

## Synthesis and characterization of zeolite derived from Buriram sugarcane bagasse ash and Narathiwat kaolinite

Pattaranun Thuadajj\*, Prasith Mukda

Department of Chemistry, Faculty of Science, Buriram Rajabhat University, Buriram, 31000, Thailand

\* Corresponding Author: [pattaranun.thad@gmail.com](mailto:pattaranun.thad@gmail.com)

Received: 31 July 2016; Revised: 7 September 2016; Accepted: 9 September 2016; Available online: 1 December 2016

### Abstract

In this research studied the synthesis of zeolite from sugarcane bagasse ash and Narathiwat kaolinite. The first step, silica was synthesized from sugarcane bagasse ash. A comparative study of NaOH concentrations was varied at 2 M 2.50 M and 3 M, respectively for 3 h at 100 °C by refluxing method. The results showed that yield of silica 55% at optimum 2.50 M NaOH concentrations. Silica was characterized by Fourier transform infrared spectroscopy (FTIR) technique. The starting materials were silica from sugarcane bagasse ash and Narathiwat kaolinite in the ratio of 3 : 7 by the refluxing method under temperature 100 °C at various NaOH concentration and crystallization times. The results found that Na-P zeolite at 3 M NaOH concentration for 10 h. The zeolite indicated that result in the research and confirmed by XRD and FTIR. The cation exchange capacity (CEC) was 351 meq/100g.

**Keywords:** Sugarcane bagasse ash; Narathiwat kaolinite; Zeolite; Cation exchange capacity

©2016 Sakon Nakhon Rajabhat University reserved

### 1. Introduction

Sugarcane bagasse is a huge by product in the sugar mills when juice is extracted from the cane. Combustion of sugarcane bagasse in boilers, used for steam and electricity generation, produces a great amount of silicon and other oxides. But the ashes obtained directly from the mill are not reactive because of these are burnt under uncontrolled conditions and at very high temperatures. The ash, therefore, becomes an industrial waste and increasing landfill problems [1]. For that reason; consequently, the advance of new procedures for its creative reuse is relevant. Actually, the growth of this waste, which is quartz-abundant, can be avoided if employed as a silicon source. By means of an alkali fusion extraction method, quartz particles can be dissolved and used as silicon source for synthesizing silica-based materials such as zeolites. But the alkali fusion method has the high energy and expensive equipment. Most researchers have used coal fly ash as a low cost silicon and aluminium source to produce zeolites. Different types of zeolites such as X [2, 3], ZSM-5 [4], hydroxysodalite [5], Na-P1 [6], and zeolite A [7, 8] were synthesized by applying many synthesis methods. Therefore, the application of this process using sugarcane bagasse ash is an important procedure to increase the value of sugarcane bagasse ash and to avoid

environmental pollution caused by this waste. The synthesis is indicated for the extraction of silica powder from sugarcane bagasse ash, making it available for zeolite synthesis [9].

The research of this study was to synthesize zeolite from sugarcane bagasse ash and Narathiwat kaolinite in two steps: extraction method was silicon from sugarcane bagasse ash by refluxing treatment for the starting material to synthesize zeolite. This work demonstrates the potential of sugarcane bagasse ash extract to be used as a reliable silica source for preparing pure zeolite and Narathiwat kaolinite as source were silica and alumina. The characterization of the resulting zeolites materials for their X-ray diffraction, cation exchange capacity (CEC) and the best Na-P zeolite was determine by Fourier transform infrared spectroscopy technique.

## 2. Materials and Methods



Fig. 1 Silica powder from sugarcane bagasse ash

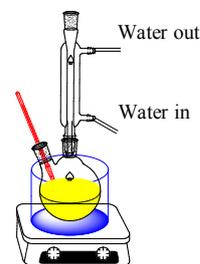


Fig. 2 Schematic of refluxing method

### Material

Sugarcane bagasse ash was obtained from Buriram sugar factory (in Buriram province), which washed with water and then dried at 110 °C for 3 h. The mineralogical composition chemical analyses of sugarcane bagasse ash were accomplished by X-ray fluorescence (XRF: Horiba Mesa-500w).

### Method

#### *Synthesis of silica from sugarcane bagasse ash*

The 10 g of sugarcane bagasse were stirred in 50 mL of sodium hydroxide (NaOH) solutions with 2.50 M in a boiling flask [10]. The reactants were placed in a water bath and heated at 100 °C for 3 h. The solution filtrated and washed with 100 mL boiling water. The filtrate was cooled down to room temperature. After that, 5 M sulfuric acid was poured into the solution obtained at first step until pH 2 and then ammonium hydroxide was also added in the filtrate to obtain pH 8.50. The filtrate was left for 3.50 h at room temperature and then dried at 120 °C for 12 h to obtain white powder, showed in Fig. 1. The powder was identified by Fourier transformed infrared spectrophotometer (FTIR: Perkin Elmer, Spectrum GX).

*Zeolite synthesis*

Zeolite synthesis process was performed of placing 10 grams of silica obtained Sugarcane bagasse ash mixed with Narathiwat kaolinite ratio of 3 : 7 (weight : weight) [11] by refluxing method showed in Fig. 2. Before synthesis, the starting materials of mixture on concentrated 3 M and 5 M in 50 ml of NaOH solutions, respectively in a breaker. The breaker was kept in a water bath at 80 °C for 3 h and stirred constantly (300 rpm). Then, the mixtures were heated at 100 °C for 6, 8 and 10 h by refluxing method without stirring. After various crystallization times, the solids were obtained by filtration process, washed repeatedly with distilled water, dried at 110 °C for 18 h and kept in powder form for further characterization. Samples were then characterized by X-ray diffraction [XRD: Bruker AXS D8 Advance diffractometer equipped with a copper anode ( $\lambda = 1.5406 \text{ \AA}$ )]. The solid product was determined the cation exchange capacity by ammonium replacement method. The best crystalline Na-x zeolite characterized by Fourier transformed infrared spectrophotometer (FTIR: Perkin Elmer, Spectrum GX).

**3. Results and Discussion***Chemical and mineralogical analyzes of materials*

The product was determined by X-ray fluorescence spectrometer (XRF) as summarized the chemical compositions of sugarcane bagasse sample are shown in Table 1. The highest amount of  $\text{SiO}_2$  is 82.70 wt% The total amounts of  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$  are 4.06, 3.55, 2.48 and 2.47 wt%, respectively and other components are 4.75 wt%. The chemical compositions of kaolinite from Narathiwat province are indicated in Table 1. It was found that the main components of kaolinite are  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  incorporating with  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{K}_2\text{O}$  and  $\text{P}_2\text{O}_5$  as minor phases.

**Table 1** Chemical compositions of sugarcane bagasse ash and Narathiwat Kaolinite

Components expressed as oxide	Sugarcane bagasse (%)	Kaolinite (%)
$\text{SiO}_2$	82.70	44.76
$\text{Al}_2\text{O}_3$	1.12	36.18
$\text{K}_2\text{O}$	4.06	1.15
$\text{CaO}$	3.55	0.13
$\text{P}_2\text{O}_5$	2.47	0.06
$\text{MgO}$	1.24	0.11
$\text{SO}_3$	1.37	-
$\text{TiO}_2$	0.42	0.84
$\text{Mn}_2\text{O}_3$	0.60	-
$\text{Fe}_2\text{O}_3$	2.48	0.83

*IR of silica from sugarcane bagasse ash*

The major chemical groups presented in silica were identified by the FTIR spectra and shown in Fig. 3. The broad band between 2800 and 3750  $\text{cm}^{-1}$  was due to silinol OH groups and adsorbed water. The predominant absorbance peak at 1320  $\text{cm}^{-1}$  was due to siloxane bonds (Si-O-Si). The peaks between 1200 and 700  $\text{cm}^{-1}$  are attributed to vibration modes of the gel network [12]. IR spectrums were not clearly show the difference between pure silica from standard chemicals and silica from sugarcane bagasse. The characteristic and position of peaks are identical.

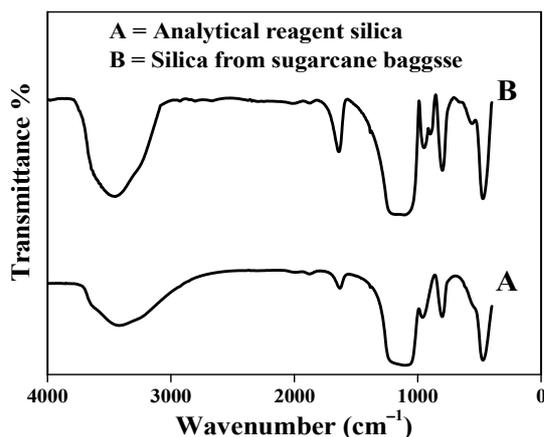


Fig. 3 Infrared spectrum of (A) analytical reagent silica and (B) silica produced from sugarcane bagasse ash.

*Synthesis experiments in NaOH media*

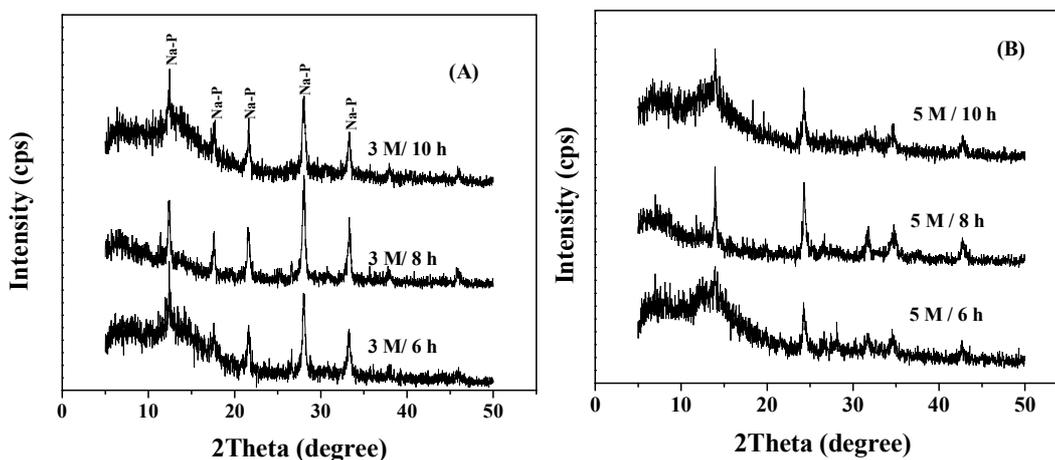


Fig. 4 X-ray diffraction patterns of the products obtained at various times

The X-ray diffraction patterns of the products obtained in 3 M and 5 M NaOH concentration in various reaction times are shown in Fig. 4(A) and 4(B) and the X-ray diffraction intensities of the above products are shown in Fig. 4(A). The amount of Na-P zeolite crystal increases with an increase time in 3 M NaOH concentration for 10 h, while the diffraction intensity of zeolite P decreases above the increase concentration due to the formation of

hydroxysodalite. Although, the refluxing method was very effective in extracting silicon species in sugarcane bagasse ash with silica and alumina from Narathiwat kaolinite. However, sodium hydroxide present in the refluxing method, acts as an activator during solution to form soluble silicate salt. The concentration of 3 M NaOH with silica produces sodium silicate and amorphous aluminosilicate, which can be easily dissolved in aqueous solution. The main phase of Na-P zeolite due to zeolite for 10 h of crystallization times, part of the silica dissolves and alumina to zeolite nuclei form on the surface of the residual material particle. Crystallization then starts at the moment the size of these nuclei reaches a certain minimum from which point further growth [13]. Therefore, as the condensation reaction of aluminosilicate and the formation of a zeolite crystal proceed, aluminate ions and silicate ions are supplied from Narathiwat kaolinite and silicate ion from synthesized silica as stating Sugarcane bagasse ash because the particle surface is covered with the deposit material, such as an aluminosilicate gel and a zeolite crystal. The first reaction product was zeolite P (Na) - sodium aluminium silicate hydrate ( $\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$ ).  $\text{Na}^+$  cation which in NaOH solution also plays an important role in zeolitization. Sodium ions ( $\text{Na}^+$ ) are known to stabilize the sub-building units of zeolite frameworks and usually are required for zeolite synthesis under refluxing method. Fig. 4(A) show the main phase crystalline of zeolite P reference with JCPDS No. 71-0962. The peaks associated with zeolite Na-P remain prominent in the pattern N. Murayama et al. [14] which report that the zeolite P synthesized in 0.50 – 3.00 M of NaOH solutions deposits as a fine crystals and the particle surface is perfectly covered with zeolite crystal with an increase in NaOH concentration. The big spherical crystal mixed with fine crystal deposits in the case of HS synthesized in more than 3.00 M of NaOH solution. It is confirmed crystallite zeolite by value cation exchange capacity. The products were evaluated in terms of CEC value as shown in Fig. 5.

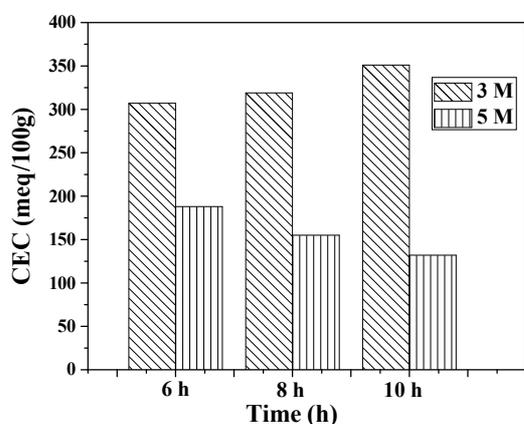


Fig. 5 CEC value of zeolites synthesis by refluxing method at various conditions

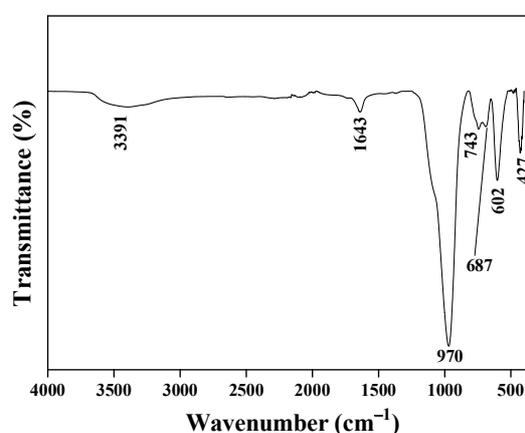


Fig. 6 FTIR spectra of the synthesized Na-P zeolite

The experiments were undertaken to determine the effects of concentration of NaOH and crystallization time on zeolite formation under the conditions described for each method. The products were evaluated in terms of CEC value as shown in Fig. 5. Clearly, there are higher CEC values of products was 351 meq/100 g in 3 M NaOH concentration for 10 h and decrease CEC values with increase concentration of NaOH for various crystallization times, respectively.

#### *IR spectra of Na-P zeolite*

Infrared spectroscopy is another to confirm the structure of Na-P zeolite, as shown in Fig. 6. The spectrum of Na-P zeolite illustrates the presence of absorptions at 427, 602, 687, 743 and 970  $\text{cm}^{-1}$ . The bands at about 970 and 427  $\text{cm}^{-1}$  are due to internal vibrations of  $(\text{Si}, \text{Al})\text{O}_4$  tetrahedral of Na-P zeolite which are insensitive to framework structure. These bands result from stretching and bending modes of the T-O (T = Si or Al) units respectively. The band at 687 and 743  $\text{cm}^{-1}$  are attributed to the symmetric stretch vibration of internal tetrahedral. The band at 602  $\text{cm}^{-1}$  is due to vibrations related to doubling stretching framework [15]. The band at 3391  $\text{cm}^{-1}$  was assigned to hydrogen bonded Si-OH groups, while the band at 1643  $\text{cm}^{-1}$  was ascribed to the bending vibration mode of residual  $\text{H}_2\text{O}$  molecules in the zeolite voids [16 – 17]. It was indicated that sample matched well with the Reference [18].

#### **4. Conclusion**

Refluxing method evaluated for synthesis of zeolite using silica from sugarcane baggase ash and Narathiwat kaolinite as raw material. The product of was generated Na-P zeolite and the high CEC value showed 351 meq/100g. Optimal reaction conditions of concentration NaOH at 3 M for 10 h of crystallization time.

#### **5. Acknowledgement**

The author is grateful to the financially supported by the Research and development institutions of Buriram Rajabhat University and Department of Chemistry, Faculty of Science, Buriram Rajabhat University. Raw fly ash sample was supplies by Buriram sugar factory (in Buriram province).

#### **6. References**

- [1] M. Balakrishnan, V.S. Batra, Valorization of solid waste in sugar factories with possible applications in India: A review, *J. Environ. Manage.* 92(11) (2011) 2886 – 2891.
- [2] N.H. Shigemoto, K.M. Hayashi, Selective formation of Na-X zeolite from coal fly-ash by fusion With sodium-hydroxide prior to hydrothermal reaction, *J. Mater. Sci.* 28(17) (1993) 4781 – 4786.
- [3] V.K. Jha, M. Nagae, M. Matsuda, M. Miyake, Zeolite formation from coal fly ash and heavy metal ion removal characteristics of thus-obtained Zeolite X in multi-metal systems, *J. Environ. Manage.* 90(8) (2009) 2507 – 2514.
- [4] M. Chareonpanich, T. Namto, P. Kongkachuichay, J. Limtrakul, Synthesis of ZSM-5 zeolite from lignite fly ash and rice husk ash, *Fuel Process. Technol.* 85(15) (2004) 1623 – 1634.
- [5] M.K. Naskar, D. Kundu, M. Chatterjee, Coral-like hydroxysodalite particles from rice husk ash as silica source, *Mater. Lett.* 65(23 – 24) (2011) 3508 – 3510.
- [6] M. Inada, Y. Eguchi, N. Enomoto, J. Hojo, Synthesis of zeolite from coal fly ashes with different silica–alumina composition, *Fuel.* 84(2 – 3) (2005) 299 – 304.

- [7] C.F. Wang, J.S. Li, L.J. Wang, X.Y. Sun, Influence of NaOH concentrations on synthesis of pure-form zeolite A from fly ash using two-stage method, *J. Hazard. Mater.* 155(1 – 2) (2008) 58 – 64.
- [8] H. Tanaka, A. Fujii, Effect of stirring on the dissolution of coal fly ash and synthesis of pure-form Na-A and -X zeolites by two-step process, *Adv. Powder Technol.* 20(5) (2009) 473 – 479.
- [9] Z.T. Yao, M.S. Xia, Y. Ye, L. Zhang, Synthesis of zeolite Li-ABW from fly ash by fusion method, *J. Hazard. Mater.* 170(2 – 3) (2009) 639 – 644.
- [10] P. Thuadaij, Production and characterization of silica powder from sugarcane bagasse ash, *J. Sci. Technol. MSU. Special* (2014) 582 – 586.
- [11] P. Thuadaij, A. Nuntiya, Preparation and characterization of faujasite using fly ash and amorphous silica from rice husk ash, *Procedia Engineering.* 32 (2012) 1026 – 1032.
- [12] U. Kalapathy, A. Proctor, J. Shultz, An improved method for production of silica from rice hull ash, *Bioresour. Technol.* 85 (2000) 285 – 289.
- [13] R.M. Barrer, *Hydrothermal chemistry of zeolites*, Academic press, London, 1982.
- [14] N. Murayama, H. Yamamoto, J. Shibata, Mechanism of zeolite synthesis from coal fly ash by alkali hydrothermal reaction, *Int. J. Miner. Process.* 64 (2002) 1 – 17.
- [15] H.L. Zubowa, H. Kosslick, D. Müller, M. Richter, L. Wilde, R. Fricke, Crystallization of phase-pure zeolite NaP from MCM-22-type gel compositions under microwave radiation, *Microporous Mesoporous Mater.* 109(1 – 3) (2008) 542 – 548.
- [16] O. Ibraheem, A. S. Mohamed, T. S Karam, E.-Nasser, M. A. Hassan, T. M. Salama, Synthesis of nanosized ZSM-5 zeolite from rice straw using lignin as a template: surface-modified zeolite with quaternary ammonium cation for removal of chromium from aqueous solution, *Microporous Mesoporous Mater.* 160 (2012) 97 – 105.
- [17] P. Pal, J.K. Das, N. Das, S. Bandyopadhyay, Synthesis of NaP zeolite at room temperature and short crystallization time by sonochemical method, *Ultrason Sonochem.* 20 (2013) 314 – 321.
- [18] D.W. Breck, *Zeolite molecular sieves: Structure, chemistry and use*, John Wiley & Sons, New York, 1974.