

Selective formation of Na–X zeolite from coal fly ash by fusion with sodium hydroxide prior to hydrothermal reaction

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Hydrothermal treatment of fly ash with alkali gives various types of zeolites such as Na–Pl, Na–A and hydroxysodalite, where the zeolite zone was formed like an egg white, covering the central core of fly ash particles, as evinced in the previous paper. By fusion with sodium hydroxide, most of the fly ash particles were converted into sodium salts such as silicate and aluminate, from which hydrothermal reaction without stirring favourably resulted in the formation of Na–X zeolite. Crystallinity of Na–X zeolite as high as 62% was attained at the optimum condition of NaOH/fly ash = 1.2 and a fusion temperature of 823 K. Fly ash contains 14 wt% mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), which was revealed to be a less-active crystalline component for zeolite formation. Aluminium-enriched fly ash gave Na–A in place of Na–X zeolite. Scanning electron microscope images of cubic and octahedral crystals characteristic of Na–A and Na–X zeolite, respectively, obtained from fly ash, are given.

1. Introduction

Coals contain various minerals (usually 10%–20%) and form coal ash as a by-product waste at coal combustion plants. In pulverized coal-fired power plants, fly ash is collected by cyclones, electric precipitators, and/or bag filters from the flue gas at the burner top, while clinker ash is recovered from the bottom as a mass of fused rock. The amount of coal ash generation is estimated to be 4 million [1] and 150 million tons/year [2] in Japan and the world in 1990, respectively. Less than a half of the fly ash is used as a raw material for cement manufacturing and construction, the remainder being still directly disposed of for on-site reclamation or piles [3], presumably leading to various environmental problems.

Typical fly ash is an agglomerate of spheres or cenospheres (hollow spheres) of 1–100 μm diameter [4, 5]. These fly ash particles contain silicon and aluminium as major elements, and are crystallographically composed of an amorphous component with some crystals such as α -quartz, mullite, haematite, and magnetite [6–8].

Hydrothermal treatment of fly ash with alkali has been made to afford various types of zeolite such as Na–Pl type zeolite, philipsite, faujasite and hydroxysodalite [9–11]. In a previous paper [12], Na–Pl, Na–A type zeolite, and hydroxysodalite were obtained by the hydrothermal reaction of fly ash with sodium hydroxide solution at 373 K under vigorous agitation. X-ray microanalysis revealed that the zeolite zone was formed like an egg white, covering the central core of fly ash particles.

Attempts were made in the present work to convert the whole of the fly ash particles into zeolite by alkali fusion prior to the hydrothermal treatment. By fusion with sodium hydroxide, most of fly ash particles were converted into sodium salts such as silicate and aluminate, the hydrothermal reaction of which, without stirring, favourably resulted in the formation of Na–X zeolite with a high yield of 62%. Aluminium-enriched fly ash gave Na–A in place of Na–X zeolite.

2. Experimental procedure

2.1. Zeolite formation

Typical alkali fusion and the succeeding hydrothermal treatment were carried out as follows. A mixture of a given amount of sodium hydroxide and 10 g fly ash was milled, and then heated in a platinum crucible to a desired temperature (773 K, unless otherwise stated), and held for 1 h. The resultant fused mixture was cooled to room temperature, milled again, and then agitated magnetically in a Teflon beaker with 100 ml H_2O for 12 h. Each 10 ml slurry was heated at 373 K in a sealed Teflon tube without stirring for a given period (6 h, unless otherwise stated). The precipitates were filtered, washed repeatedly with water, and dried overnight at 373 K.

To modify the Si/Al molar ratio, sodium aluminate was added to the fly ash before alkali fusion, where sodium hydroxide was added to adjust the sodium content to the same value in each starting material. Mullite and α -quartz were used as a source of aluminium and silicon, respectively, for zeolite formation.

2.2. Materials

Coal fly ash sample was collected from a hopper of an electric precipitator at a coal-fired power plant [12], where a mixture of Australian and Japanese (Miike) coal was burned, and used as-obtained. Table I shows the chemical composition of this fly ash.

Mullite (Commission of the European Communities, BCR 301; SiO₂ 27.8%, Al₂O₃ 71.5%) and α -quartz (Kagaku Kyoisha Ltd, Osaka, mineral standard; SiO₂ > 99%) were crushed and used as powders. Sodium aluminate (Na₂O 41.2%, Al₂O₃ 39.5%) and fumed silica (SiO₂ > 99.9%) were purchased from Wako Pure Chemical Industries Ltd, Osaka, and used as-supplied. Na-PI zeolite and hydroxysodalite were prepared by the procedure described elsewhere [12]. Na-A and Na-X zeolite were purchased from Union Showa Ltd, Tokyo, and used as standards for powder X-ray diffraction.

2.3. Analysis

Powder X-ray diffraction patterns were measured using CuK α radiation by the MXP system of MAC Science Co., Tokyo. The crystallinity of zeolite was calculated by the X-ray intensity ratio of the product to a standard at given diffraction faces as follows: Na-PI (301), Na-A (200), Na-X (111), hydroxysodalite (211). Composition of the crystalline components in the fly ash was determined by the standard addition method [8] using diffracted X-ray intensity.

An acid-soluble component was defined tentatively as the weight loss after immersion overnight of the product (0.3 g) in 1.2 N HCl (0.5 l) at room temperature. The chemical composition of the acid-soluble component was determined using an inductively coupled plasma atomic emission spectrometer (SPS-1500, Seiko Instruments Inc., Tokyo). SEM observation was made using a JSM 800 (Jeol, Tokyo).

3. Results and discussion

3.1. Alkali requirement for fusion of fly ash

Alkali fusion is a conventional method for chemical analysis to decompose materials containing silicon and/or aluminium [13]. The amount of sodium hydroxide employed in fusion affects not only the conversion of fly ash into sodium silicate and aluminate but also the alkalinity of the solution in hydrothermal treatment.

Fig. 1 shows the effect of NaOH/fly ash weight ratio (Na/ash) before fusion on the resultant zeolite crystal-

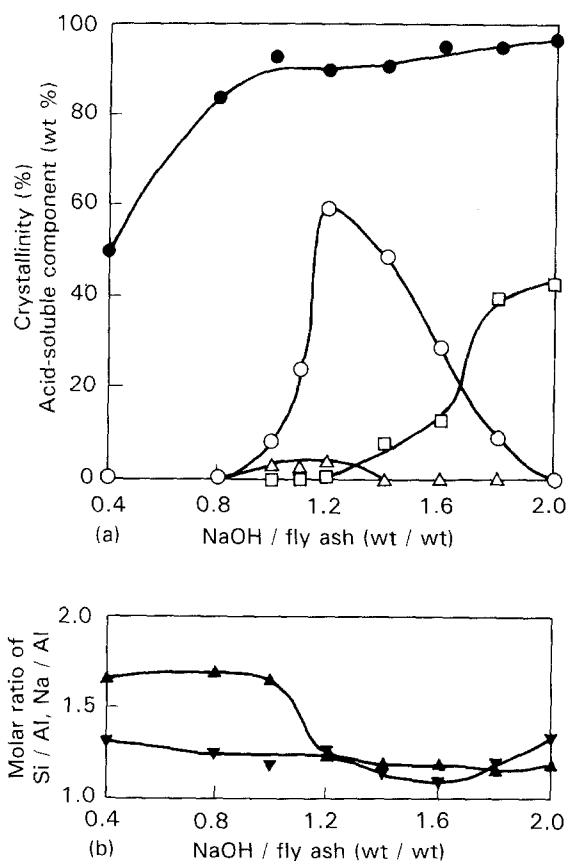


Figure 1 Effect of NaOH/fly ash ratio on zeolite formation; Fusion 773 K, 1 h; hydrothermal reaction 373 K, 6 h. (a) Crystallinity, (○) Na-X, (△) Na-A, (□) hydroxysodalite, (●) acid-soluble component. (b) Molar ratio, (▲) Si/Al, (▼) Na/Al.

linity, the weight per cent of acid-soluble component, and the molar ratio of Si/Al and Na/Al in the hydrothermal reaction products. The acid-soluble component contains zeolites and the precursor-like aluminosilicate gel as major components. Zeolites detected in the present work were completely dissolved in acid.

Faujasite was selectively formed above Na/ash = 1.0, and the crystallinity increased rather abruptly with increasing Na/ash ratio to a maximum as high as 60% at Na/ash = 1.2, followed by a decrease with further increase in Na/ash. The molar ratio of Si/Al = 1.25 in the acid-soluble component at Na/ash = 1.2, provides evidence that the faujasite is Na-X type zeolite.

No zeolite was obtained at Na/ash = 0.8, while the weight per cent of the acid-soluble component was similar to that obtained at Na/ash = 1.2. The Si/Al molar ratio of 1.70 at Na/ash = 0.8 was quite close to that of fly ash (1.78), and rather different from that of Na-X zeolite (1.0–1.5). It seems likely that alkali-deficient conditions badly affect the crystallization of zeolite. Indeed, Na-X zeolite was obtained at a rather high crystallinity of 40% by the hydrothermal treatment of the fusion product at Na/ash = 0.8 with an enriched alkaline solution of 1 N NaOH.

A further increase in Na/ash ratio over 1.2 resulted in the formation of hydroxysodalite in place of the decrease in Na-X zeolite, and only hydroxysodalite was observed at Na/ash = 2.0, where the Na/Al molar ratio in the acid-soluble component was the same as

TABLE I Chemical composition of the coal fly ash employed

Element	Content (wt %)
SiO ₂	55.4
Al ₂ O ₃	25.3
Fe ₂ O ₃	4.0
TiO ₂	2.2
CaO	4.6
MgO	0.8
Na ₂ O	0.9
K ₂ O	0.7
Ignition loss	2.0

that in hydroxysodalite (1.33). Excess alkali during fusion leads to a higher concentration of sodium hydroxide in the hydrothermal reaction, which favours the formation of hydroxysodalite rather than Na-X zeolite [14].

3.2. Effect of fusion temperature on Na-X zeolite formation

The effect of fusion temperature for a mixture at Na/ash = 1.2 on zeolite formation is given in Fig. 2, and SEM images of products obtained by alkali fusion of fly ash and the subsequent hydrothermal reaction are compared in Fig. 3.

The results in Fig. 2 may be divided into four temperature regions bordered at 373 K (b.p. H₂O), 591 K (m.p. NaOH) and 823 K (maximum zeolite yield). Below the boiling point of water (373 K), no zeolite was obtained and the weight per cent of acid-soluble component was less than 58%, showing incomplete decomposition of fly ash by heating with sodium hydroxide at lower temperatures.

In the second region, 373–591 K, the crystallinity of Na-X zeolite increased with temperature to a plateau of 42%. A high value of acid-soluble component (~90%) above 473 K and an abrupt decrease in Si/Al molar ratio near 400 K were observed. Presumably moist sodium hydroxide promoted decomposition of fly ash at elevated temperatures, leading to Na-X

zeolite in the hydrothermal reaction. A pseudo-spherical particle of approximately 20 μm diameter, reflecting the shape of the fly ash particle, was observed for the product heated at 473 K (Fig. 3a); hydrothermal treatment of these particles resulted in a surface partially covered with small particles of ~2 μm, presumably involving Na-X zeolite (Fig. 3b).

Another stepwise increase in yield of Na-X zeolite was observed at temperatures above the melting point of NaOH (591 K) to a maximum crystallinity of 62% at 823 K. The molar ratio of Na/Al = 1.25 at 832 K suggests the existence of some sodium-rich amorphous component, because Na/Al = 1.0 in Na-X zeolite. Spherical porous aggregates of 20–50 μm, composed of sintered microspheres of 2 μm, were obtained in an alkali fusion at 773 K (Fig. 3c). It is of interest that as shown in Fig. 3c and d, the microspheres seem to be converted into some distorted octahedra, details of which will be mentioned later in Fig. 6b, by the formation of crystalline zeolite Na-X in the hydrothermal treatment.

At a higher temperature above 823 K, the crystallinity of Na-X zeolite gradually decreased with increasing fusion temperature, while the acid-soluble component continued to increase. In an alkali fusion at a high temperature, 1073 K, spheres of the initial fly ash particles disappeared, and a mass of sintered glassy aggregate was seen as shown in Fig. 3e, and the hydrothermal reaction products in the SEM images in Fig. 3f were similar to that in Fig. 3d.

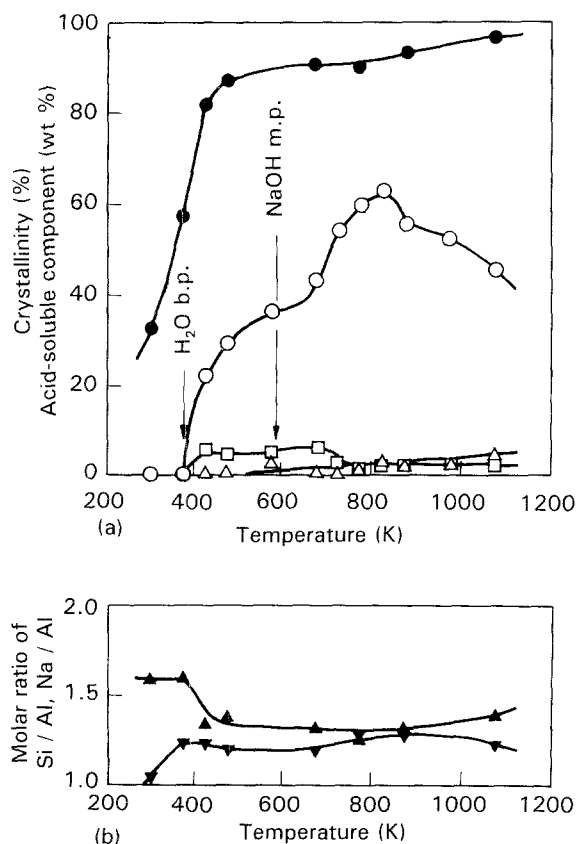


Figure 2 Effect of fusion temperature on zeolite formation; NaOH/fly ash = 1.2; fusion 1 h; hydrothermal reaction 373 K, 6 h. (a) Crystallinity, acid-soluble component; (b) molar ratio. For key, see Fig. 1.

3.3. Comparison of reactivity for zeolite formation among crystalline components containing silicon and aluminium

Table II shows the crystals detected in the coal fly ash employed, where mullite and α -quartz are crystalline components containing aluminium and/or silicon. Table III compares the reactivity of these crystalline components for zeolite formation by fusion with sodium hydroxide and the subsequent hydrothermal reaction. A mixture of α -quartz and sodium aluminate resulted in a crystallinity of Na-X zeolite as high as 88%. A similar value of 86% was obtained when using fumed silica and sodium aluminate as the reference. However, Na-X zeolite was obtained with a lower crystallinity of 53% from mullite and fumed silica.

The difference in reactivity for zeolite formation among these crystalline components might be interpreted as that α -quartz was completely changed to sodium silicate by alkali fusion but mullite was partially converted into sodium aluminate. Mullite was the only crystalline component containing aluminium in the fly ash, and aluminium in the fly ash was apportioned 40% to mullite and the remaining 60% to the amorphous component. Thus the maximum yield of Na-X zeolite could not exceed 62%, as previously shown in Fig. 2. The result appears to be adequately anticipated; i.e. as much as 40% aluminium in the fly ash exists in a less-active component of mullite.

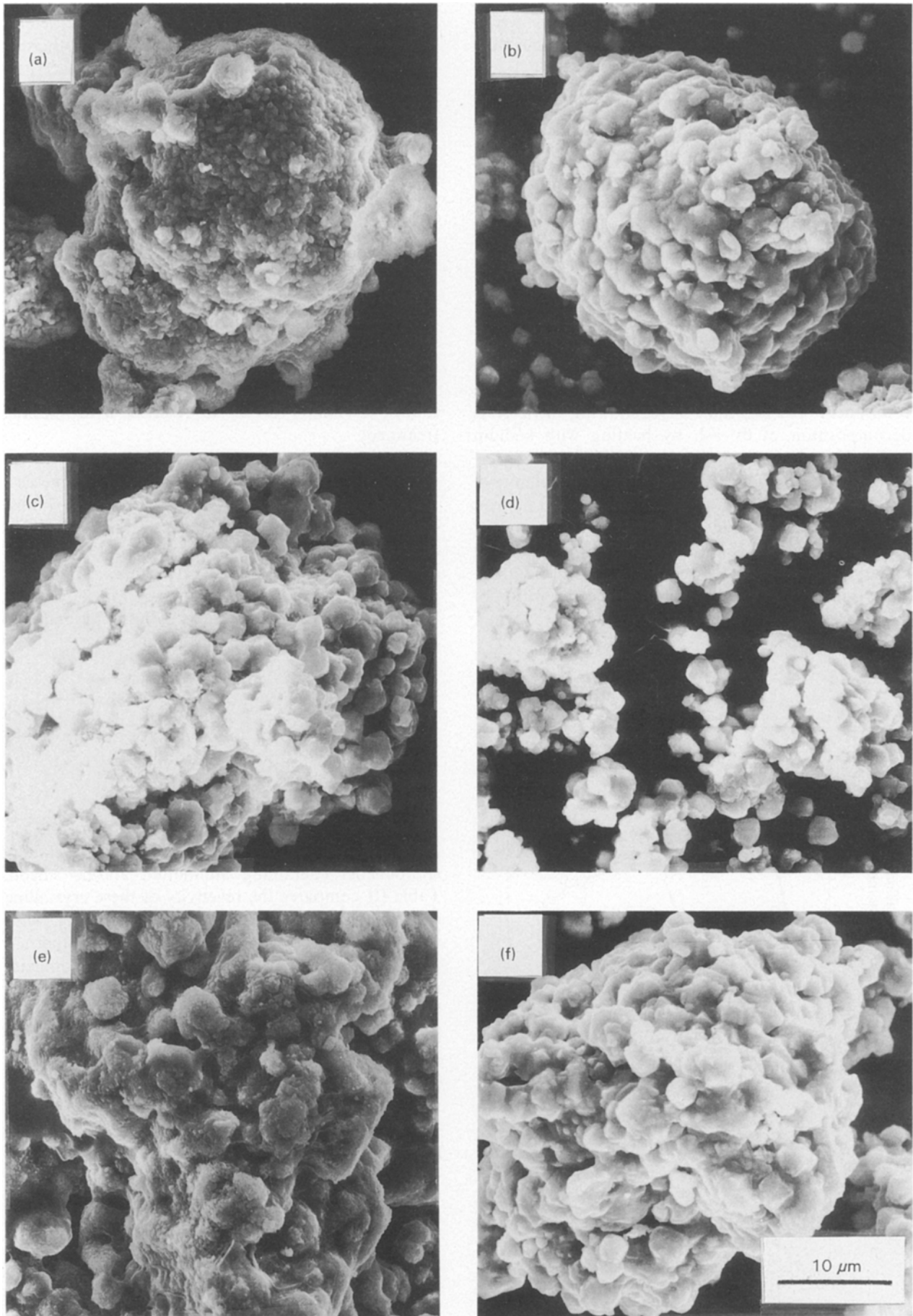


Figure 3 SEM images of products of fly ash fused with NaOH and the subsequent hydrothermal reaction; NaOH/fly ash = 1.20. Heating or fusion: (a, b) 473 K, (c, d) 773 K, (e, f) 1.073 K, for 1 h. Hydrothermal reaction: (b, d, f) 373 K, 6 h.

TABLE II Crystals detected in the coal fly ash employed

Crystal	Content (wt %)
α -quartz (SiO_2)	6.5
Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$)	13.7
Haematite ($\gamma\text{-Fe}_2\text{O}_3$)	1.5
Magnetite (Fe_3O_4)	2.3
Amorphous component	Balance

TABLE III Na-X zeolite synthesis^a from various source materials

Silicon source	Aluminium source	Crystallinity of Na-X zeolite (%)
Fumed silica	Sodium aluminate	86.0
α -quartz	Sodium aluminate	87.6
Fumed silica	Mullite	52.8

^a Composition of starting materials, Na : Al : Si = 6.1 : 1.0 : 1.9 (same at NaOH/fly ash = 1.20); fusion 773 K, 1 h, hydrothermal reaction 373 K, 6 h.

3.4. Transition of Na-X zeolite into hydroxysodalite during hydrothermal treatment

It is well known that various zeolites can themselves be transformed into different species, both zeolite and non-zeolite ([14] p. 239). Fig. 4 shows the transition of zeolite species in the hydrothermal reaction after fusion at Na/ash = 1.2 and 1.8. The crystallinity of Na-X zeolite increased abruptly after an induction period and showed a plateau of 59% after 6 h at Na/ash = 1.2 (Fig. 4a). On the other hand, the crystallinity of Na-X zeolite increased to a maximum of 27% at 4 h followed by a decrease to 8% at 24 h at Na/ash = 1.8 (Fig. 4b), where hydroxysodalite was obtained and the yield increased linearly with time of hydrothermal reaction. Na-A and Na-Pl zeolite were also observed in both series of runs.

3.5. Formation of Na-A zeolite from aluminium-enriched fly ash

It is generally known that the formation of particular zeolite species depends strongly upon the ratio of Si/Al in the starting material for hydrothermal reaction ([14] p. 188). In the present work, modification of the Si/Al molar ratio was made by the addition of sodium aluminate to the fly ash.

Fig. 5 shows the effect of added sodium aluminate on zeolite formation in the hydrothermal reaction after alkali fusion, where Na-A zeolite was obtained in place of Na-X zeolite, and increased in crystallinity with increasing added NaAlO_2 content. Na-X zeolite completely disappeared and Na-A zeolite was selectively obtained at a higher aluminium contents of $\text{NaAlO}_2/\text{fly ash} = 0.41$. The SEM image given in Fig. 6a provides evidence for cubic crystals (2 μm in size) characteristic of Na-A zeolite [15] prepared from aluminium-enriched fly ash. In contrast, Fig. 6b shows distorted octahedra (2 μm) of Na-X zeolite [15, 16] obtained from fly ash as supplied.

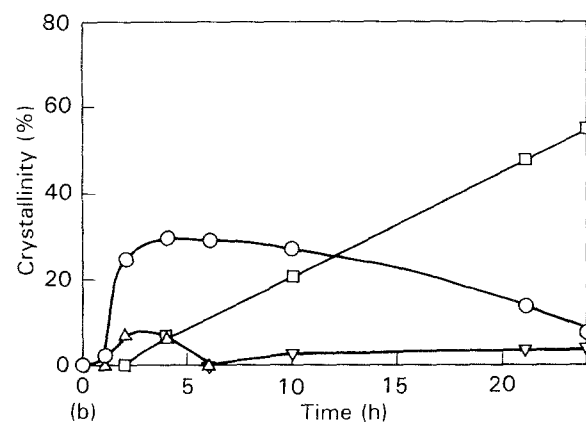
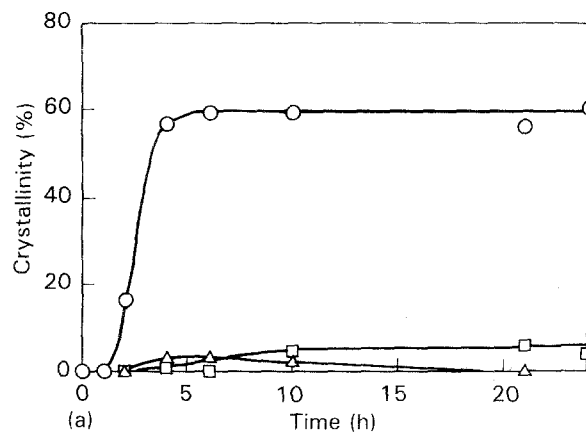


Figure 4 Transition of zeolite species during hydrothermal reaction. NaOH/fly ash: (a) 1.2, (b) 1.6. Fusion 773 K, 1 h; hydrothermal reaction 373 K. Crystallinity; (∇) Na-Pl. Other symbols as in Fig. 1.

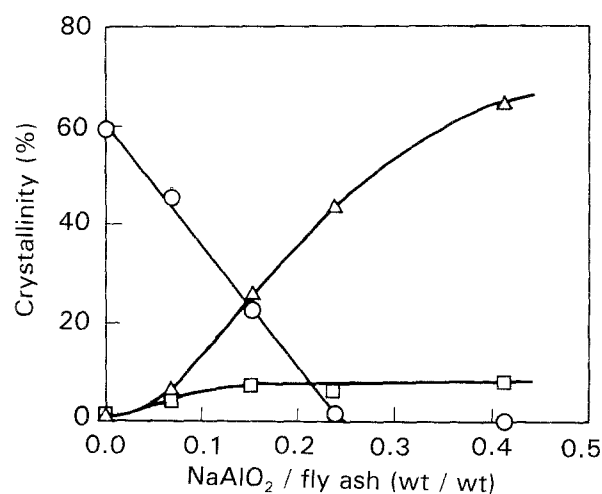


Figure 5 Effect of added aluminium content on zeolite formation. Aluminium source, sodium aluminate; fusion 773 K, 1 h; hydrothermal reaction 373 K, 6 h. For key, see Fig. 1.

4. Conclusion

Na-X zeolite was selectively obtained from coal fly ash by fusion with alkali and the subsequent hydrothermal reaction without stirring, where the ratio of NaOH/fly ash and the fusion temperature strongly affect the formation of the zeolite. Crystallinity of Na-X zeolite as high as 62% was attained at the optimum reaction conditions of NaOH/fly ash = 1.2 and a fusion temperature of 823 K.

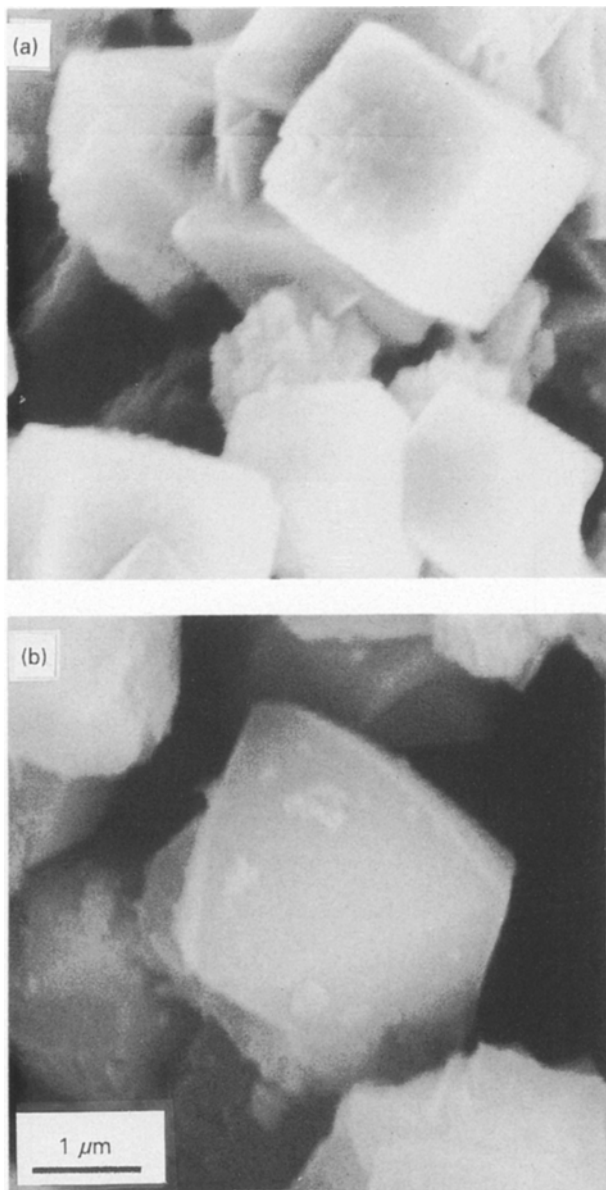


Figure 6 SEM images of (a) cubic (Na-A) and (b) octahedral (Na-X) crystals obtained from coal fly ash. Composition of the starting material: (a) NaOH:NaAlO₂:fly ash = 1.06:0.41:1.00; (b) NaOH/fly ash = 1.2. Other reaction conditions as in Fig. 5.

Fly ash contains 14 wt % mullite (3Al₂O₃·2SiO₂), which is revealed to be the less-active crystalline component for zeolite formation. Aluminium-enriched fly ash favourably resulted in the formation of Na-A zeolite in place of Na-X zeolite in the hydrothermal reaction after alkali fusion.

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