

# Synthesis and characterization of zeolite A from crushed particles of aluminoborosilicate glass used in LCD panels

Masato Tsujiguchi<sup>a,\*</sup>, Tadashi Kobashi<sup>a</sup>, Masahiko Oki<sup>a</sup>, Yasuhiko Utsumi<sup>a</sup>, Nobuaki Kakimori<sup>a</sup>, Atsushi Nakahira<sup>b</sup>

<sup>a</sup> CS and Environmental Research and Development Center, Sharp Corporation, Sakai-city, Osaka 590-8522, Japan

<sup>b</sup> Department of Material Science, Osaka Prefecture University, Sakai-city, Osaka 599-8531, Japan

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## ABSTRACT

We tried to synthesize zeolite from the sand-like particles of crushed LCD panel glass collected from discarded electronics devices. In the previous study, zeolite A was synthesized using fine glass particles of  $<10\ \mu\text{m}$ . Acid treatment was found effective toward synthesizing single phase zeolite A. Using sand-like coarse glass particles, of which the internal-core consists of glass and the surficial shell transforms into zeolite, we investigated the effect of acid-treatment by evaluating the surface of the coarse glass particles. Under acid-treatment, components other than Si eluted from the glass. The elution amounts were several percent of the total glass mass. After acid-treatment, the surface of the glass particle was discovered to be covered in a thin layer of poor components other than Si and a relatively rich quantity of Si, by scanning electron microscopy and energy dispersive spectrum analysis. The synthesized zeolite A increased the longer the acid-treatment time, which suggest the thin layer increased. When the concentration of the acid solution decreased, glass components other than Si dissolved well, and the synthesized zeolite A increased as a result. This indicates that the Si-rich layer is necessary for preferential synthesis of zeolite A from crushed particles of aluminoborosilicate glass.

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## 1. Introduction

Zeolite is a crystalline microporous aluminosilicate material with a uniform pore size of  $<2\ \text{nm}$  and chemically, mechanically, and thermally stable. Zeolite is applied as catalysts, adsorbents, gas separation membranes, detergent builders and so on because of its excellent adsorptive capacity, gas separation property, and ion-exchange capacity caused by its unique microporous structure. Zeolite has a lot of species and zeolite A ( $\{\text{Na}_{12}[\text{Al}_{12}\text{Si}_{12}\text{O}_{48}]\cdot 27\text{H}_2\text{O}\}_8$ ) has the highest concentration of Al

among these species [1]. It is hydrophilic and has the highest cation exchange capacity among zeolite species; therefore, it is used as a water purification material and a soil conditioner. It is expected to be an environmental cleanup material.

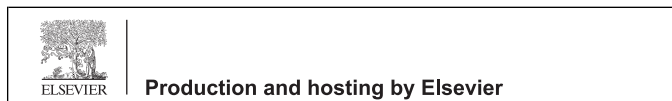
Zeolites have a disadvantage in that they are quite difficult to synthesize in bulk by conventional techniques because synthetic zeolites are powdered and seldom sinterable. Kuperman et al. [2] and Shimizu et al. [3] have reported that, by synthesizing a lot of zeolite crystalline particles on a ceramics substrate, zeolite can be generated in bulk. However, synthesizing the zeolite in bulk by modified crystal growth methods has some problems such as a long reaction time, a number of large size voids and defects, and considerable non-crystalline phases. So development of a new technique to generate zeolite in bulk is desired.

Zeolite is usually synthesized from silica, alumina, mineralizer (alkali metal hydroxide) and water. Recently, many studies have been carried out about the synthesis of zeolites from waste materials containing silica or alumina [4–7]. Murayama et al. [4,5] synthesized zeolite from coal fly ash and reported that the reaction occurred at the interface of the fly ash and the solution, and that the zeolite generated an egg-like shell to cover the fly ash particle. However, they did not refer to the synthesis of zeolite A, which is widely used in industry. Murakami et al. [6] synthesized zeolite A from blast furnace slag and reported that it was necessary to adjust components of starting materials in order to synthesize zeolite A.

\* Corresponding author at: CS and Environmental Research and Development Center, Sharp Corporation, 1, Takumi-cho, Sakai-ku, Sakai-city, Osaka 590-8522, Japan. Tel.: +81 72 282 1185; fax: +81 72 282 4578.

E-mail addresses: [tsujiguchi.masato@sharp.co.jp](mailto:tsujiguchi.masato@sharp.co.jp), [dv105009@edu.osakafu-u.ac.jp](mailto:dv105009@edu.osakafu-u.ac.jp) (M. Tsujiguchi).

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LCD panels are becoming widely used in televisions, personal computers, smartphones, tablets and digital cameras and so on because they are thin, energy-saving and lightweight. In 2011, global TV demand was about 2000 million, and more than half of that was LCD TVs. Recently, people have shown greater concern for environmental problems; therefore, it is required to make efficient use of materials from wasted LCD TVs, given that the volume of discarded LCD TVs is going to increase in the near future [8,9]. The main component of an LCD panel is the glass substrate, so the recycling of the aluminoborosilicate glass used in the glass substrate is an important issue.

Aluminoborosilicate glass mainly consists of silica and alumina. So, it is suitable as the starting material of zeolite. And, we can change the particle size of the aluminoborosilicate glass by adjusting the crushing size. We expected that, by adjusting the particle size of the aluminoborosilicate glass and synthesizing zeolite on the surface of the glass particle-like core-shell structure, we can obtain a zeolite of desired size in bulk. In this study, we tried to synthesize zeolite A, which is widely used in industry, using aluminoborosilicate glass of a few hundred micrometers in size. We tried to synthesize zeolite A covering the glass particle to obtain zeolite A in bulk. Especially, we investigated the effect of the glass components in the particle surface, by acid-treatment before hydrothermal treatment.

## 2. Experimental

### 2.1. Preparation of glass particle

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 300  $\mu\text{m}$  in median particle diameter.

The components of aluminoborosilicate glass were,  $\text{SiO}_2$ : 63,  $\text{Al}_2\text{O}_3$ : 18,  $\text{B}_2\text{O}_3$ : 10,  $\text{CaO}$ : 8,  $\text{MgO}$ : 1 wt% [10]. Aluminoborosilicate glass had silica and aluminum as its main components. So, it is suitable for a starting material of zeolite, which is crystalline aluminosilicate.

### 2.2. Acid-treatment before hydrothermal treatment

To investigate the effect of surface conditions, we prepared glass samples of various surface components by acid-treatment. By acid-treatment, we could remove components in the glass that are not original components of zeolite A.

The acid-treated glass was obtained as follows. Ten grams of the glass sample was mixed with 0.25 mL of acid solution, and stirred. The acid concentration and the treatment time were varied as described below. After that, the solution was filtered and dried at 323 K for 24 h.

At first, to evaluate the effect of treatment time, treatment using 5 mol/L nitric acid ( $\text{HNO}_3$ ; Wako Pure Chemical Industries Ltd., Japan) was varied to 0, 48 and 96 h. The treatment temperature was 348 K.

Next, the acid-treatments were carried out with  $\text{HNO}_3$  at concentrations of 1, 5 and 10 mol/L for 96 h. The treatment temperature was 348 K.

### 2.3. Synthesis of zeolite A from acid-treated glass

To investigate the relationship between acid-treatment and zeolite synthesis, we hydrothermally treated the acid-treated glass and characterized the products. Sodium aluminate ( $\text{NaAlO}_2$ ; Kanto Chemical Co., Inc., Japan) of 1.29 g was added to 0.91 g of glass powder sample for  $\text{Si}/\text{Al}=0.75$ . And, 14 mL of sodium hydroxide

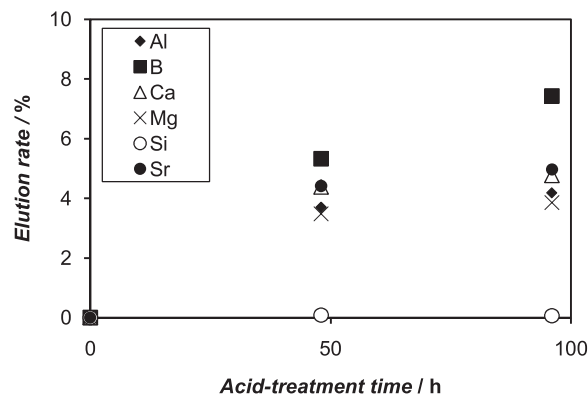


Fig. 1. Relation between acid-treatment time and elution rates of glass components.

( $\text{NaOH}$ , Wako Pure Chemical Industries Ltd., Japan) aqueous solution of a concentration of 0.5 mol/L was prepared by adding 1.1 g of  $\text{NaOH}$  to 14 mL of deionized water. They were set into a Teflon vessel of 28 mL, and stirred for 0.16 h. Then, they were hydrothermally treated at 368 K for 24 h. After hydrothermal treatment, the products were filtered, washed and then dried in oven at 323 K for 24 h.

We also hydrothermally treated the un-acid-treated glass following the same process as mentioned above, and characterized the products.

### 2.4. Characterization of products

The products obtained by hydrothermal treatment were identified by powder X-ray diffractometry (XRD, Mini Flex II, Rigaku, Japan) with  $\text{CuK}\alpha$  radiation, operating at 30 kV and 15 mA. 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. The cross-section of the glass particle was observed by polishing the particle with an argon polisher.

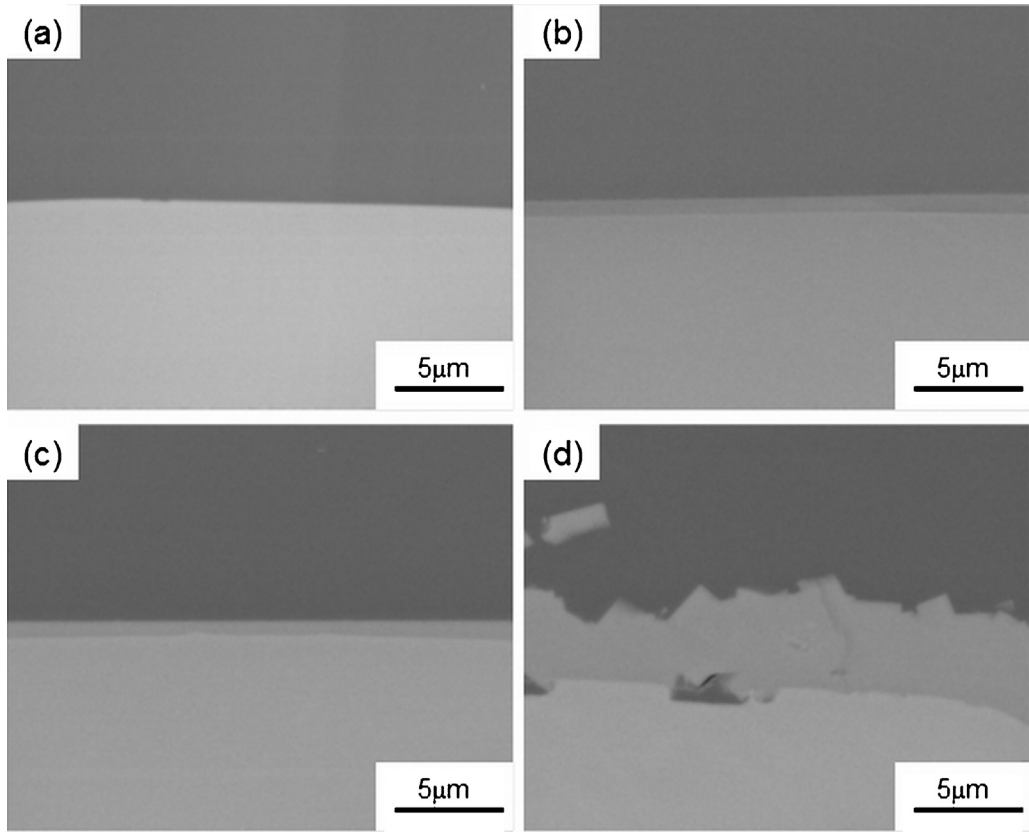
Cation exchange capacities (CEC) were evaluated as follows. At first, 1.0 g of the sample was saturated with  $\text{NH}_4^+$  ion by five sequential washings with 0.050 mL of 1 M  $\text{NH}_4\text{Cl}$  in a centrifuging tube. Then, by measuring the sample with a centrifuging tube by weight, the quantity of  $\text{NH}_4\text{Cl}$  remaining in the centrifuging tube was evaluated. Then, it was treated with five sequential extractions with 0.050 mL of 1 mol/L  $\text{KNO}_3$ . And, we gathered all supernatant solution and determined  $\text{NH}_4^+$  ion by ion chromatography (IC-2010, Touso, Japan). Then, we deducted the  $\text{NH}_4\text{Cl}$  remaining in the tube before  $\text{KNO}_3$  treatment and evaluated the CEC [11].

## 3. Results and discussion

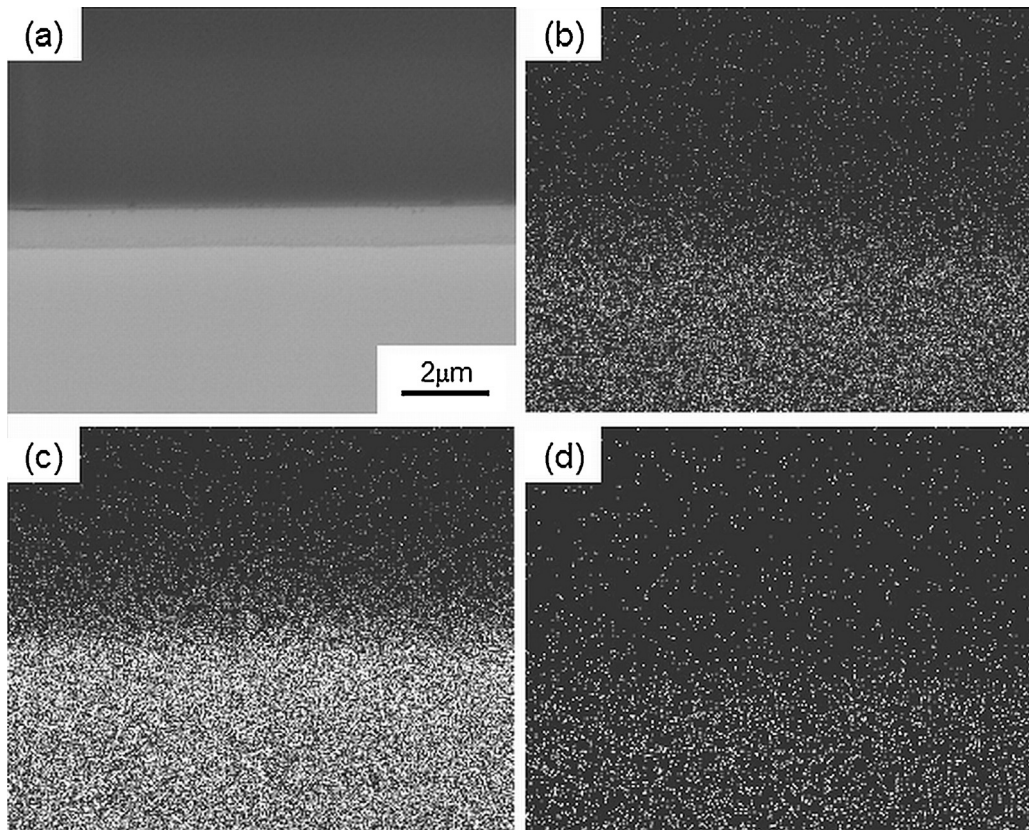
### 3.1. The effect of acid-treatment time on glass component dissolution and zeolite synthesis

Fig. 1 shows the relationship between acid-treatment time and dissolution amounts of the glass components. By acid-treatment, Al, Ca, B and Mg dissolved in the acid solution, and dissolution amounts increased with increasing time. The dissolution rates of these glass components were very much less. This indicates that only the surface layer of the glass particle was dissolved by acid-treatment. Si of the glass was seldom dissolved in the acid solution.

Fig. 2 shows SEM images of the cross-sections of the acid-treated glass particles. Fig. 2(a) shows as crushed glass, Fig. 2(b) shows the glass that was acid-treated for 48 h and Fig. 2(c) shows the glass that was acid-treated for 96 h. Fig. 2(d) shows the cross-section of



**Fig. 2.** SEM images of the cross-section on the surface of the glass particle: (a) as crushed glass, (b) glass acid-treated for 48 h, (c) glass acid-treated for 96 h and (d) hydrothermally treated glass after acid-treated for 96 h.



**Fig. 3.** Cross-sectional EDX mapping of glass acid-treated for 96 h at the surface of the glass particle. (a) SEM, (b) Al, (c) Si and (d) Ca.

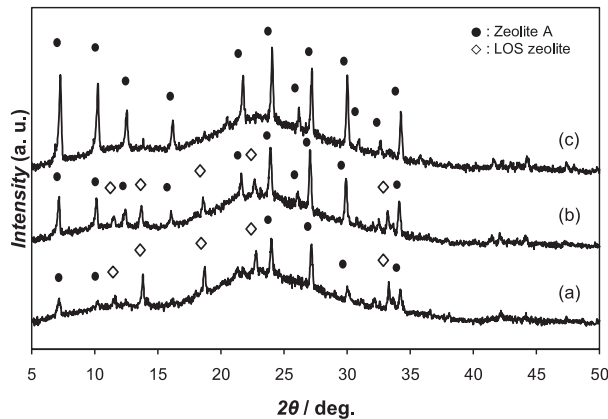


Fig. 4. XRD patterns of the products from glass acid-treated for (a) 0 h, (b) 48 h and (c) 96 h.

zeolite synthesized from the glass acid-treated for 96 h. When the glass was acid-treated, a thin layer was generated on the surface of the glass particle. The thickness of the layer did not depend on acid-treatment time. Fig. 3 shows energy dispersive X-ray (EDX) analysis mapping of the cross-section of the surface of the glass particle that was acid-treated for 96 h. As shown in the mapping, Al and Ca were poor in the surface thin layer, and Si was equal to the as-crushed glass. This result indicates that the glass components such as Al and Ca eluted preferentially by acid-treatment, and, as a result, the thin layer of poor Al and Ca was generated. In addition to these components, B and Mg were possibly poor in the surface thin layer from ICP-AES analysis.

Fig. 4 shows XRD patterns of the products from the glass samples that were un-acid-treated and acid-treated for 48 and 96 h. In the case of un-acid-treated glass, the product consisted of zeolite A,

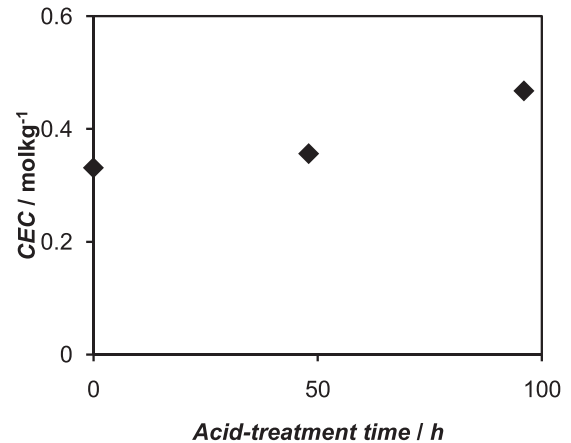


Fig. 6. Cation exchange capacities of the products as a function of the acid-treatment time of the starting glass particles.

hydroxysodalite and LOS zeolite. Furthermore, a broad peak around  $2\theta = 25^\circ$  is observed, suggesting remnants of the glass phase. With increasing acid-treatment time, the diffraction peak's intensities of hydroxysodalite and LOS zeolite became lower, and those of zeolite A became higher. This indicates that zeolite A was more easily generated with a long acid-treatment time.

Fig. 5 shows SEM micrographs of the products of various acid-treatment times. Cube-like crystals and hexagonal-disk cluster crystals were observed in the product from un-acid-treated glass. The cube-like crystals were zeolite A and hexagonal-disk cluster was presumably LOS zeolite [12]. With increasing acid-treatment time, cube-like crystals increased, and hexagonal-disk clusters decreased.

Fig. 6 shows the CEC of the products as a function of acid-treatment time. As for the un-acid-treated glass, zeolite A,

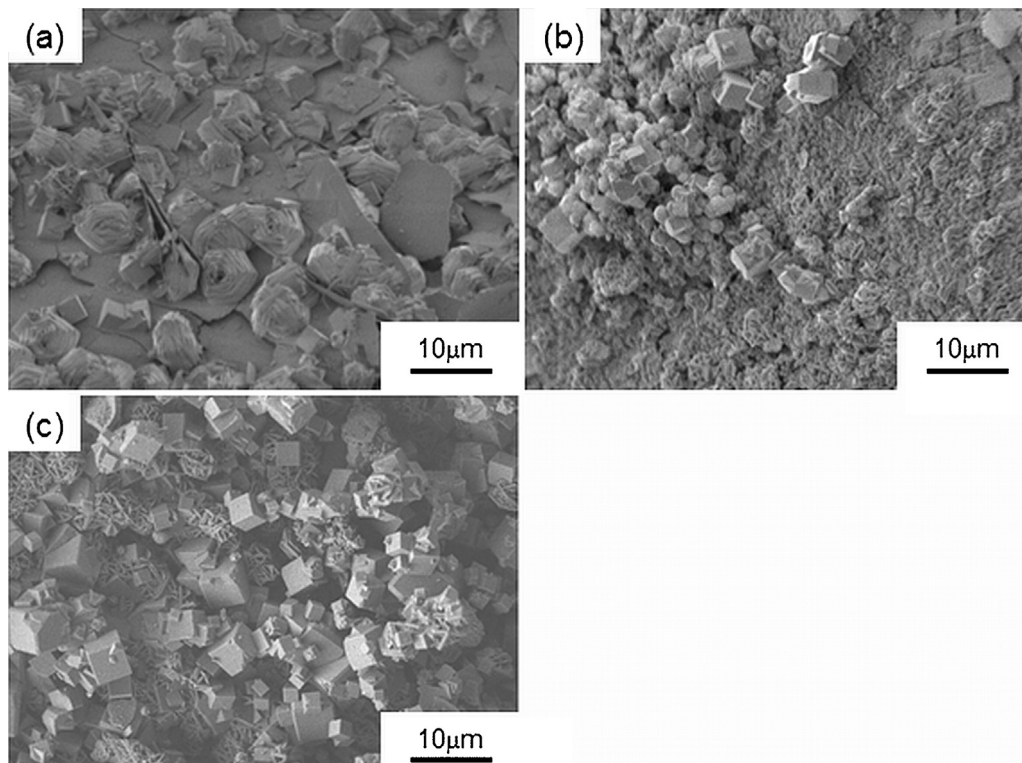


Fig. 5. SEM images of the products from glass acid-treated for (a) 0 h, (b) 48 h and (c) 96 h at the particle surface.

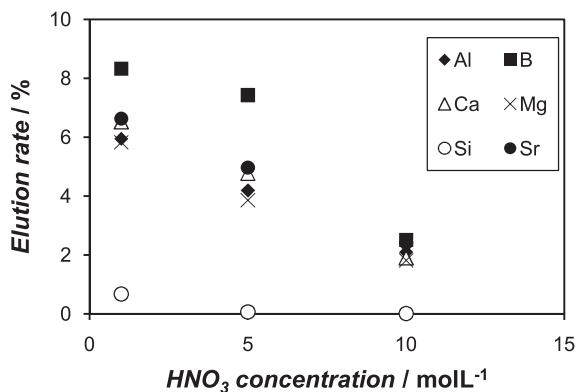


Fig. 7. Relation between concentration of HNO<sub>3</sub> and elution rates of glass components.

hydroxysodalite and LOS zeolite were synthesized. Zeolite A had the highest CEC among zeolites of 7 mol/kg [1]. Whereas the pore size of LOS zeolite is 0.256 nm [13,14], and cation mobility was low, it seldom attributed to the CEC value. This indicates that the CEC of the products was influenced by the production of zeolite A. From XRD analysis and SEM observation, when acid-treatment was carried out, the production of zeolite A increased relative to un-acid-treated glass. Thin layer of the surface grew when acid-treatment time was increased from 48 to 96 h, the crystallinity of zeolite A increased. This made CEC value increase.

### 3.2. The effect of concentration of acid-solution

Fig. 7 shows the relationship between the concentration of nitric acid solution and dissolution amounts of the glass components. By acid-treatment, Al, Ca, B and Mg dissolved in the acid solution. Dissolution amounts decreased alongside increasing concentrations. Moreover, Si dissolved in the case of dilute acid solution of 1 mol/L, which was different from the concentrated solution. However, the dissolution rate of Si was very small relative to other components. The dissolution rates of the glass components other than Si were about a few percent. In the dilute acid solution, glass components other than Si well dissolved. The elution rate decreased as the concentration of the acid solution increased.

Fig. 8 shows XRD patterns of the products from the glasses that were acid-treated with 1, 5 and 10 mol/L nitric acid solutions. In the case of using 1 mol/L nitric acid, the product consisted of zeolite A. A broad peak around  $2\theta = 25^\circ$  was observed, suggesting remnants of

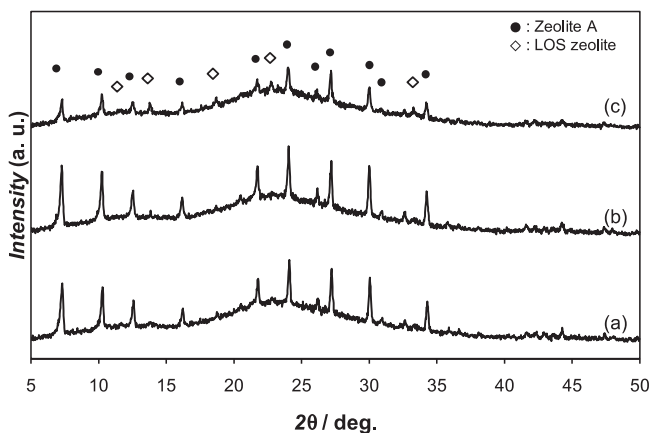


Fig. 8. XRD patterns of the products from glass acid-treated with HNO<sub>3</sub> of (a) 1 mol/L, (b) 5 mol/L and (c) 10 mol/L at 348 K for 96 h.

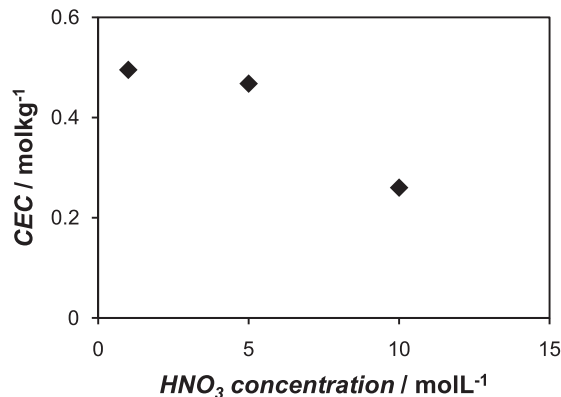


Fig. 9. Cation exchange capacities of the products as a function of the acid concentration used in the acid-treatment before hydrothermal treatment.

the glass phase. With increasing concentrations of nitric acid, the diffraction peak intensities of zeolite A became lower. This indicates that zeolite A was more easily generated with a diluted nitric acid. In the case of the dilute nitric acid solution, the surface of glass particle was well eluted, and an Si-rich layer formed. As for concentrated acid solutions, a certain amount of components other than Si, that is, Al, Ca, B and Mg eluted, whereas Si did not elute from the glass. An Si-rich layer was generated with a concentrated nitric acid of 5 mol/L. When increased to 10 mol/L, the elution rate of all components reduced relative to the case of 5 mol/L, and its crystallinity became lower.

Fig. 9 shows the CEC of the products as a function of the concentration of the acid solution. In the cases of using glass that were acid-treated with nitric acid solutions of 1, 5 and 10 mol/L, zeolite A, which has the highest CEC among zeolites, was synthesized. This indicates that the CEC of the products was determined by the production of zeolite A. From XRD analysis and SEM observation, when the concentration of nitric acid increased, the production of zeolite A decreased. As mentioned above, it is due to the decrease in the dissolution amounts of the glass components with an increase in the concentration of nitric acid, and a little thin layer was generated on the glass surface, so the synthesis of zeolite A did not proceed. Whereas, by decreasing acid concentration, a thin layer grew on the surface, the crystallinity of zeolite A increased, which made the CEC value increase.

The CEC value was positively correlated with the dissolution amounts of glass components in acid-treatment for the aforementioned reason.

## 4. Conclusions

A glass-zeolite material of a core-shell structure could be produced from aluminoborosilicate glass by hydrothermal treatment followed by acid-treatment. The material internal-core consisted of aluminoborosilicate glass and the surficial-shell consisted of zeolite A.

Without acid-treatment, zeolite A and LOS-type zeolite were synthesized by hydrothermal treatment at 368 K for 24 h, suggesting that glass components other than Si, e.g. Ca and Mg, were closely related to the generation of LOS-type zeolite. By acid-treatment using 5 mol/L nitric acid at 348 K for 96 h, glass components other than Si eluted from the glass and a thin layer that was relatively rich in Si formed on the surface of the glass particle. By hydrothermal treatment after acid-treatment, this thin layer transformed into zeolite A. LOS-type zeolite did not form because Ca and Mg were removed from the glass particle surface. The CEC of the product was 0.47 mol/kg, which is equal level to natural zeolite.

By decreasing the concentration of the nitric acid solution from 10 to 1 mol/L, the elution amounts of the glass components other than Si, i.e. Al, B, Ca, Mg, increased. The product from the glass that was acid-treated with 1 mol/L nitric acid had zeolite A of high crystallinity compared to the case of 5 or 10 mol/L nitric acid. And, the CEC of the products was lower in concentrated acid and higher in diluted acid. An Si-rich layer is necessary for synthesis of zeolite A with a high CEC.

We successfully obtained sand-like zeolite in bulk without pelletizing, by covering glass particles with a thin Si-rich layer by acid-treatment before hydrothermal treatment. By adjusting the size of the crushed glass, and transforming the surficial-shell into zeolite, the desired size of zeolite material with a core-shell structure can be produced.

These results clarified the potential of aluminoborosilicate glass as a starting material of useful sand-like bulky zeolite that has high cation exchange ability. And, these results have the potential to guide problems related to waste disposal into a resolution, by suggesting a useful process that can transform worn-out material into the practical and useful material.

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