The Optimum Operating Conditions for the Synthesis of Zeolite from Waste Incineration Fly Ash by Alkali Fusion and Hydrothermal Methods

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***Abstract*—**The fly ash of waste incineration processes is usually hazardous and the disposal or reuse of waste incineration fly ash is difficult. In this study, the waste incineration fly ash was converted to useful zeolites by the alkali fusion and hydrothermal synthesis method. The influence of different operating conditions (the ratio of Si/Al, the ratio of hydrolysis liquid to solid, and hydrothermal time) was investigated to seek the optimum operating conditions for the synthesis of zeolite from waste incineration fly ash. The results showed that concentrations of heavy metals in the leachate of Toxicity Characteristic Leaching Procedure (TCLP) were all lower than the regulatory limits except lead. The optimum operating conditions for the synthesis of zeolite from waste incineration fly ash by the alkali fusion and hydrothermal synthesis method were Si/Al=40, NaOH/ash=1.5, alkali fusion at 400 ^{o}C for 40 min, hydrolysis with Liquid to Solid ratio (L/S)= 200 at 105 ^{o}C for 24 h, and hydrothermal synthesis at 105 ^{o}C for 24 h. The specific surface area of fly ash could be significantly increased from 8.59 m^2/g to 651.51 m^2/g (synthesized zeolite). The influence of different operating conditions on the synthesis of zeolite from waste incineration fly ash followed the sequence of Si/Al ratio > hydrothermal time > hydrolysis L/S ratio. The synthesized zeolites can be reused as good adsorbents to control the air or wastewater pollutants. The purpose of fly ash detoxification, reduction and waste recycling/reuse is achieved successfully.

***Keywords*—**Alkali fusion, hydrothermal, fly ash, zeolite.

I. Introduction

FLY ash is one of the major hazardous residuals produced from the municipal solid waste (MSW) incineration plants. Currently there are 24 large-scale MSW incineration plants operated in Taiwan [1]. The total amounts of MSW treated by these incineration plants were 6 million tons per year, and 1.1 million tons of bottom ash (accounting for 18.3% of treated MSW) and 300,000 tons of fly ash stabilized products (accounting for 5% of treated MSW) were generated [1]. At present, most of the incineration bottom ash is reused in civil, road and construction engineering after proper treatment or stabilization, such as the pipe trench backfill, roadbed filling, and local base filling. However, the main treatment methods of incineration fly ash are solidification or stabilization by adding cement or chelating agents with the fly ash, so the volume of fly ash stabilized products are usually increased. Moreover, the chloride salts contained in the fly ash usually cause the setting time to be prolonged and the durability of the solidification products to be reduced. The CaO and chloride salts in the fly ash will also react with each other to form calcium chlorides which are easy to absorb moisture and cause the solidification products to expand and disintegrate. Therefore, there is still doubt that the heavy metals in the fly ash may be leached out during the long- term landfill of these solidification products. The treatment of incineration fly ash by solidification not only imposes a great loading on the landfill, but also causes problems such as hazardous doubts and poor social perception, which in turn affects the stable development of MSW incineration. The innovative treatment and reuse of incineration fly ash has become an urgent issue and Taiwan EPA also strives to find relevant feasible technologies.

Since incineration fly ash contains rich silica and aluminum components, it has great potential to be synthesized to form environmental adsorbent materials such as zeolite. However, the synthesis reactions and mechanism of zeolite are complicated. The zeolites are metastable species, different types and characteristics of zeolites may be formed due to any changes in one of the operating conditions [2]. The major impact conditions are summarized as follows:

A. Silica to Alumina Ratio

The most direct effect of silica to alumina ratio is the zeolite structure. Because zeolite is a skeleton structure formed by SiO_4^{4-} and AlO_4^{5-} tetrahedrons sharing oxygen atoms in a three-dimensional space, Xu et al. [3] addressed that a crystalline product of a certain zeolite can be synthesized only in a specific silica to aluminum ratio and crystallization region, such as low silica Faujasite (FAU) (X type, Si/Al=1~1.5), high silica FAU (Y type, Si/Al=1.5~3), Gmelinite (GME) zeolite (Si/Al=2.3~2.95), Pt type zeolite (Si/Al=1.6~2.65), Analcime (ANA) zeolite (Si/Al=1.4~4.1), and Mordenite (MOR) zeolite (Si/Al = 4.5~9.75). It is more difficult to synthesize zeolite if the silica to aluminum ratio exceeds the specific range, such as FAU zeolite with Si/Al>3, or ZSM-5, ZSM11 and other sorghum with high aluminum content. The synthesis of these zeolites cannot be promoted by increasing the ratio of silica to aluminum ratio in the raw materials. It can only be promoted by using a special structure finder under special conditions, or through secondary synthesis. In the past, some scholars studied the formation of Y-type zeolite with Si/Al>3. The result showed that the above- mentioned silica-rich Y-type zeolite

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was difficult to synthesize because it was limited by the reaction kinetics during crystallization. The silica-rich Y-type zeolite is formed by polycondensation of citrate and aluminate [4], [5]. The reaction activation energy is high and the polycondensation reaction rate is small, so that it is difficult to polymerize and crystallize.

B. Type and Concentration of Alkali Activator

Wang et al. [6] synthesized the zeolite by mixing different concentrations of NaOH (0.1~1.0 M) with the fly ash. The results showed that the higher concentration of NaOH provided higher alkalinity, better activation efficiency, and faster hydrothermal time. However, NaOH has the best activation efficiency for alkali fusion. Shigemoto et al. [7] also used NaOH as the alkali activator and mixed with fly ash in a fixed ratio. After the alkali fusion reaction at a specific temperature and hydrothermal reaction at 100 °C, zeolite with higher crystallinity can be produced. Xu [3] studied the crystallization process of type A zeolite at different alkali concentrations, the results showed that the crystallization rate was increased with higher alkali concentration, and the particle size of zeolite products were smaller and more uniform. The possible reason is presumed that the increase of alkali concentration could promote the rates of polycondensation reaction and also increase the nucleation rate during hydrothermal processes.

C. L/S

The L/S of hydrothermal synthesis solution will affect the concentration and dispersion of silica and aluminum species in the solution, and it is also one of the main parameters affecting the synthesis of zeolite. Tamura [8] used MSW fly ash to synthesize zeolites and explored the effects of different L/S of precursor solution on the synthesis of zeolite, as well as the adsorption capacity of molecular sieves for heavy metal ions. The results show that when the liquid-solid is relatively high, the Si/Al ratio in the precursor liquid is the highest, which is beneficial to the synthesis of zeolite.

D. Hydrothermal Conditions

The hydrothermal temperature, time and pressure are important factors affecting the synthesis of zeolite. Most of the hydrothermal reaction is carried out under closed conditions. Therefore, the pressure comes from the autogenous pressure in the autoclave. The pressure during the experiment is between 200 and 3000 bar. The hydrothermal temperature affects the hydrothermal reaction rate during the synthesis of the zeolite, which in turn affects the autogenous pressure in the reactor and changes the crystallized product of the zeolite [9], [10]. The hydrothermal time has an important effect on the crystalline phase of the synthesized zeolite. At proper hydrothermal time, the zeolite crystals with relatively uniform particle size can be obtained. Inada et al. [11] addressed that the formation of zeolite needs to be more than 5 hr, and the zeolite yield and species have only a small change in the hydrothermal time of 5-24 hours. Johnson and Arshad [2] pointed out that the crystallization temperature of zeolite is most suitable between 70 and 200 °C. The hydrothermal time is proportional to the crystallization effect. As the hydrothermal time is longer, the crystal phase is more stable and complete. The reaction time for the synthesis of zeolite is better at 24~120 hrs.

E. Calcination Temperature

The calcination temperature can affect the crystallinity and specific surface area of the zeolite. The literature indicates that the zeolite crystal phase will appear as the calcination temperature was above 500 °C. The crystallinity of the zeolite will increase as the calcination temperature increases [12].

According to the comprehensive literature reviews, many researches on the synthesis of zeolite mostly uses general wastes such as sludge and coal ash as raw materials, and few researches focused on the incineration fly ash [7], [12]. Different operating conditions have great influence on the characteristics and effects of synthetic zeolite. Therefore, this study aims to explore the feasibility of synthesizing zeolite from the fly ash in a large-scale waste incineration plant in Taiwan by alkali fusion and hydrothermal methods. According to the main parameters and influence factors pointed out in the literature, different experimental conditions are changed to explore the optimum synthesis conditions. The characteristics of zeolites such as the specific surface area were analyzed to provide useful information for future application and development.

II. Experimental Processes and Analysis Method

The fly ash of a large-scale MSW incineration plant in Taiwan was used as the starting material to provide the silica and aluminum source of zeolite synthesis. The zeolite was synthesized by alkali fusion hydrothermal method, and the experimental design was carried out with the Taguchi orthogonal table method. The three main control factors (silica to aluminum ratio, L/S of hydrolysis, hydrothermal time) were explored with three different operating levels, respectively. The effects of different factors and conditions on the synthesis of zeolite were investigated to seek the optimum synthesis conditions for the incineration fly ash.

The experimental procedure is shown in Fig. 1. First, the silica to aluminum ratio (10, 20, 40) of different raw materials were adjusted. Then appropriate amounts of alkali activator (NaOH) were mixed with the raw materials and the alkali to ash ratio was fixed at 1.5. The mixed sample was put in in a crucible and delivered to an electric furnace to carry out the alkali fusion reaction at 400 °C for 40 minutes. After the reaction was completed and the temperature was cooled down, the alkali fusion products was taken out and adding DI water at different L/S (100, 150, 200) to perform the hydrolysis reaction at 105 °C for 24 hr. After that, the residual and insoluble were removed by filtration. The filtrate was added with 1.2% CTAB and the pH was adjusted to about 10 with 1 M sulfuric acid. The precursor solution for the hydrothermal synthesis of the zeolite is complete. In the next hydrothermal process, the above precursor solution was placed in a hydrothermal reactor, sealed with a lid, and the reaction temperature was controlled at 105 °C and the reaction time was controlled at 12, 24, 48 hours, respectively. After the hydrothermal reaction was completed, the solid particles were taken out by filtration and dried. These