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MICROWAVE SYNTHESIS OF ZEOLITE FROM COAL FLY ASH AND THE WAY TO SCALE UP

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ABSTRACT

Coal fly ashes ejected from thermoelectric power plants were subjected to high alkaline treatment to synthesize zeolite. X-ray diffractometry (XRD) showed that the raw ashes contained quartz, mullite, and an amorphous phase. Three kinds of heating processes with a conventional refluxing method, with a domestic microwave oven, and with an industrial microwave oven were compared. Microwave heating was found to be superior to the conventional one as for the enhancement of phillipsite, which shows high cation exchange capacity (CEC). In the paper, a variety of experimental parameters, such as the alkaline concentration, addition of seed particles, and preheating (aging) prior to microwave treatment, were examined. At the optimum, the CEC value reached as high as 200 (meq/100g). Large-scale synthesis using the industrial microwave oven seems to require further optimization of the parameters and the examination of the microwave field.

Keywords: Environmental Recycle, Microwave Processing, Zeolite, Fly Ash

1. INTRODUCTION

With the increasing consumption of coal fuels in thermal power stations, a great deal of waste ash has been ejected to our environment. Though a part of the waste ash is recycled to filler materials for construction of buildings, most of the ash is still dumped into the ground and sea. As the area for them is certainly limited, we must take serious and urgent account for beneficial use of the ash[1]. Since major components in the ash are Al_2O_3 and SiO_2, zeolite materials can be produced by a relatively easy treatment with alkaline solution. A number of works have been reported on the zeolite synthesis in terms of the utilization of coal fly ash[1-3]. On the other hand, process studies for the zeolite synthesis are intensive. They are related to sonochemical[4], microwave[5], and so forth. Microwave is expected as an effective tool for the enhancement of the process. It is supposed that a lot of experimental data should be collected as to test the potential of microwave synthesis.

The present study is aimed at the combination between the use of waste ash and the accelerated synthesis using a microwave energy. In the paper, microwave process was mainly executed by using a domestic oven and partially attempted by using an industrial oven for a large-scale production.

2. EXPERIMENTAL

Raw Materials

Three kinds of coal fly ash, denoted as QM, QMII, QO, were employed in this study. Bulk composition of the ashes was determined by energy dispersive X-ray fluorescence spectroscopy (XRF; Shimadzu Co., EDX-800). In addition, the amount of crystalline phases in the ashes, quartz and mullite, were estimated from a calibration curve by using X-ray diffractometry (XRD; Rigaku Co., Miniflex). Extracting the amount of the crystalline phase from that of the bulk, the amounts of amorphous SiO_2 and Al_2O_3 were calculated. Results are summarized in **Table I**. It is confirmed that fly ashes are qualitatively similar but quite different in the content of amorphous and crystalline phases.

Table I. *Chemical Compositions of Various Fly Ashes Determined by the Combination of X-ray Fluorescences Spectroscopy and X-ray Diffractometry*

[wt%]	Bulk Composition						Crystalline			Amorphous		
	SiO_2	Al_2O_3	(SiO_2+ Al_2O_3)	CaO	Fe_2O_3	others	Quartz	Mullite	cryst. sum	silica	alumina	amor. sum
QM	59.3	24.4	(83.7)	6.3	5.6	4.4	13.7	18.4	32.1	40.4	11.3	51.7
QMII	55.2	36.6	(91.8)	3.2	2.2	2.8	17.6	41.2	58.8	26.0	7.0	33.0
QO	38.3	34.8	(73.1)	11.0	8.1	7.8	2.2	27.2	29.4	28.4	15.3	43.7

Zeolite Synthesis

Basically, 10 gram of the fly ash was charged in a Teflon container with 80cm^3 of 2M (mol/dm^3) NaOH aqueous solution. Other process parameters studied will be mentioned in each case.

Conventional refluxing was performed at ~1atm in a Teflon flask attached with a reflux condenser. The flask was kept at 120°C in an oil bath. The solution was constantly stirred by a magnetic stirrer.

Microwave synthesis was executed by using a domestic microwave oven (Toshiba Co., ER-VS1) or an industrial-type oven (TMB-5100). The former was driven at the output power of 100-500W, and the 500W process was mainly studied. While, the latter was driven at the nominal power of 1500W. An intensive microwave frequently caused rapid vaporization of the solution. If the Teflon container was tightly capped, pressure inside the container became excessive. If the container was open in air, on the other hand, the solution dried up promptly. To prevent these problems, the container was loosely covered with a lid, and distilled water was occasionally supplied.

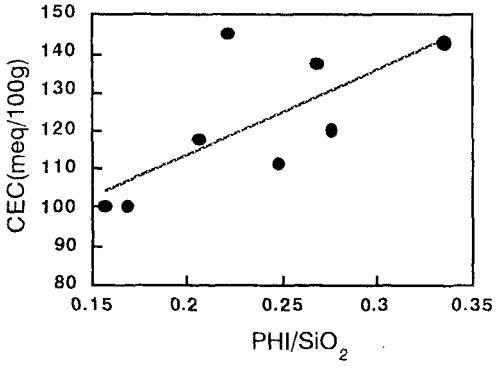


Fig.1 *Relationship between CEC value and XRD intensity of phillipsite; which was normalized by internal quartz.*

After synthesized for a certain time, precipitates were washed with distilled water, dried, and subjected to evaluation.

Evaluation

The samples obtained were mainly characterized in terms of cation exchange capacity (CEC), which was measured by using ammonium acetate[6].

XRD revealed that the crystalline phases synthesized were phillipsite [$Na_6Al_6Si_{10}O_{32}\cdot 12H_2O$] and Zeolite-A [$Na_2Al_2Si_{1.85}O_{7.7}\cdot 5.1H_2O$]. As the former has excellent CEC ability for NH_4^+, CEC increased with the increasing amount of phillipsite, as shown in Fig.1, which summarized the series using the ash QMII.

3. RESULTS AND DISCUSSION

Figure 2 shows the effect of NaOH concentration upon the CEC value. At [NaOH]=2M, we obtained the maximum CEC of 200meq/100g, which is comparable to that of commercial synthetic zeolite.

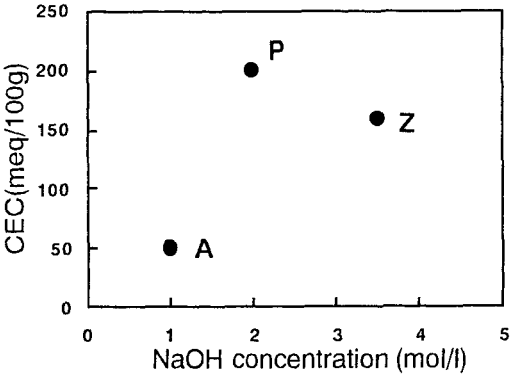


Fig.2 *CEC values as a function of NaOH concentration.*

Below and above this optimum, the phillipsite formation was no more observed, and consequently, the CEC values was found to be lower.

Unfortunately, this maximum value of CEC could not be reproduced due to the short of the ash QM, which has larger amount of amorphous phase and may be suitable for the zeolite formation. However, it is shown by another study by the authors[7] that the optimum concentration of NaOH is found to be 2M. Accordingly, the experiments below were run at [NaOH]=2M.

Effect of the microwave output power is shown in Fig.3. Phillipsite occurred only above 360W. It is curious that the CEC increased when the power increased from 80 to 190W even in the absence of phillipsite. It means that the phillipsite formation is not always necessary to increase CEC to some extent.

Figure 4 compares the conventional refluxing route and the microwave process at 500W. Distinct

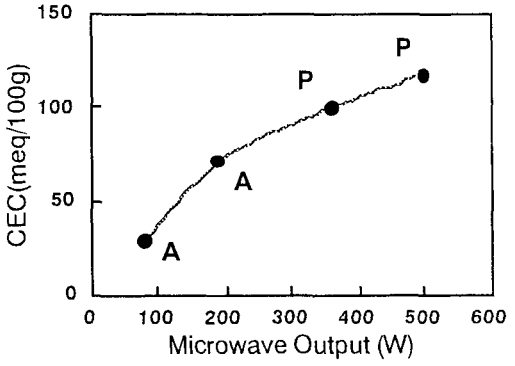


Fig.3 *CEC values as a function of output powder of domestic microwave oven*

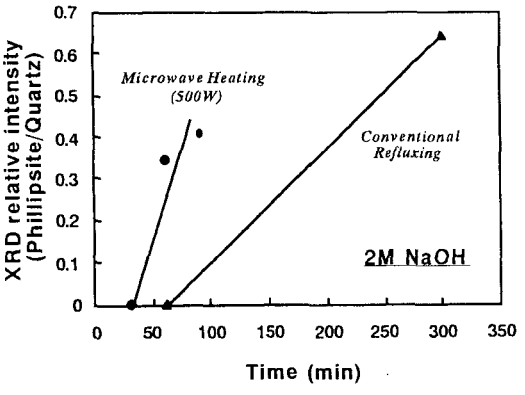


Fig.4 *Comparison of conventional refluxing method and microwave processes (domestic) in terms of the phillipsite formation.*

effect of microwave on the phillipsite formation is seen. However, the mechanism how the microwave energy enhances the formation is not well understood. It is usually known that amorphous component dissolves in an alkaline solution and deposits upon the surface of fly ash particles in the form of zeolite. Rapid heating caused by microwave may well increase the dissolution rate. But, its effect upon the reaction and the nucleation (or deposition) is not clear.

Effect of seeding, in other words, addition of nucleus of phillipsite was studied. The seed, QM15 was previously prepared by conventional refluxing of the ash QM for 24h. This powder of course contains phillipsite, and has the CEC of ~200meq/100g. Then, the seed powder was mixed with the ash QMII and processed in NaOH aq. in the microwave oven. Figure 5 shows the result. It is confirmed that the seeding not only increase the CEC but also fasten the formation of phillipsite. In fact, similar seeding effect was NOT observed in the similar experiment in the conventional refluxing. This suggest that there is a critical difference in the nucleation of the conventional case and the microwave case.

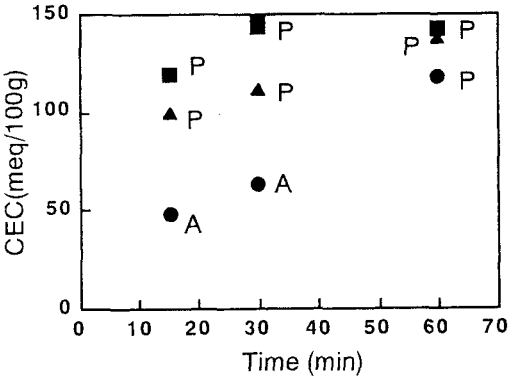
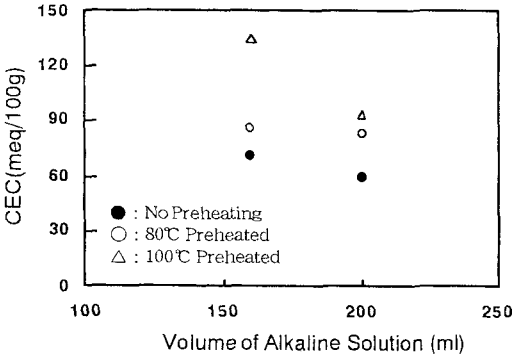


Fig.5 *CEC values as a function of microwave heating time at various seeding conditions.*

Additionally, the effects of preheating before microwave treatment and the amount of NaOH solution were examined (Fig.6). The CEC values in this series are relatively low. It may be due to the new ash (QO). Figure 6 indicates that CEC tends to increase at higher preheating temperature and at smaller amount of NaOH solution. Considering the relatively high value of the specific heat for water (~ 4.2 J/K·g), it may not be always

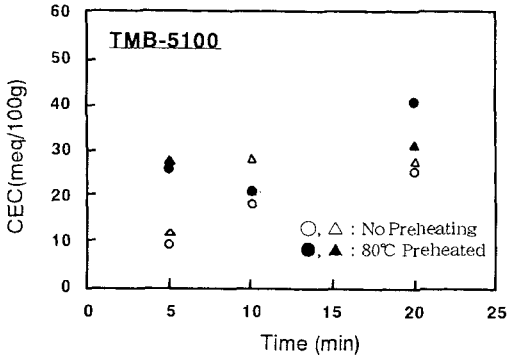
easy for a microwave energy to increase the water temperature. Figure 6 suggests that there is a room for improving the efficiency of microwave processing. As for reducing the amount of NaOH solution, in addition, it must be mentioned that there is an optimum amount in the present experiment. If the amount is to small, it is difficult to prevent the dry-up of the solution, as described in the experimental section. Accordingly, if the container is appropriately designed, there may be a more efficient way for the microwave heating.



Ash QO: 10g, [NaOH]: 2M, Microwave Output: 500W
Preheating Time: 60min, Synthesis Time: 30min

Fig. 6 *CEC values as a function of the volume of NaOH aq. under various conditions of preheating.*

Finally, the results using an industrial oven is presented in Fig.7, where the ash QO is employed. It is at first glance unsuccessful because the absolute value of CEC is quite lower than the above data, even when compared with Fig.6.



Ash QO: 300g, Alkaline Conc.: 10wt% Microwave Output: 1.5kW

●, ○ : Batch A / Ash:NaOHaq.= 1 : 0.5
▲, △ : Batch B / Ash:NaOHaq.= 1 : 1

Fig. 7 *Attempt for the large-scale synthesis by using an industrial oven (TMB-5100)*

We need further understanding and the improvement of the microwave field for the large scale synthesis.

4. CONCLUSION

Zeolite synthesis using a domestic microwave oven was found to be efficient in the enhancement of phillipsite and CEC. In addition to normal parameters (output power, alkaline concentration, etc.), specific process parameters, such as seeding, preheating, and the amount of solution were influential. Optimization of these parameter is still not perfect. Further understanding of the phillipsite formation and the microwave action is required. Besides, sophisticated flexibility against the difference of ash must be well considered in practice.

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