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

Yi-Jie Lin, Jyh-Cherng Chen

***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 °C for 40 min, hydrolysis with Liquid to Solid ratio (L/S)= 200 at 105 °C for 24 h, and hydrothermal synthesis at 105 °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

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solid particles were the synthesis products, zeolite, and they were finally calcined at 550 °C for 6 hrs. In order to study the effects of different factors and conditions on the synthesis of zeolite, this study used the Taguchi orthogonal table method to carry out the experimental design. The influence of different operating factors on the synthesis of zeolite from incineration fly ash and the optimum conditions were investigated. All the operating parameters and conditions in each experiment are shown in Table I.

The analysis items and methods for determining the characteristics of incineration fly ash and synthesized zeolite are briefly described as follows: (1) The specific surface area, pore volume and pore size of the samples are measured by a specific surface area analyzer with N2 adsorption isotherm. (2) The contents of different metals in the fly ash were analyzed by microwave digestion and inductively coupled plasma spectrometer. (3) TCLP was used to determine whether the fly ash exceeds the limits and identified as the hazardous industrial waste. (4) The major species in the fly ash and zeolite were identified by X-ray diffraction spectrometer (XRD). The XRD pattern of the sample was compared with the JCPDS standard patterns. (5) Scanning Electron Microscope (SEM) was used to observe the surface morphology and pore distribution of the samples. The energy dispersive spectrometer (EDS) was also used to qualitatively determine the elements and relative compositions on the sample surface.

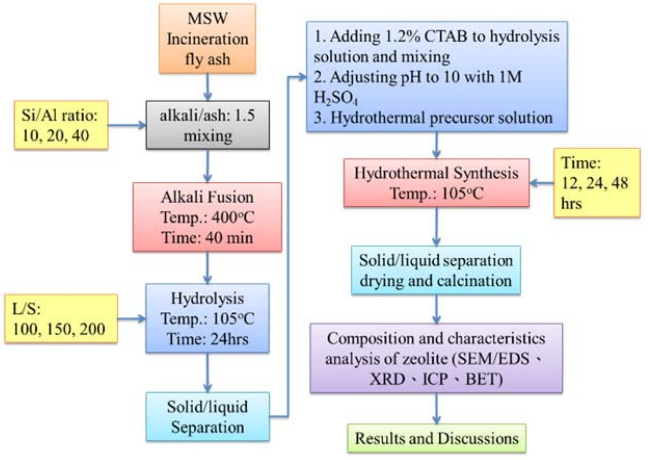


Fig. 1 The experimental flow chart

TABLE I
THE EXPERIMENTAL OPERATING CONDITIONS

Run	Si/Al	L/S	Hydrothermal time	alkali/ash ratio	Alkali fusion temp.
1	10	100	12	1.5	400
2	10	150	24	1.5	400
3	10	200	48	1.5	400
4	20	100	24	1.5	400
5	20	150	48	1.5	400
6	20	200	12	1.5	400
7	40	100	48	1.5	400
8	40	150	12	1.5	400
9	40	200	24	1.5	400
10	40	100	24	1.5	400

III. RESULTS AND DISCUSSIONS

A. Characteristics and Compositions of Fly Ash

The fly ash collected from the large-scale MSW incineration plant is pretreated by drying and then subjected to the metal composition analysis and surface property analysis, including BET specific surface area analysis, inductively coupled plasma spectrometer (ICP-AES), TCLP, and XRD spectrometer, SEM, etc., to understand the basic composition, structure, and the surface characteristics of original fly ash, as a reference for the subsequent synthesis of zeolite.

The contents of heavy metals in the original fly ash are shown in Table II. The main metals contained in the incineration fly ash are Ca, Si, K, Mg, Al, Na, Fe. The TCLP results are shown in Table III. It can be found that the leaching concentration of lead in the incineration fly ash exceeds the TCLP limits, so the fly ash should be identified as the hazardous waste.

The surface characteristics of incineration fly ash can be known from the results of specific surface area analysis (Table IV). The specific surface area of original fly ash is only 8.59 m^2/g. Fig. 2 (a) illustrates the appearance of original incineration fly ash and the morphology is full of fine gray powders. The microstructure of the fly ash is shown in Figs. 2 (b) and (c). Fig. 2 (b) shows that the surface of fly ash was mixed with many columnar and spherical structures, and the uniformity was not good. Fig. 2 (c) shows the particle agglomerations on the surface of fly ash and most of the particles are spherical. Moreover, the fly ash was also analyzed by EDS. The results are shown in Table V. The main elements of fly ash are O, Cl, Ca, K, Na, Si, S, of which the content of O, Cl, and Ca is relatively high. Fig. 4 shows the XRD results of incineration fly ash. It can be found that the main crystal species of fly ash is SiO_2 (Quartz), and the others are alkaline metal compounds such as SiO_2, Al_2O_3, CaO, Na_2O, and KCl.

TABLE II
THE CONTENT OF METALS IN THE FLY ASH

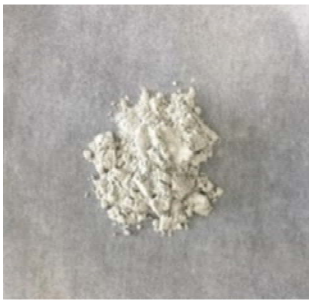
Si(%)	Al(%)	Ca(%)	Na(%)	Fe(%)	K(%)	Mg(%)	Si/Al
12.20	0.83	31.13	0.41	0.37	1.82	1.11	14.70

TABLE III
THE TCLP RESULTS OF FLY ASH (PPM)

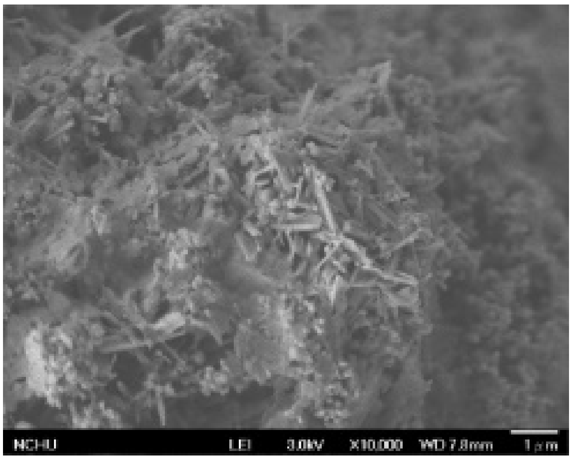
	As	Se	Pb	Cd	Cr	Ag	Cu	Hg	Ba
Regulatory value	5.0	1.0	5.0	1.0	5.0	5.0	15.0	0.2	100.0
Measured value	0.09	0.11	18.92	0.01	0.04	N.D.	0.25	N.D.	2.18

TABLE IV
THE SURFACE PROPERTIES OF INCINERATION FLY ASH

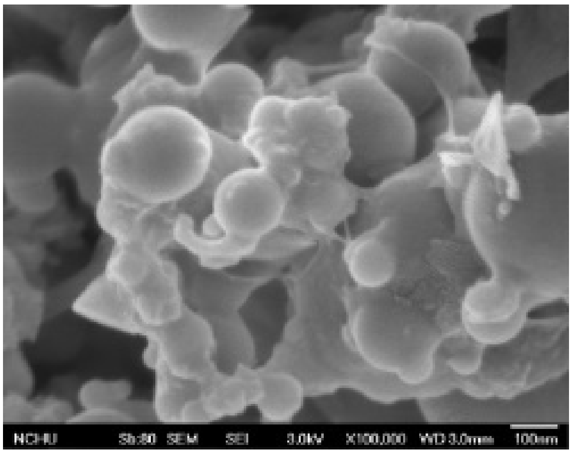
	BET Surface Area (m^2/g)	Pore Volume (m^3/g)	Pore Size (Å)
Fly ash	8.59	0.002992	13.93



(a) appearance



(b) 10kX



(c) 100kX

Fig. 2 The SEM pictures of incineration fly ash

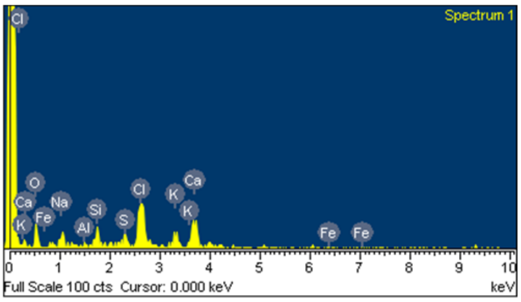


Fig. 3 The EDS pattern of incineration fly ash

TABLE V
THE EDS RESULTS OF INCINERATION FLY ASH

Element	Weight%	Atomic%
O K	34.20	52.59
Na K	7.29	7.80
Al K	-0.02	-0.02
Si K	3.99	3.49
S K	3.47	2.66
Cl K	24.84	17.24
K K	8.06	5.07
Ca K	18.16	11.15
Fe K	0.00	0.00
Totals	100	

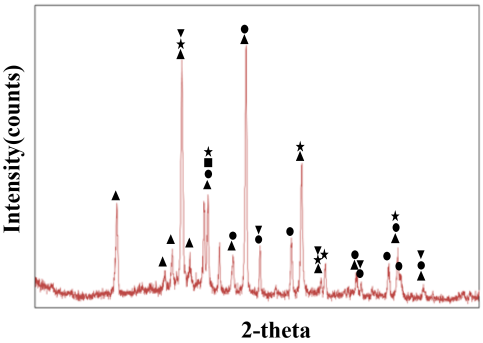


Fig. 4 The XRD pattern of incineration fly ash ▲SiO_2, ●Al_2O_3, ■CaO, ★Na_2O, ▼KCl

B. Effect of Different Synthesis Conditions on Zeolite Properties

The results of specific surface area analysis for the synthesized zeolites in different experimental condition are shown in Table VI. It can be found that the specific surface areas of the synthesized zeolites under different operating conditions are between 11 and 651 m^2/g, and the variation range is large. Comparing the data with the related literature [6], [7], [9]-[11], we can find that the synthesized zeolite in the experiment has similar specific surface area to that of the general zeolite. These zeolites have the potentials for further reuse as an adsorbent. Using the Minitab statistical software for further analysis and comparison of the above experimental results, the influence of different operating factors on the specific surface area of the synthesized zeolite can be determined from the S/N response diagram (Fig. 5) and the response value (Table VII). When the silica to aluminum ratio of the raw material increased, the S/N response value for the specific surface area of the synthesized zeolite was also increased. The L/S for hydrolysis has the largest S/N response value at 100, implying that the zeolite has the best specific surface area as the L/S is 100. For the hydrothermal time, the maximum S/N response value and the best specific surface area occurred at 24 hrs. It can be concluded from Table VII that the degree of influence of different operating conditions on hydrothermal synthesis of zeolite is as follows: the silica to aluminum ratio in the raw material > hydrothermal time > hydrolysis L/S. In addition, from the results of the optimization analysis, the optimum operating conditions for the synthesis of zeolite from MSW incineration fly ash were: silica to aluminum ratio was 40, hydrothermal time was 24 hrs, and the hydrolysis L/S was 100.

The characteristics of different synthesized zeolite under various experimental conditions were compared based on the results of XRD and SEM/EDS analysis. The effects of different operating conditions on the type and characteristics of the synthesized zeolite were investigated. The surface characteristics of zeolites synthesized in tests 1 and 9 were observed by SEM and shown in Fig. 6. Comparing the SEM pictures of the original fly ash, we can find that the surface of the zeolite synthesized under the two different operating conditions had many fine particles. The surface particles of the synthetic zeolite in Test 9 were relatively uniform and dispersed. The agglomeration of the particles on the surface of zeolite was more obvious in Test 1. The results of EDS analysis of synthesized zeolites are shown in Figs. 7, 8 and Tables VIII and IX. The main elements on the surface of synthetic zeolite in Test 1 were oxygen, silica, aluminum, lead, calcium, zinc, sulfur and sodium. The main elements on the surface of synthetic zeolite in Test 9 are in the order of oxygen, silica, sodium, aluminum, chlorine and sulfur. Moreover, it can be found that the silica to aluminum ratio of synthetic zeolite is higher than that of the raw material, indicating that the silica and aluminum had entered into the synthetic zeolite structure.

TABLE VI
THE SPECIFIC SURFACE AREA OF ZEOLITES SYNTHESIZED AT DIFFERENT OPERATING CONDITIONS

Run	Specific surface area (m^2/g)
1	514.22
2	78.23
3	11.5
4	140.75
5	66.56
6	11.42
7	80.83
8	258.79
9	651.51
10	430.50

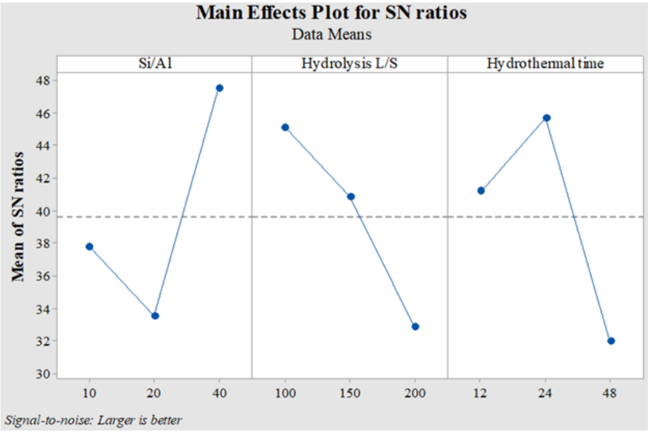
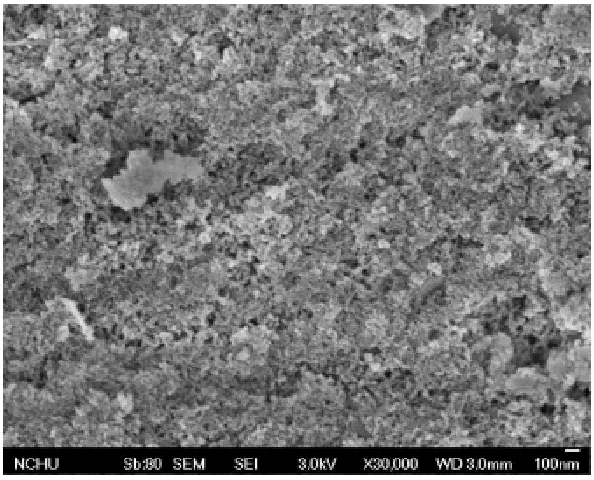
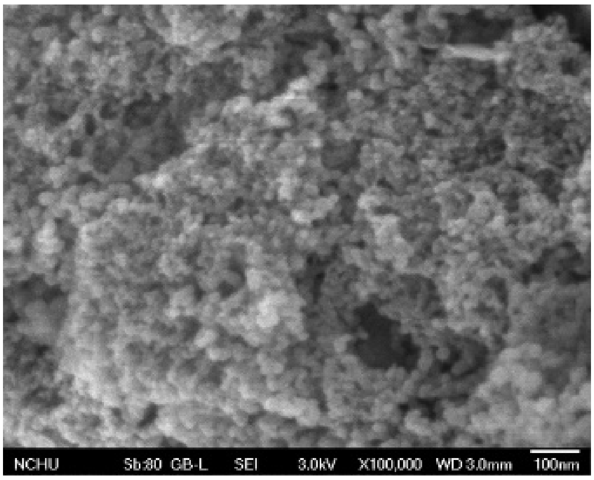


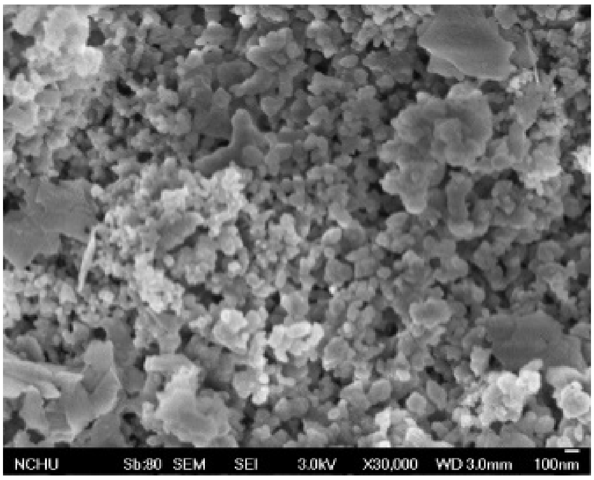
Fig. 5 The S/N response of different operating factors on the specific surface area of synthesized zeolites



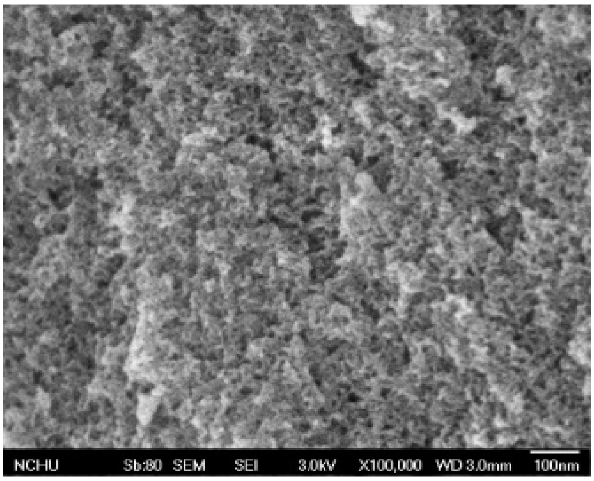
(A) Run1 (30kX)



(B) Run1 (100kX)



(C) Run9 (30kX)



(D) Run9 (100kX)

Fig. 6 The SEM pictures for the surface morphology of zeolites synthesized at different tests

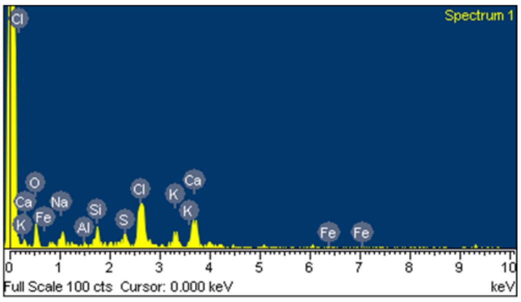


Fig. 7 The EDS pattern of zeolite synthesized in Run1

TABLE VII
THE S/N RESPONSE VALUES OF DIFFERENT OPERATING FACTORS ON THE SPECIFIC SURFACE AREA OF SYNTHESIZED ZEOLITES

Level	Si/Al	Hydrolysis L/S	Hydrothermal time
1	37.77	45.11	41.21
2	33.53	40.86	45.70
3	47.56	32.88	31.94
Delta	14.03	12.23	13.76
Rank	1	3	2

TABLE VIII
THE EDS RESULT OF ZEOLITE SYNTHESIZED IN RUN1

Element	Weight%	Atomic%
O K	51.92	68.08
Na K	1.75	1.60
Al K	7.99	6.21
Si K	26.44	19.75
S K	2.36	1.55
Cl K	-0.08	-0.05
Ca K	3.08	1.61
Zn L	2.69	0.86
Pb M	3.85	0.39
Totals	100	

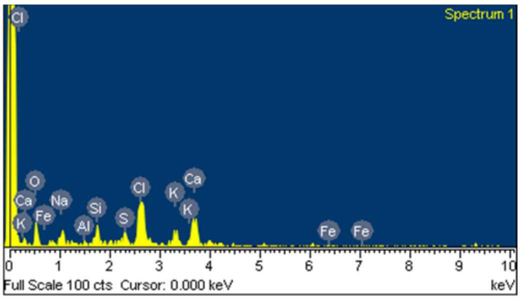


Fig. 8 The EDS pattern of zeolite synthesized in Run9

TABLE IX
THE EDS RESULT OF ZEOLITE SYNTHESIZED IN RUN9

Element	Weight%	Atomic%
O K	58.58	70.97
Na K	3.50	2.95
Al K	2.79	2.01
Si K	33.88	23.38
S K	0.14	0.08
Cl K	1.11	0.61
Ca K	0.00	0.00
Totals	100	

IV. CONCLUSIONS

In this study, the fly ash of a large-scale MSW incineration plant was selected as the original starting material for the synthesis of zeolite by alkali fusion and hydrothermal method. The effects of different operating conditions on the specific surface area of the synthesized zeolite were investigated. The comprehensive experimental results can be summarized as:

1. The specific surface area of the incineration fly ash was very low and only 8.59 m^2/g. The main components in the fly ash were Ca and Si species. The TCLP results indicated that the leaching concentrations of most metals complied with the regulatory values except lead.
2. The results of Taguchi Orthogonal Table method combined with Minitab analysis indicated that the optimum operating conditions for the synthesis of zeolite from MSW incineration fly ash were: silica to aluminum ratio was 40, alkali to ash ratio was 1.5, NaOH alkali fusion at 400 ^{o}C for 40 minutes, hydrolysis L/S was 100, and hydrothermal at 105 °C for 24 hours.
3. The influence degree of different operating conditions on the synthesis of zeolite from MSW incineration fly ash follows the sequence: silicate aluminum ratio> hydrothermal time> hydrolysis L/S.
4. The experimental results approve that the incineration fly ash can be used to synthesize zeolite by alkali fusion and hydrothermal method. The specific surface area of the synthesized zeolite can be greatly increased from the original fly ash 8.59 m^2/g to 651.51 m^2/g. The synthesized zeolite has great reuse potentials for the adsorption of various pollutants in the future. The purpose of resource recycling and sustainable development could be achieved.

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