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Effects of step change of heating source on synthesis of zeolite 4A from coal fly ash

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ABSTRACT

Effects of step change of heating sources on the crystallization of zeolite 4A from coal fly ash by hydrothermal reaction were investigated with emphasis on the change in the crystallinity of the synthesized zeolite 4A. Most of the Si and Al components were effectively transformed into zeolite 4A by step change of the first conventional heating and then the second microwave heating of synthesis mixture dissolved from coal fly ash, and maximum crystallinity of zeolite 4A obtained was 91%. The first conventional heating also plays an important role in enhancing the nuclei formation that Si and Al in synthesis mixture reacted to form ring-like structures for combining sodalites, and further to small zeolite 4A seeds. The second microwave heating increases the crystallization rates from small zeolite 4A nuclei to more zeolite 4A crystals.

The cation exchange capacity (CEC) of the zeolite 4A crystallized by step change of heating source from the conventional to the microwave was 5.5 meq/g compared to 5.7 meq/g for commercial zeolite 4A. Test results showed that removal efficiency of heavy metals by zeolite 4A synthesized from fly ash was more than 98% and similar to commercial zeolite 4A.

1. Introduction

About 6.0 million tons of coal fly ash was produced in Korea last year, of which only 70% were utilized with remaining 30% being disposed as a waste. Due to the construction of new coal power plants, the fly ash production in Korea will increase for next 5 years and is expected to reach up to 8.3 million tons in 2013. This rapid increase of the fly ash production causes serious concerns over fly ash disposal amid growing awareness of environmental issues and depletion of landfill sites [1].

Many efforts have been made at finding alternative and meaningful applications for this waste. Since fly ash contains mainly amorphous aluminosilicate (glassy phase) and some crystalline minerals (quartz, mullite, hematite, etc.), it can be used as a raw material for the synthesis of zeolite-like materials. The glassy phase plays an important role in the zeolite formation because of the high solubility into alkaline solution. However, in many of these studies [2–5], the total conversion time was generally long (72 h or more), synthesis temperature was very high (90–225 °C), and a little SiO_2 and Al_2O_3 contained in fly ash was utilized due to the low dissolution rate of conventional heating such as autoclave, heating mantle and oil (water) bath. Nowadays, microwave heating at hydrothermal process was effective for zeolite synthesis from silica–alumina gel [6,7]. The zeolite synthesis from coal fly ash by microwave heating also reported to be useful for shortening the reaction time [8]. Microwave was absorbed directly into water as a solvent, and enabled the rapid heating compared to a conventional heating. We have investigated the effect of microwave irradiation on the dissolution of Si and Al from coal fly ashes, and the crystallization of zeolite 4A from the dissolved solution [1]. It is recently found the unexpected phenomena that dissolution rate of silicon and aluminum from coal fly ash by microwave irradiation improved dramatically compared to conventional heating, but nuclei of zeolite 4A was not generated because Si and Al dissolved from fly ash less reactive and microwave have too energy to disturb the combination of among sodalites. Therefore, the conventional heating at initial step on crystallization of zeolite 4A was introduced to produce many small zeolite 4A nuclei and seeds from mixture solution.

2. Experimental

2.1. Coal fly ash sample

A fly ash sample was collected from the Tean thermal power plant owned by the Korea Western Electric Power Corporation. Table 1 shows the chemical and mineralogical composition of fly ash sample. The content of metal components was determined by X-ray fluorescence analysis and the chemical composition was presented in the form of stable oxide. The contents of major

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Table 1
Chemical and mineralogical composition of coal fly ash.

Chemical composition (wt.%)					Mineralogical composition (wt.%)			
					Crystal phase		Glass phase	
SiO_2	Al_2O_3	CaO	Fe_2O_3	Others	Quartz	Mullite	SiO_2	Al_2O_3
54.5	26.3	6.0	3.2	10.0	30.6	16.8	19.1	14.2

Others: MgO, Na_2O, TiO_2, K_2O, SO_3, P_2O_5, etc.

crystalline phases such as quartz and mullite presented in the form SiO_2 and $3Al_2O_3{\cdot}2SiO_2$ were determined by a quantitative X-ray diffraction analysis. Commercial mullite and quartz powders were used to make their calibration curves. The contents of SiO_2 and Al_2O_3 in amorphous glass phase, which included as aluminosilicate were calculated by subtracting the SiO_2 and Al_2O_3 compositions of crystal phases from the bulk compositions.

2.2. Experimental apparatus and procedures

Microwave equipment used in this study consisted of an industrial type micro-oven with a working frequency of 2.45 GHz (Korea High Frequency Inc., KMIC-2 KW) and an output power that can be varied from 0 W to a maximum of 2 kW. The microwave synthetic equipment was modified by the introduction of a thermocouple inside the cavity in order to monitor reaction temperature, and the water condenser to conduct atmospheric pressure experiments in Fig. 1. Atmospheric pressure has been chosen because atmospheric hydrothermal synthesis was the common method for manufacturing zeolite NaA on a commercial scale and allows an easy change of reaction parameters, like agitating. The agitation shaft was equipped with a SUS 316 blade and stirring rate was varied from 0 to 500 rpm. The impeller was also operated to reflect transparent microwave through Teflon lining Pyrex reactor, which has the volume of 2000 mL and the high alkali resistant materials. Appendix equipments were tuned to minimize microwave for reflecting from the reactor, the coupler for transmitting the signal of microwave strength to be reflected at reactor into both magnetron and power supply, the circulator to prevent the damage of magnetron by microwave reflected from reactor, and the dummy load which eliminates microwave inducted through circulator.

2.3. Preparation of mixed solution

A mixture of 250 g of fly ash and 1000 mL of 5 M NaOH solution (Yakuri Inc.) in a 2000-mL sealed teflon bottle was heated using a conventional insulating mantle [1] or a microwave reactor at 100 °C for 1–8 h. The solution was filtrated with filter paper lined funnels. The volume of filtrate obtained from the solution heated at 100 °C for 5 h was roughly 940 mL, the Si, Al and Na concentrations were 56.8, 0.75 and 134.2 mg/L, respectively. Next, the filtrate solution was mixed with 130 g of sodium aluminate (Daejung Chemistry Inc., Na_2O 0.31 mg/mL, Al_2O_3 0.34 mg/mL), 132 g of NaOH pellets, and 790 mL of distilled water to adjust the molar ratio of Si:Al:Na:H_2O as 1.0:1.0:2.5:100. The mixed solution was stirred with 250 rpm for 24 h at room temperature.

2.4. Synthesis of zeolite 4A

In the synthesis of zeolite 4A, four kinds of experimental methods were compared as shown in Table 2. The first method (KZ-1) was carried out only by the microwave heating without the conventional heating as insulating mantle. That is, 1750 mL of the mixed solution prepared at above section was injected into the microwave reactor and was crystallized by a microwave irradiation under agitation of 250 rpm at 100 °C for 2 h. The second and third methods were conducted only by the conventional heating

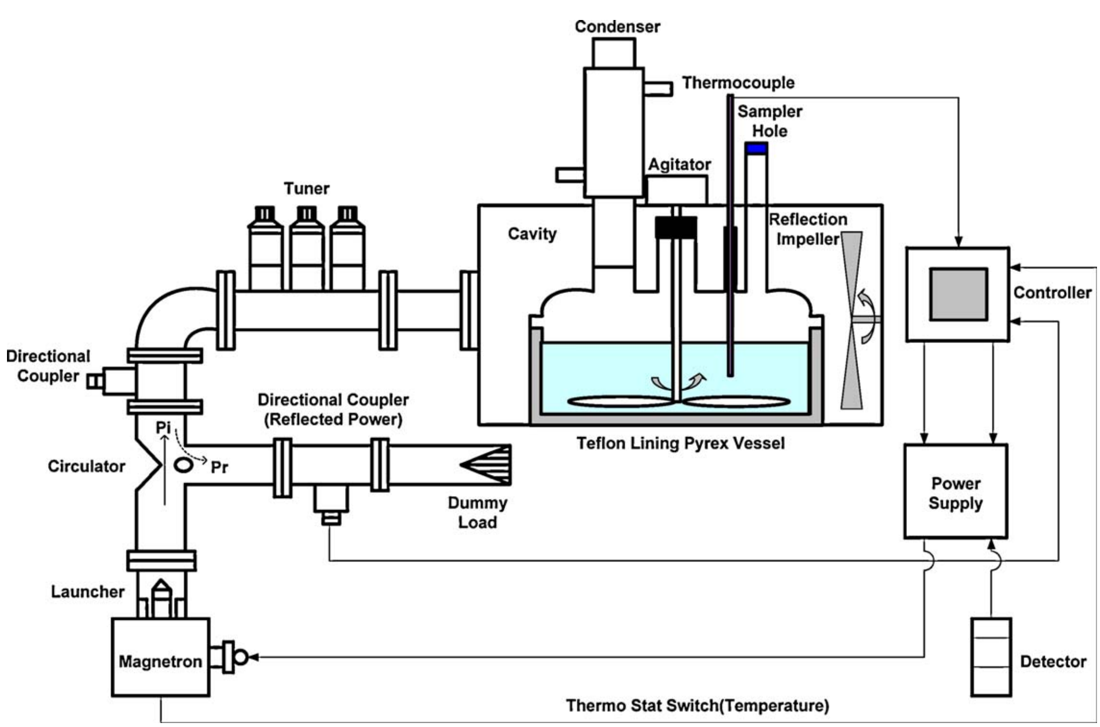

Fig. 1. The apparatus of microwave reactor for dissolution and crystallization process.