Table 1. Summary of the conditions employed in the treatments of perlite with sodium hydroxide employing modified fusion technique, and corresponding exchangeable Na^+ and K^+ ion contents. The numbers in the brackets are the standard deviations.

Perlite:NaOH(s) (weight%)	Solid:Liquid (weight%)	Synthetic Time (day)	Ion Content (mmol.g^{-1})	
			Na^+	K^+
1:1.2	1:5	7	5.52(4)	0.389(4)
		14	5.38(2)	0.396(5)
		21	4.48(2)	0.417(4)
	1:7	7	4.79(2)	0.402(4)
		14	4.87(4)	0.423(3)
		21	5.14(6)	0.453(6)
1:1	1:5	7	3.94(1)	0.422(5)
		14	4.12(2)	0.449(6)
		21	3.11(3)	0.439(4)
	1:7	7	3.25(2)	0.496(5)
		14	3.56(4)	0.498(5)
		21	3.60(5)	0.495(4)

diffraction pattern as shown in Figure 3 can be indexed based on the cell parameters of hydrated FAU of *a* about 25 Å [10], indicating the only crystalline phase formed after the treatments to be hydrated FAU. This is consistent with the scanning electron micrographs showing aggregates of well – defined cubical crystals as illustrated in Figure 4.

The presence of aluminosilicate framework in the zeolitized perlite was confirmed using FTIR spectroscopic technique [11], showing vibrational band at 770 cm^{-1} which corresponds to the vibration of Al – O fragment, and at 1000 cm^{-1} which is a characteristic band for tetrahedral SiO_4 and AlO_4. Other bands are also observed at 1640 cm^{-1} corresponding to the deformation mode of vibration of HOH, and also a broad band at 3300 – 3600 cm^{-1} due to the existence of OH group.

FAU is a zeolitic material built up of sodalite cages stacking up in a tetrahedral array and forming a diamond lattice by linking adjacent rings of 6 tetrahedra via sharing 6 oxygen atoms. The volumes enclosed by the tetrahedral array of sodalite cages are supercages, which also stacked in a tetrahedral array and connected by rings of 12 tetrahedra. The faujasite structure hence contains two independent 3D networks of cavities i.e. one of sodalite cages and another of supercages, both of which are interconnected by rings of 6 tetrahedra [12]. Due to the presence of these

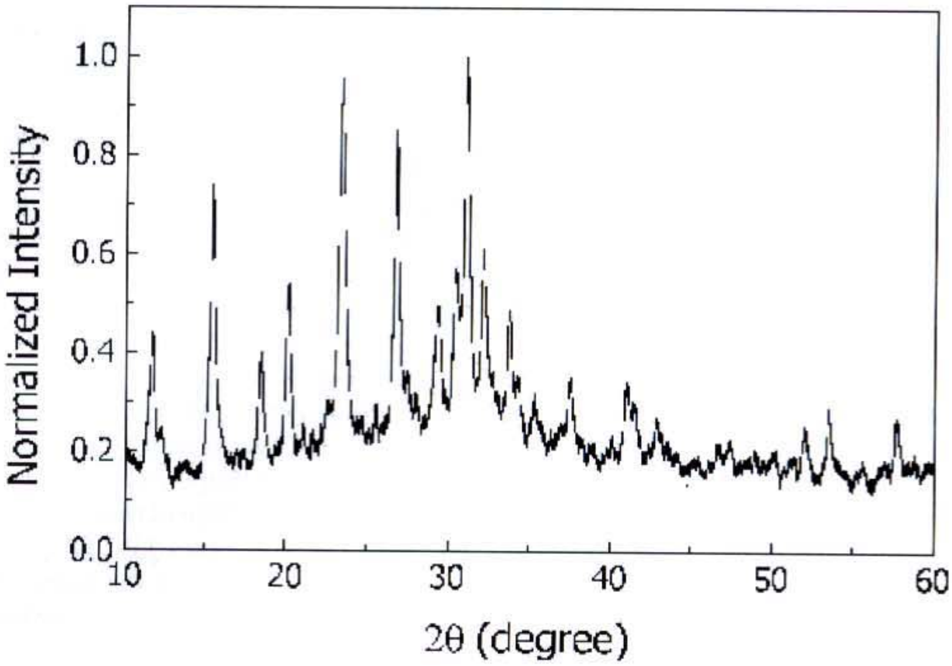

Figure 3. Powder X – ray diffraction pattern of zeolitized perlite identified as hydrated FAU zeolite.

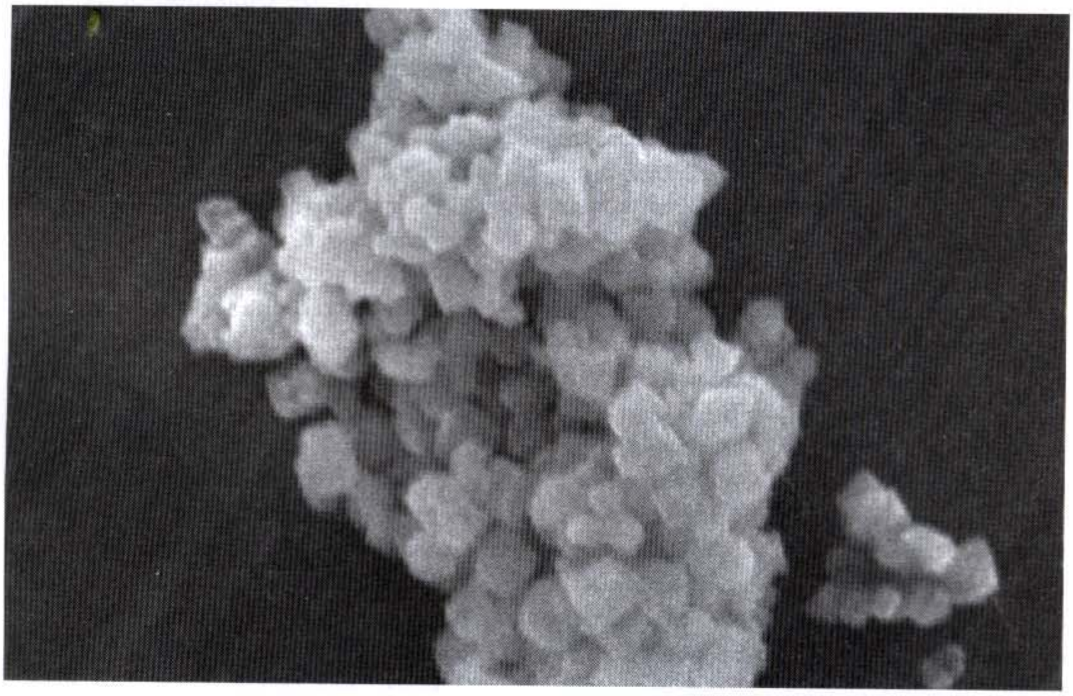

Figure 4. Scanning electron micrograph of zeolitized perlite showing an aggregate of well – identified shape crystals.

pore systems, FAU zeolite has been widely investigated and applied as a cation exchanger. The major exchangeable ion, i.e. Na^+ ion, contents in the zeolitized solid yielded under various investigated conditions were determined as preliminary assessment for cation exchange capacity. The results along with the amount of K^+ ions are summarized in Table 1. The Na^+ ion contents in the prepared FAU zeolite are varied between 3.94 (1) and 5.82 (4) $mmol.g^{-1}$, which agrees well with the reported cation exchange capability of similar zeolititc material prepared from low – grade natural zeolite in Korea, 4.1 $mmol.g^{-1}$ [13]. This study also indicates the uptake of Na^+ ion from the reaction mixture and the loss of K^+ ion, compared to 0.75 and 0.92 $mmol.g^{-1}$ for Na^+ and K^+ found in the starting perlite respec-tively. It can be noticed that more exchange-able Na^+ ion was found in the zeolitized solids when the higher weight ratio of perlite:NaOH, 1:1.2, was used, and the ion contents, both Na^+ and K^+ ion cases, generally increased slightly with increasing reaction time. These suggest more ions may be able to incorporate into the final zeolitic products if the amount of the alkali reagent is increased, or the reaction time is prolonged. The retaining of the FAU framework of the acid treated zeolitized samples were confirmed by X-ray diffraction showing identical diffraction patterns as those before the acid treatments.

4. CONCLUSIONS

Selective zeolitization of Lamnarai perlite is shown to be plausible via the inexpensive and simple treatment of perlite with sodium hydroxide pellets with prior fusion, and FAU zeolite results as the only crystalline solid product. The formation of FAU zeolite from perlite employing this modified fusion technique can occur in a wide range of treatment conditions. The exchangeable Na^+ ion content in FAU perlite was preliminary determined and shown to be potential for further investigation as a cation exchanger.

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ภาคผนวก ค

Selective Synthesis of Zeolitic Phillipsite and Hibschite Hydrogarnet from Lignite Ash Employing Calcium Hydroxide Under Mild Conditions

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Abstract

A selective synthesis of economically valuable zeolitic material, phillipsite, employing calcium hydroxide under mild chemical conditions is reported. This is to provide a potential method in reducing the amount of the waste from lignite power plant and the addition of economical value to the material. The fly ash was first activated by calcination at high temperature, and then fused with calcium hydroxide. The water was then added to the solid mixture before curing under saturated water vapor at low temperature. The treatment of as – received fly ash with either calcium hydroxide or a mixture of calcium and sodium hydroxide following as – described preparative procedure of phillipsite, but without prior calcination was also conducted, and led to the formation of Hibschite hydrogarnet, which was also evidentially selective. The following parameters i.e. type and amount of alkali reagent, the amount of added water, fusion temperature and reaction time were investigated. Powder X – ray diffraction was used to identify the type of crystalline solid products, and scanning electron microscope was employed to follow the alteration of solid morphologies. X – ray fluorescence (XRF) and atomic absorption spectroscopy (AAS) were used to trace the chemical composition of the solids and the calcium(II) ion content respectively.

Keywords: fly ash; zeolite; phillipsite; hydrogarnet; hibschite; adsorption behavior

1. Introduction

Global energy consumption has been continually increasing due to the rising of the population and industrial growth. Thailand as an agricultural country has also the same tendency as other developing countries transforming into agro-industrial base economics. Although various natural resources can be employed as fuel in generating electricity, coal still plays an important role in most part of the world including Thailand, of which lignite is the main resources. The exploration for lignite in Thailand commenced in 1917 and succeeded in 1953 when lignite resources has been found in Amphur Mae Moh, Lampang Province in the Northern part of

Thailand. Currently Mae Moh power plant is operated with 13 units in operations to generate 2,625 MW annually.[1,2] Lignite combustion causes about 25% ashes, which can be classified in to two types: 80wt% fly ash and 20wt% bottom ash. Within 10,700 ton of fly ash by-product produced daily, about 3,500 ton is exploited by selling to concrete and cement industry. Slight amount of fly ash is also spent in the agricultural research.[3] It could be seen that more than half of the fly ash produced daily is still remained and thus necessary to be discharged into fly ash ponds or landfills. This remainder can be accumulated and may lead to environmental problem in the future due to the enrichment in potentially toxic trace elements, increased demand for the storing land and also the cost of storage. Given the potential industrial value of elements present in the fly ash, high silica and alumina content, other applications such as using as raw material for zeolitization, should be investigated to enhance the value of the material and to recycle the high fly ash output, which is an advantage in reducing the environmental risk from the ash itself.

Zeolites, the open – framework hydrated aluminosilicate with general formula $M_{2/n}O.Al_2O_3.xSiO_2.yH_2O$, occur both naturally and synthetically and are widely know for their industrial and agricultural importance. The synthetic zeolites are of high purity and hence economic value, though high cost of production may obscures their widespread uses. Naturally occurring zeolites, on the other hand, exist in poor quality but cheap in price so as to apply in those applications requiring low grade materials. Potential applications of the zeolites converted from fly ash have been formerly reported e.g. in waste water treatment [4], ion exchanger and heavy metal and SO_2 sorption. [5-10]

Hydrogarnets are crystalline phases of calcium aluminumsilicates, $Ca_3Al_2[SiO_4]_{3-x}[OH]_{4x}$, in which silica units are partially or completely substituted by water existing as $[(OH_4)]^{4-}$. In nature, hydrogarnet crystallizes in an environment rich in SiO_2, Al_2O_3 and water. There are three groups of hydrogarnets worldwide; (1) typical hydrogarnets with isotropic euhedral cubic crystal grains e.g. hibschite from Czechoslovakia, Bulgaria and hydrougrandite from China, (2) massive garnets as found in New Zealand, West Australia and (3) vesuvianite mistaken for hydrogrossular such as those from Japan. Here in Thailand, there is no record of these types of minerals. The applications of hydrogarnet materials are also mainly in cement and construction industry. [11] Recently there was also a report of actual application as environmental friendly ceramic tiles, which help stabilizing temperature and humidity in the building [12,13], though the concern of unfavorable influence of its presence on the durability of concrete was also reported. [14]

It should be noted that the preparations of various zeolitic materials e.g. Na – X, Na – Y, hydroxyl sodalite and even phillipsite [15-18], from fly ash have been reported consistently during the last decades. It is however apparent to the authors that these experiments were conducted mostly with sodium hydroxide as the major alkali reagent. The other alkali reagents have been scarcely reported especially calcium hydroxide due to the significantly low solubility product constant in aqueous solution. The type of the final zeolitic products though depends considerably on the sources of the starting materials and also the alkali reagent used in the reactions and hence only a certain group of zeolites could be produced. Moreover those reported hitherto employing rather harsh conditions with poor product selectivity corresponding to the high impurities in the starting materials.

Here the preparations of zeolitic materials of phillipsite type employing calcium hydroxide as both the only and the principal alkali reagent via mild synthetic conditions are reported, along with a formation of rare hydrogarnet, hibschite, which is also the most hydrated hydrogarnet. The solids were characterized by powder X – ray diffraction whereas scanning electron microscope was employed to investigate the morphology. X – ray fluorescence (XRF) and atomic absorption spectroscopy (AAS) were used to determine the chemical compositions. The exchangeable cation contents of the typical zeolitized fly ash were also evaluated so as to assess further investigation for the environmental and agricultural applications e.g. waste treatment and controlled-released fertilizer respectively.

2. Experimental

The starting material, fly ash, was provided by the Electricity Generating Authorities Thailand (EGAT) collected from the hopper of electrostatic precipitators at Mae Moh power station in Lampang Province, Northern Thailand. The fly ash was first calcined at 880 ^{o}C in an open container, and then mixed and ground well with either calcium hydroxide pallets (BDH, 95%) in 1 : 1.2 by weight, or a mixture of calcium and sodium hydroxide in 1 : 0.60 : 0.60 by weight. The mixture was fused at various temperatures between 550^{o}C to 750 ^{o}C, and cooled down to room temperature before stirring for 6 hours with water added three – to ten – times the weight of solid. The reactions of the prepared mixtures were conducted in a closed container at 70^{o}C for varied durations from 7 to 21 days. The solid products were recovered by filtration and washing with water followed by rinsing with acetone before drying at room temperature. Powder X – ray diffraction (Siemen D500/D501, CuKα, Ni filter, λ = 1.54 Å) and scanning electron microscopy (JOEL JSM – 6335) were used to characterize the crystalline solid products and to investigate the morphology of the solids, respectively. Similar synthetic procedure was also conducted on as – received fly ash without the calcination prior to the synthesis.

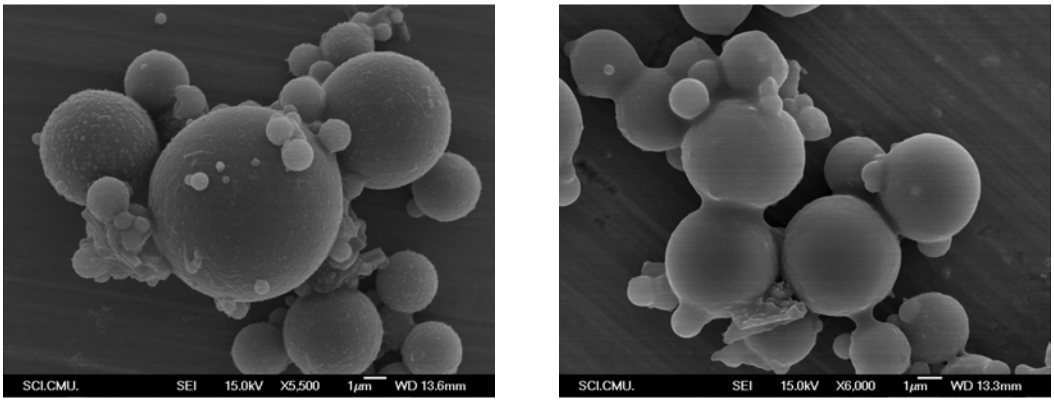
Elemental compositions of the activated fly ash and selected solid products were determined by energy dispersive X – ray fluorescence (XRF, Horiba MESA-500W) spectroscopy, compared to that of the pristine fly ash. The exchangeable cation contents of calcium(II) ion was determined on the prepared phillipsite identified by XRD using atomic absorption spectroscopy (Shimadzu AA – 680) with prior treatment with concentrated hydrochloric acid.

3. Results and discussion

The fly ash obtained from Mae Moh power plant is made up of spherical particles (Figure 1(a)), which are light brown in color. Some of these particles are opaque while some are hollow. The powder X-ray diffraction pattern (Figure 2(a)) suggests low crystallinity and possibly a multiphasic solid composing of quartz, hydrated calcium sulfate and aluminosilicates. The elemental compositions determined by X-ray fluorescence revealed high silica and alumina contents with SiO_2/Al_2O_3 of ca. 2:1. Table 1 summarizes the results of elemental analysis conducted on X-ray fluorescence spectrophotometer.

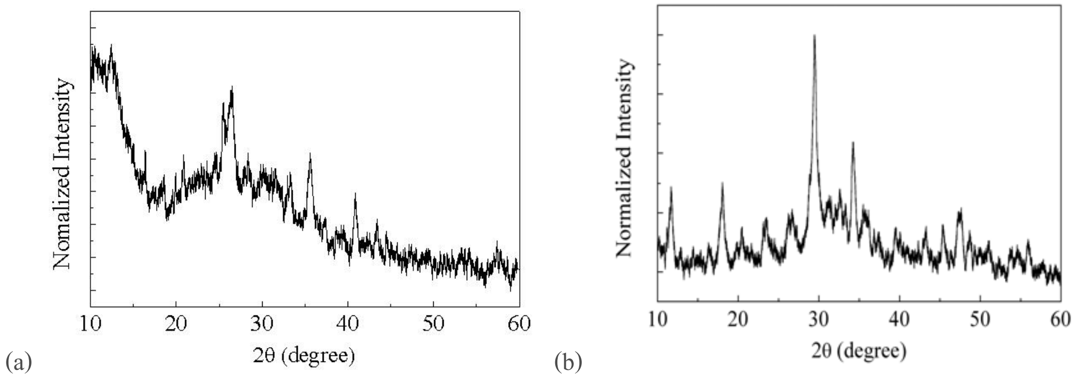
Table 1. Elemental compositions of fly ash and the activated ash compared to those of selected solids identified as phillipsite and hibschite.

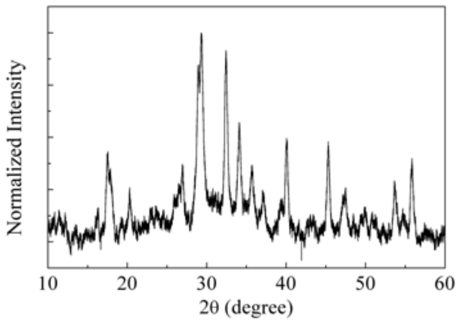
	Chemical Composition (wt%)										
	SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	MgO	Na_2O	K_2O	P_2O_5	SO_3	LOI
fly ash	40.88	20.49	11.66	12.89	0.59	1.28	0.99	4.00	0.16	2.00	4.26
activated fly ash	41.92	21.25	11.72	13.07	0.62	1.15	1.01	4.32	0.17	2.65	1.68
phillipsite	17.37	7.22	3.50	43.88	0.25	0.67	1.69	0.77	0.13	1.50	22.16
Hibschite	16.05	6.54	2.93	47.52	0.22	0.42	1.63	0.50	0.13	1.15	21.69



(a) (b)

Figure 1. Scanning electron micrograph of (a) pristine fly ash composing of spherical particles compared to that of (b) activated fly ash showing slight melting on the surface after the fusion at 880 °C.



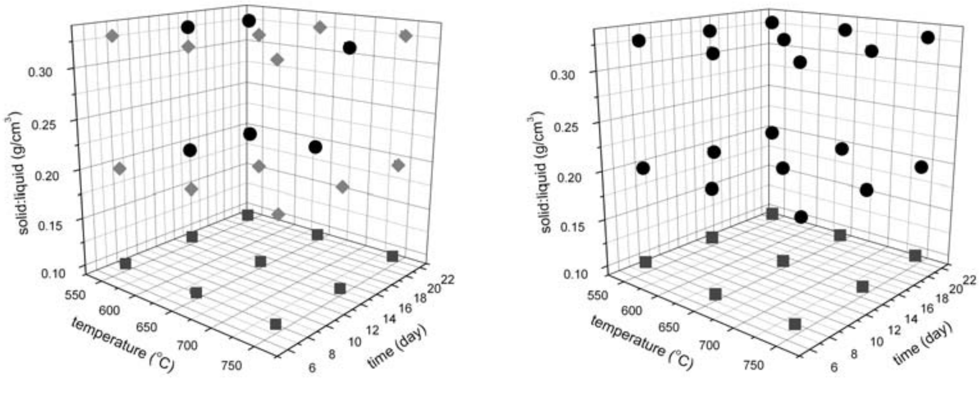


(c)

Figure 2. Powder X – ray diffraction pattern of (a) mostly amorphous fly ash compared to the patterns of (b) phillipsite and (c) hibshcite altered from the fly ash starting material.

The activation of the ash at 880 °C caused negligible difference in the powder pattern, but lower crystallinity is apparent. This is consistent with the corresponding elemental analysis showing similar SiO_2/Al_2O_3 of ca. 2:1 although with significant lower loss on ignition (LOI), which is due to the lower water content after the calcination. The scanning electron micrographs consistently revealed small degrees of melting on the surface of the particles after the activation as shown in Figure 1(b).

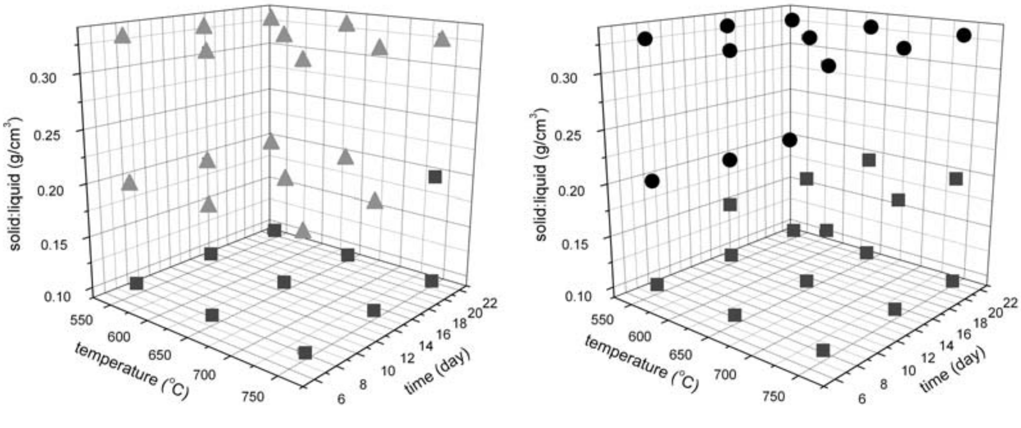
The treatments of Mae Moh fly ash under the specified conditions led to the production of phillipsite, hibschite, an unidentified phase or a mixture of these phases depending on type and amount of alkali reagents used in the reactions, the amounts of added water, fusion temperatures and reaction times. The final solid products obtained from various synthetic conditions characterized by powder X-ray diffraction are summarized as a function of three parameters, the amounts of added water, fusion temperatures and reaction times, in Figure 3 and Figure 4 and will be discussed in details later.



(a)

(b)

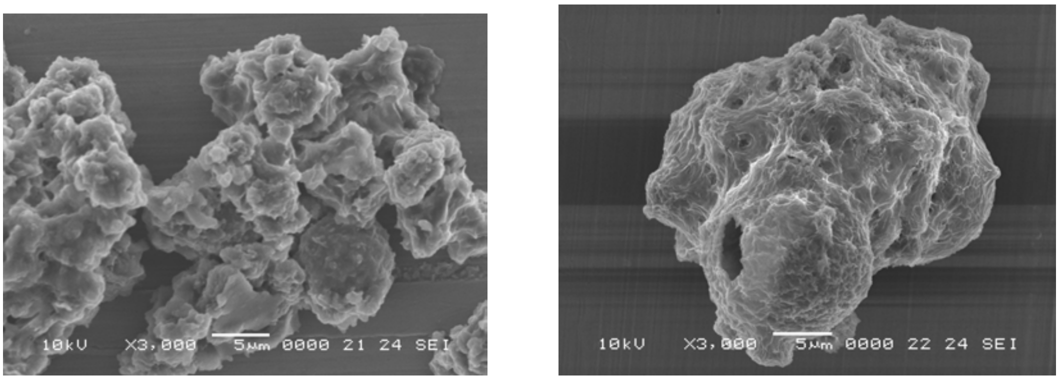
Figure 3. The Relative diagrams showing the influences of solid-to-liquid ratio, fusion temperature and reaction time on types of the solid products obtained from the reactions of as-received fly ash with (a) calcium hydroxide and (b) a mixture of calcium and sodium hydroxides at 70 °C; ● represents hibschite, ♦ is a mixture of hibschite and unidentified phases, and ■ is an unidentified phase.



(a) (b)

Figure 4. Relative diagram showing the influences of solid-to-liquid ratio, fusion temperature and reaction time on types of the solid products obtained from the reactions of the activated fly ash with (a) calcium hydroxide and (b) a mixture of calcium and sodium hydroxides at 70 °C; ● represents hibschite, Δ is phillipsite, and ■ is an unidentified phase.

It can be noticed that the zeolitic phillipsite and hibschite, each of which showed similar powder X-ray diffraction patterns, can be selectively synthesized under certain conditions. Figure 2(b) illustrates the powder X-ray diffraction pattern of the the product identified as phillipsite compared to that of the pristine ash in Figure 2(a) showing significantly higher crystallinity of the product. Every peak in Figure 2(b) can be fitted with the standard powder pattern of phillipsite although noisy background is observed. This implies the presence of glassy melt in the product coexisting with the crystalline phillipsite. This corresponds well with the electron micrograph shown in Figure 5(a) showing crystal flacks cemented by glassy melt with no spherical particles of the starting material. Comparing the elemental analysis results of the final product identified as phillipsite (Table 1) with the theoretical formula, $CaK_{0.6}Na_{0.4}Si_{5.2}Al_{2.8}O_{16}.xH_2O$, the coexistence of phillipsite and the other non-crystalline phase in the treated sample is confirmed. Elemental composition of the prepared phillipsite yielded from the reaction of the activated fly ash with calcium hydroxide also revealed the increase of calcium ion content, ca. 44 wt% CaO compared to ca. 13 wt% CaO of the activated fly ash, suggesting the uptake and cooperation of calcium ion from reaction solutions into the final zeolitized products.



(a) (b)

Figure 5. Comparison of scanning electron micrographs of (a) phillipsite and (b) hibschite dominated treated – fly ash.

Figure 2(c) exemplifies the powder X-ray diffraction pattern of the prepared hibschite. Every peak in the powder pattern shown can be indexed with the standard powder pattern of hibschite, which was hence confirmed to be the only crystalline phase in the products. The hibschite is calcium rich. This is consistent with the analyzed elemental composition as shown in Table 1, although the deviation from the weight percentages calculated from the general formula of hibschite, $Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}$ [11], is apparent. This also suggests the concurrent presence of the other amorphous phase. Electron micrographs taken on the prepared hibschite (Figure 5(b)) reveals glutinous melt with porous surface with no spherical particles of the starting materials, and hence complete collapse of the spherical particles.

The influences of the investigated parameters on the final products are closely correlated and diagrammatically shown in Figure 3 and Figure 4. It is apparent from these diagrams that the lower the water content, the higher the probability to yield selective product. The high water content in the reaction mixtures with solid-to-liquid ratio of 1g : 10cm^3 always led to the formation of unidentified phase, whereas the lower water content resulted in the selective formation of either phillipsite or hibschite depending on the other parameters. Hence the influences of other factors revealed only when the amount of water in the reaction mixtures was kept low.

The reactions of the as-received fly ash with calcium hydroxide tended to give hibschite as a mixture with other unidentified crystalline phase (Figure 3(a)) although the selective formation of hibschite can be observed at certain conditions especially those when the fusion temperatures of 550 and 650 ^oC were employed and the reactions were conducted for at least 14 days and 21 days respectively. The lower fusion temperatures and shorter reaction times were on the other hand required for the formation of hibschite as an exclusive crystalline product when a mixture of calcium and sodium hydroxide was employed (Figure 3(b)) implying the favor of sodium hydroxide toward the formation of hibschite. This can be due to the better solubility and stronger alkalinity of sodium hydroxide which prospering the presence of the hydroxyl group in the structure of hibschite. The influences of fusion temperatures and reaction times were negligible to the type of the final solid products when the fly ash was used as-received without prior calcination, especially those with the addition of sodium hydroxide.

The activation of fly ash by calcining at 880 °C in prior to the reactions led to the selective formation of the zeolitic material, phillipsite, notably when 1g : 3 cm^3 solid-to-liquid ratio was employed, which otherwise resulted in the formation of either hibschite or a mixture of hibschite and unidentified phase. (Figure 4(a)) In a similar manner to the hibschite case, the fusion temperatures and reaction times showed no significant influence on the type of the final solid products when the amount of water in the reaction mixtures was kept to the minimal of 1g : 3 cm^3, and calcium hydroxide was used as the only alkali reagent because the favor of sodium hydroxide toward the formation of hibschite over phillipsite is still evidenced (Figure 4(b)). The addition of sodium hydroxide to the reaction mixtures prohibited the formation of phillipsite, and on the other hand prompted the formation of hibschite, which was also evidentially selective. The influence of sodium hydroxide on the type of the products is more prominent than the activation of the starting material by calcination at high temperature. The calcination of the starting material though was evidenced to be the only parameter providing phillipsite as the exclusive crystalline product.

Regarding phillipsite as a zeolitic material, which is well known as a good cation exchanger, the amount of exchangeable calcium ion, the richest cation in the prepared phillipsite, was determined. High exchangeable calcium ion content of 6.9(9) $mmol.g^{-1}$, which is equivalent to 39 wt% CaO, or 89wt% of 44wt% determined by XRF, suggest potential application as a cation exchanger.

In conclusion, the selective preparation of either phillipsite or hibschite from Mae Moh lignite ash is shown to be plausible via the manipulation of the prior calcination and the presence of sodium hydroxide respectively. The activated fly ash is likely to give phillipsite as the only crystalline product when the added amount of water is kept to the minimum and calcium hydroxide is employed as the only alkali reagent. The as – received fly ash under suitable synthetic conditions especially those with the presence of sodium hydroxide can provide hibschite as an exclusive product. Other factors apparently influencing the type of the final products under the investigation are the amount of water media. Too much water in the reaction mixture can lead to other crystalline phases, which cannot be identified due to the lacking of number of diffraction peaks. The successful preparation of either phillipsite or hibschite as a single phase from Mae Moh fly ash can lead to an alternative way to enhance economical value of the ash, which is otherwise applied only in cement additives. The possibility in environmental and agricultural applications of the prepared phillipsite as ion exchanger and controlled-released fertilizer is now under investigation.

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