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Synthesis of zeolite-like material by hydrothermal and fusion methods using municipal solid waste fly ash

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Abstract

Due to the widely application of waste incineration in China, considerable waste ash were generated every year. The treatment and utilization of municipal solid waste fly ash (MSWFA) remains a challenging work. Unlike coal fly ash (CFA) that can be used to synthesize different types of zeolite-like materials, MSWFA is lacking of silicon and aluminum which are essential to the synthesis of zeolites. The aim of this research was to investigate the possibility of zeolite synthesis using MSWFA by adding silicon and aluminum sources from various solid waste to achieve recycling utilization. The raw materials were treated with alkaline using hydrothermal and fusion methods. The synthetic products were examined by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analyses (TGA). The results indicated that the products obtained from both hydrothermal and fusion treatment demonstrated the characteristics of zeolite-like materials. Compared to the raw materials, the synthetic products showed higher cation exchange capacity of 1.00 meq/g, implying the potential application by converting MSWFA into useful materials.

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Keywords: municipal solid waste fly ash, zeolite-like material, hydrothermal, fusion.

1. Background

In recent years, incineration of municipal solid waste (MSW) is becoming a favorable option for waste management. Compare to landfill and composting, incineration could effectively reduce waste volume (80-90%) and mass (70-80%), while recover energy and gain considerable revenues^[1]. Especially in China, more than 172 million tons of MSW was generated in 2013 and the incineration rate increased rapidly to 26.9% which was only 2.9% in 2004^[2]. In consequence, a portion about 3-5% of generation remains as fly ash (MSWFA). To date, only 50% of MSWFA is treated in China using stabilization/solidification and landfilling^[3]. However, serious concerns exist for both treated and untreated MSWFA because fly ash contains high levels of various heavy metals such as As, Zn, Cr, Cd etc., implying that the ash has potential risk to the environment. Furthermore, landfilling of MSWFA occupies plenty of land resources and leads to a high cost about 2000-3000 yuan/ton^[3]. This generated interests in treating and reusing MSWFA using innovative technologies such as chemical conversion of MSWFA to synthesize zeolite-like materials.

Zeolite-like materials have been widely used for adsorbent, ion exchanger, catalyst and advanced functional materials with the significant adsorption and cation exchange capacity (CEC), large specific surface area, rich micropore and good thermal stability. At present, different types of zeolites such zeolite A, X and P were synthesized from coal fly ash (CFA), MSW bottom ash, co-combustion ash of MSW and coal which had similar composition with natural zeolite^[4,5]. To adjust the Si/Al molecule ratio,

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pure silica and alumina chemical compounds were usually added as silicon and aluminum sources such as aerosol powder and sodium aluminat^{6, 7}. However, the investigation on zeolite synthesis from MSWFA is still in the start stage. Compare to other waste ash, MSWFA is lacking of silicon and aluminum which are the primary elements required for building zeolites' structure, especially in the ash of China's MSW incineration power plant. In addition, some solid wastes were rich in silicon and aluminum contents such as waste glass and aluminum scruff ash.

The aim of this research was to investigate the possibility to synthesize zeolite from MSWFA by adding silicon and aluminum sources from solid waste such as waste glass powder (GP) and aluminum oxide powder. Hydrothermal and fusion treatments were used as synthesis methods and the synthetic products were examined by multiple characterization techniques, while the CEC of the synthetic products were established. The benefit of this approach will be the recycling utilization of MSWFA together with various solid wastes.

2. Materials and Methods

2.1. Materials

The MSWFA were collected from Nanshan MSW incineration power plant in Shenzhen, China, with drying in oven at 105 °C for 24h. Table 1 presented the mainly chemical composition of raw materials, natural zeolite and synthetic products. Compare to natural zeolite, the amount of calcium was relatively high and the total amount of silicon and aluminum was very low in MSWFA. To adjust Si/Al molar ratio, waste glass powder and Al₂O₃ powder (AR, Tianjin Fuchen Chemical Reagents Factory, China) were added into the MSWFA as silicon and aluminum source. The waste glass powder was ground from beer bottle using a ball-mill grinder and sieved to a constant particle size (< 200 μm) before use which was rich in silicon content.

Table 1. The chemical composition of raw materials, natural zeolite and synthetic products

Element (%)	Si	Al	Ca	Fe	K	Br	Ti	S	Zn	Cl	Cu	Pb	Cr
MSWFA	0.3	2.2	41.7	0.7	8.9	0.9	0.1	2.5	2.1	39.7	0.2	0.3	0.01
Glass powder	56.1	3.2	33.2	3.2	1.8	-	0.2	0.5	0.1	-	0.1	0.1	0.9
Natural zeolite	58.7	12.1	12.5	5.9	0.3	-	0.7	0.5	0.2	-	0.1	-	-
Hydrothermal product	27.0	16.3	51.0	2.0	0.5	-	0.3	-	1.8	-	0.2	0.3	0.3
Fusion product	28.6	15.4	49.6	2.1	0.7	-	0.3	-	2.2	-	0.3	0.3	0.2

2.2. Hydrothermal method

In the preliminary experiment, different parameters were investigated to optimize the zeolitization process, including reaction temperature and time, sodium hydroxide concentration in the reaction solution and the liquid/solid ratio. Zeolites synthesis process by hydrothermal treatment was performed by placing 6 g MSWFA, 12 g glass powder and 7 g Al₂O₃ powder in a 250 mL round-bottom flask to obtain the silicon/aluminum molecule ratio of 1 and the total amount of SiO₂ of over 50%. Then 2.5N sodium hydroxide solution was added into the raw materials to obtain liquid/solid ratio of 10. The flask was placed on a heater with stirrer in 300 rpm and constant temperature at 60 °C for 24 h. After the hydrothermal process was completed, the reacting solution was filtrated and products were washed for several times with deionized water until the pH of solution was below 10. At last, hydrothermal products (sample 2) were separated and dried at 105 °C for 24 h before use.

2.3. Fusion method

Zeolites synthesis process by fusion treatment was performed by placing 6 g MSWFA and 7.2 g sodium hydroxide (NaOH/MSWFA ratio of 1.2) in a nickel crucible and heated in a furnace maintained at 550 °C for 1 h. Fused product was cooled in air and placed in a 250 mL Erlenmeyer flask with addition of deionized water, 12 g glass powder and 7 g Al₂O₃ powder to obtain liquid/solid ratio of 10. An aging process was carried out with vigorous shaking at room temperature for 24 h, followed by crystallizing process under stirring in 300 rpm with constant temperature at 90 °C for 24 h. After the fusion process was completed, the reacting solution was filtrated and products were washed for several times with deionized water until the pH of solution was below 10. At last, fusion products (sample 2) were separated and dried at 105 °C for 24 h before use.

2.4. Characterization Techniques

Synthetic products using different treatments were characterized and compared to the natural zeolite supplied by Yueyang Mining Factory in Hunan Province, China. The chemical composition of raw materials and synthetic products were determined by energy dispersive X-ray spectroscopy (EDX-LE, SHIMADZU) and presented in Table 1. The crystalline properties of natural zeolite and the synthetic products were examined by X-ray diffraction (XRD) with Ni-filter, Cu K_α radiation, operating at

40 kV, 200 mA. And the Joint Committee of Powder Diffraction Standards (JCPDS) software was used to identify the crystalline phases. Infrared absorption measurements were carried out using a Fourier transform infrared (FTIR, SHIMADZU) spectrophotometer. The FTIR spectra in the wavelength range from 400 to 4000 cm^{-1} were obtained with the use of the KBr pellet technique. Thermogravimetric analyses (TGA, SHIMADZU) were obtained with the use of a thermal analyser under temperature ranging from 20 $^{\circ}\text{C}$ to 1000 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$, in N_2 atmosphere.

The cation exchange capacity (CEC) of the synthetic products was determined by using sodium-ammonium acetate method number 9081 described in the Solid Waste Test Methods (SW-846), while the element concentration was determined by inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer).

3. Results and Discussion

3.1. XRD results and analysis

XRD results of natural zeolite and synthetic products prepared by hydrothermal method and fusion method were shown in Figure 1. The results suggested that natural zeolite and the synthetic products consisted of three major types of compounds: zeolites, calcium carbonate and quartz. According to the powder pattern analysis of JCPDS software, the intense peak of hydrothermal product appeared at 2θ -29.46 $^{\circ}$ and peaks at 2θ -43.30 $^{\circ}$, 49.66 $^{\circ}$ and 60.78 $^{\circ}$ may imply the presence of coesite (29.46 $^{\circ}$, 43.28 $^{\circ}$, 49.66 $^{\circ}$ and 60.73 $^{\circ}$), which belongs to quartz materials. The small peaks appeared at 2θ -23.15 $^{\circ}$ may imply the presence of perialite (23.21 $^{\circ}$), at 2θ -47.59 $^{\circ}$ (47.57 $^{\circ}$) and 48.52 $^{\circ}$ (48.51 $^{\circ}$) may imply the presence of zeolite Y and zeolite A, which belongs to zeolites. The remaining peaks appeared at 36.00 $^{\circ}$, 39.40 $^{\circ}$ and 57.47 $^{\circ}$ may imply the presence of calcium carbonate (35.99 $^{\circ}$, 39.40 $^{\circ}$, and 57.50 $^{\circ}$). For the powder pattern analysis of fusion product, the intense peak of fusion product appeared at 2θ -29.40 $^{\circ}$ and peaks at 2θ -39.38 $^{\circ}$ and 43.18 $^{\circ}$ may imply the presence of calcium carbonate (29.39 $^{\circ}$, 39.38 $^{\circ}$, and 43.15 $^{\circ}$). The small peaks appeared at 2θ -10.97 $^{\circ}$, 23.15 $^{\circ}$, 48.48 $^{\circ}$ and 67.36 $^{\circ}$ may imply the presence of perialite (11.05 $^{\circ}$, 23.21 $^{\circ}$, 48.49 $^{\circ}$ and 67.31 $^{\circ}$), which belong to zeolites. The remaining peaks appeared at 47.48 $^{\circ}$ may imply the presence of cristobalite high (47.47 $^{\circ}$), which belongs to quartz materials. Moreover, the zeolites crystals of synthetic product by hydrothermal treatment is more similar to natural zeolite than that by fusion treatment; and hydrothermal products have stronger intensity in XRD diagram with a possible contribution of richer zeolites content.

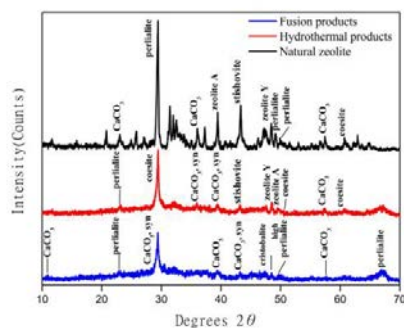


Figure 1. The XRD diagram of natural zeolite and synthetic products. All diagrams are plotted with the same intensity scale.

3.2. FTIR results and analysis

The FTIR spectrum of natural zeolite is presented in Figure 2. The bands occurring in the FTIR spectra of zeolites can be characterized as four typical types which were all showed in these results:

(a) Narrow band in the regions 1200-950 cm^{-1} attributed to the internal tetrahedron vibrations of Si-O-Si and Si-O-Al should be the strongest vibration band and assigned to a T-O stretching mode, which was showed at about 1047.35 cm^{-1} in the FTIR spectrum of natural zeolite. Furthermore, this vibration band was significant for the estimation of aluminum content in the crystalline framework, and it shifted to a lower wavenumber with increasing number of Al atoms in the framework tetrahedral sites^[8]. For instance, clinoptilolite with 6 Al atoms per formula unite showed a band at $\sim 1059 \text{ cm}^{-1}$ while heulandite with 9 Al atoms per formula unit showed a band at $\sim 1022 \text{ cm}^{-1}$ ^[9]. Moreover, substitution of Al^{3+} for Si^{4+} decreases T-O-T angle, and the resulting frequency is lower, due to the weaker character and increased length of the Al-O bond; the force constant for the mode in an Al-O-Si bond is lower than the corresponding mode in a Si-O-Si linkage^[8]. The FTIR spectrum results of natural zeolite

indicated that natural zeolite has an intermediate content in Al atoms per formula unit and the similar crystal structure with mordenite.

(b) Narrow band in the regions 500-420 cm^{-1} attributed to the Si–O–Si and Si–O–Al vibrations should be the next strongest band and assigned to a T–O bending mode, which was showed at about 470.63 cm^{-1} in the FTIR spectrum of natural zeolite.

(c) Bands in the regions 800-500 cm^{-1} attributed to the pseudo-lattice vibrations was showed at about 601.79 cm^{-1} in the FTIR spectrum of natural zeolite, these vibrations are insensitive to the nature of the channel cations, as well as to the Si/Al ratio^[10].

(d) Bands in the regions 3700-1600 cm^{-1} was attributed to the presence of zeolite water. More specifically, broad band at about 3440 cm^{-1} is the characteristic of hydrogen-bonded OH to oxygen ions; sharp band at about 3619 cm^{-1} is the typical of isolated OH stretching; board band at about 1640 cm^{-1} is the usual bending vibration of water. In the FTIR spectrum of natural zeolite, broad band in the regions 3626.17-3444.87 cm^{-1} and band at about 1645.28 cm^{-1} all appeared.

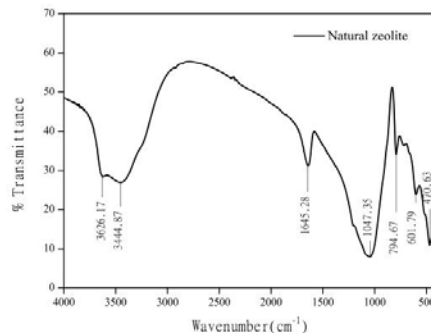


Figure 2. The FTIR spectrum of the natural zeolite.

The FTIR spectra of the synthetic products by hydrothermal and fusion methods were presented in Figure 3. The strongest bands due to the T–O stretching vibration of hydrothermal and fusion products appeared at about 996.34 cm^{-1} and 970.19 cm^{-1} , respectively, indicating that the number of Al atoms in hydrothermal product was higher than that in fusion product; the next strongest bands due to the T–O bending vibration appeared at about 447.49 cm^{-1} and 443.63 cm^{-1} , respectively. Board bands due to the presence of zeolite water were also presented respectively. Different from natural zeolite, synthetic products showed IR bands in the regions of 1490-1420 cm^{-1} (Figure 3(a) and Figure 3(b)) and at about 871 cm^{-1} (Figure 3(b)), which were assigned to the vibration of CO_3^{2-} ^[11, 12]. Moreover, bands due to the pseudo-lattice vibrations were very weak in the spectra of hydrothermal and fusion products, these bands were connected with the internal tetrahedral bonds typical for the ordered crystal structure, suggested a lower ordered structure for the synthetic products than the natural zeolite^[13]. In general, those FTIR results were in agreement with the XRD results.

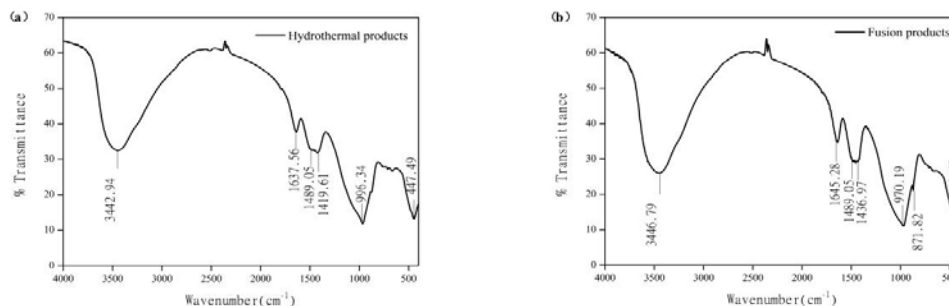


Figure 3. (a) The FTIR spectrum of the synthetic product by hydrothermal method; (b) The FTIR spectrum of the synthetic product by fusion method.

3.3. TG results and analysis

Water on the silicate minerals is usually in two forms as intact molecules and as hydroxyl (-OH) groups formed on dissociation of water interacting with metal ions such as Si^{4+} , Al^{3+} , and O^{2-} [14]. The TG analysis results of natural zeolite and synthetic products were presented in Figure 4. The physical elimination adsorbed water of natural zeolite and synthetic products were observed up to 100°C and 80°C , respectively. At temperature ranging from $100\text{--}300^\circ\text{C}$ or higher, removal of hydroxyl groups by associative desorption were observed. Moreover, hydroxyl groups left the surface mainly at $200\text{--}500^\circ\text{C}$ while the isolated hydroxyl groups were eliminated at higher temperature, leading to the slow weight loss in both TG curves. At temperature above 400°C , the TG curve of natural zeolite reached a stable phase due to the dissociation of almost all -OH groups on the silicate surface. However, the curves of synthetic products sharply dropped at temperature $600\text{--}700^\circ\text{C}$, indicating the existence of calcium carbonate, which was decomposed to carbon dioxide and calcium oxide above initial temperature of 600°C [15,16]. The existence of calcium carbonate was also verified by XRD and FTIR. Furthermore, according to the weight loss at temperature $600\text{--}700^\circ\text{C}$, it could be calculated that the calcium carbonate contents of synthetic products by hydrothermal and fusion treatments were 7.5 % and 5.9 %, respectively. The calcium carbonate contents of fusion product was slight lower than that of hydrothermal product, in agreement with the result showed in Table 1. In addition, natural zeolite showed the best thermal stability than the synthetic products, followed by the hydrothermal product.

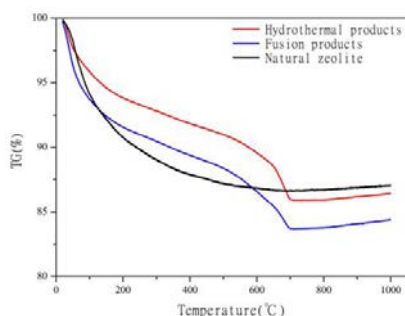


Figure 4. The TG diagram of natural zeolite and synthetic products.

3.4. CEC analysis

Zeolites are crystalline aluminum-silicates with structures made up of a framework of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra linked to each other at the corners by sharing their oxygens. The tetrahedra makes up a three-dimensional network with lots of voids and open spaces. These voids define the various special properties of zeolites, such as the adsorption of molecules in the huge internal channels. Moreover, the substitution of Si^{4+} by Al^{3+} in the tetrahedral accounts for a negative charge of the structure, which may give rise to high CEC when the open spaces allow the access of cations; some studies have shown that CEC of synthetic zeolites ranged from $0.3\text{--}4.7\text{ meq/g}$ [4]. Thus, synthetic zeolites from waste ash have the potential in the application of wastewater treatment and have been used as adsorbents to remove selected pollutants from wastewater[17, 18]. The CEC values of raw materials as well as natural and synthetic zeolites were presented in Table 2. It can be seen that the CEC value of 1.00 meq/g for synthetic products was 5 folds of the raw materials due to the conversion of MSWFA into crystalline zeolites. The CEC value of products synthesized by two different treatments were the same, indicating that high quality zeolites were synthesized from MSWFA by both hydrothermal and fusion methods. Compared to natural and synthetic zeolites presented in other studies, the synthetic products in this research demonstrated reasonable CEC values, however, the optimum synthesis conditions need to be further studied.

Table 2. The CEC values of raw materials and synthetic products

Material	MSWFA	GP	Hydrothermal product	Fusion product	Natural zeolites ^[19]	Synthetic zeolites from waste fly ash ^[4]
CEC (meq/g)	0.20	0.22	1.00	1.00	0.64-2.29	0.3-4.7

4. Conclusion

By adding silicon and aluminum sources from solid waste such as waste glass and aluminum oxide powder, zeolite-like materials were synthesized from MSWFA using hydrothermal and fusion methods. The XRD results showed that the main materials in synthetic products were zeolites, quartz and calcium carbonate. Zeolites such as perlielite, zeolite A and Y, quartz such as stishovite and coesite, natural and synthesis calcium carbonate were all detected. The results also showed that synthetic

product by hydrothermal treatment had higher similarity in zeolite crystalline properties with natural zeolite than that by fusion treatment. The stronger intensity in XRD diagram implied a possible contribution of richer zeolites content in hydrothermal product than that in fusion product. The results of FTIR spectra showed that bands due to the internal tetrahedron stretching and bending vibrations of Si–O–Si and Si–O–Al in synthetic products were all presented. Moreover, bands due to the presence of zeolite water and the vibration of CO_3^{2-} also appeared, in agreement with the TG results. The results of TG also indicated that the thermal stability of hydrothermal product was higher than that of fusion product. In addition, synthetic products from MSWFA with the CEC value of 1.00 meq/g was 5 folds of the raw materials due to the conversion of raw materials into crystalline zeolites. By incorporation with silica and alumina solid waste, MSWFA can be utilized to synthesize zeolite-like materials. There is no significant difference between the products synthesized by two methods, however, in consideration of energy consumption, hydrothermal treatment has been demonstrated to be the preferred method in zeolite synthesis from MSWFA.

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