Hydrothermal Synthesis of Zeolite A Using Blast Furnace Slag

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Alkali hydrothermal synthesis of zeolite A using blast furnace (BF) slag was investigated. The preliminary experiment was conducted in use of synthetic slag consisting of SiO₂, Al₂O₃, and CaO powders, and it was made clear that the most optimum slag compositions to synthesize zeolite A were the molar ratio of Si to Al (Si/Al) of 1 and reduction of CaO content down to 15 mass%, and that hydrothermal treating conditions were the temperature range from 328 to 358 K, NaOH solution of 1 M (=mol/L) and the ratio of the volume of NaOH solution to total mass of slag (V_{NaOH}/V_{slag}) of 15 (mL/g). It was also found that synthetic slag with such a higher content of CaO as 40% resulted in formation of tobermorite and hydrogarnet. In the experiment using BF slag, zeolite A could be successfully synthesized by optimizing both conditions of the compositions of raw material powders and hydrothermal treatment as noted above, where optimization of the compositions of raw material powders such as Si or Al content were performed by the suitable amount of addition of SiO₂ powder or NaAlO₂ powder as a source of Si and Al. The ball milling type reaction vessel containing numerous small SiC balls which was first adopted in this hydrothermal treating study was confirmed to be very effective for acceleration of synthetic reaction rate, shortening markedly the time period needed for fully synthesis of zeolite A. Temperature dependence of heat capacity of zeolite A powder synthesized in use of BF slag was measured after absorption of vapor at the ambient temperature, showing endothermic behavior with the peak at the temperature of around 473 K.

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

1. Introduction

Zeolite, which is one of the candidate materials used for heat-storage, is aluminosilicate containing the molecular size of pores in its crystal structure, and its chemical formula is expressed by \( {\text{M}}_n{[\text{Al}_{m}\text{SiO}_{2(m+n)}]} \cdot x\text{H}_2\text{O} \). A lack of a positive charge is brought about due to substitution of \( \text{Al}^{3+} \) ion for \( \text{Si}^{4+} \) ion in tetrahedron of oxygen which is component of zeolite. Exchangeable cations like Na⁺ ion exist in its mobile form in M site of the above formula for covering this lack of a positive charge, and therefore zeolite has ion exchangeability. Moreover, zeolite has functions of gas adsorption, molecular sieve and catalytic ability due to its porous crystal structure. The reaction caused by adsorption of water vapor is exothermal reaction and it is possible to store the heat in use of this reversible chemical reaction. The ratio of Al to Si has the marked effect on the hydrophilic property of zeolite and the property of surface of zeolite changes from hydrophobic into hydrophilic with the increase of Al content. Zeolite A with the composition of \( \{\text{Na}_{12}([\text{Al}_{12}\text{Si}_{12}\text{O}_{48}] \cdot 27\text{H}_2\text{O})\} \) has Si/Al molar ratio of 1 and is one kind of the zeolites containing the largest amount of Al. Exchangeable cations and water molecules exist in pores. In the case that exchangeable cation is Na⁺ ion, the pore size of zeolite A crystal is 4 Å and this zeolite is called zeolite 4A (NaA). It has been reported that adsorption of water vapor amounted to about 30% of the total mass of the zeolite. Dehydrated zeolite A possesses the high capability of heat-storage and it is possible to use as a heat-storage material for the low-grade heat source like heat waste of industrial plant. Moreover, the total amount of the hydration energy of zeolite is proportional to the water content, because the hydration enthalpy (the exothermic energy per hydration of 1 mol water vapor) is a steady value of around \(-65 \text{kJ/mol}\). Additionally, zeolite has a couple of advantages to amorphous materials regarding on water vapor-adsorption and desorption properties. The first one is that it can work under the low water vapor pressure condition differently from the amorphous materials like silicagel, and the second one is the very little degradation of adsorption property due to numerous operation cycles of adsorption and desorption. Mizota et al. have been reported that the heat-storage energy of zeolite A amounted to about 470 kJ/kg and that of zeolite A with substitution of Mg for Na dehydrated at 473 K increased to about 1 MJ/kg, of which value is equal to the energy density of the most advanced alkali cell.

Zeolite is hydrothermally synthesized by heating raw materials at the high temperature for a certain period of time under high pressure, and raw materials used in general con-
sist of compounds like the oxide of Si or Al (hereinafter called as a Si or Al source, respectively), alkali source for alkali solution and water. One of the objectives in the present study is to utilize blast furnace slag (BF slag) as both sources of Si and Al for framework structure of zeolite. The world production of pig-iron amounted to 81.5 million tons in 2002, resulting in bi-product of BF slag with the amount of 23.5 million tons. Three quarter of total amount of BF slag product was water-quenched slag and one quarter was slow-cooled slag.6) Most slag has been re-used as a material substituted for cement, a material for roadbed and a concrete aggregate. However, the amount of use of BF slag in these fields tends to be saturated in this country, and so exploitation of new utilization of BF slag becomes important.

**Table 1** shows an example of compositions of water-quenched slag, of which main components consist of SiO\(_2\), Al\(_2\)O\(_3\), CaO and MgO. On taking account of substitutability Ca and Mg for Na in zeolite A, water-quenched slag may possibly become one of the available raw materials for synthesis of zeolite. There have been many reports of the synthesis of zeolite-type materials by hydrothermal treatment in use of fly ash,7–9) but there was no report on synthesis of zeolite A in use of fly ash except the report by Holloman et al. They studied zeolite A synthesis using the solution including Si and Al ion by two step synthesis process. There has been no report on alkali hydrothermal synthesis of hydrophilic zeolite in use of BF slag. It surely contributes to save resources and the electric power through the effective recycle use of the industrial waste of BF slag, if BF slag can be utilized as a raw material for synthesis of zeolite A and it can be successfully applied to the heat-storage material.

The main purpose of this study is to clarify the synthesis conditions of zeolite A using water-quenched slag with taking into consideration of its effective utilization as a heat storage material. The synthesis conditions investigated in the present alkali hydrothermal treatment include the compositions of raw material powders, the synthesis temperature and the reaction time period, the concentration of alkali solution and the ratio of volume of solution to the weight of raw material powders. The newly devised experimental procedure adopted in this study was use of a rotating reaction vessel containing numerous small SiC balls together with raw material powders, which was expected to increase reaction rate of hydrothermal synthesis of zeolite A. It was suggested by studies on alkali hydrothermal treatment for synthesis of zeolite A using fly ash that the compositional control of raw material powders was needed to be the molar ratio Si/Al of 1.7–10) However, its ratio in the compositions of water-quenched slag is 1.95 as shown in Table 1. Consequently, three kinds of experiments for zeolite A synthesis were carried out in this study. First, three kinds of synthetic slag with SiO\(_2\)-Al\(_2\)O\(_3\)-CaO system were prepared using a respective oxide powder and the basic conditions for synthesis of zeolite A such as the optimum compositions of raw material powders or the hydrothermal treating conditions were made clear. Secondly, the experiment of zeolite A synthesis was performed using water-quenched slag containing MgO and FeO\(_2\) besides three oxides noted above. The raw material powders used in this experiment consisted of BF slag and other oxides, of which compositions were optimized for synthesis of zeolite A by additions of oxide powders for Si and Al sources based on the results obtained in the first experiment. These mixed powders were re-melted and water-quenched in advance, and then the ground powders were hydrothermally treated. The last experiment was the direct hydrothermal synthesis of zeolite A using BF slag. After the compositions of raw material powders were optimized similarly to the second experiment, hydrothermal treatment was conducted without preliminary melting of raw material powders. Finally, several synthesized products were absorbed water vapor at 298 K, and then the heat capacity changes with the temperature in these products were evaluated using a differential scanning calorimeter.

**2. Experimental**

**Table 2** shows the chemical compositions of three kinds of synthetic slag used for the first hydrothermal synthesis experiment of this study. Synthetic slag is in SiO\(_2\)-Al\(_2\)O\(_3\)-CaO ternary system, and powders of amorphous SiO\(_2\) with 99.9% purity (Kanto Chem. Ltd.), α-Al\(_2\)O\(_3\) with the first grade (Wako Pure Chem. Ind. Ltd.) and CaO with 99.9% purity (Kanto Chem. Ltd.) were used for the synthetic slags. The slag compositions were adjusted to become the Si/Al molar ratio of 1.0, and CaO content of 40, 20 and 15 mass% in slag A, B and C, respectively. CaO powder was used after burning at 1 273 K for 3.6 ks in air. Mixed powders were put into a melting pot made of platinum, and were melted by heating at the temperature of 1 943 K for 7.2 ks in the electric resistance furnace under argon gas atmosphere, followed by water quenching. All of synthetic slags were confirmed to be amorphous. The synthetic slag was grounded to powder with a size of around 3 μm in an agate mortar.

The second hydrothermal synthesis experiment was performed by using the water-quenched slag supplied from one of the steel mill works in Japan and its composition were listed in Table 1. This BF slag was grounded to powder similarly to the synthetic slag. The some amount of SiO\(_2\) and Al\(_2\)O\(_3\) powders were added into BF slag to control the Si/Al molar ratio of 1.0 and to optimize the content of CaO. All powders were mixed, and were melted, followed by water-quenching in the same conditions with the synthetic slag preparation described above. The grassy type of amor-
phous slag was also obtained. The last experiment was direct synthesis of zeolite A, which was performed without preliminary melting of mixed powders consisting of BF slag and Si or Al source powders. Powders of α-Al₂O₃ or NaAlO₂ with the first grade (Wako Pure Chem. Ind. Ltd.) and amorphous SiO₂ were used as Al and Si sources, respectively, were used for control of compositions of raw materials.

The experimental apparatus for alkali hydrothermal synthesis used in this study is shown in Fig. 1. This apparatus consists of the ball milling type reaction vessel and the heating system, and the former was designed to rotate during reaction at elevated temperatures. The autoclave consisted of the outer vessel made by stainless steel and inner one made by Teflon with a diameter of 40 mm and the volume of 60 ml. Raw material powders, NaOH solution and SiC balls were put into the inner vessel. NaOH solution was prepared by dissolution of granular NaOH powder with purity over 96% (Wako Pure Chem. Ind. Ltd.) into water, and 30 numbers of SiC balls with a diameter of 10 mm were put into a vessel, which were used to enhance synthetic reaction rate during hydrothermal treatment. In fact, it was confirmed that reaction was markedly accelerated in comparison with synthetic treatment without use of the rotating vessel containing these balls.

The volume of NaOH solution and the concentration of NaOH were changed in the ranges from 6 to 35 mL and 0.5 to 10 M, respectively. The mass of raw material powder ranged from 0.4 to 2 g including powders added to control the compositions. The synthetic temperatures were varied in the range from 328 to 473 K. Rotating velocity of the autoclave was 75 rpm. The synthetic time period at a respective temperature was varied in the range from 3.6 to 86.4 ks. After synthetic reaction was terminated, synthesized products were pulled out from the vessel. After being filtered and washed with distilled water, these products were dried at the same temperature as synthesis, and then analyzed for phase identification of compounds by X-ray diffraction.

This was carried out in use of a powder diffractometer (Philips, X’Pert) with Ni-filtered Cu Kα radiation in the 2θ ranged from 4 to 60°.

The experiment for adsorption of water vapor was conducted as follows. The synthesized products with a weight of 0.1 g were heated at 373 K for 3.6 ks in air. Then, these products on dish were put into the closed vessel containing water, where setting of synthesized products was devised not to directly contact with water, but to contact with water vapor equilibrated at 298 K. After keeping at 298 K for 21.6 ks, products were withdrawn from the vessel, and were left in air until no weight change was observed. The heat capacity change with the temperature in synthesized products absorbed water vapor was evaluated using a differential scanning calorimeter (NETZSCH, DSC 404/6/F-S). The scanning temperature ranged from 323 to 773 K and the heating rate was 10K/min.

3. Results

3.1. Synthesis of Zeolite A in Use of Synthetic Slag

Figure 2 shows XRD patterns of the products obtained by alkali hydrothermal treatment in use of three kinds of synthetic slag with CaO content of 40, 20 and 15 mass% in slag A, B, and C, respectively. The alkali hydrothermal treatment was carried out at 373 K for 86.4 ks in NaOH solution of 15 mL under a given amount of synthetic slag of 1.0 g. Formation of zeolite A was found in slag of B and C, but not A. Other kinds of compounds such as hydroxycancrinite with 3(Na₂O·Al₂O₃·2SiO₂)·0.5Na₂SiO₃·3H₂O, tobermorite with Ca₅Si₆O₁₈H₂·4H₂O and hydrogarnet with 3CaO·Al₂O₃·(3-x)SiO₂·2xH₂O(x=0–3) were also detected in slag B and C. It was found from this figure that slag C resulted in the larger amount of zeolite A synthesis compared with slag B. On the other hand, products obtained by slag A consisted of mostly tobermorite and hydrogarnet. Consequently, it can be noted that the decrease of CaO content in the compositions of synthetic slag is essentially needed for synthesis of zeolite A in alkali hydrothermal treatment. Therefore, a raw material powder of slag C was used in the following investigations.

Effects of the temperature, the NaOH concentration and the ratio of the volume of NaOH solution to the total amount of slag, \( V_{\text{sol}}/W_{\text{slag}} \) (mL/g), on formation of zeolite A in hydrothermal treatment were investigated in use of slag C, of which results were shown in Figs. 3, 4 and 5, respective-
The hydrothermal treating time period at a respective temperature was all 86.4 ks. For evaluation of the relative amount of zeolite A among various synthesized compounds, the highest peak value of a respective compound phase detected in XRD profile were all summed, and the ratio of the highest height peak value of zeolite A to this total value was evaluated. It was found from results shown in these figures that the optimum ranges of hydrothermal treating conditions for synthesis of zeolite A were the temperature range from 328 to 393 K, the range of NaOH concentration from 0.5 to 3 M NaOH and the ratio of $V_{sol}/W_{slag}$ below 37.5 mL/g. The higher temperature over the optimum range resulted in a marked reduction of zeolite A formation as seen in Fig. 3. Similarly, the maximum amount of formation of zeolite A in the products was observed at 1 M NaOH concentration and $V_{sol}/W_{slag}$ of 15 mL/g as shown in Figs. 4 and 5, respectively. Thus, hydrothermal treatment in the following all experiments was performed in these best conditions for synthesis of zeolite A, if otherwise stated. It was detected by XRD that the main synthesized products obtained by hydrothermal treatment at 473 K or in $V_{sol}/W_{slag}$ of 87.5 mL/g were sodalite with Na$_6$(AlSiO$_4$)$_6$ ·4H$_2$O together with some amounts of hydroxycancrinite, nepheline hydrate with Na$_2$O·Al$_2$O$_3$·2SiO$_2$·H$_2$O and tobermorite.

Thermal stability of zeolite A which was synthesized by the best conditions was investigated by reheating in air at various temperatures in the range from 573 to 1 073 K in a holding time period of 3.6 ks. Various phases in the compounds obtained after reheating were examined by XRD as shown in Fig. 6. It was confirmed that synthesized zeolite A was stable at the temperature until 873 K, but that it was decomposed to other products such as hydroxycancrinite at 973 K, then the whole products being transformed into nepheline with NaAlSiO$_4$ at 1 073 K.

3.2. Synthesis of Zeolite A in Use of Blast Furnace Slag

Various product phases obtained by hydrothermal treatment in use of only BF slag powder are listed in the right side column of No. 1 in Table 3. Nevertheless the hydrothermal treatment was performed under the best synthetic condition, no synthesis of zeolite A was observed, indi-
cating essential necessity of the compositional optimization of raw material powders in use of commercial BF slag. Therefore, the experiment for zeolite A synthesis in use of BF slag was carried out under the most optimum compositions of raw material powders as well as the best alkali hydrothermal treating condition. That is, the compositions of raw material powders were adjusted as to become the Si/Al ratio of 1 and CaO content of 15 mass%, and these raw material powders were re-melted, water-quenched and ground to powders. Hydrothermal treating conditions were heating at 373 K for 86.4 ks, 1 M NaOH solution of 15 mL and the amount of slag of 1.0 g. No. 2 in Table 3 shows the product phases obtained under these conditions. On quantitative evaluation of the product ratio of hydrogarnet and tobermorite, the maximum peak height of these compounds was used because it was difficult to quantify separately both compound phases in the XRD pattern as shown in Fig. 7. It was confirmed that zeolite A could be synthesized by using raw material powders prepared by preliminary re-melting. While the small amounts of tobermorite and hydrogarnet were synthesized, hydroxycancrinite which was observed in the experiment in use of synthetic slag C was not detected, resulting in the larger amount of zeolite A synthesis in use of BF slag compared with the case of synthetic slag C.

Figure 8 shows the effect of the hydrothermal treating time period at 373 K on the ratio of the amount of zeolite A to the total amount of products. Raw material powders still remained as an amorphous phase after the treating time period of 3.6 ks, but crystals of zeolite A were synthesized after 14.4 ks, after then, the ratio of zeolite A in various products increasing slowly with a further extension of the treating time.

Results of direct hydrothermal treatment in use of a BF slag powder are shown in Table 3 and Fig. 7. In this experiment, the some amounts of SiO2 and Al2O3 or NaAlO2 powders were put into the reaction vessel together with a BF slag powder for optimization of the chemical compositions of raw material powders, which had the Si/Al molar ratio of 1 and CaO content of 15 mass%. No. 3 and 4 in Table 3 or Fig. 7 show various phases in products obtained in this experiment. For use of α-Al2O3 powder, non-reacted α-Al2O3 powder remained among products and the small amount of Na–P1 (Na4Al4Si10 · 12H2O) compound was synthesized. These results suggest that the amount of Al ion dissolved into a solution was not enough for formation of

### Table 3. Hydrothermal treatment using BF slag and products obtained.

<table>
<thead>
<tr>
<th>No.</th>
<th>Raw material powders</th>
<th>Compositions</th>
<th>Hydrothermal treatment</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BF slag</td>
<td>Si/Al=1.95</td>
<td>Direct</td>
<td>tobermorite hydrosilicate (100%)</td>
</tr>
<tr>
<td>2</td>
<td>BF slag, SiO2, Al2O3</td>
<td>Si/Al=1</td>
<td>Remelting</td>
<td>zeolite A (82%) tobermorite hydrosilicate (18%)</td>
</tr>
<tr>
<td>3</td>
<td>BF slag, SiO2, Al2O3</td>
<td>Si/Al=1</td>
<td>Direct</td>
<td>Na–P1 (50.0%) tobermorite hydrosilicate (50.0%)</td>
</tr>
<tr>
<td>4</td>
<td>BF slag, SiO2, NaAlO2</td>
<td>Si/Al=1</td>
<td>Direct</td>
<td>zeolite A (75%) tobermorite hydrosilicate (25%)</td>
</tr>
</tbody>
</table>

zeolite A. On the other hand, for the use of NaAlO₂ powder, much large amount of zeolite A was synthesized similarly to the case of use of re-melting slag. The cause for different synthetic behavior of zeorite A exerted by use of different powders as an Al source is discussed later.

Figure 9 shows scanning electron micrographs of synthesized products obtained by hydrothermal treatment at 373 K for various treating time periods in use of raw material powders including a BF slag powder. It could be observed that non-reacted BF slag still remained at the treating time period of 3.6 ks. Zeolite A was synthesized first at the treating time period of 14.4 ks, corresponding to XRD results shown in Fig. 8. The cubic shape of zeolite A crystals with a size of about 1.5 μm became to be observed clearly at the treating time of 86.4 ks. The morphology of synthesized zeolite A crystals was very similar to that of commercial one.

Figure 10 shows the effect of the mass ratio of BF slag to the total amount of raw material powders on the ratio of the synthesized amount of zeolite A to the total amount of products obtained by hydrothermal treatment. Raw material powders in use of 80% BF slag resulted in synthesis of only tobermorite and hydrogarnet, but no zeolite A. It was found that the ratio of the amount of BF slag to the total amount of raw material powders was needed to reduce down to 60% for zeolite A synthesis.

Several synthesized products which contained the different amount of zeolite A were prepared by use of different raw material powders and also the different hydrothermal treating conditions, and they were treated for water vapor absorption at 298 K. Then, the apparent specific heat changes of these products with the temperature were measured using a differential scanning calorimeter, which were compared with that of commercial zeolite 4A or silicagel as shown in Fig. 11. For products obtained by raw material powders with the total content of CaO and MgO of 15 mass% under use of BF slag, the temperature dependence of apparent specific heat was very similar to that of commercial zeolite 4A, showing endothermic behavior due to vapor desorption with the peak at the temperature of around 473 K. The value of specific heat was also similar to that of commercial zeolite 4A, although the peak value of specific heat in synthesized zeolite A was slightly low. It was also found from comparison between data of No. 1 and No. 2 in Fig. 11 that there was little effect of treating time periods between 28.8 and 86.4 ks on apparent specific heat. However, for products synthesized by use of raw material powders containing the total content of CaO and MgO of 40 mass%, the specific heat value and the change of endotherm with the temperature were much lower compared with results of other products. These results indicate that the enough amount of zeolite A is needed to be synthesized by alkali hydrothermal treatment when synthesized prod-
products are used for a heat storage material.

4. Discussion

4.1. Synthesized Compounds in SiO₂–Al₂O₃–CaO Ternary Phase Diagram

Figure 12 shows the equilibrium phase diagram of SiO₂–Al₂O₃–CaO ternary system together with the composition ranges of synthetic slag and commercial BF slag used in this study. Zeolite A, tobermorite and hydrogarnet were main synthesized products obtained in this study. The composition ranges of these compounds were also included in this figure, and the last two compounds were indicated by lines showing the composition range of solid solution in these compounds according to results of past studies.⑪,⑫) The composition ranges of BF slag or compounds shown in this figure were drawn based on a couple of assumptions. First, BF slag used in this study included MgO besides three oxides, and CaO content in BF slag shown in this figure was represented by summation of both contents of CaO and MgO, because both alkaline-earth metal oxides assumed to behave similarly in alkaline hydrothermal treatment. Secondly, the range of composition of zeolite A was indicated by excepting for H₂O, and the amount of alkaline-earth metals of Ca or Mg with two-valences ion which could substitute for one-valence ion of Na in the structure of zeolite A was assumed to be at most a half number of moles of Na. It is predictable from Fig. 12 that the increase of CaO content in raw material powders tends to approach to the compositional ranges of tobermorite and hydrogarnet, and in fact, the present experimental results showed tendency of formation of these compounds. Consequently, it is very clear from Fig. 12 that reduction of CaO content below 30 mass% in raw material powders is needed for synthesis of zeolite A.

4.2. Mechanism for Zeolite A Synthesis

It was reported in the study of mechanism for synthesis of zeolite A in alkaline hydrothermal treatment in use of fly ash that the first step of reaction was the elution process of Si and Al ion from raw material powders into an alkali solution, followed by formation of zeolite due to reaction between eluted ions and the surface layer of the raw material powder.⑨,⑩ It is suggested from this mechanism that hydrothermal treating conditions for fully synthesis of zeolite A such as the synthetic temperature, the alkalai concentration or the V_{slag}/W_{slag} ratio are needed to be optimized so as to obtain enough amount of eluted metallic ions from raw material powders. Figure 13 shows the changes of Si and Al concentrations in NaOH solution with the treating time period of hydrothermal treatment at 373 K. Two kinds of raw material powders with the best compositions for synthesis of zeolite A were used. One kind of powders was prepared by preliminary re-melting in use of BF slag, and the other was prepared by mixing BF slag powder and other oxide powders including NaAlO₂ powder in place of Al₂O₃ powder without preliminary re-melting. For raw material powders prepared by re-melting, Al concentration first increased with the treating time, and then tended to be saturating at the treating time period of around 7.2 ks. Si concentration showed the peak value at around 7.2 ks, and then tended to decrease, followed by a steady state value. The onset time of reduction of Si concentration or saturation of Al concentration was almost same with the starting time for synthesis of zeolite A detected by XRD analysis. That is, the increase of the synthesized amount of zeolite A appears to accompany with the decrease of Si or Al concentration in NaOH solution, while both ions are continuously eluted from raw material powders. On the other hand, for raw material powders prepared by mixing without re-melting, Si concentration varied similarly to the result of raw material powders prepared by re-melting, but Al concentration showed the peak value immediately after the start of hydrothermal treatment, and then decreased continuously with the longer treating time. The marked different kinetics of Al ion elusion shown in this figure appears to be due to different powders used for an Al source rather than difference in preparation route of raw material powders. That is, NaAlO₂ powder is much easily soluble into NaOH solution compared with α-Al₂O₃ powder. This difference of Al elusion behavior between two kinds of oxide powder for an Al source appeared to yield marked difference of zeolite A synthesis as shown in Fig. 7.
The much shorter hydrothermal treatment time period for synthesis of zeolite A was obtained in this study compared with the treating time period reported for zeolite A synthesis in use of fly ash. This advantageous result obtained in this study was brought about by adoption of stirring raw material powders in use of the ball mill type of the rotating reaction vessel in hydrothermal treatment. The large amount of zeolite A was synthesized by hydrothermal treatment at 373 K for 86.4 ks as shown in No. 4 of Fig. 7, but extremely tiny formation of zeolite A was detected for both cases of statically holding raw material powders into the vessel and rotating the vessel without containing SiC balls under the same treating condition. It was made clear from SEM observation of products after hydrothermal treatment in these two cases that zeolite A was formed only in the surface thin layer of raw material powders. That is, the present hydrothermal treatment system was devised based on the following idea. Products synthesized in the surface layer of powders may be stripped off by hard SiC balls, and the fresh surface of powders be revealed, which may enhance elusion of ions and be enable to synthesize zeolite A incessantly.

4.3. Effective Use of BF Slag for Zeolite A Synthesis

The amount of BF slag or its ratio to total amount raw material powders which can utilized in hydrothermal treatment for synthesis of zeolite A is very important from point of view of its recycle use. The results showed in Fig. 2 and Fig. 10 suggested that the decrease of CaO content in raw material powders in use of BF slag was essentially needed to synthesize zeolite A. The amount of synthesized zeolite A in use of raw material powders with the optimized compositions under use of BF slag was larger compared with for the case of use of synthetic slag C, and the formation of hydroxycancrinite was avoided in the former procedure. These results appear to be brought by the following causes. On the optimization of raw material powders compositions, the MgO content in BF slag was added to the CaO content, resulting in the decrease of the CaO content by the amount of MgO content in the optimized powder compositions in raw material powders. MgO contained in raw material powders appears to be much preferable to synthesize zeolite A differently from CaO.

Hollman et al. reported to have succeeded synthesis of zeolite A in use of fly ash by two-steps process. In the first step, solution containing the enough amounts of eluted ions of Si and Al was prepared by controlling the treating time period, and in the second step, hydrothermal treatment was performed by using this solution and new fly ash. Similarly, the preliminary treatment of BF slag appears to be effective for high purity zeolite A synthesis in use of the large amount of BF slag, where CaO content in BF slag should be reduced as lean as possible as well as elimination of non-preferable impurity elements.

There is still possibility of the further improvements of the processing conditions for zeolite A synthesis in this study. It was reported that the heat storage capacity of zeolite depended on the drying temperature of the synthesized products before adsorption of water vapor. The drying temperature was fixed at 373 K in the present experiment for evaluation of the heat capacity. The heat capacity may possibly become higher than the value obtained in this study by optimizing the drying temperature. There is possibility that zeolite A synthesized in this study might include not only crystallized one, but also some amount of amorphous one. The peak of specific heat in synthesized zeolite A shown in Fig. 11 was observed at around 473 K, which was lower compared with that of commercial zeolite 4A. C. Kosanovic et al. reported that the peak temperature in the endotherm curve of amorphous zeolite A was lower than that of crystalline one. These results appear to indicate possibility of synthesized zeolite A containing some amount amorphous phase.

5. Conclusions

Alkali hydrothermal synthesis of zeolite A in use of blast furnace (BF) slag and NaOH solution was studied by utilizing a newly devised rotating type of the reaction vessel, and the following results were obtained.

(1) The preliminary experiments in use of synthetic slag powders consisting SiO$_2$–Al$_2$O$_3$–CaO system made clear that the most optimum compositions of raw material powders had CaO content of 15 mass% under the content ratio of Si to Al of 1.0, and that the best synthetic conditions for zeolite A were the temperature range from 328 to 358 K, NaOH concentration of 1 M and the ratio of the amount of NaOH solution to mass of slag of 15 mL/g.

(2) Synthesized zeolite A was found to be stable at the heating temperature until 873 K.

(3) For hydrothermal synthesis of zeolite A in use of BF slag, the amount of zeolite A in synthesized products increased with the decrease of CaO+MgO contents in raw material powders. That is, the decrease of CaO+MgO contents in raw material powders down to 15% is needed to synthesize zeolite A.

(4) It was found that use of NaAlO$_2$ powder as an Al source in optimization of raw material powders compositions could much enhance zeolite A synthesis compared with Al$_2$O$_3$ powder, which enabled to practice direct hydrothermal synthesis without preliminary re-melting of raw material powders.

(5) The newly devised rotating ball mill type of the reaction vessel containing small SiC balls was confirmed to accelerate markedly hydrothermal reaction, and a large amount of zeolite A could be synthesized at the reaction time period of 28.8 ks at 373 K.

(6) Temperature dependence of heat capacity of zeolite A synthesized in the present experiments was measured after subjecting to vapor absorption at the ambient temperature, and endotherm phenomenon due to vapor desorption in the temperature range from 70 to 500 K was observed, suggesting possible utilization of zeolite A as a heat storage material.

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