Synthesis of FAU zeolite from aluminoborosilicate glass and elution behavior of glass components

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We tried to synthesize FAU zeolite from aluminoborosilicate glass used in liquid crystal displays, of which the discard volume is supposed to increase in the near future. The effect of hydrothermal process factor on the synthesis of FAU zeolite using aluminoborosilicate glass, which is poorly alkaline-soluble, was investigated. From X-ray diffraction, with increasing aging time before hydrothermal treatment, the production of FAU zeolite increased, whereas, that of zeolite P decreased. From inductively coupled plasma atomic emission spectrometry, the concentration of Si in the solution increased and that of Al decreased during aging. This indicates that aluminosilicate was generated from Si from aluminoborosilicate glass and Al from sodium aluminate. With aging time, generated aluminosilicate was aged, resulting in preferential synthesis of FAU zeolite. From scanning electron microscopy, increasing aging time resulted in a small crystal particle size of the synthesized FAU zeolite. At higher aging temperature than room temperature, the dissolution of aluminoborosilicate glass was accelerated, zeolite P increased. When NaOH concentration of aqueous solution decreased, zeolite A was synthesized. This indicates that aluminoborosilicate glass did not elute substantially, therefore low silica zeolite was generated. At higher NaOH concentration, FAU zeolite was generated because Na⁺ ion stabilized FAU zeolite and more Si eluted from aluminoborosilicate glass. Zeolite P which is a stable phase was generated when hydrothermal treatment temperature was high and treatment time became long. From nitrogen adsorption/desorption measurements, the microstructure of the obtained product was almost the same as the pure FAU zeolite. We clarified the potential of aluminoborosilicate glass as a starting material of FAU zeolite, widely used in catalysts, adsorbents, gas separation agents and so on.

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1. Introduction

LCD panels are widely used in televisions, personal computers, smartphones, tablets, digital cameras and so on. In 2011, global TV demand was about 2000 million, more than half of which was for LCD TVs.¹⁾

Recently, people have become more concerned about environmental problems, therefore it is necessary to make efficient use of materials from discarded LCD TVs, given that the discard volume of LCD TVs is going to increase in the near future. The main component of an LCD panel is a glass substrate, therefore the recycling of the aluminoborosilicate glass used in the glass substrate is an important issue.

By the way, zeolites are microporous aluminosilicate materials with a uniform pore size of less than 2 nm and chemically, mechanically, and thermally stable.²⁾ Zeolites are applied as catalysts, adsorbents, gas separation membranes, detergent builders and so on because of their excellent adsorptive capacity, gas separation property and ion-exchange capacity, which owes to the unique microporous structure.

Generally, zeolites are synthesized from a silica source, an alumina source, a mineralizer (alkali metal hydroxide) and water.²⁾ There are many previous studies on the synthesis process of zeolite A and FAU-type zeolite, which are widely used for indus-

trial purposes.^{2)–11)} Zeolites with an FAU-type framework are classified into zeolite X and zeolite Y according to the Si/Al molar ratio.^{12),13)} The synthesis of FAU zeolite attracts much attention because of its wide industrial use, such as a fluid catalytic cracking catalyst that utilizes the solid acid properties of zeolite Y^{14)–17)} and a gas separation agent that utilizes the adsorptive performance of zeolite X.¹⁸⁾ Accordingly, many studies of the synthesis of FAU zeolite have been carried out. As for the synthesis of FAU zeolite, many studies have been focused on suppressing the development of phases other than FAU.^{3)–7)} Generally, it is synthesized by hydrothermal treatment after aging aluminosilicate gel generated from the starting material for a few hours.^{3)–5)} Colloidal silica is one of the preferred sources of silica for obtaining zeolite Y. In the previous research into the synthesis of zeolite from blast furnace slag using a starting material that was pre-treated to have an SiO₂ content of 90%, highly-pure FAU zeolite was synthesized by hydrothermal treatment.^{8)–10)} Starting materials that contains high-pure SiO₂, such as colloidal silica and pre-treated blast furnace slag, readily elute alkaline solution during hydrothermal treatment, whereby generating homogeneous Si solution. Therefore, FAU zeolite could be synthesized by brief hydrothermal treatment.

Aluminoborosilicate glass mainly consists of SiO₂, Al₂O₃, B₂O₃ and alkaline earth oxides, and is probably suitable for zeolite ingredient because SiO₂ and Al₂O₃ are the main components. We can also make effective use of aluminoborosilicate glass as a mechanically-excellent and transparent substrate or base material such as large particles or plates. Furthermore, hydro-

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thermal treatment which is a typical method to synthesize zeolites is at low temperature relative to fusing process. The high softening temperature of aluminoborosilicate glass is not a problem for hydrothermal treatment. In a previous paper about the synthesis of zeolites from aluminoborosilicate glass,¹⁹⁾ relatively high silica and stable zeolite such as GIS zeolite (zeolite P) and ANA zeolite were obtained by hydrothermal treatment.

We tried to synthesize FAU zeolite to increase the potential of aluminoborosilicate glass as a starting material of zeolite. Aluminoborosilicate glass has chemical resistance and is less soluble in alkaline solution than colloidal silica. The generation of aluminosilicate species, which occurs in alkaline solution, is difficult with aluminoborosilicate glass. Therefore, it was predicted that FAU zeolite nucleation would be difficult to promote. Moreover, the glass components, which are not original framework components of zeolites, such as alkaline earth oxide, may block the generation of zeolites.

In this study, the synthesis of FAU zeolite from aluminoborosilicate glass was tried. The microstructure of the product was also investigated. We focused on the relationship between the elution behavior of aluminoborosilicate glass and FAU zeolite synthesis, because aluminoborosilicate glass is barely soluble in alkaline solution and FAU zeolite is susceptible to the solution composition. The effect of the composition, aging process and hydrothermal condition were investigated. And, we discuss the relationship between the elution of glass and zeolite synthesis.

2. Experimental

2.1 Glass sample preparation

In this study, a commercial aluminoborosilicate glass was used as a starting material. Glass sample was treated with ball milling for a few hours until the particle size was approximately 8 μm in median particle diameter.

The composition of aluminoborosilicate glass was SiO_2 : 63, Al_2O_3 : 18, B_2O_3 : 10, CaO : 8, MgO : 1 wt%.¹⁹⁾ Aluminoborosilicate glass had silica and aluminum as its main components. Therefore, it is suitable for a starting material of zeolites, which are crystalline aluminosilicates.

By acid treatment, we tried to remove components of the glass that were not the original components of the zeolites, as carried out in the synthesis of zeolite from blast furnace slag.¹¹⁾ The acid-treated glass was obtained as follows. 10 g of the glass powder sample was mixed with 250 mL 5 mol/L nitric acid solution (HNO_3 ; Wako Pure Chemical Industries Ltd., Japan), then stirred at 348 K for 3 h. After that, it was filtered, washed and dried at 323 K for 24 h. From inductively coupled plasma atomic emission spectrometry (ICP-AES, ICPE-9000, Shimadzu, Japan) of the acid solution, the dissolution rates of B_2O_3 , CaO and MgO were 7, 5 and 4 wt%, respectively. SiO_2 has seldom eluted into the acid solution.

2.2 Effect of Si/Al ratio and NaOH concentration on the synthesis of FAU zeolite

First, the effect of the mixing ratio of starting materials, which determine Si/Al ratio, was investigated. Sodium aluminate (NaAlO_2 ; Kanto Chemical Co., Inc., Japan) of 0.25, 0.17 and 0.10 g were added to 0.91 g of glass powder sample to create Si/Al = 1.9, 2.1 and 2.3. And, 14 mL of sodium hydroxide (NaOH) aqueous solution with a concentration of 2.0 mol/L was prepared by adding 1.1 g of NaOH (Wako Pure Chemical Industries Ltd., Japan) to 14 mL of deionized water. The mixture of sodium aluminate and NaOH aqueous solution was set into Teflon vessel of 28 mL, then stirred for 0.16 h and aged at room temperature for

96 h without stirring. Then, they were hydrothermally treated at 348 K for 96 h. After hydrothermal treatment, the products were filtered, washed and then dried in an oven at 323 K for 24 h.

The effect of the concentration of NaOH aqueous solution was also investigated. 1.0, 2.0 and 3.0 mol/L NaOH aqueous solutions were prepared. 0.91 g of glass powder sample and 0.17 g of NaAlO_2 were mixed with NaOH aqueous solutions to create Si/Al = 2.1. Then, the solutions were aged for 96 h and hydrothermally treated at 348 K for 96 h.

2.3 Effect of aging time and aging temperature on the synthesis of FAU zeolite

The effect of aging was investigated. A mixture of glass and sodium aluminate with an Si/Al ratio of 2.1, and NaOH aqueous solution with a concentration of 2.0 mol/L were prepared. The samples were aged for 0, 24, 48, 96, 144, 196 and 240 h, followed by hydrothermal treatment at 348 K for 96 h. To investigate the relationship between the elution of glass during aging and zeolite synthesis, compositions of solutions after aging were evaluated by ICP-AES.

The effect of aging temperature was also investigated. A mixture of glass and sodium aluminate with an Si/Al ratio of 2.1, and NaOH aqueous solution with a concentration of 2.0 mol/L were prepared. The samples were aged for 96 h at 298, 313 and 323 K followed by hydrothermal treatment at 348 K for 96 h.

2.4 Effect of hydrothermal treatment conditions on the synthesis of FAU zeolite

The effects of hydrothermal treatment conditions were investigated in the case of an Si/Al ratio of 2.1, NaOH concentration of 2.0 mol/L and aging time of 96 h at 298 K. Synthesis temperatures were 338, 348, 358 and 368 K, while synthesis time was 48, 96, 144, and 192 h.

2.5 Characterization of products

The products obtained by hydrothermal treatment were identified by powder X-ray diffractometry (XRD, Mini Flex II, Rigaku, Japan) with $\text{Cu K}\alpha$ radiation, operating at 30 kV and 15 mA. The XRD of the commercial FAU zeolite (HS-320, Wako Pure Chemical Industries Ltd., Japan) was measured as a standard material. The micromorphologies of the products were observed by field emission scanning electron microscopy (FE-SEM, JSM-7401F, JEOL, Japan) at an acceleration voltage of 5 kV.

Ratios of produced zeolite phases were evaluated by reference intensity ratio (RIR) method,²⁰⁾ in which diffracted X-ray intensity ratio was compared to a standard α -alumina.

The crystallinities of zeolites were determined from the X-ray intensity ratio of the product to a standard at given diffraction faces as follows: zeolite A (200), hydroxysodalite (110), zeolite P (301).¹⁷⁾

Nitrogen adsorption isotherms at 77 K were obtained by an automatic gas adsorption measure apparatus (BELSORP-miniII, BEL Japan, Inc., Japan). The samples were pretreated at 473 K for 12 h. The specific surface area of the samples was calculated by the BET (Brunauer-Emmet-Teller) method using adsorption data from $P/P_0 = 10^{-3}$ to 10^{-2} .

3. Results and discussion

3.1 Effect of Si/Al ratio and NaOH concentration on the synthesis of FAU zeolite

XRD patterns of products obtained from the mixture of glass and sodium aluminate with Si/Al = 1.9, 2.1 and 2.3 are summarized in Fig. 1. In the case of Si/Al = 1.9, zeolite A, which is

Fig. 1. XRD patterns of the products obtained by hydrothermal treatment at 348 K for 96 h, after 96 h aging, with 2.0 mol/L NaOH, when Si/Al ratio was (a) 1.9, (b) 2.1 and (c) 2.3.

Fig. 2. XRD patterns of the products obtained by hydrothermal treatment at 348 K for 96 h, after 96 h aging, with (a) 1.0, (b) 2.0 and (c) 3.0 mol/L NaOH, when Si/Al ratio was 2.1.

low silica zeolite, was generated. In the case of Si/Al = 2.1 and 2.3, FAU zeolite and zeolite P were generated simultaneously. Zeolite P is relatively high silica zeolite and easily generated from waste materials such as coal fly ash and blast furnace slag.²¹⁾ From X-ray diffractions, the production volume of FAU was highest in Si/Al = 2.1.

The effect of NaOH concentration of the solution on the synthesis of FAU zeolite was investigated. **Figure 2** shows XRD patterns of the products using 1, 2 and 3 mol/L NaOH aqueous solutions. In 1 mol/L NaOH, zeolite A and FAU zeolite were synthesized, whereas in 2 and 3 M NaOH, FAU zeolite and zeolite P were generated. Aluminoborosilicate glass did not elute sufficiently in lower NaOH concentration, therefore the Si concentration in the solution was low and resultantly zeolite A, which is low silica zeolite, was generated. In higher NaOH concentrations, Si eluted well from glass and Na^+ ion had the effect of stabilizing FAU zeolite; as a result, FAU zeolite was generated. On the other hand, zeolite P, which is a more stable phase, was also generated. In 3 mol/L NaOH, the production of zeolite P increased relative to 2 mol/L NaOH.

3.2 Effect of aging time and aging temperature on the synthesis of FAU zeolite

Figures 3(a) to 3(c) shows XRD patterns of the products obtained after aging for (a) 48, (b) 96, (c) 240 h. **Figure 4(d)** shows the XRD pattern of the commercial FAU zeolite. From XRD patterns, FAU zeolite is dominant phase of the product with 240 h

Fig. 3. XRD patterns of (a) the commercial FAU zeolite and the products obtained by hydrothermal treatment at 348 K for 96 h, after (b) 48, (c) 96 and (d) 240 h aging, with 2.0 mol/L NaOH, when Si/Al ratio was 2.1.

Fig. 4. Ratio of the product phases as a function of aging time when hydrothermally treated at 348 K for 96 h with 2.0 mol/L NaOH. Si/Al ratio was 2.1.

aging. From **Fig. 3**, the crystallinity of FAU zeolite obtained with aging time of 0 h was almost 0%. Those of aging time of 48 and 96 h was about 14% and 43%, respectively. This indicated that about half of glass phase was remained unreacted with long period of aging. Almost all of zeolite phases transformed into FAU zeolite in the case of 240 h aging.

In the synthesis of FAU zeolite, aging the solution is effective towards suppressing the development of other phases such as zeolite P.³⁾ **Figure 4** shows the ratio of each crystalline zeolite phase produced by hydrothermal treatment as a function of aging time. **Figure 4** was evaluated without consideration of non-crystalline phase, which was unreacted glass. In the previous report on the synthesis of FAU zeolite from colloidal silica, the production of FAU zeolite increased up to 12 h of aging.⁴⁾ However, in this study, the quantity of produced FAU zeolite was not so high after aging for 24 h, but it gradually increased up to aging for 96 h. And, it also increased from 96 to 240 h slightly, as shown in **Fig. 4**.

Figure 5 shows the concentrations of Si and Al in the solution after aging as a function of aging time. Si concentration in the solution, which was supplied from aluminoborosilicate glass, was almost 0 mol/L just after mixing the starting materials, and it increased with aging time. Initially, Al was abundant in the solution because NaAlO_2 , which is water-soluble, was added as a starting material. But, Al concentration in the solution decreased

Fig. 5. Si and Al concentrations in the solution after aging as a function of aging time with 2.0 mol/L NaOH. Si/Al ratio was 2.1.

with aging time. These results indicate that Si eluted from aluminoborosilicate glass and Al dissolved in the solution generated insoluble aluminosilicate gel, and, as a result, Al concentration in the solution decreased. The solid phases aged for 0 to 240 h were non-crystalline, which means no crystalline phases were obtained. This indicates that insoluble aluminosilicate was of non-crystalline phase. According to the previous study on the synthesis of FAU zeolite from pure reagent,³⁾ by aging the solution for long hours, Si and Al reacted to generate aluminosilicate gel. The production of aluminosilicate gel increased with aging time and it causes preferential growth of FAU zeolite. In the synthesis of FAU zeolite from aluminoborosilicate glass, because aluminoborosilicate glass was hardly soluble, Si eluted into the alkaline aqueous solution very slightly during aging. And, it reacted with Al dissolved in the solution previously, to generate aluminosilicate gel. As a result, the production of FAU zeolite increased in the following hydrothermal treatment.

Figures 6(a) to 6(c) show SEM images of the products obtained after aging for 48, 96 and 240 h, followed by hydrothermal treatment at 348 K for 96 h. The crystals of the products appeared as octahedral-like crystals, which are typical in FAU zeolite.³⁾ Crystalline particles of FAU zeolite became smaller with aging time, which is consistent with previous reports. The synthesized FAU zeolite crystal was 5 to 6 μm in size in the case of 96 h aging, and 2 to 3 μm in the case of 240 h aging. These results indicate that the size of crystal particle became smaller with aging time, as reported in the previous studies.^{3),22)}

Figure 7 shows XRD patterns of the products obtained after aging for 96 h at 398, 413 and 423 K. When the aging temperature rose with the same hydrothermal treatment, the production volume of zeolite P increased. This result indicated that the dissolution amount of Si increased substantially during aging at higher temperature, therefore the solution became Si-rich. This possibly resulted in alternation in the kind of the predominant zeolite phase.

3.3 Effect of hydrothermal treatment conditions on the synthesis of FAU zeolite

Then, we investigated the effect of the time of the hydrothermal treatment at 348 K. Figure 8 shows the ratio of each produced zeolite phase as a function of synthesis time. Figure 8 was evaluated without consideration of non-crystalline phase. With only aging and without hydrothermal treatment, the product was of non-crystalline phase. By hydrothermal treatment for 48 h, FAU zeolite was generated. The diffraction peak intensity was

Fig. 6. SEM images of the products obtained by hydrothermal treatment at 348 K for 96 h with 2.0 mol/L NaOH, after aging for (a)48, (b)96 and (c)240 h. Si/Al ratio was 2.1.

Fig. 7. XRD patterns of the products obtained by hydrothermal treatment at 348 K for 96 h, after aged at (a)298, (b)313 and (c)323 K for 96 h, with 2.0 mol/L NaOH, when Si/Al ratio was 2.1.

relatively weak; it was estimated that the production volume of FAU zeolite was small and a lot of non-crystalline phase remained. After hydrothermal treatment of 96 h, zeolite P was generated in addition to FAU zeolite. This is because parts of FAU zeolite transformed into zeolite P, which is a more stable

Fig. 8. Ratio of the product phases as a function of synthesis time when hydrothermally treated at 348 K after 96 h aging, with 2.0 mol/L NaOH. Si/Al ratio was 2.1.

Fig. 10. Ratio of the product phases as a function of synthesis temperature when hydrothermally treated for 96 h with 2.0 mol/L NaOH. Si/Al ratio was 2.1.

Fig. 9. Si and Al concentrations in the solution as functions of synthesis time when hydrothermally treated at 348 K after 96 h aging, with 2.0 mol/L NaOH. Si/Al ratio was 2.1.

Fig. 11. Adsorption/desorption isotherms for the commercial FAU zeolite and the product obtained by hydrothermal treatment at 348 K for 96 h, after aged at 298 K for 96 h, with 2.0 mol/L NaOH, when Si/Al ratio was 2.1.

phase than FAU zeolite, by hydrothermally treating for a long time period. This result agreed with previous reports.⁷⁾

Figure 9 shows Si and Al concentrations in the solution evaluated by ICP-AES analysis. Just after starting hydrothermal treatment, Si concentration in the solution increased significantly. This indicates that the elution of Si was accelerated by heating the solution. Meanwhile, Al concentration in the solution decreased substantially just after starting hydrothermal treatment. This is because Al in the solution was used for generating aluminosilicate species and zeolites. Si concentration in the solution increased with treatment time, despite parts of Si in the solution being consumed for the formation of non-crystalline aluminosilicate species and zeolites. This means that the elution of Si was accelerated dramatically by heating the solution. The produced aluminosilicate was also aged during hydrothermal treatment. As a result, the production of FAU zeolite increased slightly during hydrothermal treatment.

Figure 10 shows the ratio of each produced zeolite phase as a function of synthesis temperature. Figure 10 was evaluated without consideration of non-crystalline phase. When treatment temperature rose, the production of zeolite P increased and that of FAU zeolite decreased. These results indicate that at higher temperature zeolite P, which is a more stable phase, was generated, therefore, to suppress the synthesis of zeolite P, the lowest possible temperature that can promote the FAU zeolite synthesis reaction is desired.

Table 1. Specific Surface Areas of the commercial FAU zeolite and the product obtained by hydrothermal treatment at 348 K for 96 h, after aged at 298 K for 96 h

Samples	Specific surface area/m ² g ⁻¹
Commercial FAU	927
The product from glass	447

3.4 Microporus structure of synthesized FAU zeolite from aluminoborosilicate glass

Figure 11 shows N₂ adsorption/desorption measurements of the commercial FAU zeolite and the product obtained by aging at 298 K for 96 h followed by hydrothermal treatment at 348 K for 96 h. The products showed the adsorption/desorption isotherms the typical Langmuir-type isotherms (type-I), which were derived from microporous structures of materials. The results of specific surface areas for the both samples are summarized in **Table 1**. The product obtained after aging for 96 h from aluminoborosilicate glass had the specific surface area of 447 m²/g. The commercial FAU zeolite had the specific surface area of 927 m²/g. The specific surface area of the product was 48% of the commercial FAU zeolite. This value was in reasonably good agreement with the crystallinity derived from the XRD peak intensity of 43%. Difference between the ratio of the specific surface area and the crystallinity from XRD was possibly due to coexistence of zeolite

P. This result indicated that FAU zeolite obtained from aluminoborosilicate glass, which constituted about half of the product, had almost the same microporous structure with the pure FAU zeolite.

4. Conclusions

FAU zeolite was successfully synthesized by aging the solution before hydrothermal treatment, however zeolite P was also generated slightly. We clarified that it is necessary to select the appropriate NaOH concentration, aging time and synthesis conditions to obtain highly pure FAU zeolite because of the difficult solubility of aluminoborosilicate glass.

With diluted NaOH solution, aluminoborosilicate glass did not elute sufficiently, therefore zeolite A, which is low silica zeolite, was generated. With increasing aging time before hydrothermal treatment, the production of synthesized FAU zeolite increased. Aluminoborosilicate glass eluted gradually, and aluminosilicate species were generated. During the aging process, the precursor increased with aging time. Different from using pure reagent as a starting material, relatively long-term aging was necessary to generate FAU zeolite.

A high hydrothermal treatment temperature and long treatment time accelerated the elution of aluminoborosilicate glass, whereas stable phase zeolite P was generated. To suppress the synthesis of zeolite P, the lowest possible temperature that can promote the FAU zeolite synthesis reaction is desired.

In this study, the framework structures of the products, such as the location of Al, Al-deficiency have not been clearly understood. These properties have relationship with the stability of zeolite materials. There are potential of future work about obtained products from aluminoborosilicate glass toward the practical use of catalysts, adsorbents and so.

In this study, FAU zeolite with the good microporous structure was successfully obtained. A longer aging period was necessary than using silica as a starting material. This result may cause cost rise. Meanwhile, the expectation to recycle waste glass from LCD-TV to a functional material, which costs to dispose now, will take economical advantage, as well as benefits to the environmental.

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