (TGA) using a high-resolution mode with a maximum heating rate of 5 $Kmin^{-1}$. The specific surface area of SBA-15 produced was confirmed by the Brunauer–Emmet-Teller (BET) method.

III. RESULTS AND DISCUSSION

A. Percentage of silica in fly ash

XRF analysis for the sample is shown in Table 1. The result indicated that silica has the highest percentage up to 36.26% of the total composition of FA. This indicates that FA can be used as an alternative source to synthesis SBA-15. After acid treatment, the amount of silica constituting increases by approximately 14% to 49.85%.This is because the acid treatment method helps to remove the impurities from the fly ash. [7]

Table 1 Chemical composition of raw fly ash and silica extracted

Constituent	Concentration (%)	
	Raw Fly Ash	After Treatment By 1M of HCL
SiO_2	36.26	49.85
Al_2O_3	27.35	27.44
Fe_2O_3	24.80	14.06
MgO	4.48	3.30
Na_2O	2.56	2.40
CaO	2.44	1.03
TiO_2	1.06	1.12
K_2O	0.75	0.76
SO_3	0.33	0.03

B. Effect of calcination temperature on the characteristics of SBA-15

In this study, the silica extracted from fly ash was used as silica source to synthesis SBA-15. SBA-15 was synthesized using tri-block copolymer poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), which is commercially available as pluronics P123 ($EO_{20}PO_{70}EO_{20}$)[8]. SBA-15 synthesis was calcined at different temperature of 450ºC, 550ºC and 650ºC in order to remove the P123. The effect of temperature on the XRD pattern of SBA-15 was illustrated in Figure 1-3.

XRD patterns of the calcined SBA-15 samples prepared at higher temperatures exhibited three clear peaks characteristic of hexagonally ordered structure. Relative intensities of (110) and (200) peaks varied as the synthesis temperature was increased. The calcined SBA-15 sample prepared at 450ºC exhibited strong (110) reflection whereas the (200) reflection was hardly visible [9] The X-ray diffraction (XRD) patterns in Figure 2 and 3 had three well-resolved peaks that could be indexed as (1 0 0), (1 1 0) and (2 0 0) diffraction peaks, which indicated the typical two-dimensional hexagonally ordered mesostructure (p6mm) of SBA-15.[10]

Fourier transform infrared spectroscopy was carried out to study the surface chemical modification of samples in the range of 400–4000 cm^{-1}. FTIR spectra of SBA-15 samples calcined under different experimental runs are shown in Figure 4. SBA-15 samples calcined at different temperature displays almost similar FTIR spectra. The broad band around 3408 cm^{-1} was attributed to vibrations of OH group within the silanol groups. The band near at 1737 cm^{-1} is commonly associated to the bending of H–O–H from adsorbed water, whereas band at 1070 cm^{-1} belonged to asymmetrical and symmetrical stretching of Si–O–Si.[11]

Thermogravimetry analysis on the sample SBA-15 calcined at 450ºC, 550ºC and 650ºC (Figure 5-7) shows that the samples started to experience about 50% TGA weight loss at temperature of 863℃. This weight loss may be due to the decomposition and desorption of the polymeric. It might also due to the release of the water formed from the condensation of silanols in the silica framework. The thermal stability of the silica from TGA analysis indicates that an endurance limit of hydrophobicity of the silica in the structure can be maintained up to 600ºC. Therefore, when the temperature of the heat treatment was increased to 600ºC, the synthesized SBA-15 shows hydrophilic character due to conversion of the surface CH groups to OH groups.[12]

Field emission scanning electron microscopy (FE-SEM) images revealed the morphology of the crystals, SBA-15 as shown in Figure 9-11. The SBA-15 prepared did agglomerate in the form of irregular particles confirmed the presence of ordered hexagonal mesoporous channels in the final product [13]. The SBA-15 synthesized at 650ºC displays a highly ordered and well-defined pore structure. [5]

SBA-15 is a mesoporous silica sieve based on uniform hexagonal pores with a narrow pore size distribution and a tunable pore diameter between 5 and 15 nm. The thickness of the framework walls is about 3.1 to 6.4 nm, which gave the material a higher hydrothermal and mechanical stability. Typically, SBA-15 has a high internal surface area of ranging from 400–900 m^2/g makes SBA-15 a well-suited material for many applications in industry. SBA-15 are used in environmental analytics, for adsorption and separation, advanced optics, as a support material for catalysts and as a template for the production of nanostructured carbon or platinum replica.[14]

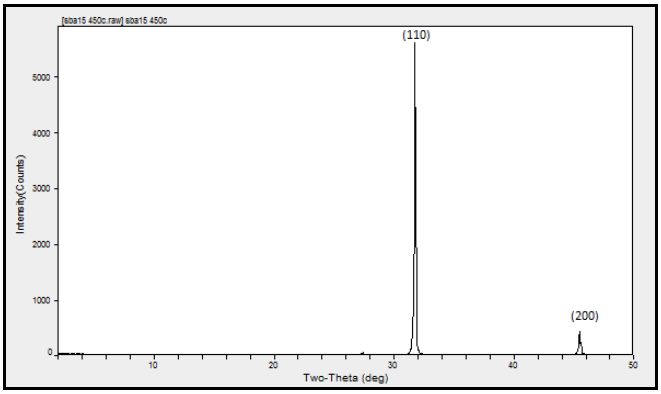

Figure 1 Powder XRD samples of SBA-15 calcined at 450ºC

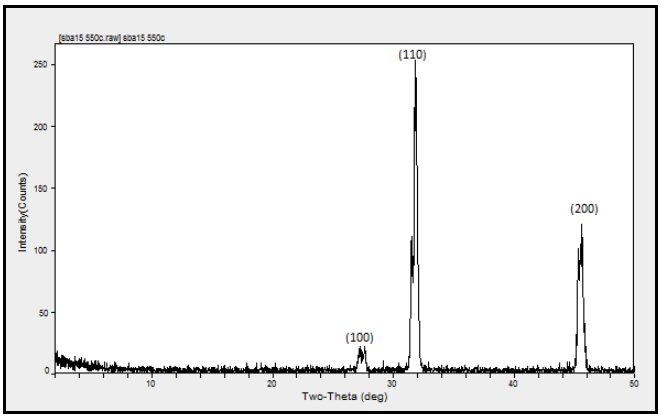

Figure 2 Powder XRD samples of SBA-15 calcined at 550ºC

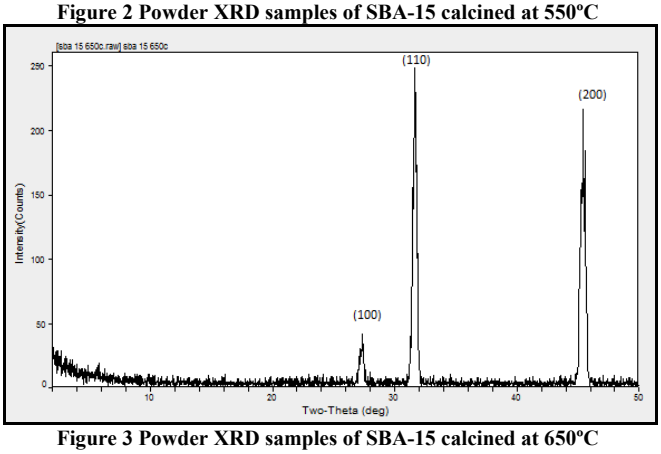

Figure 3 Powder XRD samples of SBA-15 calcined at 650ºC

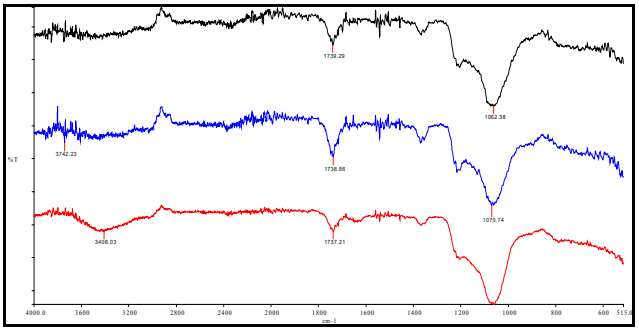

Figure 4 FTIR spectra of SBA-15 calcined at (i) 450ºC (ii) 550ºC and (iii) 650 ºC

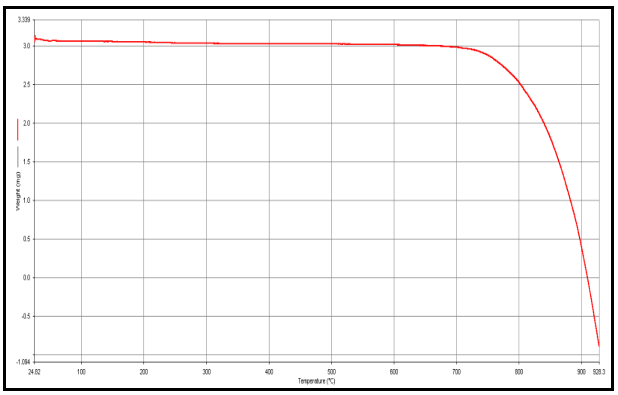

Figure 5 TGA curves of SBA-15 calcined at 450ºC

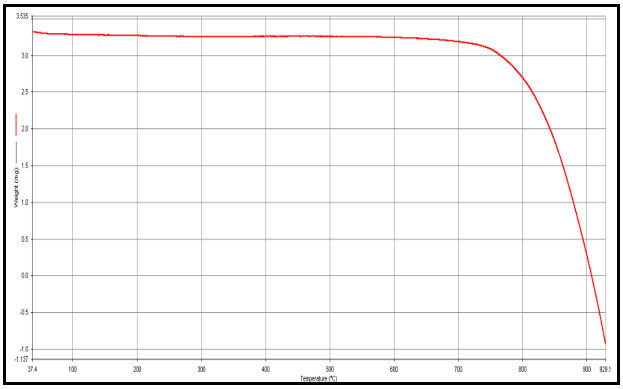

Figure 6 TGA curves of SBA-15 calcined at 550ºC

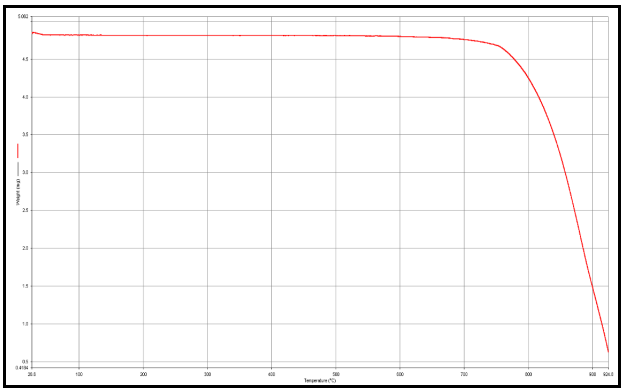

Figure 7 TGA curves of SBA-15 calcined at 650ºC

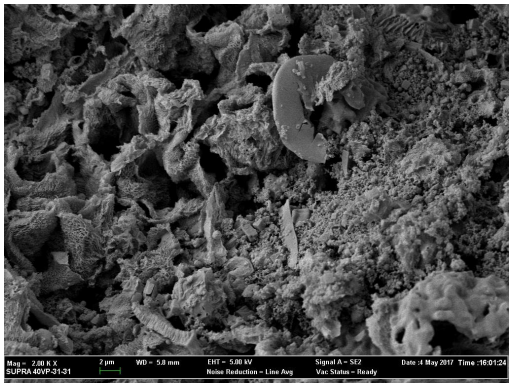

Figure 8 FE-SEM image of SBA-15 synthesis at 450ºC

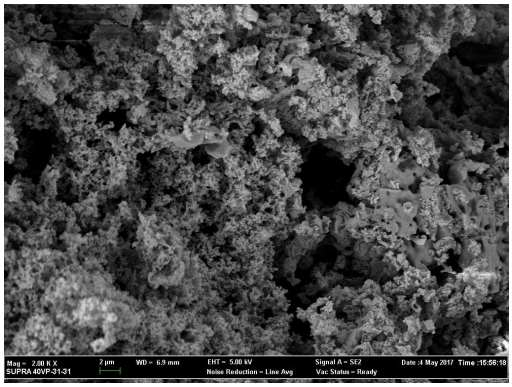

Figure 9 FE-SEM image of SBA-15 synthesis at 550ºC

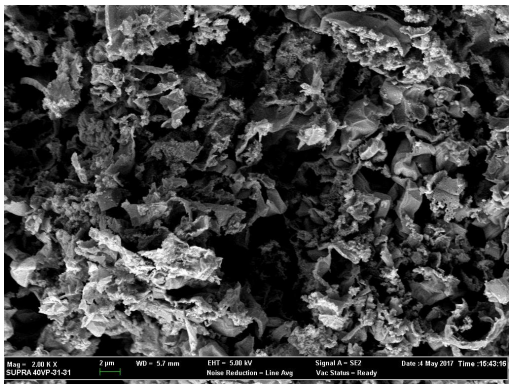

Figure 10 FE-SEM image of SBA-15 synthesis at 650ºC

IV. CONCLUSION

Silica extracted from fly ash was successfully converted into SBA-15. The fly ash consist about 36% SiO_2 and the composition was increased with HCl treatment. Different temperature used for calcination of SBA-15 effect the physical and chemical properties of SBA-15 synthesized. The SBA-15 synthesized at 650ºC is highly ordered and well-defined pore structure.

ACKNOWLEDGMENT

Thank you to my supervisor, Dr Fazlena Hamzah and Universiti Teknologi Mara for providing support in order to complete this research.

References

1. Ramezanianpour, A.A., *Fly Ash.* 2014: p. 47-156.
2. Shi, F., et al., *Cost-effective synthesis of silica aerogels from fly ash via ambient pressure drying.* Journal of Non-Crystalline Solids, 2010. **356**(43): p. 2241-2246.
3. Shcherban, S., *ASH UTILIZATION WITH SILICA AND METALS RECOVERY.* 1996.
4. Nordin, N., et al., *UTILIZATION OF FLY ASH WASTE AS CONSTRUCTION MATERIAL.* International Journal of Conservation Science, 2016. **7**(1).
5. Zhao, H., et al., *A facile strategy to synthesize spherical SBA-15 silicas by the addition of poly(vinyl alcohol).* Materials Letters, 2013. **92**: p. 33-35.
6. Norsuraya, S., H. Fazlena, and R. Norhasyimi, *Sugarcane Bagasse as a Renewable Source of Silica to Synthesize Santa Barbara Amorphous-15 (SBA-15).* Procedia Engineering, 2016. **148**: p. 839-846.
7. Kruk, M. and M. Jaroniec, *Characterization of the Porous Structure of SBA-15.* 2000.
8. Katiyar, A., et al., *Synthesis of ordered large pore SBA-15 spherical particles for adsorption of biomolecules.* J Chromatogr A, 2006. **1122**(1-2): p. 13-20.
9. Kruk, M. and M. Jaroniec, *Characterization of the Porous Structure of SBA-15.* American Chemical Society, 2000. **12**(7): p. 8.
10. Lu, B. and K. Kawamoto, *A novel approach for synthesizing ordered mesoporous silica SBA-15* 2012.
11. Sari Yilmaz, M. and S. Piskin, *Evaluation of novel synthesis of ordered SBA-15 mesoporous silica from gold mine tailings slurry by experimental design.* Journal of the Taiwan Institute of Chemical Engineers, 2015. **46**: p. 176-182.
12. Cheng, Y., et al., *Effect of surface modification on physical properties of silica aerogels derived from fly ash acid sludge.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2016. **490**: p. 200-206.
13. Jiang, J., et al., *Economical synthesis of amorphous carbon nanotubes and SBA-15 mesoporous materials using palygorskite as a template and silica source.* Materials Letters, 2014. **132**: p. 425-427.
14. Thielemann, J.P., et al., *Pore structure and surface area of silica SBA-15: influence of washing and scale-up.* Beilstein J Nanotechnol, 2011. **2**: p. 110-8.