Alkali Hydrothermal Synthesis of Zeolite A Using Oxide By-products

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The alkali hydrothermal synthesis of zeolite A using oxide by-products such as blast furnace (BF) slag and aluminum dross was investigated. Na-P1 ($\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{32} \cdot 12\text{H}_2\text{O}$) was synthesized directly in NaOH aqueous solution for 86.4 ks at 373 K using BF slag, Al_2O_3 , and SiO_2 . On the other hand, zeolite A was successfully synthesized by a two-step method including an elution treatment of Al_2O_3 . Under optimal conditions, the formation ratio of zeolite A in various compounds contained in the product was 56 %. The utilization of dross residue squeezed out from the aluminum dross as a raw material to synthesis of zeolite A let this ratio increase to 60 %. The heat of water adsorption of the product synthesized by the two-step method using BF slag, SiO_2 , and aluminum dross residue was measured, and it was 184 J/g, being higher than that of commercial zeolite A.

KEY WORDS: zeolite A; hydrothermal synthesis; heat-storage materials; slag.

1. Introduction

Heat storage systems that utilize the heat generated by water adsorption of zeolite can contribute to reducing the difference between the amounts of the electric power consumption in the daytime and nighttime. These systems also contribute to the effective utilization of exhaust heat at low temperatures.¹⁾ Zeolite is hydrothermally synthesized by heating raw materials at high temperatures under high pressure for a certain period of time. In general, the raw materials used for the synthesis of zeolite consist of compounds such as Si or Al oxide (hereinafter described as a Si or Al source, respectively), which are alkali sources for alkali aqueous solutions. Zeolite A, with a composition of $\{\text{Na}_{12}[\text{Al}_{12}\text{Si}_{12}\text{O}_{48}] \cdot 27\text{H}_2\text{O}\}_8$, has a Si/Al molar ratio of 1 and contains the largest amount of Al among various zeolites. It has been reported that the amount of water vapor absorbed was approximately 30% of the total mass of zeolite A.²⁾ However, the production cost of zeolite A is high, which may prevent a practical use of zeolite A as a heat storage material.

In 2008, 78.5 million tons of pig iron were produced in Japan, resulting in 27.3 million tons of blast furnace slag (BF slag) as a by-product, of which 82% was water-quenched slag and 18% was slow-cooled slag. Most slag is re-used as raw materials for cement, roadbed, and concrete aggregate. However, the amount of BF slag produced in Japanese steel industry tends to become much higher than the total amount of slag consumption in these fields and

therefore, exploring new applications of BF slag has become increasingly important. The major components of BF slag are SiO_2 , Al_2O_3 , CaO, and MgO. Since Ca and Mg can be substituted for Na in the synthesis of zeolite A, BF slag may possibly become one of the available raw materials for the synthesis of zeolite. If BF slag can be used as a raw material for the synthesis of zeolite A, the manufacturing cost of zeolite A is much reduced. If the product synthesized by use of BF slag can be successfully applied to heat-storage materials, this development contributes to saving resources due to the effective recycle use of industrial waste. Other utilizations of zeolite include can also be used for the purification of industrial liquid waste and soil, the humidity control material for buildings, deodorants, and so on.

Many studies on the synthesis of zeolite-type materials by hydrothermal treatment using BF slag have been reported. Tae *et al.*³⁾ and Yoshikawa *et al.*⁴⁾ reported that tobermorite ($\text{Ca}_5\text{Si}_6\text{O}_{18}\text{H}_2 \cdot 4\text{H}_2\text{O}$) can be synthesized in NaOH aqueous solution. Kuwahara *et al.*⁵⁾ successfully synthesized composite materials of hydroxyapatite and zeolite X using aqueous solution of H_3PO_4 and NaOH mixture. However, they did not report on the alkali hydrothermal synthesis of zeolite A. We have previously⁶⁾ reported the synthesis of zeolite A using water-quenched BF slag. The synthesis of zeolite A was carried out using BF slag, SiO_2 , and NaAl_2O_4 , where BF slag was used to adjust the composition of the raw material. It was elucidated that the most optimum slag composition required to synthesize zeolite A was a molar ratio of Si/Al of 1, and that the content of CaO

and MgO was needed to be reduced down to 15 mass%. The hydrothermal treatment conditions adopted in the previous study were as follows: the temperature range was from 328 to 358 K, NaOH solution had a concentration of 1 M, and the ratio of the volume of NaOH solution to the total mass of slag ($V_{\text{sol}}/W_{\text{slag}}$) was 15 (mL/g). Commercial reagents were used to adjust the composition of the raw materials.

Waste glass, fly ash, and waste diatomite can be used as a Si source. Many studies^{7–11)} on the synthesis of zeolite-type materials by hydrothermal treatment using fly ash have been reported. However, the synthesized product is zeolite with high Si/Al ratio and there are only a few reports on the synthesis of zeolite A as a main product. Hollman *et al.*¹⁰⁾ and Tanaka *et al.*¹¹⁾ reported the two-step process that consisted of Si elution from fly ash and hydrothermal synthesis with NaOH.

On the other hand, aluminum dross can be used as an Al source. The so-called aluminum dross can be recovered from the refining process of aluminum and its alloys, and aluminum content in this dross is generally higher than 60%. The residue forms in the recovery process of aluminum dross (hereinafter described as dross residue), and the dust also forms. These contain high levels of Al_2O_3 and AlN. 100 000 tons per year of the aluminum dross was deposited in landfills in Japan. Furthermore, given the uses of other by-products with aluminum oxide, it is important to discuss whether Al_2O_3 , which is a poorly water-soluble oxide, can be used as a raw material for the synthesis of zeolite A.

The objectives of this study are to clarify the synthesis conditions of zeolite A using oxide by-products such as water-quenched BF slag and dross residue, and then to evaluate heat capacity of the synthesized zeolite A, taking into account its effective utilization as a heat storage material. First, the optimum synthesis conditions using BF slag, SiO_2 , and Al_2O_3 are investigated. Secondly, synthesizing condition of zeolite A using the dross residue is studied. Finally, the heat of water adsorption of several synthesized products is measured using a Tian–Calvt type calorimeter.

2. Experimental

Raw materials used in this study were water-quenched BF slag, dross residue, amorphous SiO_2 with 99.9% purity (Kanto Chem. Ltd.), first-grade Al_2O_3 (Wako Pure Chem. Ind. Ltd.), and first-grade NaAlO_2 (Wako Pure Chem. Ind. Ltd.). BF slag and the dross residue were supplied from plants of a respective industry in Japan. Their compositions are listed in **Tables 1** and **2**, respectively. BF slag was grounded to a powder with a size less than 30 μm in an agate mortar.

Zeolite A was synthesized in NaOH aqueous solution using a ball-milling-type reaction vessel with a volume of 60 mL, in a heater.⁶⁾ The composition of the raw materials was adjusted so that the molar ratio of Si/Al was 1.0, and the content of CaO and MgO was 15 mass%. In this study, the direct and two-step synthesis methods were investigated. In the direct synthesis method, 1.0 g of raw material powders, a number of 240 SiC balls with a diameter of 5 mm, and 15 mL of NaOH aqueous solution were put into

Table 1. Chemical compositions of water-quenched blast furnace slag (mass%).

SiO_2	Al_2O_3	CaO	MgO	Total-Fe	FeO
33.8	14.7	42.5	6.65	0.25	0.05

Table 2. Chemical compositions of aluminum dross (mass%).

Al	AlN	Al_2O_3	MgAl_2O_4	MgO
33.94	32.11	9.14	20.27	4.54

the vessel. NaOH aqueous solution was prepared by dissolving granular NaOH powder with purity greater than 96% into distilled water. The concentration of NaOH was changed in the range from 1.0 to 3.0 mol/L. The synthesis temperature and time periods were varied in the ranges from 343 to 403 K and from 14.4 to 86.4 ks, respectively. The two-step synthesis method consists of an elution process of Al_2O_3 , followed by the synthesis of zeolite A as the second step. In the Al_2O_3 elution step, Al_2O_3 , the dross residue, a number of 240 SiC balls, and NaOH aqueous solution were put into the vessel. The elution temperature was 473 K. The concentration of NaOH was changed in the range from 1.0 to 3.0 mol/L. The elution time periods were varied in the range from 3.6 to 86.4 ks. Subsequently, BF slag and amorphous SiO_2 powders were added to the vessel, and the synthesizing was conducted. The synthesis temperature and time periods were varied in the range from 363 to 413 K and from 3.6 to 43.2 ks, respectively. In both the aluminum elution and synthesizing steps, the rotating velocity of the autoclave vessel was 75 rpm.

After the synthesis reaction was terminated, the synthesized products were removed from the vessel. After filtering and washing these products by distilled water, they were dried at the synthesis temperature. Then, the products were analyzed for phase identification of compounds by X-ray diffraction. The ratio of identified phases in the product was determined by the calibration curve method using MgO as the standard reagent.

The heat of water adsorption was measured using a Tian–Calvt type twin calorimeter.^{12,13)} **Figure 1** shows the schematic drawing of the calorimeter made in this study. Two reaction cells, *i.e.*, the working and reference cells, were set up in a copper block held at a constant temperature. In each of these twin units, the difference between the temperature in the reaction cell and the constant temperature in the block was detected using a 96-couple K-type thermopile. The synthesized product was granulated with a diameter of approximately 3 mm by the addition of colloidal silica. The granulated product with a weight of 0.3 g was dried at 673 K for 3.6 ks under vacuum of 10^{-1} Pa, followed by cooling to room temperature. Distilled water with a 1.0 mL was poured into the cells. After the temperature of the copper block was stabilized at room temperature, the granulated product was dropped into the reaction cell. The enthalpy change accompanied with the reaction of the product with distilled water was defined as the heat of water ad-

Fig. 1. The schematic diagram of twin calorimeter assembly.

sorption. The calorimeter was calibrated using the measured heat in dilution of HCl into distilled water.

3. Results

3.1. Synthesis of Zeolite A Using Al_2O_3 as an Al Source

Figure 2 shows the XRD patterns of the products obtained by the direct synthesis of zeolite A using BF slag, SiO_2 , and Al source from a) NaAlO_2 and b) Al_2O_3 . The alkali hydrothermal treatment was carried out at 373 K for 86.4 ks in 1 mol/L NaOH solution. Zeolite A was formed using NaAlO_2 , though small amounts of tobermorite and hydrogarnet ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot (3-x)\text{SiO}_2 \cdot 2x\text{H}_2\text{O}$ ($x=0-3$)) were also formed. However, when Al_2O_3 was used as Al source, Na-P1 ($\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{32} \cdot 12\text{H}_2\text{O}$) with a 5/3 in Si/Al ratio was formed instead of zeolite A, and much of the Al_2O_3 powder remained. The higher ratio of Si/Al in the solution is attributed to the poor elution ability of Al_2O_3 . The water adsorption property of Na-P1 is less than that of zeolite A, since only a dozen H_2O molecules can be adsorbed to Na-P1, whereas 27 water molecules can be adsorbed to zeolite A.

Figure 3 shows XRD patterns of the products obtained by the two-step synthesis of zeolite A, of which conditions were an elution treatment at 373 K for 14.4 ks and the hydrothermal treatment at 473 K for 86.4 ks. The concentration of NaOH in the solution was varied in the range from 1 to 5 mol/L. The formation of zeolite A was detected under all conditions, though small amounts of tobermorite, hydrogarnet, and sodalite ($\text{Na}_8(\text{AlSiO}_4)_6 2\text{X} \cdot n\text{H}_2\text{O}$, $\text{X} = 1/2 \text{CO}_3^{2-}$, $1/2 \text{SO}_4^{2-}$, Cl^- , OH^- or NO_3^-) were also identified. However, the X-ray peak intensity of zeolite A synthesized using 1 M NaOH solution was considerably lower than that synthesized under other conditions. Furthermore, the amorphous phase was detected. As shown in Fig. 4, the ratio of zeolite A in the product increases with increasing the concentration of NaOH and its peak value is observed at 3 mol/L of NaOH concentration, followed by a reduction of its value with a further increase of NaOH concentration higher than 3 mol/L. It should be noted that Al_2O_3 was not identified for all NaOH concentrations, suggesting that most of the Al contained in Al_2O_3 was eluted during elution treatment in the first step.

Figure 5 shows the changes in the concentration of Al ions released from Al_2O_3 and the volume ratio of zeolite A in the product according to the Al elution time. The product was synthesized at 373 K for 14.4 ks, after elution treatment for various elution time periods at 473 K in 3 mol/L NaOH

Fig. 2. XRD patterns of products obtained by hydrothermal treatment in use of (a) NaAlO_2 and (b) Al_2O_3 as Al source.

Fig. 3. XRD patterns of products obtained by hydrothermal treatment at 373 K for 14.4 ks after Al elution treatment at 473 K for 86.4 ks in (a) 1 mol/L, (b) 3 mol/L and (c) 5 mol/L NaOH solutions.

Fig. 4. The effect of NaOH concentration on the volume ratio of zeolite A in products obtained by hydrothermal treatment at 373 K for 14.4 ks after Al elution treatment at 473 K for 86.4 ks.

solution. The dashed line represents the concentration of Al ions when all the Al_2O_3 added in the vessel dissolves in the solution. Al elution from Al_2O_3 begins after a short incubation time (less than 10 ks) and is complete within 18.0 ks. No zeolite A formed at the elution time of 7.2 ks, and the product only contained Al_2O_3 and an amorphous phase.

Fig. 5. Changes in Al ion concentration released from Al₂O₃ by Al elution treatment and the ratio of zeolite A in product with Al elution time. Synthesis and Al elution treatments were conducted at 373 K for 14.4 ks and at 473 K in 3 mol/L NaOH solution, respectively.

The formation of zeolite A was first identified after the elution time of 10.8 ks, when the concentration of Al ion was 340 ppm. A further increase in the elution time leads to an increase in the ratio of zeolite A up to 56%. Consequently, synthesis of zeolite A necessitates elution of Al ion, and the amount of this product increases with the increase of eluted Al ion concentration.

Figure 6 shows the effect of the time in synthesis treatment on the ratio of zeolite A in the product, where the elution treatment was conducted at 473 K for 14.4 ks. Other synthesis conditions were identical to those shown in Fig. 5. Zeolite A formed after 7.2 ks, and the ratio of zeolite A shows a peak value for 14.4 ks. The further extension in the synthesis time decreases this ratio. The crystal structures of metastable phases such as zeolite A may be change to the stable form in such an extended heating time.¹⁴⁾ It can be concluded from this result that the optimum time for the synthesis of zeolite A is 14.4 ks for the case of the temperature of 373 K and 3 mol/L NaOH solution. **Figure 7** shows changes in the product ratio of crystalline phases with the synthesis time under elution treatment at 473 K for 14.4 ks. Zeolite A, sodalite, and tobermorite+hydrogarnet were considered as the crystalline phases in the product, though the ratio of zeolite A in Fig. 6 was calculated directly by the calibration curve method in XRD measurements. The product ratio of the crystalline phases was calculated from the given peak of each phase; zeolite A: $2\theta=27.08$, sodalite: $2\theta=24.23$, and tobermorite+hydrogarnet: $2\theta=29.07$. The product ratio of zeolite A decreases continuously with an extension of the synthesis time. The ratios of sodalite and tobermorite+hydrogarnet increase with increasing the synthesis time up to 21.6 ks. The ratio of sodalite increases in longer synthesis times, whereas the ratio of tobermorite+hydrogarnet remains constant.

Figure 8 shows the effect of the synthesis time periods on the product ratio of the crystalline phases under both synthesis solutions of 1 mol/L and 5 mol/L NaOH. The elution time was 86.4 ks, and the temperatures in the Al

Fig. 6. The change in zeolite A content in products with synthesis time in 3 mol/L NaOH solution after Al elution treatment at 473 K for 14.4 ks.

Fig. 7. The change in the ratio of product phases with synthesis time at 373 K after Al elution treatment at 473 K for 14.4 ks.

Fig. 8. The change in the ratio of product phases with synthesis time at 373 K after Al elution treatment at 473 K for 86.4 ks in (a) 1 mol/L and (b) 3 mol/L NaOH solution.

elution and synthesis treatments were 473 K and 373 K, respectively. When 1 M NaOH solution was used, tobermorite+hydrogarnet was not produced in the synthesis time of 14.4 ks. It seems that the concentration of Ca ions in the

solution was not sufficiently high for the formation of these phases. The ratio of these phases increases with an increase in the synthesis time from 14.4 to 28.8 ks. The reason may be that the concentration of Ca ions was sufficiently high for the reactions to proceed. On the other hand, when the 3 mol/L NaOH solution was used, the synthesis time has no effect on the ratio of these phases. Under these conditions, sodalite was also formed, and its ratio increases with increasing the synthesis time periods. It seems that zeolite A was transformed to sodalite as a stable phase during an extension of the synthesis time.

The effect of the synthesis temperature on the product ratio of the crystalline phases is shown in Fig. 9. The concentration of NaOH in the solution was 3 mol/L, and the time periods of elution and synthesis treatments were 14.4 ks and 7.2 ks, respectively. The product ratio of zeolite A decreases at the synthesis temperature over 383 K, whereas the product ratio of sodalite increases. On the other hand, the product ratio of tobermorite+hydrogarnet was independent of the synthesis temperature. At temperatures below 363 K, only the amorphous phase was obtained. Therefore, it is clear that the optimum temperature for the synthesis of zeolite A is a narrow range from 373 to 383 K.

Hence, it is concluded that zeolite A can be synthesized by a two-step method using BF slag, amorphous SiO₂, and Al₂O₃ powders, where the Si/Al molar ratio was 1.0, and the content of CaO and MgO was less than 15 mass%. The optimum conditions for the synthesis of zeolite A are that the concentration of NaOH in the solution is 3 mol/L, and the temperature and time of elution treatment are 473 K and 14.4 ks and those of synthesis treatment are 373–383 K and 14.4 ks, respectively.

Figure 10 shows the scanning electron micrographs of zeolite A obtained from (a) the two-step method using optimal conditions, (b) the direct method using NaAlO₂, and (c) commercial zeolite A. The synthesized zeolite A crystals obtained from the two-step method have a similar cubic shape to that of commercial zeolite A and zeolite A crystals obtained using the direct method. However, the synthesized crystals are smaller than the commercial crystals. This may be attributed to the short synthesis time and the ball-milling

Fig. 9. The effect of synthesis temperature on the ratio of product phases obtained by synthesis for 7.2 ks after Al elution treatment at 473 K for 14.4 ks in 3 mol/L NaOH solution.

type of reaction vessel that was used in the synthesis of zeolite A.

3.2. Synthesis of Zeolite A Using Al Dross Residue

The two-step synthesis of zeolite A was carried out using dross residue as an Al source. The concentration of NaOH in the solution was 3 mol/L. The temperature and time in the first and second steps were 473 K and 14.4 ks and 373 K and 7.2 ks, respectively. Figure 11 shows the XRD patterns of the product and the dross residue. The components of the dross residue were identified as Al, AlN, MgAl₂O₄, and MgO. The major compound in the product was zeolite A. Tobermorite and hydrogarnet slightly formed similarly to use of Al₂O₃ as the Al source. MgAl₂O₄ was also present after the reaction was complete, indicating that the Al source in the dross residue was not fully consumed during

Fig. 10. Scanning electron micrographs of synthesized zeolite A by (a) two-step synthesis method and (b) direct synthesis method and (c) commercial zeolite A.

Fig. 11. XRD patterns of (a) Al dross residue and (b) products obtained by two-step synthesis method using aluminum dross.

Fig. 12. The effect of synthesis time in the direct synthesis method on the ratio of zeolite A in the products obtained by direct to two-step methods. Two-step synthesis was carried out in 3 mol/L NaOH solution, and the temperature and time of Al elution and synthesis treatments were at 473 K for 14.4 ks, and at 373 K for 7.2 ks, respectively.

the synthesis treatment. In this case, the ratio of zeolite A in the product was 60%, which is slightly higher than that synthesized by the two-step method using Al_2O_3 .

Figure 12 shows the change in the volume ratio of zeolite A in the product obtained by the direct synthesis to that by the two-step one using dross residue. The two-step synthesis was carried out using 3 mol/L NaOH solution. The temperature and time of elution and synthesis treatments were 473 K for 14.4 ks and 373 K for 7.2 ks, respectively. Direct synthesis was carried out in 3 mol/L NaOH solution at 373 K. The synthesis time was varied in the range from 14.4 to 28.8 ks in both treatments. The ratio of zeolite A shows a peak value for 21.6 ks, but only 90% of the amount of zeolite A produced by the two-step synthesis was generated in direct synthesis treatment. This is because Al_2O_3 , which is 9% of the dross residue, does not dissolve in the solution for the synthesis, though Al source originated from metallic Al and AlN could be used for the synthesis. Consequently, it was found that the two-step synthesis method using dross residue increased the production of zeolite A as compared to the direct synthesis.

Figure 13 shows the scanning electron micrographs of the product obtained from the two-step synthesis of zeolite A using the dross residue. Particles of zeolite A are indicated by the white arrow. The shape of these particles is the same as that synthesized using Al_2O_3 , as shown in Fig. 10(a). The size of these is smaller than that of commercial zeolite A particles. However, part of the produced particles has same size as that of commercial one as shown in Fig. 13(a).

3.3. Heat of Water Adsorption of the Product

Figure 14 shows the relation between the heat of water adsorption of the products and the ratio of zeolite A. The products were obtained by the two-step synthesis treatment. The two-step synthesis was carried out in 3 mol/L NaOH solution, and the temperature and time of the first and second steps were 473 K and 14.4 ks and 373 K and 7.2 ks, respectively. The heat of water adsorption of the commercial

Fig. 13. Scanning electron micrographs of the product obtained by two-step hydrothermal treatment using the dross residue.

Fig. 14. Relation between heat of water adsorption of the products and ratio of zeolite A. The products were obtained by two-step synthesis.

zeolite A is $164 \text{ J} \cdot \text{g}^{-1}$. A proportional relationship between the heat of water adsorption and the ratio of zeolite A was not observed. The heat of water adsorption of all products in this study becomes higher than that predicted by the proportional relation. When zeolite A is prepared from SiO_2 and Al_2O_3 , the difference between the measured and the predicted values is small. However, a large difference is observed when BF slag is used to prepare zeolite A. The heat of adsorption of the product obtained using BF slag, amorphous SiO_2 , and the dross residue is $184 \text{ J} \cdot \text{g}^{-1}$, which is greater than the heat of adsorption of commercial zeolite A.

4. Discussion

4.1. Evaluation of By-products as Raw Materials for Zeolite A Synthesis

In this study, oxide by-products were used as raw materials for the synthesis of zeolite A. The formation ratio of zeolite A in the product depended a great deal on the character of raw materials including by-products. Therefore, the availability of by-products as the raw materials will be discussed in the following paragraph.

4.1.1. Blast Furnace Slag

The amount of BF slag or its ratio to total amount raw material powders, which can be utilized in hydrothermal treatment for synthesis of zeolite A, is very important from point of view of its recycle use. From the previous study,⁶⁾ it was found that the decrease of CaO content in raw material powders in use of BF slag was essentially needed to synthesize zeolite A. Under the optimum conditions, the addition ratio of BF slag has to be controlled less than 30% of the raw materials. The method to utilize more BF slag should be developed.

4.1.2. Al Dross Residue as an Al Source

It is difficult to synthesize zeolite A using only the Al dross residue because SiO₂ content in the Al dross residue is very low. Therefore, in this study, the Al dross residue was used as an Al source. The surface of the dross residue particles obtained from the production of Al alloy series of #1000 is covered with an Al₂O₃ layer. The dross residue surfaces originated from Al alloy series of #5000 and #6000 alloys, which contain Mg as an alloying element, are coated with Al₂O₃, MgAl₂O₄, and MgO layers, while AlN is contained in the subsurface layer.¹⁵⁾ The dross residue used in this study contained 20 mass% of MgAl₂O₄. Therefore, this dross residue appears to be originated from the refining process of Al alloy series of #5000 and #6000. The dross residue containing Mg is unsuited for use as an Al source for the synthesis of zeolite A because MgAl₂O₄ is very stable and does not dissolve during the elution treatment at 473 K for 86.4 ks. On the other hand, residues that do not contain Mg, such as #1000 alloys, are the most suitable raw materials for the synthesis of zeolite A.

4.2. Transformation of Zeolite A to a Stable Phase

In this study, the percentage of sodalite presented as a stable phase increased with increasing the synthesis time, temperature, and the NaOH concentration. As previously described, the major product obtained by the direct synthesis of zeolite A under high ratio of solution to powder material was sodalite.⁶⁾ Many researchers have investigated the transformation of zeolite A to sodalite. Subotic *et al.*¹⁶⁾ reported that zeolite A transformed to zeolite P in 1 mol/L NaOH solution and to hydroxysodalite under high concentrations of NaOH. Walton *et al.*¹⁷⁾ reported that higher temperatures and concentrations of NaOH resulted in the transformation of zeolite A to hydroxysodalite in a shorter period of time. At higher temperatures, the direct formation of sodalite, but not zeolite A, was reported by Breuer *et al.*¹⁸⁾ The results presented in this study are in agreement with those reported previously.

4.3. Relation between the Heat of Water Adsorption and the Production Ratio of Zeolite A

The reason why the heat of water adsorption of zeolite A produced by the two-step synthesis is larger than that predicted by the proportional relation described above will be discussed. Basaldella *et al.*¹⁹⁾ reported that zeolite A particles synthesized in solutions with high Al concentration showed the cubic with beveled edges. Zeolites A particles synthesized by the two-step method shown in Figs. 10 and

13 have beveled edges. It is estimated that zeolite A with high Al content, namely low Si/Al ratio, was synthesized because the concentration of Al ions in the solution at the beginning of the synthesis treatment was high as shown in Fig. 5. On the other hand, commercial zeolite A does not have beveled edges. It means that Si/Al ratio of commercial zeolite A is high.

It is known that the Si/Al ratio in zeolite has the marked effect on the hydrophilic property of zeolite.²⁰⁾ Zeolite becomes more hydrophilic with an increase in the Al content. It is concluded that the reason why the heat of water adsorption of the product was greater than the predicted value is that the Si/Al ratio of the synthesized zeolite A is less than that of commercial zeolite A. Further, not only the formation of zeolite A but also that of tobermorite and hydrogarnet, which had a certain heat storage capacity,⁶⁾ was detected. This is also one of reasons why the products have greater heats of water adsorption. Therefore, it is concluded that products containing tobermorite and hydrogarnet can be used as heat storage materials.

5. Conclusions

The alkali hydrothermal synthesis of zeolite A using oxide by-products such as BF slag and Al dross residue was studied, and the following results were obtained:

(1) Zeolite A could be successfully synthesized using BF slag, amorphous SiO₂, and Al₂O₃ by applying a two-step synthesis method, which consists of an Al₂O₃ elution process and a synthesis process. The optimum condition for this method is that the concentration of NaOH in solution is 3 mol/L, the temperature and time of first and second steps are 473 K and 14.4 ks, 373–383 K and 14.4 ks, respectively. The ratio of zeolite A in the synthesized product was 56% under the optimum condition.

(2) The dross residue was found to be used as an Al source for the synthesis of zeolite A. Although zeolite A can be synthesized directly, the amount of zeolite A in the product increases when the two-step method is used. However, the percent yield of zeolite A was not 100% on account of the presence of CaO and MgO in the BF slag and MgAl₂O₄ in the dross residue.

(3) The heat of water adsorption of the product synthesized by the two-step method using BF slag, amorphous SiO₂, and the dross residue is greater than 180 J·g⁻¹. The obtained heat is larger than that of commercial zeolite A. The heats of water adsorption for all products prepared by the two-step synthesis are greater than the predicted values. This discrepancy is explained by difference in the Si/Al ratio in zeolite A.

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