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Optimization of crystal growth of sub-micron ZSM-5 zeolite prepared by using $Al(OH)_3$ extracted from fly ash as an aluminum source

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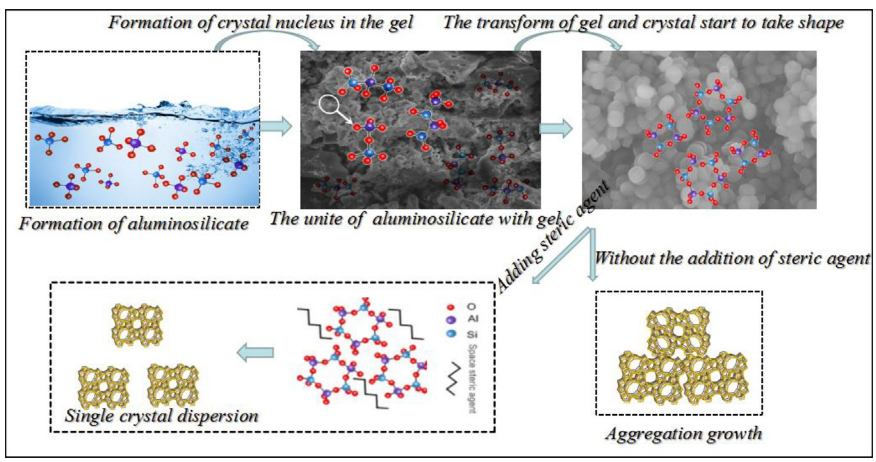
HIGHLIGHTS

- A novel approach was proposed to prepare ZSM-5 zeolite by using Al(OH)3 extracted from fly ash, as an aluminum source.
- The variations of crystallization curves for ZSM-5 growth under different hydrothermal conditions were investigated.
- The formation of ZSM-5 crystal was investigated.
- Growth process regulation of ZSM-5 was discussed under the effect of organic steric hindrance agents.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel approach was proposed to prepare ZSM-5 zeolite via hydrothermal synthesis by using $Al(OH)_3$, which was extracted from fly ash by a staged treatment, as an aluminum source. The synthesis parameters and crystal growth of ZSM-5 were optimized. The optimization of crystal growth for ZSM-5 was investigated under the effect of organic steric-hindrance agents. The crystal phase and morphology of the ZSM-5 were characterized by X-ray diffractometry and scanning electron microscopy, and the particle size distribution was measured by laser particle-size analyzer. The crystal growth of ZSM-5 under different hydrothermal conditions obeyed the "S" regulation. According to the analysis, the formation of ZSM-5 crystal occurred via four steps: (1) the formation of amorphous aluminosilicate by the condensation of silicate ions and aluminate ions; (2) the particle growth and aggregation of the amorphous aluminosilicate; (3) crystallization and crystal growth of ZSM-5; (4) Gentle growth after the zeolite crystal reaches a certain size. The addition of organic steric hindrance agents resulted in a decrease in grain size and crystal-particle formation with a narrow size distribution. Single-grain dispersion resulted and the micropore volume, mesopore volume, and specific surface areas were improved by the presence of organic steric agents.

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Table 1
Chemical composition of raw CFA.

Composition	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	MnO_2	P_2O_5	LOI
wt. %	51.44	30.91	6.76	0.53	3.54	1	0.8	0.54	0.16	0.22	4.1

(LOI = loss on ignition).

1. Introduction

Coal fly ash (CFA) is an industrial solid waste that is generated during coal combustion and transformation, and resulting in serious pollution. According to statistics, CFA from coal combustion exceeded 5.8×10^8 metric tons in 2014 [1], and has become the largest solid-waste resource. The large amount of CFA deposition occupies infield, contaminates water resources and the atmosphere, and is harmful to human health. Unfortunately, only ~50% CFA is used. Because of its compositional similarity to volcanic materials with high SiO_2 and Al_2O_3 contents, CFA is an ideal raw material for zeolite production. Bukhari et al. described the efficient conversion of CFA to zeolites such as ZSM-5 [2]. Na-A zeolite [3], Na-X zeolite [4,5], Na-P zeolite [6–8] and MCM zeolite [9] are produced using fly ash as a raw material, and zeolites are used widely for the purification of pollutant water and refining of oil products and chemicals of catalytic synthesis.

ZSM-5 zeolites were extended infinitely as three-dimensional crystalline aluminosilicates with corner-sharing $[AlO_4]^{5-}$ and $[SiO_4]^{4-}$ tetrahedra that form frameworks with a high SiO_2/Al_2O_3 ratio [10]. They have been used mainly in practical applications, such as catalyst carriers in the petroleum refining industry [11,12], and for separating and extracting organic compounds in water for environmental protection in water purification because of their favorable adsorption performance [13,14]. Therefore, the preparation of zeolites with a smaller grain size and the reduction of production costs are two issues of crucial importance for industrial applications. It is of vital importance to reduce costs to contrast with the high-cost chemical raw materials of silica and aluminum salts.

We selected CFA as a source of aluminum components by activation and separation to synthesize ZSM-5 zeolite via hydrothermal synthesis. The process parameters for the synthesis (crystallization temperature, crystallization time, water–silica ratio) and the crystal growth of ZSM-5 zeolite were optimized. The influences of organic steric-hindrance agents on the grain growth of ZSM-5 zeolite were investigated. The crystal phase and morphology of the ZSM-5 zeolite was characterized by X-ray diffractometry (XRD) and scanning electron microscopy (SEM). The specific surface area and pore volume were measured by Brunauer–Emmett–Teller (BET) and the particle size distribution (PSD) was determined by laser particle analyzer. The results provide a theoretical basis for a new approach to fly ash utilization — the synthesis of ZSM-5 zeolites with $Al(OH)_3$ as an aluminum resource as extracted from fly ash.

2. Experimental section

The chemical composition of CFA is provided in Table 1. Tetrapropylammonium hydroxide (TPAOH, 25% aqueous solution) was from Kente Chemical Ltd., Zhejiang Province, China. Tetraethoxysilane (TEOS) was from Damao Chemical Ltd., Tianjin City, China. Ethanol, polyethylene glycol (PEG), polyvinylpyrrolidone (PVP), triethanolamine (TEA) and sodium hydroxide from Bomao Chemical Ltd., Shandong Province, China, were commercial analytical grade reagents.

The CFA samples were calcined at 800 °C to remove unburned carbon, washed with deionized water to remove soluble impurities and dried at 120 °C for 12 h. To increase the leaching efficiency of the silicon and aluminum compounds and the utilization of CFA, a dried sample (10 g) was mixed with Na_2CO_3 powder (Waco; 97 wt.% Na_2CO_3) at a mass ratio of CFA: Na_2CO_3 = 1:1.5 and calcined at 840 °C for 4 h.

The above powder was mixed with 3 mol L^{-1} HCl in a mass/volume ratio of powder:HCl = 1:10 g mL^{-1} and aged for 2 h at 80 °C with stirring at 250 rpm. The solution was centrifuged to separate the silica gel and $AlCl_3$ solution that contained impurities. By adjusting the pH of the $AlCl_3$ solution with 6 wt.% NaOH solution to pH = 3.8, we make sure that all iron ions were converted to $Fe(OH)_3$ and removed by centrifugation to obtain $NaAlO_2$. Continuous CO_2 was inlet to yield $Al(OH)_3$, and Na_2CO_3 can be obtained and recycled. The SEM image and XRD pattern of the $Al(OH)_3$ samples as extracted from the fly ash is shown in Fig. 1.

The alcohol and TPAOH were diluted with deionized water with stirring at 300 rpm at 50 °C for 1 h. The quantity of deionized water depended on the different H_2O/SiO_2 ratios. The TEOS was added

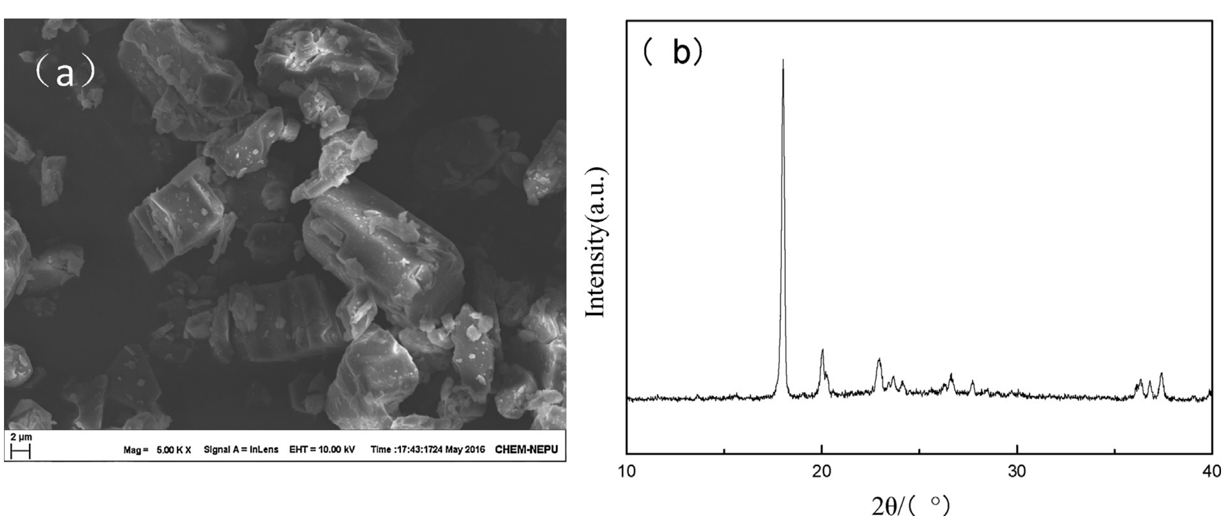

Fig. 1. The SEM image(a) and XRD pattern(b) of $Al(OH)_3$ samples.