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Formation process of Na-X zeolites from coal fly ash

H. TANAKA*, S. MATSUMURA, R. HINO
Department of Material Science, Faculty of Science and Engineering,
Shimane University, 1060 Nishikawatsu, Matsue, Shimane 690-8504, Japan
E-mail: hidekazu@riko.shimane-u.ac.jp

In order to synthesize Na-X zeolite from coal fly ash (Fa), Fa was pretreated under stirring condition at various temperatures of 20–50°C for 72 h and then aged at 85°C for a given period with NaOH solutions. The resulting materials were characterized by various means. When Fa was aged for 72 h without pretreatment, species P were formed. As the pretreating temperature raised from 20 to 50°C, the degree of crystallinity of faujasite increased, while that of species P decreased. The faujasite species formed was identified as Na-X zeolite with molar ratio $SiO_2/Al_2O_3 = 2.4$. When Fa was pretreated at 50°C and aged for 60 h, the only species formed was Na-X zeolite. Increasing the pretreating temperature up to 50°C results in the increase of Si^{4+} and Al^{3+} concentrations in the treating solution by dissolution of amorphous material in Fa. With the conditions used, the crystalline phase, such as α-quartz and mullite, was poorly dissolved during the treatment. Hence, the higher pretreating temperature would give the uniform nucleation and crystal growth of Na-X zeolite during the aging. © *2004 Kluwer Academic Publishers*

1. Introduction

Coal ash is formed by combustion of coal in power station as a waste product. In the world and Japan, the coal ash production reaches approximately 500 and 6 million tons per year, respectively, and is predicted to increase [1]. The coal ash can be separated into two forms: one is fly ash (Fa) and another is bottom ash or slag. The Fa is collected at the top of burner using cyclones, electric precipitators or mechanical filters. Whereas, the bottom ash or slag is obtained from bottom of furnace as a mass of fused rock. The proportion of Fa generated accounts for 84% of total coal ash [2]. In the world, only 15% of the Fa are used as a raw material, mainly for cement and concrete production, and the remaining Fa is disposed of for reclamation [2]. Although, Fa contains various hazardous heavy metals, for instance, As, Pb, Sn and Cd [3]. Therefore, resource recover of Fa is concerned at present.

Fa is mainly composed of amorphous material with high molar ratio SiO_2/Al_2O_3 and some crystals, such as α-quartz (SiO_2), mullite ($2SiO_2{\cdot}3Al_2O_3$), hematite (α-Fe_2O_3) and magnetite (Fe_3O_4) [4] and can be converted to zeolites in alkali solutions by hydrothermal treatment [5–12]. There are many reports for synthesis of zeolites from Fa, e.g., faujasite [4–10], phillipsite [11] and hydroxysodalite [12]. Since Na-X zeolite, one of the faujasite type zeolite, possesses large pore openings and large cavities, this material is used as catalysts, washing builder, cation exchanger, adsorbents and so forth. The conversion of Fa to Na-X zeolite has been studied by Henmi [5] and LaRosa *et al.* [7]. They treated Fa in NaOH solutions at 80–90°C to produce Na-X zeolite. However, not only Na-X zeolite but also other zeolites such as species P and phillipsite were formed. Recently, we reported the suitable formation condition of Na-X zeolites from Fa [13]. Although, the detailed formation process of Na-X zeolite has not been fully established.

The aim of this study was to synthesize Na-X zeolite from Fa and to clarify the formation process of Na-X zeolite. The Fa particles were pretreated by stirring in NaOH solutions at 20–50°C for 72 h and then aged at 85°C for various periods. The products thus obtained were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and Fourier transform infrared (FTIR). The formation process of Na-X zeolites is discussed on the basis of results obtained.

2. Experimental

2.1. Materials

The chemical composition of Fa supplied from Nippon Steel Co. was determined by a Rigaku X-ray fluorescence spectrometer (XRF) and is listed in Table I. The amounts of crystallized SiO_2 and Al_2O_3 such as α-quartz and mullite were assayed by a quantitative X-ray diffraction (XRD) method [14]. The concentrations of amorphous SiO_2 and Al_2O_3 were calculated by subtracting crystallized SiO_2 and Al_2O_3 contents from total SiO_2 and Al_2O_3 contents, respectively. The amount of crystallized and amorphous components is listed in

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*Author to whom all correspondence should be addressed.

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TABLE I Chemical composition of Fa

	wt%
SiO_2	71.0
Al_2O_3	18.3
CaO	0.8
K_2O	0.7
Na_2O	0.3
$Fe_2O_3 + Fe_3O_4$	3.6
C	1.0

TABLE II Crystal and amorphous contents in Fa

	wt%
Crystalline SiO_2 (α-quartz, mullite)	13.0
Amorphous SiO_2	58.0
Crystalline Al_2O_3 (mullite)	10.8
Amorphus Al_2O_3	7.5

Table II. The Fa used in this study possesses higher SiO_2 content and lower molar ratio SiO_2/Al_2O_3 compared to most of Fa. Although, the reason has not been clarified at present.

The amorphous SiO_2 and Al_2O_3 components in Fa were used as Si and Al sources for synthesis of zeolites. The conversion of Fa to zeolites was carried out as follows. An amount of 6.0 g of Fa was added into NaOH solutions in a sealed polypropyrene vessel, of which the molar ratio SiO_2/Al_2O_3:Na_2O/SiO_2:H_2O/Na_2O in the staring materials was 13.2:6.0:50.0. The slurry thus prepared was pretreated under stirring condition at different temperatures of 20–50°C for 72 h and then aged at 85°C for various periods from 0 to 72 h in an air oven without stirring. The resulting materials were separated into solid phase and treating solution by filtration. The solid phase was thoroughly washed with distilled-deionized water and dried at 110°C for 24 h in an air oven.

2.2. Characterization

The materials thus prepared were characterized by various conventional methods. Powder X-ray diffraction (XRD) patterns were taken on a Rigaku X-ray diffractometer using a Ni filtered Cu K_α radiation (30 kV, 16 mA). For the XRD measurements, 20.0 mg of anatase (TiO_2) used as an internal standard were added in 200.0 mg of the samples. The degree of crystallinity of zeolite was estimated from the diffraction intensity ratio of the zeolite to an internal standard at given diffraction faces: Na-X zeolite (111), species P [Na-Pt (110) + Na-Po (001)] and anatase (101). Similarly, the proportion of amorphous material was estimated from the diffraction intensity ratio of the top of a halo pattern from $2\theta = 15$ to 35° to an internal standard. Particle morphology was observed by a Hitachi scanning electron microscope (SEM). Transmission IR spectra were recorded by a JASCO Fourier transform infrared (FTIR) spectrometer with a resolution of 2 cm^{-1} using a KBr method. Si^{4+} and Al^{3+} concentrations in the treating solutions were assayed by molybdenum yellow method and EDTA chelate titration, respectively.

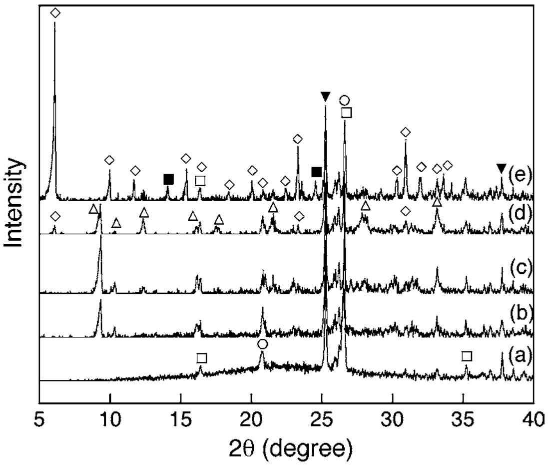

Figure 1 XRD patterns of (a) original Fa and (b–e) Fa pretreated at various temperatures for 72 h and aged at 85°C for 72 h. Pretreating temperature (°C), (b) without pretreatment, (c) 20, (d) 35, (e) 50. (□) mullite, (○) α-quartz, (△) species P, (◇) faujasite, (■) hydroxysodalite, (▼) anatase.

3. Results and discussion

3.1. Influence of pretreatment of Fa on the formation of Na-X zeolite

Fig. 1 displays XRD patterns of original Fa and Fa pretreated at various temperatures for 72 h and then aged at 85°C for 72 h. Pattern a of the original Fa possesses some diffraction peaks and a halo pattern except for the peaks due to internal standard, meaning that the material is mainly composed of α-quartz, mullite and amorphous material. When Fa is aged without pretreatment, the diffraction peaks due to species P are developed (pattern b). Pattern c of the Fa pretreated at 20°C is almost identical with pattern b. On pretreating at 35°C, new diffraction peaks at $2\theta = 6.1$, 23.9 and 31.0° appear and the peaks due to species P are weakened (pattern d). These new peaks can be assigned to faujasite. Upon raising the pretreating temperature up to 50°C, the peaks of faujasite are suddenly developed and those of hydroxysodalite are found at $2\theta = 14.1$ and 24.6°, while no peaks due to species P are observed (pattern e). From these results, it is indicative that the pretreatment of Fa and its temperature significantly affect on the formation of faujasite.

The synthetic faujasite type zeolite can be distinguishable into two forms with the same crystal structure. One is Na-X zeolite with $2.0 \leq$ molar ratio $SiO_2/Al_2O_3 \leq 3.0$ and another is Na-Y zeolite with $3.0 \leq$ molar ratio $SiO_2/Al_2O_3 \leq 6.0$. Dempsey *et al.* [15] have reported the relationship between molar ratio SiO_2/Al_2O_3 of faujasite and lattice constant ao of Na-X and Na-Y zeolites. The faujasite formed in this study has a lattice constant ao = 25.0 Å and can be assignable to the Na-X zeolite with molar ratio $SiO_2/Al_2O_3 = 2.4$.

3.2. Influence of pretreating temperature on the dissolution of amorphous material in Fa

Fig. 2 plots the proportion of amorphous material in Fa as a function of pretreating period. On pretreating at 20 and 35°C, no remarkable decrease in proportion of amorphous material is found. Upon pretreating at 50°C, the proportion of amorphous material is dramatically decreased with elapsing the pretreating period. These results suggest that the dissolution of amorphous material is accelerated by raising the pretreating temperature up to 50°C. The dissolution of Fa during the pretreatment was also confirmed by SEM observation. Fig. 3 depicts the SEM pictures of original Fa and Fa pretreated at various temperatures of 20–50°C for 72 h. The original Fa is spherical particles with a diameter ranging from 10 to 120 μm and the particle surface is very smooth (Fig. 3a). When Fa is pretreated at 20°C, the particle morphology is almost unchanged (Fig. 3b). Fig. 3c shows that Fa particles pretreated at 35°C are only slightly dissolved, although no marked change in the particle shape is recognized. Upon raising the pretreating temperature at 50°C, the surface of Fa particles becomes rough and several cracks can be observed

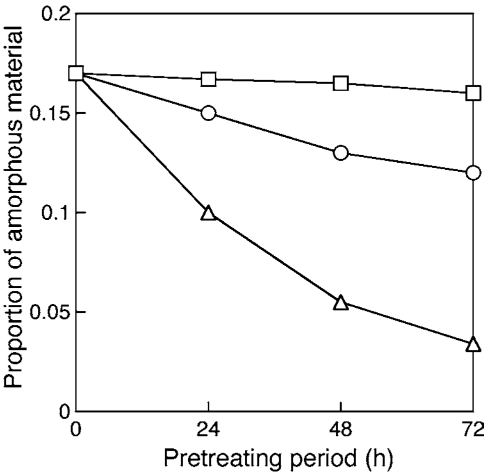

Figure 2 Change in proportion of amorphous material against pretreating period. Pretreating temperature (°C): (□) 20, (○) 35, (△) 50.

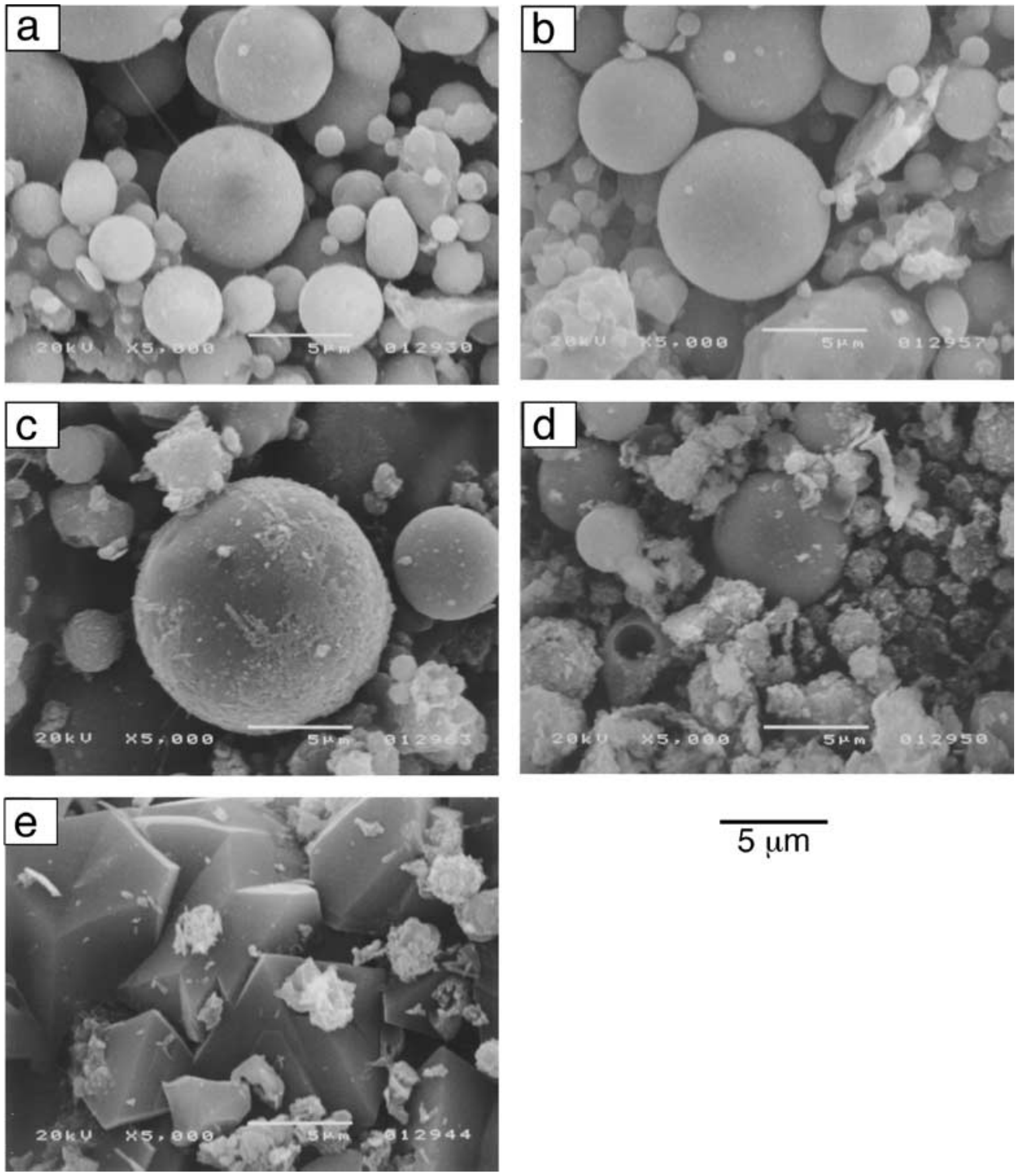

Figure 3 SEM pictures of Fa pretreated at various temperatures for 72 h: (a) original Fa, (b) pretreated at 20°C, (c) 35°C, (d) 50°C, and (e) pretreated at 50°C and agied for 60 h.

(Fig. 3d). Besides, no new particle is generated during the pretreatment. Henmi [4] reported that the amorphous material in Fa is mainly composed of aluminosilicate. Furthermore, Shigemoto *et al.* [8] and Catalfamo *et al.* [16] have indicated that the amorphous material is much dissolved than crystalline phase such as α-quartz and mullite in alkali solutions. Indeed, a halo pattern due to amorphous material was completely diminished as shown in XRD patterns b–e of Fig. 1. Whereas, the peak intensity of α-quartz and mullite was not changed during the treatment. From the aforementioned results, it is though that the pretreatment at 50°C induces only dissolution of amorphous materials in Fa and the Si^{4+} and Al^{3+} ions eluted are reacted to form Na-X zeolite and species P. Since the species P was formed after aging at 85°C for 72 h without pretreatment as shown in XRD pattern b of Fig. 1, pretreatment of Fa above 50°C seems to induce the dissolution of amorphous material in Fa and crystallization of zeolites.

3.3. Formation process of Na-X zeolite

In order to elucidate the formation process of zeolites such as Na-X zeolite, species P and hydroxysodalite, XRD patterns of Fa pretreated at 20–50°C for 72 h and aged for different periods were taken. Fig. 4 plots the change in degree of crystallinity of zeolites and in proportion of amorphous material estimated from the XRD patterns against aging period. As it can be seen in this figure, the proportion of amorphous material is decreased with increasing the aging period. In any pretreating temperature, no zeolite is formed until the amorphous material is completely dissolved. As the pretreating temperature is raised, the degree of crystallinity of Na-X zeolite is developed, while that of species P is decreased. When Fa is pretreated at 50°C, the degree of crystallinity of Na-X zeolites is increased with elapsing the aging period and is maximum at 60 h. Whereas, no formation of other zeolite such as species P is recognized. These facts reveal that the only species formed is Na-X zeolite. When aged for 72 h, the degree of crystallinity of Na-X zeolite is slightly decreased and that of hydroxysodalite is increased. The formation of Na-X zeolite was also confirmed by SEM observation. Fig. 3e shows the SEM picture of Fa pretreated at 50°C for 72 h and aged at 85°C for 60 h. The octahedral particles can be clearly seen. Since the Na-X zeolite possesses the FAU type framework, the morphology of Na-X zeolites generally exhibits octahedral particles. Hence, these particles can be ascribed to the Na-X zeolites.

Fig. 5 compares IR spectra of Fa pretreated at 50°C and then aged. Spectrum a of the original Fa possesses three absorption bands at 1086, 791 and 463 cm^{-1}. The 1086 and 463 cm^{-1} bands are due to the asymmetric stretching and the bending vibration modes of T—O bonds, respectively (where T = Si or Al) [17]. The 791 cm^{-1} band is assigned to the symmetric stretching vibration mode of O—T—O groups [17]. Aging for 12 h appears new bands at 1174 and 1011 cm^{-1} (spectrum e). As confirmed by SEM observation, the amorphous material such as precursor of zeolite was formed at the same period (not shown here). Thus, the 1174 and 1011 cm^{-1} bands can be assigned to the asymmetric stretching vibration modes of external linkages and internal T—O bonds in TO_4 tetrahedra of formed amorphous materials, respectively [17]. These bands gradually shift to a lower wavenumber and strengthen with increasing the degree of crystallinity of Na-X zeolites. It has been reported that the wavenumber of the stretching vibration band decreases with an increase of Al content in the zeolite structure [17]. Hence, the shift of the T—O bands to a lower wavenumber indicates the incorporation of Al in the amorphous aluminosilicate such as precursor of zeolites to form Na-X zeolites. Further, the molar ratio SiO_2/Al_2O_3 of the amorphous aluminosilicate formed by aging for 12 h would be much higher than 2.4 of the Na-X zeolites formed. Spectrum f of the Fa aged for 24 h possesses new bands at 760 and 559 cm^{-1}. Since the Na-X zeolites are formed at

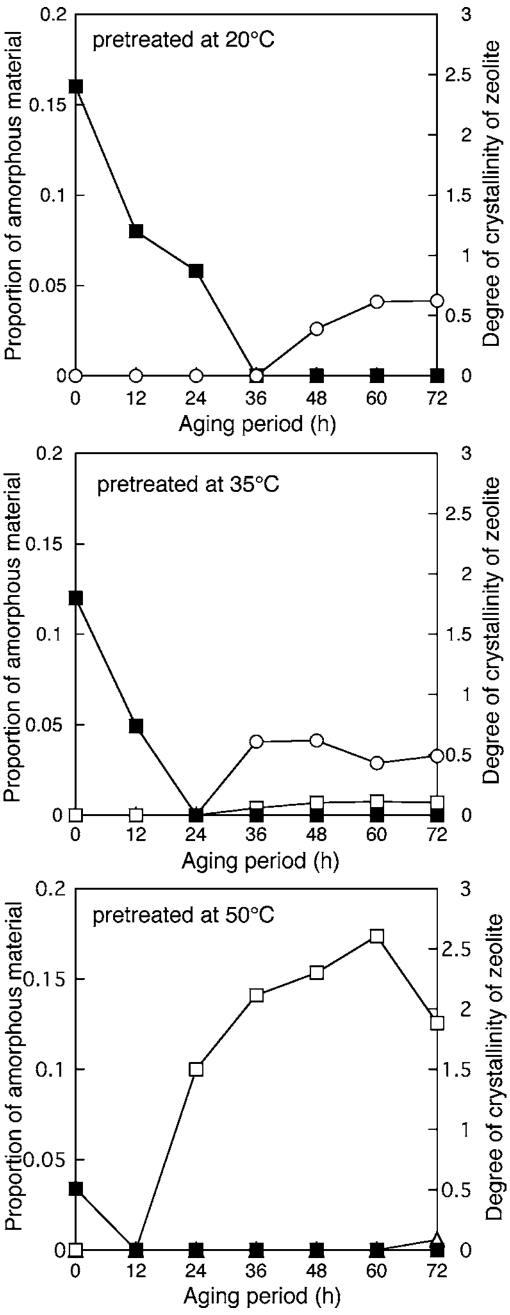

Figure 4 Change in degree of crystallinity of zeolites and in proportion of amorphous material against aging period: (□) Na-X zeolite, (○) species P, (△) hydroxysodalite, (■) amorphous material.

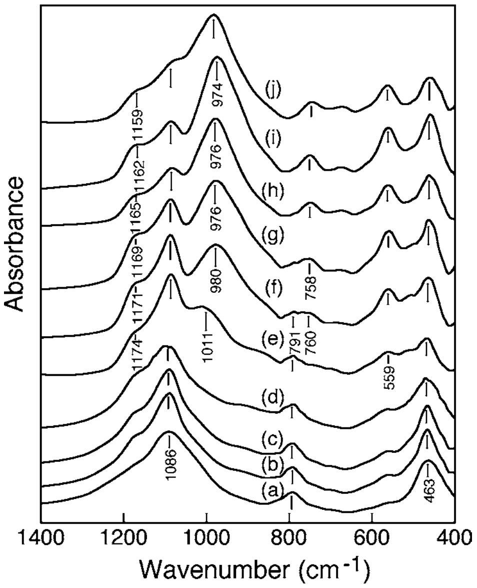

Figure 5 IR spectra of Fa pretreated at 50°C and then agied for different periods: (a) original Fa, (b) pretreated for 24 h, (c) 48 h, (d) 72 h, (e) agied for 12 h, (f) 24 h, (g) 36 h, (h) 48 h, (i) 60 h, and (j) 72 h.

the same period, the 760 and 559 cm^{-1} bands can be ascribed to the symmetric stretching vibration band of O—T—O groups and double six-membered rings (D6R), respectively [17]. These bands are also intensified with increasing the degree of crystallinity of Na-X zeolite.

To get insight into the change of cation concentration in the treating solution during the treatment, Si^{4+} and Al^{3+} concentrations were determined at various preparation periods. The results are displayed in Fig. 6. The Si^{4+} and Al^{3+} concentrations are increased with elapsing the pretreating period and with raising the pretreating temperature up to 50°C. As has been already mentioned, the Si^{4+} and Al^{3+} ions eluted from amorphous material in Fa are reacted to form zeolites. When Fa is pretreated at 20 and 35°C for 72 h, aging for 12 h abruptly increases the Si^{4+} and Al^{3+} concentrations, meaning that the amorphous material is suddenly dissolved. Whereas, when Fa is aged for 12 h after pretreatment at 50°C for 72 h, the Si^{4+} concentration is slightly increased, while the Al^{3+} concentration is decreased. This is because about 80% of amorphous material is dissolved during the pretreatment as shown in Fig. 2. On aging above 24 h, the Si^{4+} concentration becomes almost constant and the Al^{3+} concentration is gradually reduced. It can be, therefore, inferred that the Al^{3+} ions are incorporated into aluminosilicate framework with a higher molar ratio SiO_2/Al_2O_3 than Na-X zeolite, corresponding to the IR results. The formation process of various zeolites from Fa has been reported by Shigemoto *et al.* [8], Lin and Hsi [18], and Murayama *et al.* [19]. They concluded that the formation of zeolites from Fa occurs through the following three steps: (1) dissolution of Fa, (2) formation of amorphous aluminosilicate and (3) crystallization of zeolites. Furthermore, it has been reported that the difficulty in preparing pure faujasite such as Na-X and Na-Y zeolites is due to the fact that this more porous zeolite is thermodynamically metastable compared to species P and phillipsite [20]. Therefore, it is required to synthesize Na-X zeolite that the uniform nucleation and crystal growth of Na-X zeolite. When Fa is pretreated at 50°C for 72 h, most of amorphous materials are dissolved and the Si^{4+} and Al^{3+} concentrations in the treating solution are 111.6 and 27.0 mmol dm^{-3}, respectively. Interestingly, molar ratio SiO_2/Al_2O_3 in the solution is 8.3, close to $SiO_2/Al_2O_3 = 8.0$ for suitable formation condition of Na-X zeolites as reported previously [21–23]. Hence, the higher pretreating temperature would give the uniform nucleation and crystal growth of Na-X zeolite during the aging.

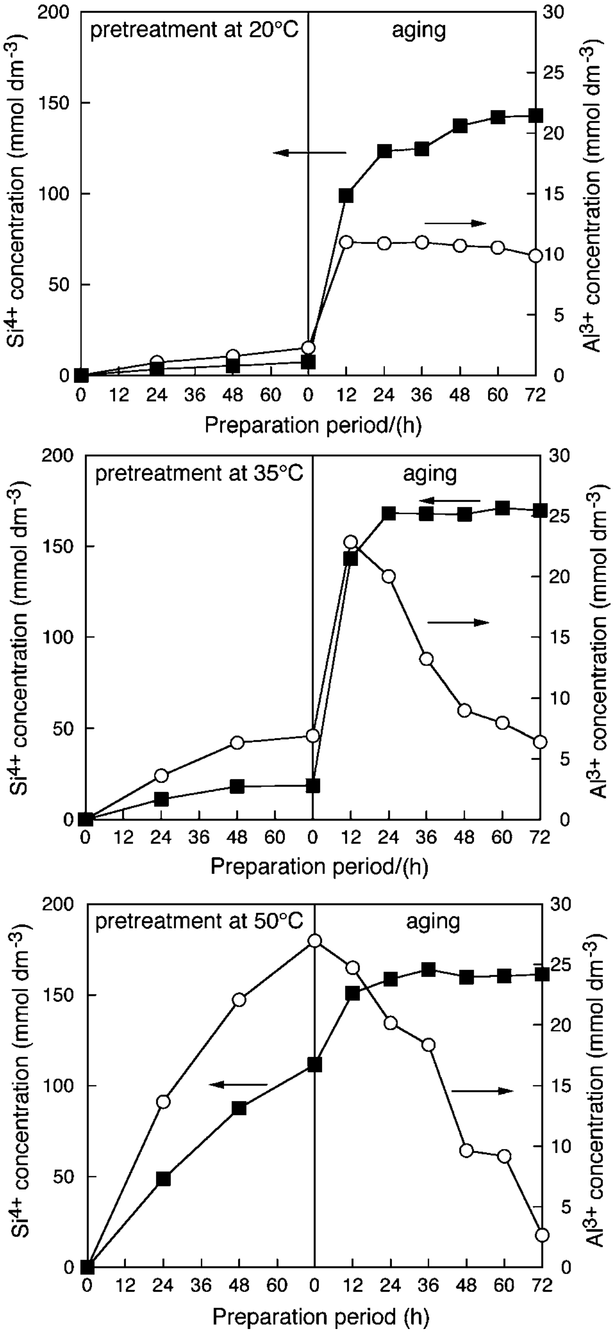

Figure 6 Change of (■) Al^{3+} and (○) Si^{4+} concentrations in the treating solution vs. preparation period.

From these results, we can proposed a formation mechanism of the Na-X zeolite from Fa by pretreating at 50°C and aging as follows. The amorphous material in Fa is dissolved during the pretreatment and no new materials are formed (step 1). Aging for 0–12 h forms the amorphous aluminosilicate with a higher molar ratio SiO_2/Al_2O_3 than Na-X zeolite (step 2). The Al^{3+}

ions are incorporated into the amorphous aluminosilicate during the aging to yield Na-X zeolite (step 3). Since the amorphous material is poorly dissolved during the pretreatment at 20 and 35°C and is suddenly dissolved by aging, steps 1 and 2 take place at the same aging time. As a result, uniform nucleation of Na-X zeolite does not occur and the amorphous aluminosilicate formed at step 2 possesses no homogeneous chemical composition. Consequently, a little amount of Na-X zeolite is formed during the aging.

4. Conclusions

The results obtained in the present study can be summarized as follows. The pretreatment of Fa and its temperature significantly affect on the formation of Na-X zeolites. About 80% of amorphous material in Fa were dissolved by pretreating at 50°C for 72 h. With raising the pretreating temperature up to 50°C, the degree of crystallinity of faujasite was increased while that of species P was decreased. The faujasite formed was identified as Na-X zeolites with molar ratio $SiO_2/Al_2O_3 = 2.4$. When Fa was pretreated at 50°C for 72 h and aged at 85°C for 60 h, the only species formed was Na-X zeolites. The higher pretreating temperature would give the uniform nucleation and crystal growth of the Na-X zeolite during the aging.

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