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Effect of the SiO_2/Al_2O_3 ratio on the synthesis of Na-x zeolite from Mae Moh fly ash

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ABSTRACT: In this study, a Na-x zeolite was synthesized by using metakaolin from Narathiwat kaolinite, amorphous silica from rice husk ash, and high CaO fly ash from the Mae Moh electrical plant by using the alkaline fusion method. The mixture of fly ash, amorphous silica and metakaolin was fused in NaOH followed by incubation at 70 °C for 24 h. An amorphous silica from rice husk ash and metakaolin were added to high CaO fly ash to increase the SiO_2/Al_2O_3 ratio of fusion materials. The fused mixtures of high CaO fly ash, amorphous silica and metakaolin were mixed in the weight ratio of 1:3:6 giving a SiO_2/Al_2O_3 ratio of 3.25 to achieve a Na-x zeolite phase. The synthesized zeolite was characterized by XRD, SEM, FTIR, and BET techniques. The CEC and specific surface area of the Na-x zeolite were 420 meq 100 g^{-1} and 398 m^2/g, respectively.

KEYWORDS: amorphous silica, metakaolin, alkaline fusion method, incubation

INTRODUCTION

Zeolites are crystalline, microporous, hydrated aluminosilicate of alkaline or alkaline earth metals with the frameworks which are composed of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral, corner-share to form different open structures[1]. Zeolites with particular structural and chemical features have been produced commercially for fluidized catalytic cracking in petroleum refining, drying reagents for gases and liquids, and selective molecular absorbents for pollution abatement[2]. Generally, zeolites are synthesized from sodium aluminosilicate gels, which are prepared from various silica and alumina sources[3–5]. However, Mae Moh power plant in the northern part of Thailand uses lignite coal as fuel to generate electricity; fly ash is the by-product of this process[6]. The main constituents of fly ash are SiO_2 and Al_2O_3. The significant amounts of Si and Al in amorphous and crystalline phases make a possibility to apply fly ash as a source material for synthesizing zeolites[7]. Although fly ash is currently used for the production of cement and concrete as backfilling in mining and agriculture, it is also exploited in a variety of civil engineering applications[8]. The most interesting applications of fly ash that emerged in the middle of the 1980s is the synthesis of zeolites[5]. New applications of fly ash still need to be developed.

Nevertheless, fly ash from the Mae Moh electrical plant contains low silica and high CaO which can be classified as a high CaO class C fly ash (CaO $>$ 15%). Miyake et al[9] reported that fly ash can be treated with acid to reduce the inherent CaO. Then, the treated fly ash is subjected to hydrothermal treatment at operating temperatures between from 60–180 °C, in 0.5–3.5 N for 10–48 h. This procedure generates zeolite A, zeolite P, and sodalite. In general, the findings of most studies reveal that zeolites can be obtained by adjusting the ratio of SiO_2/Al_2O_3 by adding silica sand and alumina powder[10,11].

However, Na_2SiO_3 and $NaAlO_2$ powders have also been added to fly ash to synthesize zeolites[12]. Fotovat et al[4] synthesized Na-A, -X and -Y zeolites by adding $NaAlO_2$ (Merck) to high silicon fly ash in Si/Al ratio from 1.6–3.0. Sutarno et al[13] studied the conversion of fly ash into faujasite zeolite by reflux in 5 M HCl at 90 °C for 1 h. It was found that Si/Al mol ratio, specific surface area, and crystallinity of faujasite zeolite were increased. Several studies have reported addition of silica and alumina powders from commercial grade and treatment with HCl solution, in an attempts to produce zeolite material by increasing the ratio of SiO_2/Al_2O_3 in fly ash. Therefore, silica and alumina should be from different sources.

In this study, the wastes from Mae Moh electrical plant and amorphous silica from rice husk ash were obtained from Brick Factory in Chiang Mai Province. These raw materials were applied to synthesize Na-x zeolite. Thuadaij et al[14] synthesized amorphous silica powder from rice husk ash by precipitation method and it was found that agglomerated size and specific surface area were 189.73 µm and 138.74 m^2 g^{-1}, respectively. Amorphous silica powder from rice husk ash has a chemical composition which is similar to silica fume, but their physical specifications are different. However, the kaolinite has been reported as an ideal, source of silica and alumina to synthesize a zeolite. The zeolites from kaolinite are always contaminated with the traced amounts of Fe, Ti, Ca, Mg, which are originally present the ancillary minerals in the naturally occurring kaolinite[15]. Nuntiya et al[16] found that the main components of the Narathiwat kaolinite were Al_2O_3 and SiO_2, with the minor components Fe_2O_3, TiO_2, Na_2O, K_2O, CaO, MgO, and P_2O_5. Thus the mixture of Mae Moh fly ash, amorphous silica from rice husk ash, and Narathiwat kaolinite can be possibly used as starting materials to synthesize Na-x zeolite. Little work has been done so far to synthesize high cation exchanging capacity of Na-x zeolite from high CaO fly ash.

Therefore, the purpose of this study was to synthesize the Na-x zeolite from metakaolin, amorphous silica from rice husk ash and high CaO fly ash from the Mae Moh electrical plant by the alkaline fusion followed by incubation method. The effect of the SiO_2/Al_2O_3 ratio on the synthesis conditions was considered.

MATERIALS AND METHODS

Materials

The fly ash was obtained from the Mae Moh electrical plant in Lampang province as raw material and iron oxide impurity was removed by magnetic separation. Kaolinite sample from Narathiwat province was calcined in the furnace at 900 °C with a uniform gradation giving a soaking period for 1 h. After the calcination process, the kaolinite sample was transformed to metakaolin and ground by a ball mill for 24 h. The metakaolin after calcination was carried out as starting material for the synthesis of zeolite. The raw materials were characterized by wavelength dispersive X-ray fluorescence spectrometer (XRF: Megix Pro MUA/USEP T84005, Philips), X-ray diffractometer (XRD: X' Pert MPD, Philips), particle size analyser (Mastersizer S), specific surface area (BET: Quanta Chrome Autosorp-1) and cation exchange capacity (CEC) by the ammonium replacement method, respectively. The results are summarized in Table 1.

Table 1 Chemical composition of pretreated fly ash, fly ash after removing iron oxide, and metakaolin.

Characteristics	Pretreated fly ash	Fly ash after rem. Fe_2O_3	Metakaolin
Chemical composition (wt.%)			
SiO_2	35.43	35.95	49.57
Al_2O_3	22.82	22.52	49.51
Fe_2O_3	11.47	4.01	0.18
CaO	20.89	23.47	–
K_2O	2.12	2.50	0.47
SO_3	6.76	6.98	–
TiO_2	0.41	0.44	0.25
Mn_2O_3	0.09	0.12	–
P_2O_5	–	–	0.02
SiO_2/Al_2O_3	1.55	1.60	1.00
Mean particle size (µm)	37.05	8.25	6.60
Specific surface area ($m^2 g^{-1}$)	2.32	19.69	31.37
CEC (meq $100g^{-1}$)	5.30	7.50	11.85

Amorphous silica powder (98.63 wt.%) was used as a source of white powder-SiO_2 according to the method previously described[14].

Zeolite synthesis

Zeolite synthesis was performed by using 10 g of dry mixture of fly ash, amorphous silica and metakaolin in the weight ratios of 10:0:0, 7:3:0, 5:3:2, and 1:3:6, respectively. The mixtures were mixed with NaOH (Merck, 99% AR grade) in the weight ratio of 1:1. A suitable weight ratio of the starting materials/NaOH was selected from previous work[17]. Then, the mixtures were fused in a muffle furnace at 550 °C in air atmosphere for 1 h. A heating rate of 5 °C/min was applied to elevate the temperature from ambient to 550 °C[18,19]. The fusion products were identified by determining the chemical composition using wavelength dispersive X-ray fluorescence spectrometer (XRF) to compare SiO_2/Al_2O_3 ratio of Na-x zeolite reference (Table 2). The fused products were ground and mixed with 100 ml distilled water[4,20], followed by vigorous shaking in Dual-Action Shakers (NB-101 MT, N-Biotex, Inc., Korea) at room temperature for 3 h. After ageing for 24 h, the slurry was incubated and crystallized autogenously at 70 °C for 24 h[21]. The solid crystalline products were recovered by filtration method and then washed with distilled water until the filtrate pH was 10–11. The synthesis products were dried in the oven at 120 °C for 12 h. Subsequently,

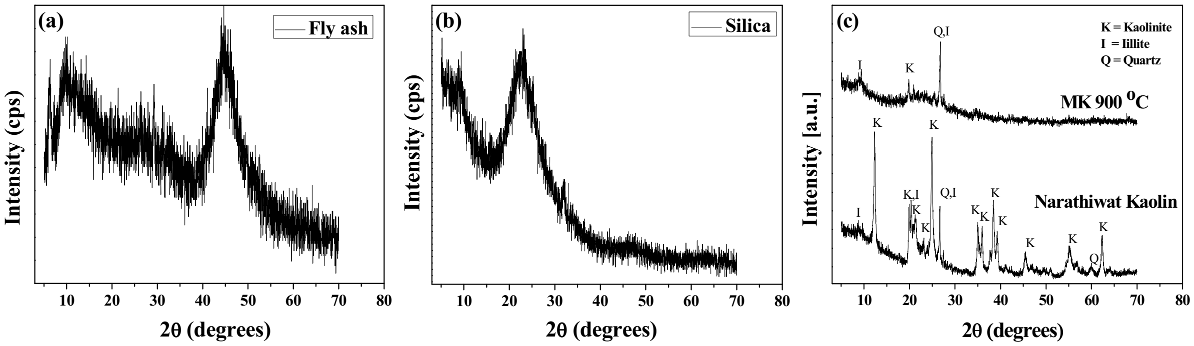

Fig. 1 X-ray diffractograms of starting materials (a) fly ash, (b) amorphous silica, (c) Narathiwat kaolinite and metakaolin.

Table 2 The experimental conditions used in this study.

Sample	Composition (g)			SiO_2/Al_2O_3		
	FA*	AS*	MK*	Before fusion	Fused material (XRF)	Na-x zeolite Ref. 22
A1	10	0	0	1.6	2.16	
A2	7	3	0	3.06	3.05	3–5
A3	5	3	2	3.01	2.75	
A4	1	3	6	3.53	3.25	

* FA = fly ash from Mae Moh electrical plant,
AS = amorphous silica powder from rice husk ash,
MK = metakaolin.

products of the crystalline phase were characterized by means of X-ray diffraction technique and morphology using a scanning electron microscope (SEM: JSM-5910: JEOL). Cation exchange capacity (CEC) was also determined using a modified ammonium acetate method. According to our observations, the above times that were allotted for fusing, ageing and incubation method resulted in the highest crystalline product. It was found that the optimum weight ratio of fly ash, amorphous silica from rice husk ash and metakaolin was 1:3:6. The highest crystalline product was identified by Fourier transform infra-red spectroscopy (FTIR: Perkin Elmer; Spectrum GX) using KBr method and specific surface area was determined by BET method.

RESULTS AND DISCUSSION

Characterization of starting materials

The chemical compositions of fly ash, fly ash after removing iron oxide by magnetic separation, and metakaolin are as listed in Table 1.

From Table 1, the iron oxide content of the fly ash sample was reduced to 65% after treating it by magnetic separation technique. Fe content was associated with the presence of magnetite which can behave as an inert material for zeolite synthesis[23]. The total amounts of SiO_2, Al_2O_3, and CaO were 35.95, 22.52, and 23.47 wt. %, respectively. However, CaO was found to be present in relatively high amounts, which can also affect zeolite synthesis as calcium competes with sodium cation to occupy the active sites of the formed zeolite[24]. SiO_2/Al_2O_3 ratio is an important parameter for zeolite synthesis. However, the SiO_2/Al_2O_3 ratio of fly ash after removing iron oxide was not sufficient to synthesize Na-x zeolite. Then, the metakaolin, which is the main source of SiO_2 and Al_2O_3, needs to be applied in the mixture to produce Na-x zeolite.

Fig. 1a shows the diffractogram of fly ash from the Mae Moh electrical plant after removing iron oxide. The hump which was noticed in the diffractogram indicated that the presence of amorphous materials, which are likely to be glass portion which is the main phase amorphous aluminosilicate and silicate[25]. Fig. 1b shows the strong broad peaks of pure silica which was centred from range of 22–23° (2θ), keeping the strong broad peaks of a characteristic of amorphous SiO_2[26]. It can be concluded that the silica from fly ash is in an amorphous state. On the other hand, Fig. 1c shows the diffractogram of kaolinite sample consists of kaolinite, illite, and quartz. However, metakaolin being calcined at 900 °C showed the main amorphous phase and remaining peaks due to quartz and illite and slightly kaolinite phase.

Zeolite synthesis

From Fig. 2, Na-x zeolite phase was not found in A1 but it showed amorphous aluminosilicate and calcium silicate hydrate phases. It may be due to the effect of high CaO and slightly iron oxide contents (Table 1). Fe is usually present in the form of magnetite which can behave as an inert material for zeolite synthesis. Through the formation of calcium

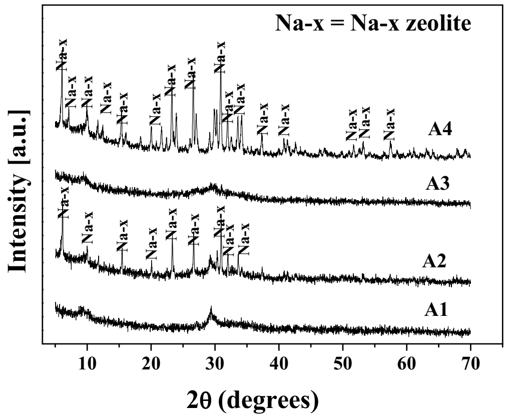

Fig. 2 X-ray diffractograms of the Na-x zeolite after the alkaline fusion followed by incubation method.

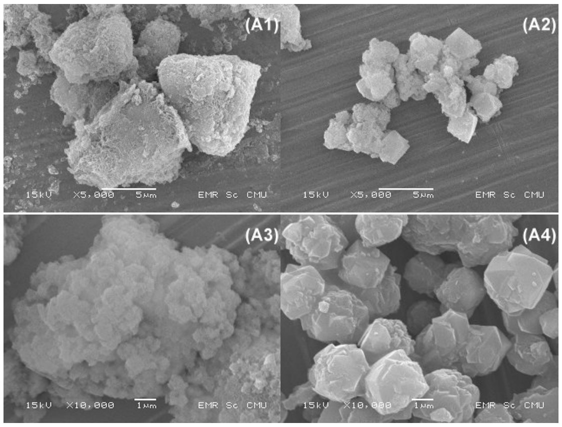

Fig. 3 SEM micrographs of Na-x zeolite after the alkaline fusion followed by incubation method (see text).

silicate, Ca-compounds could also act as a zeolite synthesis inhibitor[27]. A2 showed a poorly crystalline Na-x zeolite phase possibly due to a small amount of CaO residue in the mixture which may behave as an inhibitor in the synthesis reaction[27]. However, the reaction history of zeolite synthesis developed in this study can explain that Si and Al released from alkaline fusion process can form an amorphous aluminosilicate hydrogel[1, 18] and involve two steps to form crystalline Na-x zeolite. Firstly, Na-x zeolite nuclei formation was triggered by the formation of D6R sub-unit in the solution by interaction between amorphous silica from rice husk ash and fly ash to increase the SiO_2/Al_2O_3 ratio and form sodium silicate and sodium aluminate by alkaline fusion. The alkaline fusion approach included a previous ageing step of the aluminosilicate hydrogels which promotes the increase of ionic species in solution. Secondly, Na-x zeolite nuclei were formed solely in aluminosilicate hydrogels after heat treatment. The addition of amorphous silica from rice husk ash may help to increase the nuclei of Na-x zeolite in the system. The nuclei continue their growth by consuming constituents from the gel phase or the solution phase. It was not possible to verify which path led to Na-x zeolite formation. From the experimental results, it can be concluded that the addition of amorphous silica from rice husk ash was the key factor in initiating Na-x zeolite nuclei. The diffractogram of A3 showed the occurrence of an amorphous aluminosilicate phase with a geopolymeric paste appearance, particularly using metakaolin, fly ash and amorphous silica as a starting materials and revealed non-successful zeolite synthesis process. It can be explained in terms of the SiO_2/Al_2O_3 ratio of the fused starting materials which are dissolved in the solution not being enough to form metastable gel stage. As a result, it may not initiate Na-x nuclei high enough to form secondary building units (D6R subunits). Conversely, the peak intensities of Na-x zeolite increased progressively with fly ash, amorphous silica from rice husk ash and metakaolin in the weight ratio of 1:3:6 which gave a SiO_2/Al_2O_3 ratio of 3.25 as shown in A4. According to Tanaka et al[28], fly ash was pretreated in aqueous NaOH solution with stirring at 85 °C for 18 h and then the treated fly ash was adjusted to a controlled SiO_2/Al_2O_3 ratio of 0.5–4.5 by adding $NaAlO_2$ solution and heated at 85 °C for 24 h. A weight ratio of SiO_2/Al_2O_3 equal to 4.5 showed a single phase of Na-x zeolite.

SEM images of products are shown in Fig. 3. The agglomerated amorphous aluminosilicate particles are shown in A1. A2 shows small crystals and a flaky appearance. A3 indicates the agglomerated amorphous phase and irregular shape. On the other hand, A4 demonstrates good octahedral crystals of Na-x zeolite consistent with the work of Yaping et al[29] who showed that Na-x zeolite types were octahedral crystals with sizes ranging from 0.5–1 µm. Subsequently, the synthesis products were evaluated in terms of CEC values (Fig. 4). The results indicated that the CEC value of the zeolite was affected by the degree of zeolitization.

Characterization of zeolite

Fourier transform infra-red spectroscopy was used to determine the functional group of zeolite sample and specific surface area was measured by BET method. Fig. 5 and Table 3 showed typical infrared spectrum and data of the synthesized Na-x zeolite compared with the results of Novembre et al[30] and Flaningen

Table 3 Infrared data of Na-x zeolite (A4).

Sample	Asymmetric stretch	Symmetric stretch	Double rings	T-O bends
Na-x zeolite (A4)	1060(M)-980(S)	751(M)-667(M)-674(M)	560(M)	460(M)
Na-x zeolite (Novembre et al)[30]	1067(M)-986(S)	753(M)-671(M)-691(M)	566(M)	466(M)
Na-x zeolite (Flaningen et al)[31]	1060(M)-971(S)	746(M)-668(M)-690(M)	560(M)	458(M)

Qualitative intensity of the peaks: W = weak, M = medium, S = strong.

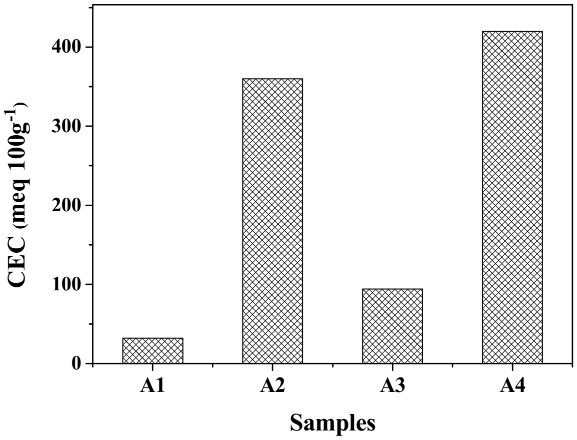

Fig. 4 CEC values of Na-x zeolite after alkaline fusion followed by incubation method.

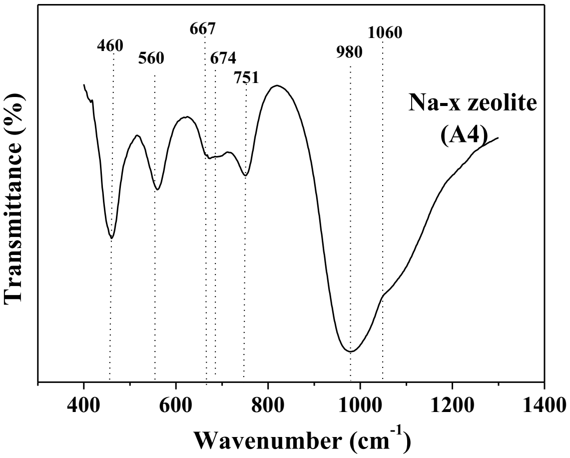

Fig. 5 FTIR spectra of the synthesized Na-x zeolite (A4).

et al[31]. The spectrum of Na-x zeolite exhibited absorptions at 460, 560, 667, 674, 751, 980, and 1060 cm^{-1}. The 980 cm^{-1} and 1060 cm^{-1} bands were due to the Si–O–Al antisymmetric stretching vibration mode of T–O bonds, (where T = Si or Al)[32–34]. According to Novembre et al[30], Na-x zeolite from metakaolin can be achieved from the presence of two characteristic peaks in the region between 1060 and 971 cm^{-1} and this is in good agreement with data proposed by Flaningen et al[31]. The band at 751 cm^{-1} was due to the S4R T–O–T symmetric stretching, while the absorption at 560 cm^{-1} was attributed to the D6R T–O–T symmetric stretching. The three bands at 460, 667, and 674 cm^{-1} were assigned to Si–O–Al symmetric stretching and S4R symmetric bending modes, respectively. The specific surface area and cation exchange capacity (CEC) of the synthesized Na-x zeolite were 398 m^2 g^{-1} and 420 meq 100 g^{-1}, respectively.

CONCLUSIONS

Na-x zeolite can be synthesized by using high CaO fly ash, amorphous silica from rice husk ash and metakaolin as the starting materials and then fusing them by alkaline fusion followed by incubation at 70 °C for 24 h. The fused mixtures of high CaO fly ash, amorphous silica and metakaolin in the weight ratio of 1:3:6 provided a rich source of SiO_2 and Al_2O_3. The starting material SiO_2/Al_2O_3 ratio of 3.25 could be successfully converted into Na-x zeolite and displayed the octahedral shape of Na-x zeolite. FTIR spectra exhibited the presence of internal Si-O-Si and Si-O-Al asymmetric stretching mode. The CEC and specific surface area of Na-x zeolite were 420 meq 100 g^{-1} and 398 m^2 g^{-1}, respectively.

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REFERENCES

1. Ríos CA, Williams CD, Fullen MA (2009) Nucleation and growth history of zeolite LTA synthesized from kaolinite by two different methods. *Appl Clay Sci* **42**, 446–54.
2. Mumpton FA (1978) *In Natural Zeolites: Occurrence, Properties, Use*, Pergamon Press, Oxford, pp 3–27.
3. Inada M, Eguchi Y, Enoto N, Hojo J (2005) Synthesis of zeolite from coal fly ashes with different silica-alumina composition. *Fuel* **84**, 299–304.
4. Fotovat F, Kazemian H, Kazemeini M (2009) Synthesis

of Na-A and faujasitic zeolites from high silicon fly ash. *Mater Res Bull* **44**, 913–7.

5. Marion GL, Michel S, Philippe C, Joël P, Edgar M, Isabelle S (2010) Conversion of coal fly ashes into faujasite under soft temperature and pressure conditions: Influence of additional silica. *Micropor Mesopor Mat* **127**, 41–9.
6. Cheerarot R, Jaturapitakkul C (2004) A study of disposed fly ash from landfill to replace Portland cement. *Waste Manag* **24**, 701–9.
7. Walek T, Saito F, Zhang Q, Kano J (2007) Zeolite synthesis from fly ash: Current processes and their benefits and drawbacks. Japan 86-95.
8. Belardi G, Massimilla S, Piga L (1998) Crystallization of K-L and K-W zeolites from fly-ash. *Resour Conservat Recycl* **24**, 167–81.
9. Miyake M, Tamura C, Matsuda M (2002) Resource recovery of waste incineration fly ash: Synthesis of zeolite A and P. *J Am Ceram Soc* **85**, 1873–5.
10. Lucas S, Tognonvi MT, Gelet JL, Soro J, Rossignol S (2011) Interactions between silica sand and sodium silicate solution during. *J Non Cryst Solids* **357**, 1310–8.
11. Fukui K, Nishimoto T, Takiguchi M, Yoshida H (2006) Effects of NaOH concentration on zeolite synthesis from fly ash a hydrothermal treatment method. *J Soc Powder Tech* **24**, 497–504.
12. Wang CF, Li JS, Wang LJ, Sun XY (2008) Influence of NaOH concentrations on synthesis of pure-form zeolite A from fly ash using two-stage method. *J Hazard Mater* **155**, 58–64.
13. Sutarno Arryanto Y (2007) Synthesis of faujasite from fly ash and its applications for hydrocracking of petroleum distillates. *Bull Chem React Eng Catal* **2**, 45–51.
14. Thuadaij N, Nuntiya A (2008) Preparation of nanosilica from rice husk ash by precipitation method. *Chiang Mai J Sci* **35**, 206–11.
15. Chandrasekhar S, Pramada PN (2001) Sintering behaviour of calcium exchanged low silica zeolites synthesized from kaolin. *Ceram Int* **27**, 105–14.
16. Nuntiya A, Prasanphan S (2006) The rheological behavior of kaolin suspensions. *Chiang Mai J Sci* **33**, 271–81.
17. Thuadaij P, Nuntiya N (2011) Synthesis of Na-x hydrate zeolite from fly ash and amorphous silica from rice husk ash by fusion with caustic soda prior to incubation. In: Proceeding of the International Conference on Chemistry and Chemical Process, Bangkok, pp 69–73.
18. Ojha K, Pradhan NC, Samanta AN (2004) Zeolite from fly ash: Synthesis and characterization. *Bull Mater Sci* **27**, 555–64.
19. Kazemian H, Naghdali Z, Ghaffari Kashani T, Farhadi F (2010) Conversion of high silicon fly ash to Na-P1 zeolite: Alkaline fusion followed by hydrothermal crystallization. *Adv Powder Tech* **21**, 279–83.
20. Shigemoto N, Hayashi H, Miyaura K (1993) Selective formation of Na-x zeolite from coal fly ash by fusion with sodium hydroxide prior to hydrothermal reaction. *J Mater Sci* **28**, 4781–6.
21. Thuadaij P, Nuntiya N (2012) Preparation and characterization of faujasite using fly ash and amorphous silica from rice husk ash. In: Proceeding of the 3rd International Science Social Science Engineering and Energy Conference, Nakhon Pathom, pp 1026–32.
22. Milton RM (1959) Molecular sieves adsorbents. US Patent No. 2882244.
23. Juan R, Hernandez S, Andres J, Ruiz C (2007) Synthesis of granular zeolitic materials with high cation exchange capacity from agglomerated coal fly ash. *Fuel* **86**, 1811–21.
24. Barrer RM (1982) *Hydrothermal Chemistry of Zeolite*, Academic press, London.
25. Arvelakis S, Folkedahl B, Frandsen FJ, Hurley J (2008) Studying the melting behaviour of fly ash from the incineration of MSW using viscosity and heated stage XRD data. *Fuel* **87**, 2269–80.
26. Jo BW, Kim CH, Tae GH, Park JB (2007) Characteristics of cement mortar with nano-SiO_2 particles. *Construct Build Mater* **21**, 1351–5.
27. Zhang M, Zhang H, Xu D, Han L, Niu D, Zhang L, Wu W, Tian B (2011) Ammonium removal from aqueous solution by zeolites synthesized from low-calcium and high-calcium fly ashes. *Desalination* **277**, 46–53.
28. Tanaka H, Fujii A (2009) 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 Tech* **20**, 473–9.
29. Yaping Y, Xiaoqiang Z, Weilan Q, Mingwen W (2008) Synthesis of pure zeolites from supersaturated silicon and aluminum alkali extracts from fused coal fly ash. *Fuel* **87**, 1880–6.
30. Novembre D, Di Sabatino B, Gimeno D, Pace C (2011) Synthesis and characterization of Na-X, Na-A and Na-P zeolites and hydroxysodalite from metakaolinite. *Clay Miner* **46**, 339–54.
31. Flaningen EM, Khatami HA, Szymanski HA (1971) Infrared structural studies of zeolite frameworks. *Adv Chem* **101**, 201–29.
32. Joshi UD, Joshi PN, Tamhankar SS, Joshi VV, Rode CV, Shiralkar VP (2003) Effect of nonframework cations and crystallinity on the basicity of Na-x zeolites. *Appl Catal Gen* **239**, 209–20.
33. Kowenje CO, Doetschma DC, Schulte J, Kanyi CW, Decoste J, Yang SW, Jones BR (2010) Effects of copper exchange levels on complication of ammonia in Cu (II)-exchanged X zeolite. *S Afr J Chem* **63**, 6–10.
34. Mozgawa W (2001) The Relation between structure and vibrational spectra of natural zeolites. *J Mol Struct* **596**, 129–37.