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

Lulu Deng [a], Qiyong Xu [a], Huanan Wu [a,*]

[a]Shenzhen Engineering Laboratory for Eco-efficient Polysilicate Materials, School of Environment and Energy, Shenzhen Graduate School, Peking University, Shenzhen 518055, China

**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,

* Corresponding author: WU Huanan. Tel.: +86-13689563140 ; fax: +86-755-26032670 .
*E-mail address:* wuhn@pkusz.edu.cn


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pure silica and alumina chemical compounds were usually added as silicon and aluminum sources such as aerosol powder and sodium aluminate[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℃ 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 $Al_2O_3$ 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 $Al_2O_3$ powder in a 250 mL round-bottom flask to obtain the silicon/aluminum molecule ratio of 1 and the total amount of $SiO_2$ 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 ℃ 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 ℃ 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 ℃ 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 $Al_2O_3$ 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 ℃ 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 ℃ 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 $K_\alpha$ radiation, operating at