



Conventional hydrothermal synthesis of Na-A zeolite from cupola slag and aluminum sludge

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ARTICLE INFO

Article history:

Received 20 March 2008

Received in revised form 9 November 2008

Accepted 10 November 2008

Available online 17 November 2008

Keywords:

Cupola slag

Zeolite

Synthesis

Fusion method

Hydrothermal

ABSTRACT

Na-A type zeolites were prepared from two industrial wastes: the solid by-product of cupola slag and aluminum sludge from an aluminum plating plant. Two preparation methods using the same starting material compositions were carried out. In the first method, alkaline fusion was introduced, followed by the hydrothermal treatment to obtain sodium aluminosilicate which was then crystallized in NaOH solution under the condition of $90 \pm 3^\circ\text{C}$ for 1–9 h with different $\text{H}_2\text{O}/\text{SiO}_2$ ratios. The result shows that higher $\text{H}_2\text{O}/\text{SiO}_2$ ratio increases the rate of crystallization. The largest amount of crystallinity for Na-A was found at 3 h. In the second method, alkaline hydrothermal treatment without fusion was carried out in the same condition as the first method. No Na-A zeolite was obtained by this method. The changes of the dissolved amounts of Si^{4+} and Al^{3+} in 3 M NaOH were investigated during the hydrothermal reaction.

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1. Introduction

Cupola slag is the industrial waste generated from ferrous foundry processing. The cupola slag is composed of lime, a substantial amount of amorphous silica as well as other impurities in the iron. The slag is separated from the molten iron during the melting process, and cooled down in water. The water-quenched cupola slag is composed of SiO_2 (ca. 47 wt. %), CaO (ca. 24 wt. %), Al_2O_3 (ca. 12 wt. %), MgO (ca. 9 wt. %), Fe_2O_3 (ca. 5 wt. %), and some other compounds such as Na_2O , K_2O , TiO_2 and MnO in trace amounts (< 1 wt. %). The world production of iron amounted to 81.5 million tons in 2002 resulting in 23.5 million tons of the slag [1]. At present in Thailand, large amounts of the cupola slag are stockpiled within the factories constituting a hazardous waste problem. Utilization of the slag as a supplemental material for cement and road-base consumes a small amount of slag. Another possible solution to manage the cupola slag problem is to use the waste slag as a silicon source for the synthesis of zeolite. Zeolites are crystalline microporous aluminosilicates that have the general formula: $\text{M}_{x/n}[(\text{AlO}_2)_x(\text{SiO}_2)_y] \cdot z\text{H}_2\text{O}$, where n is the charge of an cation M, and the values of x , y and z depend on the type of zeolite. The typical zeolite synthesis involves mixing together aluminates and silicates under basic condition followed by heating at temperatures between 25 and 200°C for a period of time that may range from hours to days [2]. The Si/Al ratio of the produced zeolites can vary greatly but the nature of the start-

ing material can have an effect on the types of zeolite obtained. Therefore, attempting to use the industrial waste as a silicon and/or aluminum sources will require a basic understanding of how this complex and heterogenous mixture affects zeolite crystallization.

Zeolites can be synthesized from many different industrial wastes. For example, the hydrothermal treatment of coal fly ash [3–10], paper sludge ash [11], oil shale ash [12] and metakaolin [13] under alkaline conditions have been reported. By fusing a mixture of fly ash and NaOH (weight ratio of 1:1.2) at 550°C , followed by hydrothermally heating at $60\text{--}100^\circ\text{C}$ for 6–24 h, the fused powder was converted into the faujasite type zeolites X and Y [14]. A conventional synthesis of zeolite ZSM-5 from the cupola slag was made and the result was compared with the microwave heating technique [15]. The results show that the ZSM-5 produced by the conventional heating and the microwave heating have the Si/Al molar ratio of 28 and 29, respectively. The conventional heating produced ZSM-5 particles $3\ \mu\text{m}$ in diameter while the microwave-heating produced smaller ZSM-5 particles only $0.3\ \mu\text{m}$ in size.

Because of the low aluminum content in the cupola slag used for the synthesis of zeolite in this study, another source of aluminum waste from another industry was brought in to control the Si/Al ratio. This requirement will enhance the environmental benefit by utilizing dual wastes. Although, the present market price for Na-A zeolite is not high, large quantities are used in detergent industries, as ion exchangers and adsorbent, etc. An economic study on converting these dual wastes into zeolite A versus the cost of landfill should be further pursued. It has been reported that the landfill method for managing hazardous wastes has become increasingly expensive. The acquisition of landfill for hazardous

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Table 1
Chemical composition of the untreated cupola slag, acid treated cupola slag, purified aluminium sludge and fused precursor.

Compound	Untreated cupola slag (wt %)	Acid treated cupola slag (wt %)	Purified aluminum sludge (wt %)	Fused precursor (wt %)
SiO ₂	47.31	87.72	0.81	18.19
Al ₂ O ₃	12.12	0.45	60.72	11.90
Fe ₂ O ₃	5.05	0.12	0.41	0.05
CaO	24.09	4.13	2	0.79
LOI at 500 °C	<0.09	2.78	32.55	10.82
Na ₂ O	<0.01	0.00	0.27	57.31
K ₂ O	0.1	0.07	0	0.06
TiO ₂	0.12	0.43	0	0.08

LOI=loss on ignition.

wastes is strictly controlled by environmental law. Most hazardous wastes also require substantial chemical pretreatments prior to being disposed of in landfills.

2. Experimental

2.1. Preparation of raw materials

Cupola slag was obtained from the Ti-Heng foundry factory in Samutprakarn Province, Thailand. The slag was ground using a Los-Angeles Miller and sieved to obtain a fine powder having a particle size between 20 and 50 μm, and then magnetized to eliminate magnetic particles. The powder was then stirred with a 1:1 (v/v) mixture of 3 M HCl to remove Ca content and 4 M H₂SO₄ to remove Fe content at 60 °C for 1.5 h in which their presence will compete with aluminum for the zeolite framework formation during synthesis. The mass ratio between the powdered cupola slag and acid solution was 1:2. The solid phase was separated from the acid solution by vacuum filtration and rinsed with deionized water until the pH of the filtrate was 6–7. The washed acid treated solid was dried in an air-circulating laboratory oven at 105 °C for 24 h, then calcined at 700 °C for 3 h to remove the incorporated organic matter. The precursor was cool-down and stored in a desiccator over dry silica gel. The chemical composition of the acid treated cupola slag (see Table 1) was determined by X-ray Fluorescence Spectroscopy (XRF). The residual was further analyzed to recheck the compositions of those removed substances from the cupola slag after the acid digestion using an ICP (PerkinElmer; Model; Plasma-100). Aluminum sludge was obtained from the wastewater plant of the Muang Tong aluminum factory, Thailand, and purified by etching with 0.005 M sulfuric acid for 10 min to remove the impurities. The etching helps in removing dust, ash and small impurities content in the aluminum sludge. Again, the acid used for this etching is the sulfuric acid waste recovered from the aluminum raw material cleaning line. This study looks into all possibilities to utilize the discharge hazardous wastes and hence, to minimize the wastes. The purified aluminum sludge was separated from the solution by vacuum filtration, washed with deionized water, dried in an air-circulating laboratory oven at 105 °C for 24 h and then cooled and stored in a desiccator over dry silica gel. The chemical composition of the purified aluminum sludge (see Table 1) was determined by XRF.

2.2. Preparation of the synthesis precursors

The acid treated cupola slag is rich in SiO₂, whereas the Al₂O₃ content is small in the sample. SiO₂/Al₂O₃ molar ratios of the raw cupola slag and acid treated cupola slag are 6.64 and 331.39, respectively. Therefore, there is a need to add Al₂O₃ in the reaction mixture to obtain the desired SiO₂/Al₂O₃ molar ratio. Using the same starting materials (acid treated cupola slag as silicon source and purified aluminum sludge as aluminium source), synthesis precursors were prepared by mixing together acid treated cupola slag, purified aluminum sludge and commercial grade NaOH with the weight ratio

1:1:3 and then fused at 700 °C for 1 h [16]. After cooling, the resulting solid were pulverized in an agate mortar and kept in tightly sealed plastic bottles. The chemical composition of the fused precursor was determined by XRF and shown in Table 1.

2.3. Preparation of Na-A zeolite

2.3.1. Conventional heating

The fused precursor was added to 3 M NaOH solution. The H₂O/SiO₂ ratios were varied at 2.36, 4.17, 5.07, 5.46, 7.88, 35.47 and 70.94, respectively. The reaction mixtures were stirred at room temperature for 10 min, and then transferred to a Teflon™-lined stainless steel autoclave and heated at 90 ± 3 °C for 1–9 h. The contents in the autoclaves were removed at the specified time (1–9 h) from the oven and quenched with cold water. The solid product was filtered and washed with deionized water until the filtrate pH dropped to 7. The products were dried at 105 °C for 24 h.

The same experiment was repeated using as received waste as the starting material (the fusion step was omitted). This is the direct synthesis of Na-A zeolite and the product was used as the control sample.

2.3.2. Characterization

The crystalline phase identification and % crystallinity were determined by X-ray diffraction (Rigaku Ultima III with CuKα radiation). The % crystallinity was calculated by Eq. (1). A commercial zeolite A was used as the standard.

$$\% \text{Crystallinity} = \left(\frac{\sum \text{intensity of XRD peaks of product}}{\sum \text{intensity of XRD peaks of standard}} \right) \times 100 \quad (1)$$

The SEM images were collected using a LEO 1530 field emission scanning electron microscope. The concentrations of Si and Al in the liquid phase of the reaction mixture were determined by an Inductively coupled plasma atomic emission spectrometer (ICP; PerkinElmer; Model; Plasma-1000). The chemical compositions of the different solids were measured by a APL 9400 X-ray fluorescence spectrometer.

To determine the calcium exchange capacity of the products of crystallization, 0.5 g of solid sample was put into the vessel containing 200 ml of 0.005 M CaCO₃ solution. The obtained suspension was stirred at 25 °C for 15 min, and then the liquid phase was separated from the solid phase by vacuum filtration. The liquid phase was determined for calcium concentration using atomic absorption spectroscopy, Varian Techtron model 30/40 atomic adsorption spectrophotometer. From the known mass *m* of the sample, volume *V* of the CaCO₃ solution, concentrations *C*_{Ca}(0) and *C*_{Ca}(*t*) of calcium ions before and after phase separation, the calcium exchange capacity Γ_{Ca} (in mg of CaO/g of solid) was calculated as

$$\Gamma_{Ca} = \frac{\{V[C_{Ca}(0) - C_{Ca}(t)]M_{CaO}\}}{m} \quad (2)$$

where *M*_{CaO} is the molecular mass of calcium oxide.

3. Results and discussion

3.1. Conventional heating

The chemical compositions of the untreated cupola slag, acid treated cupola slag, purified aluminum sludge and fused precursor (FP) are presented in the form of oxides in Table 1. The thermal and acid treatments resulted in a material with significant reduction of Fe₂O₃ (97.6%) and CaO (82.9%) as well as a reduction in the Al₂O₃ content (96.3%). The trace elements of the residual were also analyzed and found to be in very small quantity (Ti=0.05, As=0.005, Mn=0.001, K=0.074 and Na<0.0001 mg/L).

Quartz is the major crystalline silica present and is not affected by the acid treatment. To obtain a lower Si/Al ratio zeolite such as Na-A zeolite will require the addition of aluminum. Aluminum sludge powder was added into the acid treated cupola slag to control the Si/Al molar ratio of 1.0 and fused at 700 °C for 1 h. The sodium aluminum silicate (Na_{1.45}Al_{1.45}S_{0.55}O₄-JCPDS 49-0002) was formed at the fusion temperature of 700 °C as shown in Fig. 1.

The diffraction intensities of quartz and gibbsite which contained in acid treated cupola slag and aluminum sludge, respectively are gradually reduced through the fusion stage. The X-ray diffraction intensity of sodium aluminum silicate increases with fusion temperature. Fig. 1 showed that at the fusion temperature of 700 °C, quartz and gibbsite were significantly transformed into more reactive species. These newly formed compounds dissolved in water more readily than quartz and gibbsite in the acid treated cupola slag and aluminum sludge.

Table 2 shows different types of zeolites obtained from the alkaline fusion of the acid treated cupola slag (ATCS) and aluminum sludge followed by hydrothermal treatment and only by hydrothermal treatment without preliminary fusion. Without the preliminary fusion, non-reacted aluminum sludge (gibbsite) powder remained in the products. These results suggest that the amount of Al dissolved in the solution was not sufficient for the formation of Na-A zeolite. On the other hand, addition of aluminum sludge in the fusion process resulted in the formation of an appreciable amount of Na-A zeolite. Sodium aluminosilicate was formed at the fusion temperature of 700 °C from the reaction between a mixture of NaOH powder, the crystalline phase of ATCS and the aluminum sludge.

The highest calcium exchange capacity and the percent crystallinity of the obtained Na-A zeolite products at different reaction times, as shown in Table 2, are as follows: 442.8 mg CaO/g of product with 64% crystallinity at 3 h, 364.1 mg CaO/g of product with 50% crystallinity at 5 h, 281.3 mg CaO/g of product with 33% crystallinity at 7 h, 177.5 mg CaO/g of product with 12% crystallinity at 9 h.

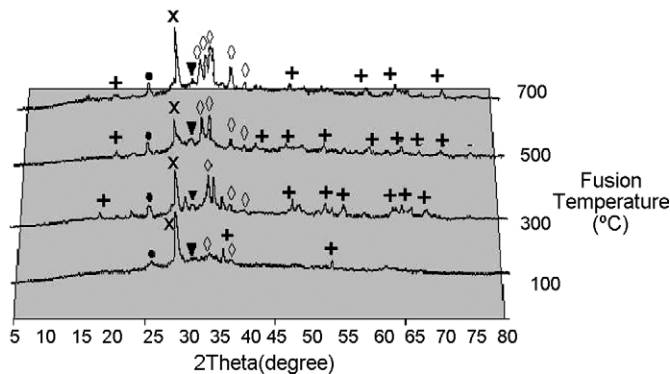


Fig. 1. X-ray diffraction intensities of the products obtained at various fusion temperatures. (●) Quartz, (◇) sodium aluminum silicate (▼) Gibbsite (X) NaOH and (+) impurities.

Table 2 Hydrothermal treatment using acid treated cupola slag (ATCS) and relative crystallinities of the zeolite material.

Sample no.	Raw materials	Composition	Synthesis method	Reaction time (h)	Calcium exchange capacity (mg CaO/g product)	% crystallinity of zeolite	Total products
1	ATCS and Al-sludge	Si/Al = 1	Alkaline fusion, followed by hydrothermal treatment	1	78.2	11.5% (A)	Am + A
				3	442.8	64% (A) + 3% (HS)	Am + A + HS
				5	364.1	50% (A) + 13% (HS)	Am + A + HS
				7	281.3	33% (A) + 38% (HS)	Am + A + HS
				9	177.5	12% (A) + 66% (HS)	Am + HS
2	Na-A zeolite ATCS and Al-sludge	Si/Al = 1	Hydrothermal treatment without preliminary fusion	1	-	0%	Gibbsite
				3	-	0%	Gibbsite
				5	-	1% (HS)	Gibbsite + HS
				7	78.1	41.4% (HS)	HS
				9	162	83.7% (HS)	HS

Am = amorphous.

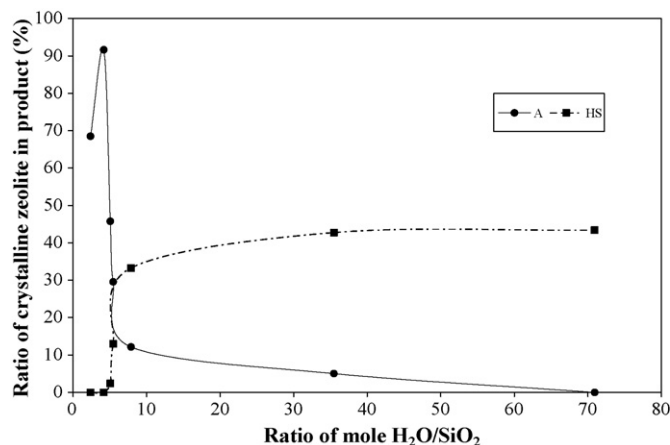


Fig. 2. Effects of the molar ratio of H₂O/SiO₂ on the amount of Na-A and HS zeolite formed in the products by hydrothermal treatment.

The yields of Na-A and HS zeolites as a function of H₂O/SiO₂ in 3 M NaOH at 90 °C by the hydrothermal treatment are shown in Fig. 2.

In these figures, the highest yield of Na-A zeolite occurs at H₂O/SiO₂ of 4.17. When H₂O/SiO₂ reaches 5.45, the yield of HS zeolite is steeply increased while that of Na-A zeolite is suddenly reduced. Aging H₂O/SiO₂ at the ratio of 71 forms a single phase of the HS zeolite. It can be concluded that the higher molar ratio of H₂O/SiO₂ resulted in marked reduction of Na-A zeolite formation. On the other hand, since the thermodynamic stability of Na-A zeolite is less than the thermodynamic stabilities of other zeolites (e.g., P, X, HS), the Na-A zeolite formed in the first step of the crystallization process spontaneously transforms into thermodynamically more stable hydroxysodalite. Transformation of Na-A zeolite into just hydroxysodalite is probably caused by relatively high molar ratios of H₂O/SiO₂ and a longer reaction time. The result found in this experiment is in agreement with the study by Subotic et al. [17]. It is concluded that the higher molar ratio of H₂O/SiO₂ will increase the rate of crystallization.

3.2. Effect of reaction time

The effect of the reaction time on the formation of Na-A zeolite was investigated at 90 ± 3 °C, and the XRD pattern is shown in Fig. 3. The zeolite products made from the fusion precursor are in the form of amorphous sodium aluminum silicate and change to a crystalline structure when they are subjected to hydrothermal treatment.

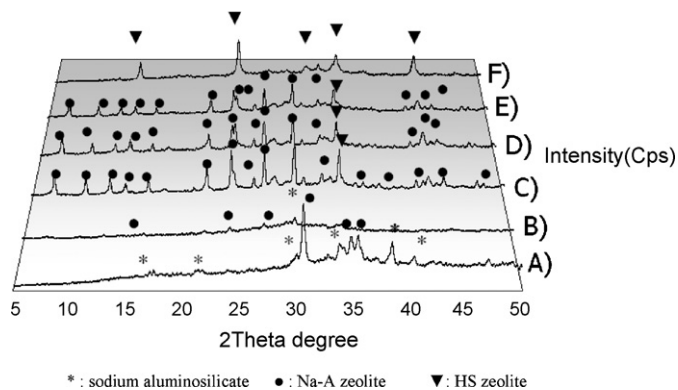


Fig. 3. X-ray diffraction patterns of the obtained zeolite products obtained from the fusion precursors at different reaction times (A) sodium aluminosilicate precursor, (B) 1 h, (C) 3 h, (D) 5 h, (E) 7 h and (F) 9 h.

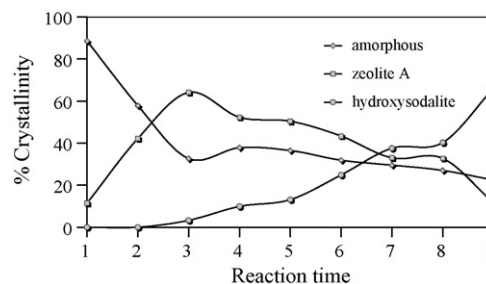


Fig. 4. Effect of the reaction time on the percentage crystallinity of products obtained by hydrothermal treatment of fusion raw materials at 90 ± 3 °C.

There was a small variation in the Na-A zeolite content at 90 ± 3 °C. However, Na-A zeolite crystallinity increased with increasing time after 1 h, and then the diffraction intensities of zeolite Na-A increased to the optimum value in about 3 h of the reaction time. It also verified the previous observation that the HS zeolite starts to appear after 3 h. After 9 h of the crystallization time, Na-A zeolite was mostly transformed to a more stable phase, the HS-zeolite, as shown in Fig. 3 F.

Fig. 4 shows the effect of the reaction time at 90 ± 3 °C on the percentage crystallinity of the products. After the reaction time of 1 h, the percentage of Na-A zeolite increased slowly with further extension of the reaction time. The results suggest that the amount of Al ion dissolved in the solution slowly reacted to form Na-A zeolite. Therefore, most of the product remained as gibbsite at a lower reaction time. However, after 2 to 3 h of hydrothermal treatment, the rate of formation of Na-A zeolite increased rapidly. The crystallinity of Na-A zeolite reached the optimal yield of around 64% at 3 h of reaction time (calcium exchange capacity, CEC = 442.8 mg CaO/g of product). After 5 h of crystallization, the sample consisted of zeolite-type materials within 63.6% of total crystallinity (50.4% Na-A zeolite + 13.1% HS zeolite) (CEC = 364.1 mg CaO/g of product). After 7 h of reaction time, Na-A zeolite was transformed to more stable phase, the HS zeolite (CEC = 177.5 mg CaO/g of product). The results of this experiment are in agreement with the previous study. Thus, the best conditions for synthesis of Na-A zeolite by hydrothermal treatment at 90 °C is the molar ratio of H₂O/SiO₂ of 4.17 and 3 h for the reaction time.

The formation of Na-A zeolite goes through the following steps: dissolution of Si and Al ions from raw materials into an alkaline solution, followed by formation of zeolite during which reaction

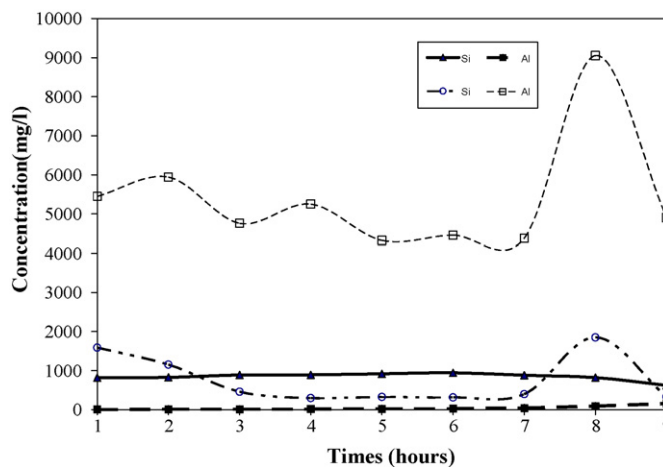


Fig. 5. Variation in concentrations of aluminum and silicon in the filtrate at different reaction times, (a) ■: Al, ▲: Si of reference material and (b) □: Al, ○: Si of fusion material.

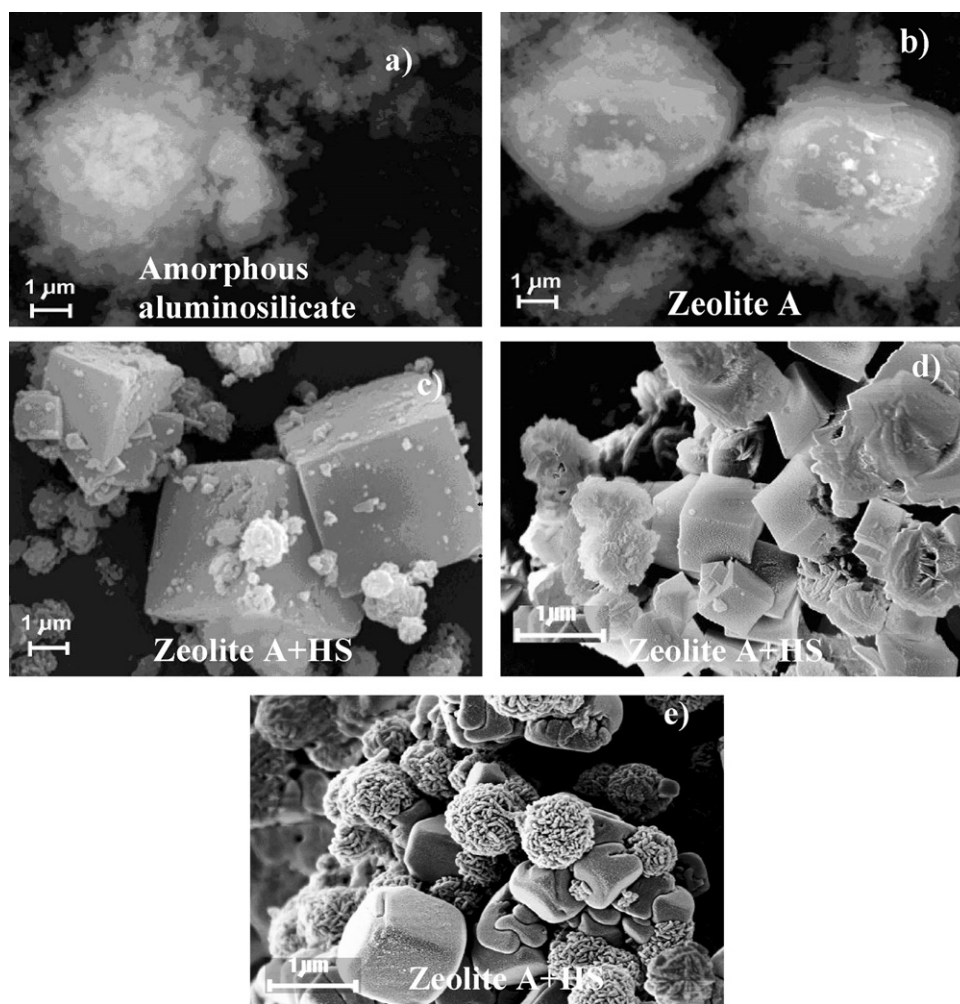


Fig. 6. SEM image of fused precursor at $90 \pm 3^\circ\text{C}$ hydrothermal treatment for (a) 1 h: aluminosilicate, (b) 3 h: zeolite A, (c) 5 h: zeolite A, (d) 7 h: zeolite A + HS and (e) 9 h: zeolite A + HS.

occurs between the dissolved ions and the surface layer of the raw materials, deposition of aluminosilicate gel as zeolite precursor, and crystallization of zeolite. It is considered here that when a large quantity of silicate ion exists in the liquid phase, aluminate and silicate ions are condensed to become an aluminosilicate gel with increase in reaction time.

Fig. 5 shows the changes of Si and Al concentration in NaOH solution at different of reaction time at $90 \pm 3^\circ\text{C}$. For the prepared fusion raw materials, Al concentration increased with the reaction time, and then saturated at the reaction time around 8–9 h. The Si concentration followed almost the same trend as Al concentration. The increase of synthesized amount of Na-A zeolite appears to accompany the decrease of Si and Al. It was found that the fusion material (sodium aluminosilicate) is much more easily soluble into NaOH solution compared with $\text{Al}(\text{OH})_3$ powder and amorphous silicon in slag without fusion (reference materials). In this study, the acid treatment of the raw cupola slag and calcined at 700°C for 3 h can remove impurities (non-reactive phase and organic matter) and the conversion of amorphous aluminosilicate glass to quartz and mullite is initiated. Both the quartz and aluminum hydroxide that remained in the reference materials have low reactivity to alkaline solution compared with the aluminosilicate glass phase in the fusion material. Therefore, they were not sufficient to form Na-A zeolite when using the reference raw materials. Fig. 5a also showed that silicon concentration in alkaline solution is higher than aluminum concentration under the hydrothermal treatment.

Although $\text{Al}(\text{OH})_3$ can dissolve in excess hot alkaline solution but without fusion, $\text{Al}(\text{OH})_3$ in the aluminum sludge is not readily dissolved in the short reaction time (1–8 h). Without the pre-step of fusion, only gibbsite $\text{Al}(\text{OH})_3$ was found in the main product.

On the other hand, sodium silicate and sodium aluminate by fusion prior to the hydrothermal treatment, can readily be transformed into more soluble forms of sodium aluminosilicate, due to $\text{Al}(\text{OH})_3$ decomposition at 300°C . Fig. 5b shows that the aluminum concentration is higher than the silicon concentration because of their transformation into sodium aluminosilicate, deposition of aluminosilicate gel (1 h), and crystallization of Na-A zeolite. Heat treatment by the fusion can transform the insoluble phase (quartz and aluminium hydroxide) into the soluble phase (sodium silicate and sodium aluminate). Hence, crystallization to Na-A zeolite required a shorter time.

Fig. 6 shows SEM of synthesized products obtained by hydrothermal treatment at $90 \pm 3^\circ\text{C}$. The Na-A zeolite appeared first at the reaction time of 3 h. The cubic shape of Na-A zeolite with a size of about $3\ \mu\text{m}$ was observed clearly at reaction time of 3 h as shown in Fig. 6b–d. The spherical shape of HS zeolite with a size about $1\ \mu\text{m}$ is shown in Fig. 6e,

4. Conclusions

This study has shown that fused sodium aluminosilicate (treated cupola slag: NaOH: aluminum sludge) can be successfully con-

verted into Na-A zeolite. The optimum precursor is the mixture of treated cupola slag:NaOH:aluminum sludge in the ratio of 1:3:1 at 700 °C for 1 h. The higher H₂O/SiO₂ will increase the rate of crystallization. The suitable reaction time for Na-A zeolite is 3 h. The fusion (heat treatment) is effective for enhancing the formation of Na-A zeolite. In a similar attempt for control of the precursor (without fusion method), gibbsite is the product at 1–5 h, because Al(OH)₃ cannot dissolved into the alkaline solution without fusion method.

Acknowledgements

This research was supported by Thailand Research Fund under the Royal Golden Jubilee award (TRF-RGJ).

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