Utilization of NaCl for Phillipsite Synthesis from Fly Ash by Hydrothermal Treatment with Microwave Heating

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Abstract

The coal fly ash was treated hydrothermally with the mixture of NaOH aqueous solution with NaCl aqueous solution at 373 K with using the microwave heating and the conventional heating in order to clarify influences of the NaCl concentration in the hydrothermal solution on the the growth rate and the crystalline phase of synthesized zeolites.

As a result, it was found that phillipsite crystallinity of product powder increases with the additive NaCl concentration in the hydrothermal solution when the concentration of NaOH is so low as not to generate the zeolite from fly ash. On the other hand, in case that NaOH concentration relatively high, the addition of NaCl to the hydrothermal solution with using the conventional heating hardly affect phillipsite crystallinity of product powder, however, the generation of hydroxysodalite is enhanced by the microwave heating .

Moreover, it was revealed that the necessary treatment time to complete the crystallization of phillipsite increases with increasing concentration of NaCl in the hydrothermal solution. This is because the substitution of NaCl for NaOH reduces the dissolution rate of aluminate and silicate ions from fly ash and the generation rate of the precursor aluminosilicate gel. However, this delay of the completion of the crystallization can be shortened by the microwave heating method.

These experimental results concluded that the utilization of NaCl for the hydrothermal solution is effective in phillipsite synthesis from fly ash only when the NaOH concentration is relatively low in the hydrothermal solution and especially, the microwave heating is used.

(Key Words)

Fly ash, Microwave, Phillipsite, Sodium chloride, Hydrothermal treatment

1. INTRODUCTION

In Japan, over 8 millions tons of fly ash are excreted per year by thermal power plants and so on as industrial wastes. The amount of discharged fly ash is expected to increase monotonously in the years ahead [1]. "Law for the Promotion of Effective Utilization of Resources [1991]" and "Fundamental Law for Establishing a Sound Material-Cycle Society [2000]" established by the Japanese government obligate to reuse fly ash. Therefore, effective ways to reuse fly ash should be quickly developed. As a way to reuse fly ash, the synthesis of phillipsite, which can be used as adsorbents, catalysts and so on, by hydrothermal treatment with NaOH aqueous solution has been proposed [2-6]. Previously we have reported effects of the synthesis conditions on the growth rate and the crystal structure of generated zeolite and proposed the new method to improve the purity and yields of synthesized product powder [7-13]. Furthermore, we also reported effects of microwave irradiation on the zeolite synthesis from fly ash [14-15].

However, in order to spread this reuse method, costs of the hydrothermal solution and the treatment of the waste solution must be reduced. Here, NaCl is more inexpensive than NaOH and the waste NaCl solution can be treated more easily than the waste NaOH solution. On the other hand, a saltern usually has a thermal power plant because the saltern needs much electric power for making NaCl by the electroosmosis method. A large amount of fly ash is also excreted from the saltern.

Consequently, it is effective in the reduction of the cost and the environment load that the product of the saltern, NaCl can be utilized for the phillipsite synthesis from fly ash by hydrothermal treatment as a substitute of NaOH.

In this study, we will investigate effects of NaCl concentration in the hydrothermal solution on the the growth rate of phillipsite and the crystalline phase of synthesized zeolites. Moreover, effects of the microwave irradiation on them will be also clarified.

2. EXPERIMENTAL

The properties of tested coal fly ash are listed in **Table 1**. This fly ash, which has relatively high silica content and the crystalline phase of quartz, was supplied from Shin-Onoda thermal power plant (Chugoku Electric Power Co. Inc.) .

The schematic diagram of the microwave heating equipment is shown in **Figure 1(a)**. 2.45 GHz microwave generated by the magnetron attains to the vessel by way of the wave guide. The slurry, which contains 50.0 ml of hydrothermal solution and 2.0 g of fly ash, is irradiated and heated up by the microwave. With using this equipment, the fly ash was treated hydrothermally at 373 K. The hydrothermal solution was the mixture of NaOH aqueous solution with NaCl aqueous solution, each concentration of which was varied from 0 to 2.0 mol/*l*. Here, the treatment pressure was 1.0 10^{5} Pa and the rotational speed of the stirrer was set 250 rpm. The fly ash was also treated hydrothermally under the same conditions with the conventional electric heater shown in **Figure 1(b)**.

After the hydrothermal treatment, the slurry was cooled down to the room temperature. The product powder was separated from the hydrothermal solution by Buchner funnel, washed with distilled water thoroughly and dried at 393 K for 48 hours. Therefore the product powder consists of unreacted fly ash and generated zeolite.

The properties of obtained product powder were evaluated by the crystalline phase and ammonium ion adsorption capacity. The crystalline phase was identified by XRD (Rigaku RINT-2000). The concentration of ammonium ion was measured by ion meter (Horiba F23). The concentration of Si and Al elements in hydrothermal solution was also measured by ICP (SEIKO SPS3000). The concentrations of Si and

Al elements were regarded as the concentration of silicate ion and aluminate ion, respectively.

3. RESULTS AND DISCUSSION

Figure 2 shows the XRD peak charts of the product powders obtained by hydrothermal treatment for various hydrothermal solutions. In any cases, it can be observed the peaks of quartz in unreacted fly ash and newly generated zeolites. However, using a certain solution, hydroxysodalite ($Na_4Al_3Si_3O_{12}OH$) as a by-product as well as phillipsite ($Na_6Al_6Si_{10}O_{32}$ $13.5H_2O$) are generated. Therefore, it can be said that the crystalline phase of synthesized zeolites depends on the concentrations of NaCl and NaOH in the hydrothermal solution.

The crystalline phase and the adsorption capacity of product powder was investigated. The crystallinity was evaluated by [022] peak intensity of phillipsite and [110] peak intensity of hydroxysodalite of the product powder. The fly ash was treated hydrothermally for 9 hours with the mixed hydrothermal solution of 0.5 mol /*l* $NaOH_{aq.}$ and various concentration $NaCl_{aq.}$. **Figure 3** shows the relationship between XRD peak intensity of product powder and the concentration of NaCl in the hydrothermal solution for conventional heating and microwave heating. Here, the index of the peak intensity reflects the degree of crystallinity of the generated zeolite itself mainly but the zeolite content in the product powder also effects on it to some extent. Any peak intensity can not be detected by XRD at 0 mol/*l* and the phillipsite peak intensity increases monotonously with the concentration of NaCl. After that it keeps almost constant. The heating method makes no difference in the change of the peak intensity of product powder.

Figure 4 shows the relationship between the ammonium ion adsorption capacity of product powder and the concentration of NaCl in the hydrothermal solution for conventional heating and microwave heating. Here, the index of the adsorption capacity reflects the zeolite content in the product powder mainly. In any heating methods, the adsorption capacity increases to constant value of about 40 mg/g as the concentration of NaCl increases. Here, in our previous study, the adsorption capacity of product powder which was acquired by conventional hydrothermal treatment with 2.0 mol/*l* $NaOH_{aq.}$ was 40.8 mg/g [14].

The SEM images of product powders acquired by the hydrothermal treatment with 2.0 mol/*l* $NaOH_{aq.}$ and the mixed solution of 0.5 mol/*l* $NaOH_{aq.}$ and 1.5 mol/*l* $NaCl_{aq.}$ are shown in **Figure 5**. In any cases, it can be observed that newly generated crystallized phillipsite particles deposit on the surface of the unreacted fly ash. It can be hardly found that the difference in the appearance of phillipsite particles between them. Besides, Cl could not be detected in any product powders by EDX measurement. Accordingly, it can be said that $NaCl_{aq.}$ can be utilized for the hydrothermal solution as a substitute of $NaOH_{aq.}$. Namely, it is thought that NaCl can act effectively for Na source just like NaOH.

Next, the fly ash was treated hydrothermally for 9 hours with the mixed hydrothermal solution of 1.5 mol/*l* $NaOH_{aq.}$ and various concentration $NaCl_{aq.}$. **Figure 6** shows the relationship between XRD peak intensity of product powder and the concentration of NaCl in the hydrothermal solution for conventional heating and microwave heating. In the case of the conventional heating, the phillipsite peak intensity increases little by little with the concentration of NaCl and the peaks of hydroxysodalite can not be observed. On the other hand, in the case of the microwave heating, the peak intensity of phillipsite decreases and the peak intensity of hydroxysodalite increases with the concentration of NaCl. It is thought this is because the Na concentration in the hydrothermal solution is so high [8]. This result suggests that the microwave heating promotes the formation of hydroxysodalite and this phenomena was reported in our previous work [15]. Hence, the advantage of the microwave heating can not be found in this condition.

Figure 7 shows the relationship between the ammonium ion adsorption capacity of product powder and the concentration of NaCl in the hydrothermal solution for conventional heating and microwave heating. In the case of the conventional heating, the adsorption capacity increases gradually with NaCl concentration. On the contrary, in the case of the microwave heating, an increase in the NaCl concentration lessens the adsorption capacity since the ratio of hydroxysodalite to the newly generated zeolite, which does not the adsorption ability of the ammonium ion, increases. Consequently, it is found that the addition of NaCl to the hydrothermal solution is effective only when the concentration of NaOH is so low as not to generate the zeolite from fly ash.

Then, it was examined the crystal growth rate and the change in the adsorption capacity of product powder with treatment time. The fly ash was treated hydrothermally with 2.0 mol/l $NaOH_{aq.}$ and the mixed solution of 0.5 mol/l $NaOH_{aq.}$ and 1.5 mol/l $NaCl_{aq.}$ for various treatment time. The change in the peak intensity of the product powder with treatment time was shown in **Figure 8**. Using 2.0 mol/l $NaOH_{aq.}$, the peak intensity can not be detected by XRD at first and after 1 hour waiting time for crystallization, the peak intensity increases with treatment time. After that it keeps almost constant. This tendency does not depend on the heating method. On the other hand, Using the mixed solution of 0.5 mol/l $NaOH_{aq.}$ and 1.5 mol/l $NaCl_{aq.}$ needs 3 hours waiting time for crystallization and longer treatment time until the end of the crystallization than 2.0 mol/l $NaOH_{aq.}$. Furthermore the mixed solution of 0.5 mol/*l* $NaOH_{aq.}$ and 1.5 mol/*l* $NaCl_{aq.}$ has a larger peak intensity at the steady state than 2.0 mol/*l* $NaOH_{aq.}$. This suggests that the mixed solution enhances the degree of crystallinity of the generated phillipsite itself. Besides, it was found that the microwave heating requires the shorter treatment time to complete the crystallization than the conventional heating since the microwave heating gives the larger increasing rate of the peak intensity, which corresponds to the crystal growth rate, than the conventional heating. It is thought that the promotion of the crystal growth rate is induced by the improvement in the sensitivity of product powder against the microwave on the basis of the polarization which is caused by the adsorption of Cl^- on the surface of phillipsite.

The change in the adsorption capacity of the product powder for ammonium ion is shown in **Figure 9**. In any cases, the adsorption capacity increases with treatment time and then it keeps almost constant. The constant value of the adsorption capacity does not depend on the heating method and the hydrothermal solution. This result suggests that the product powders at the steady state are almost equal in content of phillipsite. Similarly to the change in the peak intensity shown in Fig.8, only when the mixed solution of 0.5 mol/*l* $NaOH_{aq.}$ and 1.5 mol/*l* $NaCl_{aq.}$ is used, the microwave heating reduces the necessary treatment time until the end of the reaction. From these results, it can be revealed that the microwave heating is effective in reducing the necessary treatment time when NaCl is substituted for NaOH.

Here, it is thought that phillipsite is synthesized from coal fly ash through the following heterogeneous reaction processes mainly [15]. At first, aluminate ion and silicate ion dissolved from coal fly ash in the hydrothermal solution form the precursor aluminosilicate gel. This precursor is attacked by sodium ion and it is crystallized to phillipsite crystal. Hence, the concentration of silicate and aluminate ions in the hydrothermal solution was measured in order to acquire the information about effects of the substitution of NaCl for NaOH on the phillipsite formation. The change in the concentration of silicate ion and aluminate ion with treatment time is shown in **Figure 10**. As shown in Fig.10(a), in the case of 2.0 mol/*l* $NaOH_{aq.}$, the concentrations of both ions increase considerably and acquires the maximum value at about 45 minutes. After that they decrease to the constant concentrations monotonously. On the other hand, the mixed solution of 0.5 mol/*l* $NaOH_{aq.}$ and 1.5 mol/*l* $NaCl_{aq.}$ makes the change in the aluminate ion concentration resemble to that of 2.0 mol/*l* $NaOH_{aq.}$, but it gives the lower maximum concentration at about 30 minutes and slower decreasing rate than that of 2.0 mol/*l* $NaOH_{aq.}$. This fact means that the substitution of NaCl for NaOH reduces the dissolution rate of ions from fly ash. This is because pH of the hydrothermal solution decreases with decreasing NaOH concentration in the hydrothermal solution. Since the substitution of NaCl for NaOH reduces the aluminate ion concentration especially, the generation rate of the precursor aluminosilicate gel also decreases. For this reason, it is thought that the generation rate of phillipsite was also reduced. Furthermore, it can not be found clearly that the change in ion concentrations depends on the heating method. This result suggests that the microwave heating does not enhance the dissolution of silicate ion and aluminate ion from fly ash and the formation of the precursor aluminosilicate gel. Accordingly it can be said that the microwave heating effects on the nucleation and the crystal growth of phillipsite mainly when NaCl is substituted for NaOH [14, 15].

4. CONCLUSION

Influences of NaCl concentration in the hydrothermal solution and the microwave irradiation on the the growth rate of phillipsite and the crystalline phase of synthesized zeolites were investigated. The results obtained in this work can be summarized as follows.

1) When the concentration of NaOH is so low as not to generate the zeolite from fly ash, phillipsite synthesized from fly ash increases with the additive NaCl concentration in the hydrothermal solution. Under this condition, the heating method does not affect the phillipsite generation.

2) When the concentration of NaOH is so high as to generate the zeolite from fly ash, the microwave heating enhance the generation of hydroxysodalite and the phillipsite generation hardly depends on the addition of NaCl to the hydrothermal solution in the case of the conventional heating.

3) The substitution of NaCl for NaOH needs longer treatment time to complete the crystallization than 2.0 mol/*l* $NaOH_{aq.}$.

4) The microwave heating reduces the treatment time until the end of the reaction and develop the crystal growth rate of phillipsite when NaCl is substituted for NaOH.

5) The microwave heating does not enhance the dissolution of silicate ion and aluminate ion from fly ash and the formation of the precursor aluminosilicate gel but promotes the nucleation and the crystal growth of phillipsite mainly when NaCl is substituted for NaOH.

6) The substitution of NaCl for NaOH reduces the dissolution rate of ions from fly ash and the generation rate of precursor aluminosilicate gel.

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Table 1　Properties of tested fly ash

Fig.1　Schematic diagram of experimental set-up

Fig. 2　XRD peak charts of product powders synthesized with various hydrothermal solutions (treatment time = 9 h)

Fig.3　Relationship between XRD peak intensity of product powder and the concentration of NaCl in the hydrothermal solution for conventional heating and microwave heating　(NaOHaq. = 0.5 mol/*l*)

Fig.4　Relationship between ammonium ion adsorption capacity of product powder and the concentration of NaCl in the hydrothermal solution for conventional heating and microwave heating (NaOHaq. = 0.5 mol/*l*)

Fig.5　SEM images of product powders treated hydrothermally with conventinal heating method for 9 hours a) hydrothermal solution : 2.0 mol/*l* NaOHaq. , b)hydrothermal solution : 0.5 mol/*l* NaOHaq. and 1.5 mol/*l* NaClaq.

Fig.6　Relationship between XRD peak intensity of product powder and the concentration of NaCl in the hydrothermal solution for conventional heating and microwave heating　(NaOHaq. = 1.5 mol/*l*)

Fig.7　Relationship between ammonium ion adsorption capacity of product powder and the concentration of NaCl in the hydrothermal solution for conventional heating and microwave heating (NaOHaq. = 1.5 mol/*l*)

Fig.8　Change in [022] phillipsite peak intensity of product powder with treatment time for various heating methods and hydrothermal solutions

Fig.9　Change in adsorption capacity of product powder for ammonium ion with treatment time for various heating methods and hydrothermal solutions

Fig.10　Change in concentration of silicate ion and aluminate ion in hydrothermal solution with treatment time for various heating methods and hydrothermal solutions