PHASE TRANSFORMATION IN THE FORMATION OF FAUJASITE FROM FLY ASH

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ABSTRACT

Faujasite was hydrothermally synthesized from fly ash at 100^oC in alkaline solution by reflux with 5M HCl and fusion with NaOH pretreatments. Phase transformation in the formation of faujasite was performed by variation of NaOH/fly ash weight ratios and hydrothermal times. The solid products were characterized by X-ray diffraction method. Results showed that faujasite was formed through dissolution of fly ash components such as quartz, mullite and amorphous aluminosilicates followed by crystallization to form faujasite. Arranging the NaOH/fly ash weight ratio as well as hydrothermal time can selectively form faujasite. Faujasite with crystallinity of 97.06%, Si/Al ratio of 2.68, and specific surface area of 452.93 m^2/g was successfully formed using NaOH/fly ash weight ratio of 1.2 for hydrothermal time of 72 hours. In more concentrated alkaline solution as well as for longer hydrothermal time, faujasite was completely transformed into hydroxysodalite as the final product.

INTRODUCTION

It was known that a series of zeolitic materials could be synthesized under hydrothermal condition. Such syntheses entail the combination of a silica component, an alumina component, and inorganic and/or organic bases. This mixture forms a gel or viscous liquid, which is allowed to crystallize, usually under autogeneous pressure, for a period of time between a few hours to several weeks at temperatures between $\sim60^oC$ and 200^oC. Kinetic control implies that nucleation phenomena will be important, and the courses of zeolite crystallization are generally sensitive to slight changes in the chemical and physical environment. Changes in the relative Na_2O-SiO_2-Al_2O_3-H_2O gel composition and/or crystallization conditions give rise to a wide range of possible products from this system. This diversity implies the possibility of simultaneous crystallization of more than one phase, and multiphase products are common [1].

The process of zeolite crystallization generally involves initial gel formation, slow dissolution of gel components into the aqueous component, nucleation (from either solution or gel), crystal growth, and then further evolution, perhaps by redissolution of this first phase and nucleation and growth of second crystalline phase. Silicate gels and solutions generally support equilibriums between large numbers of distinct silicate anions (in various states of condensation) [1].

In alkaline solution, aluminate solutions are relatively simple with $Al(OH)_4^-$ as the dominant anionic species. When silicates are dissolved either in water or in acid, according to their solubility characteristics, the silicate anion or silicic acid corresponding with that in the parent compound. When aluminates and silicates are present in the solutions, various polymeric species are known to occur [2].

According to Oswald's rule [3], in the formation of polymorphs of a given element or compound the first polymorph to be formed from vapor, liquid or solution tend to be the least stable thermodynamically which is then in succession replaced by more stable polymorphs. In the hydrothermal systems, Oswald's rule (phase transformation), in general, can be caused by higher temperature, longer crystallization time, as well as higher concentration of alkaline solution. Synthetic zeolites, although stable under the particular conditions of their synthesis, may undergo transformation with time. For example, zeolite A when exposed to dilute sodium hydroxide solutions for prolonged periods of time converted to the zeolite P phase. In more concentrated solutions, it converted further to the hydroxysodalite hydrate.

Recently, many researchers showed that various types of zeolites could be produced from fly ash by hydrothermal reaction in alkaline solution. Although zeolites have been synthesized from fly ash, most previous studies, however, showed that the final products were generally a mixture of zeolite

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materials, such as zeolite P, zeolite A, faujasite, analcime, and hydroxysodalite [4-8]. Because the zeolite materials obtained from fly ash almost always contain undesired impurity phases, therefore, efforts to achieve the single phase (selective) zeolite are very important. Attempts to convert fly ash into selective zeolite have been done using many treatments before hydrothermal reaction such as fusion with NaOH [9-11] as well as ageing and seeding [12]. In this present paper, an attempt has been made to obtain an understanding of phase transformation in the hydrothermal formation of faujasite from fly ash. Faujasite was synthesized from fly ash via reflux with 5 M HCl and fusion with various NaOH/fly ash weight ratios as reported earlier [13]. In this experiment, the temperature of reaction was kept constant around $100^{o}C$. Phase transformation was studied by variation of both NaOH/fly ash weight ratio in the fusion and hydrothermal time.

EXPERIMENTAL SECTION

The fly ash sample was taken from Suralaya Power Plant, Serang-Banten, Indonesia. A mixture of 10 g of fly ash sample and 100 mL of 5M HCl was refluxed at $90^{o}C$ for 1 hour with magnetically stirring. The solid was repeatedly washed with water and dried at $100^{o}C$ overnight. The refluxed-fly ash was added with NaOH pellets (the NaOH/fly ash weight ratio was varied), milled, and subsequently heated in a nickel crucible at $550^{o}C$ for 1 hour. The resultant fused-refluxed-fly ash was cooled to room temperature, milled again, and then stirred magnetically in a Teflon beaker with 100 mL water overnight. The slurry was heated in stainless steel autoclave with Teflon beaker inside under autogenously pressure at $100^{o}C$ for 72 hours without any stirring. After cooling to room temperature, the resulting solid product was recovered by filtration on a Buchner funnel, washed repeatedly with water and dried in an oven at $100^{o}C$ overnight.

The chemical compositions (silicon to aluminum ratios) of the selected zeolites obtained were measured by UV-Vis spectrometer (Hitachi 150-20 UV-Visible). X-ray diffraction (XRD) patterns were obtain by powder method using Ni-filtered CuKα radiation at 40 kV and 30 mA with scanning speed of 4°/minute (Shimadzu XRD-6000). Samples were normally scanned in the 2θ range of 5 to 40°. Nitrogen adsorption measurements of selected samples were performed on a NOVA 1000 microanalyzer (QUANTACHROME) at liquid nitrogen temperature. The sample was normally outgassed at $200^{o}C$ for at least 4 hours under

vacuum (10^{-4} torr). The sample was then subjected to automatic analysis.

RESULT AND DISCUSSION

Influence of NaOH/Fly Ash Weight Ratio on the Zeolite Obtained

Figure 1 showed that faujasite could be resulted at NaOH/fly ash weight ratio from 1.0-1.5 with the highest intensity at NaOH/fly ash weight ratio of 1.2. At lower NaOH/fly ash weight ratio (1.0), faujasite appeared with low intensity and the initial phase, i.e. quartz, still appeared. As the NaOH/fly ash weight ratio increased (1.5), the intensity of faujasite abruptly decreased and quartz disappeared but a new phase, i.e. hydroxysodalite, appeared. At higher NaOH/fly ash weight ratio (2.0-3.0) faujasite disappeared and hydroxysodalite appeared accordingly as the only result.
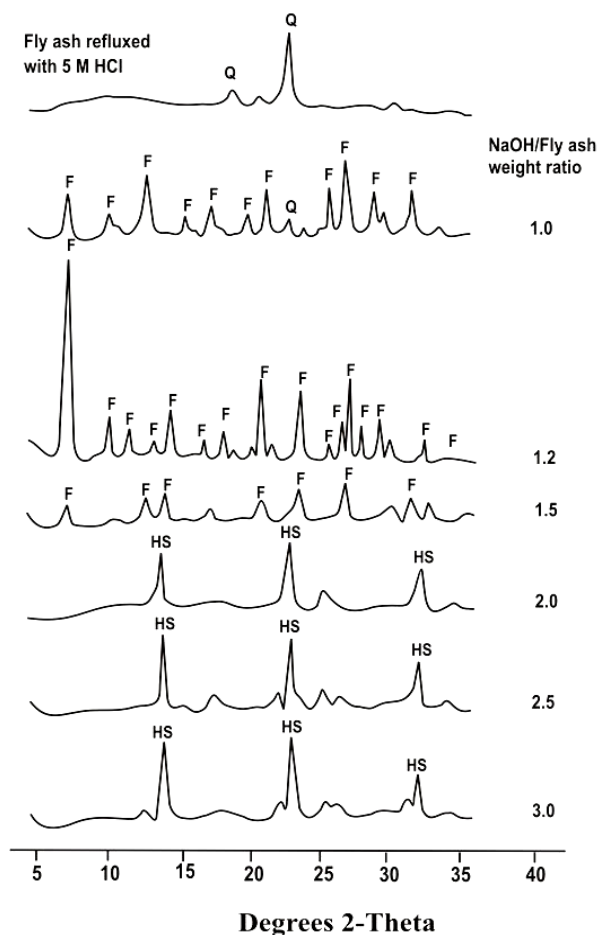
Figure 1 XRD pattern of the zeolite obtained by fusion with various NaOH/fly ash weight ratios for hydrothermal time of 72 hours (F=faujasite, HS=hydroxysodalite and Q=quartz)

Table 1 The influence of fusion with various NaOH/fly ash weight ratios on the crystallinity, Si/Al mol ratio, and specific surface area of the faujasite obtained for hydrothermal time of 72 hours

NaOH/fly ash weight ratio	Crystallinity of faujasite (%)	Si/Al mol ratio	Specific surface area (m^2/g)
Refluxed-fly ash[a]	-	2.79	66.32
1.0	73.00	1.99	407.30
1.2	97.06	2.68	452.93
1.5	30.67	1.71	362.45
2.0	00.00	*nd*	*nd*
2.5	00.00	*nd*	*nd*
3.0	00.00	*nd*	*nd*
Commercial zeolite NaY[b]	100.00	3.31	569.76

[a]Fly ash refluxed with 5M HCl, [b]Commercial zeolite NaY was used as reference of 100% crystallinity, *nd*=not determined

It was clearly shown that the higher the weight ratio of NaOH/fly ash, the lower the intensity of quartz. Disappearance of quartz at higher weight ratio of NaOH/fly ash showed that the dissolution of Si species from its crystalline was more effective. However, the higher alkalinity of the reaction mixture was not likely for the formation of faujasite. According to Breck [3], the higher alkalinity supports the transformation of faujasite and zeolite P into hydroxysodalite. The secondary building unit (SBU) of faujasite and hydroxysodalite is double-six ring (D6R) and single-six ring (S6R), respectively.

The influences of fusion with various NaOH/fly ash weight ratios on the crystallinity, Si/Al mol ratio, and specific surface area of the faujasite obtained were shown in Table 1. Table 1 showed that at NaOH/fly ash weight ratios of 1.0 to 1.2, it was shown that the crystallinity, Si/Al mol ratio, and specific surface area of faujasite obtained increased with the increase of NaOH/fly ash weight ratio. The relatively low crystallinity and specific surface area of faujasite synthesized with NaOH/fly ash weight ratio of 1.0 compared to those of NaOH/fly ash weight ratio of 1.2 may be caused by uncompleted dissolution of Si and Al source in fly ash as demonstrated by the presence of initial phase, i.e. quartz, in faujasite obtained. The relatively low Si/Al mol ratio of faujasite obtained at NaOH/fly ash of 1.0 may be caused by the lower Si/Al mol ratio of precursor solution. At lower NaOH concentration, the dissolution of Al was easier than that of Si, therefore, the Si/Al mol ratio in the precursor solution was lower and leads the formation of faujasite with lower Si/Al mol ratio. This phenomenon agreed well with the previous investigation [9].

Furthermore, at NaOH/fly ash weight ratio of 1.5, the crystallinity, Si/Al mol ratio and specific surface area of faujasite abruptly decreased. The peaks broadening of faujasite also accompanied the decrease of crystallinity. It was reported that peaks broadening were attributed to the presence of an extra amount of amorphous phase [14].

A further increase of NaOH/fly ash weight ratio (2.0-3.0) resulted in the formation of hydroxysodalite as the only phase in place of faujasite. Although the dissolution of fly ash phases was completed at higher NaOH/fly ash weight ratio, it forms a higher alkalinity of precursor solution. Excess alkalinity during fusion leads to a higher concentration of sodium hydroxide in the hydrothermal reaction mixture, which favors the formation of hydroxysodalite rather than faujasite [2]. It was reported earlier that zeolite A and faujasite in dilute alkaline solution for prolong time can change into zeolite P, whereas in concentrated alkaline solution may change further into hydroxysodalite [3]. However, in this experiment zeolite P did not appear as a metastable phase before the formation of hydroxysodalite. This phenomenon may be caused by higher concentration of alkaline solution in hydrothermal reaction mixture.

Influence of Hydrothermal Time on the Zeolite Obtained

Figure 2 showed XRD patterns of samples synthesized at hydrothermal temperature of 100°C for various hydrothermal time via reflux with 5M HCl followed by fusion pretreatment with NaOH/fly ash weight ratio of 1.2 (reflux 5M-fusion 1.2). The relatively high background of samples at hydrothermal time of 0-3 hours was explained by the presence of amorphous phases [14]. The XRD patterns of samples obtained at hydrothermal time of 6-72 hours contained all peaks corresponding to faujasite phase without any other phases. At hydrothermal time over 72 hours (120 hours), hydroxysodalite peaks appeared as the only phase in place of faujasite. This phenomenon indicated the transformation of faujasite into hydroxysodalite by prolong hydrothermal time [2]. The crystallinity and

Si/Al mol ratio of faujasite obtained were summarized in Table 2.
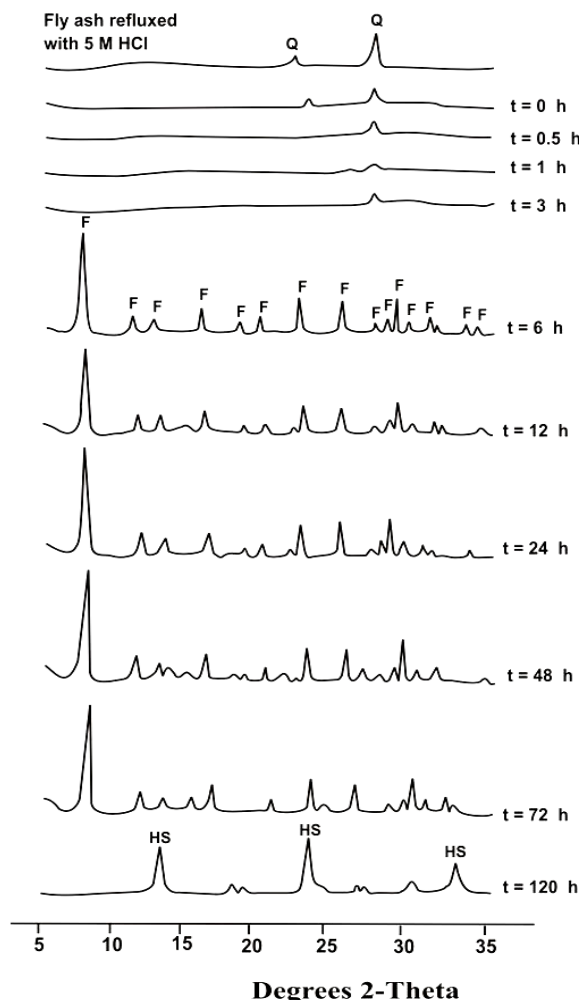
Figure 2 XRD pattern of the zeolite obtained at various hydrothermal times via reflux with 5M HCl and fusion with NaOH/fly ash weight ratio of 1.2 (F=faujasite, HS=hydroxysodalite, and Q=quartz)

Table 2 The crystallinity and Si/Al mol ratio of faujasite obtained at various hydrothermal times

Hydrothermal time (h)	Faujasite obtained	
	Crystallinity (%)	Si/Al mol ratio
6	95.79	1.86
12	79.55	1.05
24	94.59	1.36
48	96.50	1.72
72	97.06	2.68
120	00.00	*nd*
Commercial zeolite NaY[a]	100.00	3.31

[a]Commercial zeolite NaY was used as reference of 100% crystallinity, *nd*=not determined

Based on Figure 2 and Table 2, it revealed that the process of faujasite formation from fly ash under the experimental condition might be divided into three steps. Firstly, the formation of faujasite from fly ash was started by the dissolution of unfused quartz and amorphous aluminosilicates phases of fly ash as indicated by the decrease of both the quartz peaks and the background at hydrothermal time of 0-3 hours. Although fly ash has been fused with NaOH before hydrothermal reaction, however, the fusion has not completed as demonstrated by the presence of quartz. The disappearance of quartz at hydrothermal time of 3 hours showed that the dissolution of unfused quartz from fly ash seemed to be completely occurred.

Secondly, the formation of faujasite was promoted over 3 hours and was almost completed with crystallinity of 95.79% over hydrothermal time of 6 hours. Although at hydrothermal time of 6-72 hours, except at 12 hours, the crystallinity of faujasite was almost similar (94.59-97.06%), however, the Si/Al mol ratio of faujasite obtained at 72 hours was too high compared to that of 6-48 hours. The exceptionally low crystallinity of faujasite obtained at 12 hours (79.55%) may be due to the faster dissolution of aluminosilicates than the crystallization of aluminosilicates [3], whereas the very high value of Si/Al mol ratio of faujasite obtained at 72 hours (2.68) may be caused by the completed crystallization of aluminosilicates.

Thirdly, at hydrothermal time over 72 hours (120 hours), hydroxysodalite peaks appeared as the only phase in place of faujasite. This phenomenon strongly supported the phasetransformation of faujasite into hydroxysodalite by prolong hydrothermal time. Although zeolites are stable at certain condition, however, for prolong hydrothermal time they may transform into other phases. It was reported earlier that zeolite A and faujasite in dilute alkaline solution for prolong time can change into zeolite P, whereas in concentrated alkaline solution may change further into hydroxysodalite [3]. It was clearly shown that in this experiment zeolite P did not appear as a metastable phase before the formation of hydroxysodalite. This phenomenon confirmed the influenced of higher concentration of alkaline solution in hydrothermal system that favors the formation of hydroxysodalite rather than zeolite P [2].

CONCLUSION

Faujasite was formed through dissolution of fly ash components such as quartz, mullite and amorphous aluminosilicates followed by crystallization to form faujasite. Arranging the NaOH/fly ash weight ratio as well as hydrothermal

time can selectively form Faujasite. Faujasite with crystallinity of 97.06%, Si/Al ratio of 2.68, and specific surface area of 452.93 m^2/g was successfully formed using NaOH/fly ash weight ratio of 1.2 for hydrothermal time of 72 hours. In more concentrated alkaline solution as well as for longer hydrothermal time, faujasite was completely transformed into hydroxysodalite as the final product.

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