

Synthesis of Na-A and Na-X zeolites by using rice husk ash from biomass power plant

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Abstract— Rice husk ash (RHA), a solid waste from biomass power plant was used as a raw material to synthesize Na-A and Na-X zeolites. In fact, high silica content inside this material opens a possibility to become a potential zeolite precursor. In this study, a medium particle of RHA has been reused to prepare zeolite with high purity. After segregated by mechanical sieving, the medium particle fraction of RHA was subjected to alkali fusion treatment followed by dissolution and then residue separation to produce clear silicate supernatant as the silica source for preparing the low-silica zeolites. High purity of Na-A and Na-X zeolites were prepared using hydrothermal treatment by optimizing the process condition, curing time, hydrothermal temperature and Si/Al molar ratio in the reaction mixture.

Keywords— Zeolite, Fly ash, Synthesis, Catalyst, Hydrothermal treatment

I. Introduction

Rice has been one of the most important agricultural products of Thailand. It was cultivated not only for domestic consumption but also for export [1]. The byproduct which is rice husk has been used as a major energy source to generate electricity. The rice husk ash obtained after combustion is often dumped or used only as landfilling materials, materials for soil improvement, or raw materials in cement production [2].

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The study of rice husk ash showed high content of silica and alumina similar to raw materials typically used in zeolite synthesis [3]. These raw materials can be coal fly ash [4,5], oil shale ash [6], bagasse fly ash [7], or rice husk ash [1,8,9]. Therefore, rice husk ash is a potential raw material for zeolite synthesis.

Among many types of zeolites, zeolite Na-A and Na-X has been attracted a lot of attention. Na-A and Na-X zeolites possess unique structural properties and are extensively used in industries as catalyst supports, gas or liquid dryers, and ion-exchanger. The studies on synthetic zeolite are usually focused on the use of chemicals with high purity while artificial zeolites use waste materials such as coal fly ash. Generally, there are two main methods for zeolite synthesis using solid wastes as the silica-alumina source. The methods are widely recognized as single step and two step method. The single step method aims to utilize whole part of the silica containing solid waste for zeolite production without any separation. Usually this method employs hydrothermal treatment in a single pot for all preparation sequences, i.e. dissolution of silica and alumina from the bulk solid in alkali solution and then re-crystallization of the two components into zeolites covering the un-dissolved solid. By employing this method there will be no leftover residue, however particles irregularities and crystal variety in the end zeolite products become the major drawbacks of this method. On the other hand, the two step method requires solid residue separation after most of silica and alumina content have been dissolved in the alkali solution. The residue removal increases the possibility in producing desired type of zeolite with high purity and particle regularity (shapes and sizes) but leaving a new solid waste along with very low production yield. Meanwhile, for eliminating any waste generation, a combination between the two methods has been proposed to produce high purity zeolite from the supernatant and also low grade zeolite from the mixture of the solid residue and the spent reaction time [7].

This study was aimed to investigate the effect of reaction condition in hydrothermal treatment of supernatant (Silica extraction solution) such as alkali concentration for silica extraction method, treatment temperature, treatment time and amount of sodium aluminate added for zeolite preparation method.

II. Experimental

A. Silica extraction from rice husk ash

Rice husk ash was obtained from Roi-Et Green power plant in the Northeastern of Thailand with combustion

temperature of 650°C. The sample was then sieved to remove dirt and was dried in an oven at 100°C overnight. The particle fraction was separated from the bulk rice husk ash by mechanical sieving using standard sieve of 25 mesh (particle size less than 0.710 mm). The first preparation step was the extraction of silicon and aluminum content from medium RHA particles proposed by Purnomo et al. (2012) [7]. 10 g of ash was mixed with sodium hydroxide powder (Waco; 97 wt.% NaOH) with different at weight ratios of RHA:NaOH (1:1 and 1:2) and heated different temperature of 100, 200, 300, 400 and 500°C for 1 or 2 hours. The mixture was then cooled to room temperature and milled for several minutes. The obtained powder was mixed with deionized water with weight ratio of powder to water of 1:5 followed by aging for 2 hours with agitation at room temperature. Then solid in the mixture were filtered to obtain a clear supernatant by using Whatman™ filter paper 540 hardened ashless. The concentrations of silicon, aluminum and sodium in the supernatant were measured with Inductively Couple Plasma-Atomic Emission Spectroscopy (ICP-AES) method using SPS 7800 (SII).

TABLE I. THE ELEMENT COMPOSITION OF THE RICE HUSK ASH

Element	Si	Al	Na	Mg	K	Fe	Others
Content (wt. %)	27.05	5.03	41.59	0.87	0.42	0.11	24.93

B. Zeolite preparation

The synthesis of zeolite was prepared from the concentration of silicon and aluminum in the supernatant after measured by ICP. A mixture of zeolites were synthesized from the high silica supernatant mixed with sodium aluminate solution from dissolution of sodium aluminate powder (Waco; 0.77M ratio of Al/NaOH) into deionized water for preparing the reaction mixture with Si/Al molar ratio of 0.5, 1.0, 1.5, 1.8 and 2.0. The mixture were then stirred for 1 hour, after that the mixture was mixed thoroughly and treated at 90° and 120°C for 10 to 24 hour in Teflon™ – lined stainless steel vessels of 15 mL capacity without agitation. The final procedures were filtering, washing and drying of the precipitates. For identification, zeolite sample names follow this rule: ZRxTytz where x is the Si/Al molar ratio in the parent solution, y is the hydrothermal temperature in °C and z is the hydrothermal time in hours.

C. Characterization of rice husk ash and zeolite

The elements of Si, Al, Na, Mg, K, Fe and others in the RHA was analyzed using ICP-AES. N₂ adsorptions of synthesized materials were carried out using Autosorb 1 (Quantachrome) and the specific surface areas were calculated using BET method. X-ray diffraction (XRD) analyses using Multiflex (Rigaku) with Cu-Kα radiation were carried out to determine the crystalline type of zeolites produced. Scanning electron microscopy using JSM-5310LV (JEOL) was conducted to observe the surface morphology of RHA and products.

The loss of ignition (LOI) test was done by placing 1 g of dried sample of the rice husk ash in a crucible and ignited in the furnace at 1000°C for 30 minutes to achieve a constant mass left, followed by cooling at room temperature. The loss of ignition, as a percentage by mass given by the formula:

$$LOI = \frac{M_o - M_1}{M_o} \times 100, \% \quad (1)$$

where M_o is the mass of the sample and M₁ is the mass of the sample after ignition.

The cation exchange capacity (CEC) of zeolites synthesized was measured using sodium acetate method to exchange all the cations in the material with sodium using sodium acetate and then extract all of them using ammonium acetate. The extracted sodium ions will then be analyzed using ICP-AES.

III. Results and Discussion

A. Characterization of rice husk ash and the supernatant after extraction

Table I shows the chemical composition of the rice husk ash from power plant Si was 27.05 wt.%, Al was 5.03 wt.%, Na was 41.59 wt.%, Mg was 0.87 wt.%, K was 0.42wt.%, Fe was 0.11wt.%, the others were 24.93 wt.% and the loss of ignition (LOI) was 5.15%. The surface area of RHA was 17.13 m²/g. The XRD pattern of rice husk ash showed in Figure 1 confirms the main composition of SiO₂ with crystalline type of quartz and cristobalite. The broad peak between 2θ of 21 – 32° implied the presence of amorphous phase of carbon and silica.

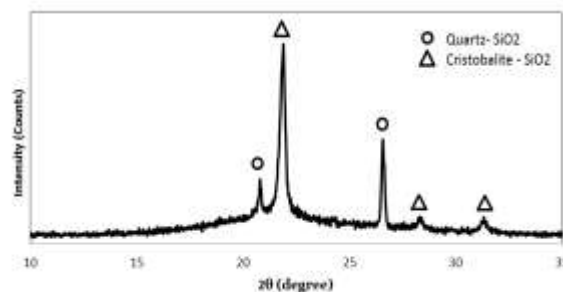


Fig. 1. XRD pattern of rice husk ash from power plant at 650°C

TABLE II. COMPOSITION OF SUPERNATANTS AT VARIOUS EXTRACTION CONDITIONS OF RHA.

RHA:NaOH	Heating Temp, °C	Heating Time, hour	Silicon, mg/L	Aluminum, mg/L
1:1	500	1	21,400	500
1:1	400	1	23,809	952
1:1	300	1	23,333	476
1:2	300	2	24,286	952
1:1	200	2	22,857	952
1:2	100	2	6,667	476

The composition of supernatants obtained from RHA extractions with different conditions were listed in Table II. At RHA:NaOH ratio of 1:1 and heating time of 1 hour, the change of temperature from 500°C to 400°C and 300°C resulted in the change of silicon content from 21400 mg/L to 23809 mg/L and 23333 mg/L, respectively and the change of aluminum content from 500 mg/L to 952 mg/L and 476 mg/L, respectively. For the condition of heating time = 2 hours, RHA:NaOH ratio = 1:2, temperature = 300°C, the silicon and aluminum dissolved were 24286 mg/L and 952 mg/L, respectively.

For heating time of 2 hours with RHA:NaOH ratio of 1:1 and temperature of 200°C, the amount of silicon has been changed to 22,857 mg/L and heating time of 2 hours with RHA:NaOH ratio of 1:2 and temperature of 100°C, the amount of silicon and aluminum have been changed to 6,667 mg/L and 476 mg/L, respectively. The supernatant extracted at RHA:NaOH of 1:1, heating temperature of 300°C and heating time of 1 hour was used in the next step of hydrothermal treatment of the supernatant

B. The effect of Si/Al molar ratio

Adjusting the ratio of Si/Al in the reaction mixture prior to undergoing crystallization by hydrothermal treatment is the most important aspect in determining crystal structure of the end zeolite product. Because the supernatant has very low aluminum content, sodium aluminate solution was added to increase its concentration in the mixture. The Si/Al molar ratio of 1.8 was critical ratio to prepare pure zeolite X (PDF 38-0237: $\text{Na}_2\text{Al}_2\text{Si}_2.5\text{O}_9.6.2\text{H}_2\text{O}$). Increasing the ratio higher than 1.8, the mixture of zeolite Na-X and Na-P1 (PDF 39-0219: $\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32}.12\text{H}_2\text{O}$) was formed, while using lower ratio zeolite Na-A (39-0222: $\text{Na}_9\text{Al}_9\text{Si}_9\text{O}_{384}.216\text{H}_2\text{O}$) was formed in the ratio of 1.0 and 0.8. This raw material could prepared a pure zeolite both Na-X and Na-A in this ratio, and it has a good agreement with a previous studied using coal fly ash as the silica source [10]. By using lower molar ratio Si/Al ≤ 1 , pure zeolite Na-A could not be achieved due to sodalite and amorphous aluminosilicate impurity.

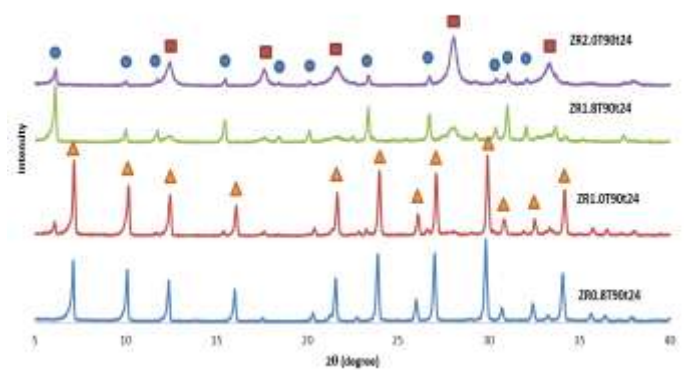


Fig. 2. XRD patterns of produced zeolite by hydrothermal treatment at 90°C, ● is Na-X, ■ is P1 ▲ is Na-A.

Fig. 2 shows the XRD patterns of synthesized zeolites at lower temperature (90°C). The figure confirms that high purity of zeolite Na-A and pure zeolite Na-X can be prepared from the reaction mixture with proper Si/Al ratio. All the appeared peaks correspond to Na-X and P1 zeolite pattern for ZR1.8T90t24 and ZR2.0T90t24 and Na-A zeolite pattern for ZR1.0T90t24 and ZR0.8T90t24, respectively. The purity was also confirmed by SEM images of the two main zeolite types. It can be seen that typical octahedral particle shape of faujasitic zeolite X and cubic shape of zeolite A are clearly showed in Figure 3a and 3b, respectively. The surface area and the cation exchange capacity (CEC) of the synthesis Na-A zeolite prepared at 90°C for 24 hours were 134.7 m²/g and 470 meq/100g, respectively. The surface area and the cation exchange capacity (CEC) of the synthesis Na-X zeolite prepared at 90°C for 24 hours were 703.2 m²/g and 503 meq/100g, respectively. According to H. Katsuki and S. Komarneni, 2009 [8], the surface area of the Na-A zeolite was lower than Na-X zeolite because nitrogen molecule cannot enter into Na-A zeolite due to its small pores, while Na-X zeolite has larger pores which let nitrogen molecules go in and that is why the surface area is very high in the Na-X zeolite.

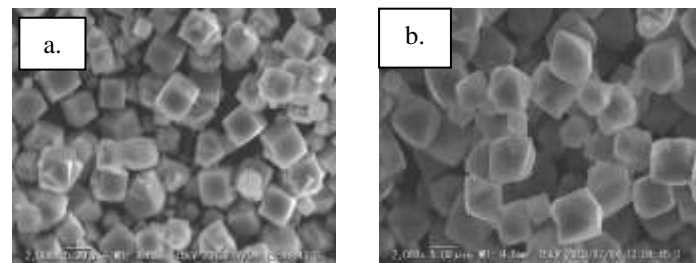


Fig. 3. SEM images of 90°C hydrothermal method: (a) ZR1.0T90t24 and (b) ZR1.8T90t24.

The IR spectra of absorption bands due to the formation of structural unit during zeolite crystallization are shown in Fig. 4. All of the band assignments of rice husk ash, zeolite A and X follow the work pioneered by Flaningen et al. [11]. The

formation of rice husk ash after combustion at 650°C from biomass power plant showing the presence of absorptions at 459, 792 and 1090 cm^{-1} . The band at 459 and 792 cm^{-1} are due to the S4R T-O-T (where T = Si or Al) symmetric stretching, while the absorption at 1090 cm^{-1} is due to siloxane bonds; Si-O-Si. The spectrum of Na-A zeolite exhibited absorptions at 459, 554 and 1001 cm^{-1} . The 1001 cm^{-1} band was due to the Si-O-Si siloxane bond. The band at 554 cm^{-1} was attributed to the D6R T-O-T symmetric stretching. On the other hand, the spectrum of Na-X zeolite exhibited absorptions at 456, 554, 670, 753 and 974 cm^{-1} . The 974 cm^{-1} band was due to the Si-O-Si siloxane bond. The 753 cm^{-1} band was due to the S4R T-O-T symmetric stretching while the absorption at 670 cm^{-1} was attributed to the Si-O-Al symmetric stretching. The 554 cm^{-1} and 456 cm^{-1} bands were due to the D6R T-O-T symmetric stretching and S4R T-O-T symmetric stretching, respectively.

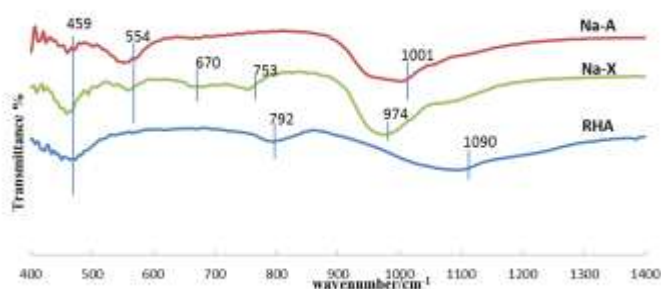


Fig. 4. FTIR spectra of rice husk ash, Na-A zeolite and Na-X zeolite.

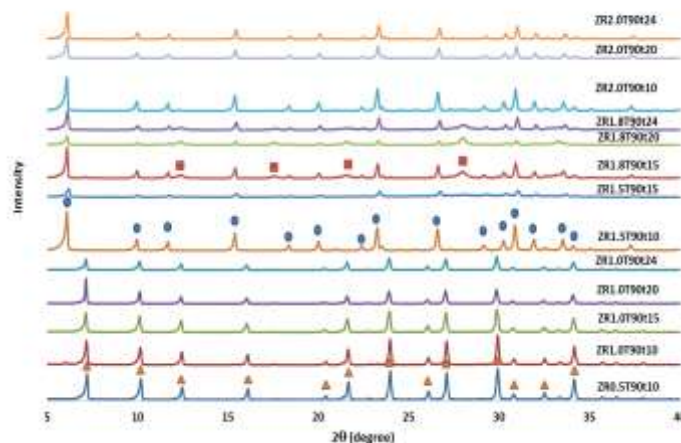
C. The effect of hydrothermal heating time and temperature

In the case of energy conservation we tried to decrease the heating time for zeolite preparation in the same condition of Si/Al ratio of 0.5, 1, 1.5, 1.8, and 2; and heating temperature of 90°C and 120°C. The results can be seen in Fig. 5a and 5b which are the results from hydrothermal heating time of 24, 20, 15 and 10 hours are shown. It can be seen that at the hydrothermal temperature of 90°C, pure Na-A zeolite formed in the ratio of 0.5 to 1.0 and there was no change when hydrothermal time was increased. Na-X zeolite formed together with Na-P1 zeolite at Si/Al ratio of 1.5 to 1.8, and there was no change when hydrothermal time increased as well, but at ratio of 2.0 with heating time of 10 to 24 hours, pure Na-X zeolite was formed. On the other hand, Na-A zeolite was formed in the ratio of 1.0 at hydrothermal time of 10 hour while increasing the time to 24 hours resulting in the formation of sodalite without any Na-A or Na-X zeolites. Na-X and P1 zeolite were formed when Si/Al ratio increased to 2.0 with hydrothermal time from 20 to 24 hour.

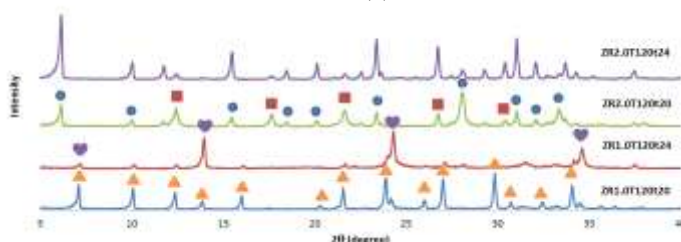
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(a)



(b)

Fig. 5. XRD pattern of produced zeolite by hydrothermal treatment at 90°C (a) and 120°C (b) in different Si/Al ratio and heating time

● = Na-X ■ = Na-P1 ▲ = Na-A ▼ = Sodalite

iv. Conclusion

After the text edit has been completed, the paper is ready for The rice husk ash waste from power plant in Thailand can be used for synthesized Na-X zeolite and a pure Na-A zeolite by using it as silica source by employing alkali fusion and then extraction with residue removal followed by hydrothermal treatment. Zeolite A was formed at 90°C hydrothermal temperature for 10 to 24 hours by varying Si/Al molar ratio from 0.5 to 1.0. On the other hand, Na-X zeolite were formed in the same hydrothermal heating time as zeolite A by varying Si/Al ratio from 1.5 to 2.0 with heating time of 10, 20, and 24 hours, respectively. Zeolite P1 was formed together with zeolite X at the ratio of 1.8 with heating time of 15 to 24 hours. Na-A and Na-X zeolites synthesized with the optimal condition possessed a maximum value of cation exchange capacity of 470 meq/100 g and 503 meq/100g, respectively.

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References

- [1] P. Thuadajj, and A. Nuntiya, "Synthesis of Na-x Hydrate Zeolite form Fly ash and Amorphous Silica from Rice Husk Ash by Fusion with Caustic Soda Prior to Incubation," International Conference on Chemistry and Chemical Process, 2011, vol. 10, pp. 69-74.
- [2] S. Tangtermsirikul. Development of fly ash usage in Thailand. The International Workshop on Project Management, Kochi, Japan. 2005, 1.
- [3] J.Y. Huang. Beneficial use of fly ash. Michigan Technological University.
- [4] H. Tanaka, H. Eguchi, S. Fujimoto, and R. Hino, "Two-step process for synthesis of a single phase Na-A zeolite from coal fly ash by dialysis", Fuel, vol. 85, 2006, pp. 1329-1334.
- [5] H. Tanaka, and A. Fujii, "Effect of stirring on the dissolution of coal fly ash and synthesis of pure-form Na-A and -X zeolite by two-step process" Advanced Powder Technology, vol. 20, 2009, pp. 473-479.
- [6] N.R.C.F. Machado and D.M.M. Miotto, "Synthesis of Na-A and -X zeolite from oil shale ash" Fuel, vol. 84, 2005, pp. 2289-2294.
- [7] C.W. Purnomo, C. Salim, and H. Hinode, " Synthesis of pure Na-X and Na-A zeolite form bagasse fly ash" Microporous and Mesoporous Materials, vol. 162, 2012, pp. 6-13.
- [8] H. Katsuki and S. Komarneni, "Synthesis of Na-A and/or Na-X zeolite/porous carbon composites from carbonized rice husk", Journal of Solid State Chemistry, vol. 182, 2009, pp. 1749-1753.
- [9] Z. Ghasemi and H. Younesi, "Preparation and Characterization of Nanozeolite NaA from Rice husk at Room Temperature without Organic Additives", Journal of Nanomaterials, 2011.
- [10] G.G. Hollman, G. Steenbruggen, and M. Janssen-Jurkovicova, Fuel, vol. 78, 1999.
- [11] E.M. Flaningen, H. Khatami, H.A. Szymanski, Adv. Chem. Ser. vol 101, 1971.