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Preparation, characterization and adsorption properties of sodalite pellets

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ABSTRACT

This paper explores the capability of the combined processes of extrusion molding and hydrothermal synthesis for the creation of porous granular single-phase zeolitic products which were prepared from coal fly ash. The key is to introduce the plasticizer of sodium carboxymethyl cellulose (CMC) in order to tailor the relative plasticity of the paste. Furthermore, CMC also acts as a kind of pore-forming agent. The crystalline phase, purity and morphologies of the semi-finished products and the products were characterized by XRD and SEM. Effects of material ration, concentration, crystallinity temperature and time were explored and optimal conditions were shown. The adsorption properties of the as-prepared sodalite pellets were evaluated by the removal of Pb^{2+}. In comparison with commercial activated carbon particles, the as-prepared sodalite pellets exhibit good adsorption performances.

1. Introduction

Since the discovery of their adsorption properties, zeolites have been widely studied as a kind of adsorbent in applications such as water treatment and purification [1–3]. In the most of applications it is a problem that the costs of artificial zeolites are expensive. Many strategies have been proposed to reduce the cost. One possibility is to reduce energy consumption, such as decrease the crystallization temperature and time [4–6]. Several synthesis methods have been reported to prepare zeolites at lower temperatures or shorter crystallization time, even at room temperature. Instead of reducing energy consumption, another possibility is to reduce the materials cost, and this idea has led to the discovery of novel synthesis methods of zeolites which were prepared by using coal fly ash (CFA) as the raw material [7]. It is a promising approach because of reducing the cost of artificial zeolites and improving the utilization rate of CFA. Since the initial study was reported, many kinds of zeolites have been prepared [8,9]. High-quality artificial zeolites can be obtained through hydrothermal alkaline conversion of silicate and aluminate which are extracted from CFA with hot alkaline solution [10]. But this process has the disadvantage of forming the solid residue, implying a low utilization rate of CFA. Furthermore, zeolitic materials synthesized from CFA are powdery, which limits their practical applications.

We report herein the design and synthesis, by combining extrusion molding and hydrothermal synthesis processes, of a highly efficient, cost-effective zeolite-based adsorbent with the desired properties mentioned above. This kind of adsorbent, sodalite pellets, was obtained by controlling the material ration, concentration, reaction time and temperature. The good adsorption properties of as-synthesized sodalite pellets for removing Pb^{2+} were studied.

2. Materials and methods

CFA used in this study was collected from the electrostatic precipitators at the Yangzi Petrochemical thermal power plants in Nanjing. All chemicals obtained from Shanghai Chemical Reagent Co., are of analytical grade and used without further purification. Activated carbon particles are commercial products from Ningshi Chemical Plant (Nanjing, China), which were washed to pH 7 with deionized water and dried at 60 °C for 48 h before use.

The fabrication of sodalite pellets mainly includes the preparation of CFA pellets and their zeolitization. In a typical synthesis of CFA pellets, 45 g CFA, 10 g NaOH, 18 g $Al(OH)_3$ and 6 g CMC were mixed by a rotating disintegrator for 5 min, followed by the addition of 34 mL H_2O. The resulting mixture was stirred until

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homogeneity and aged in a water bath of 60 °C for 5 h. Then, the product was extruded and cut into pellets. After that, the resulting pellets were heated under air atmosphere to 700 °C at a rate of 1 °C/min and heated for another 6 h. After being calcined, CFA pellets were washed several times to remove the excess NaOH and dried at 80 °C for 12 h. Zeolitization of CFA pellets was conducted according to our earlier procedure [11]. Typically, CFA pellets (4 g) and NaOH solution (60 mL) were sealed in a PTFE reactor and kept at 120 °C for 36 h. After cooling to room temperature, the final product was washed with deionized water to remove NaOH and dried at 60 °C for 48 h before use.

X-ray diffraction (XRD, Bruker D8 powder diffractometer) patterns and scanning electron micrographs (SEM, JSM-6380LV microscope) were examined to characterize the intermediate and final products. Decontamination tests were performed using artificial solution containing 20 mg/L of Pb^{2+}, and 0.1 g adsorbents were added to 50 mL artificial solution in 100 mL Erlenmeyer flasks which were shaken at 30 °C and 150 rpm. Then the solutions were filtered by 0.45 μm syringe filters, and the concentrations of Pb^{2+} in the solutions were determined by atomic absorption spectrometer (AAS, AA-320-CRT, Shanghai). Experimental values of the concentrations were the average of triplicate experiments reported.

3. Results and discussion

For the synthesis of zeolites from CFA, amorphous aluminosilicates is the available Si and Al source, which can be obtained by digesting of mullite and quartz [12]. In this study, the digestion was controlled by tuning the mass ratio of NaOH/CFA during the process of preparing CFA pellets. As shown in Fig. 1a, mullite and quartz are the main crystals in the absence of NaOH, which decreases as more NaOH is added. However, when the ratio is up to 2/9 or more, some new crystalline phases are observed. Fig. 1b shows the corresponding amorphous content, which there is an apparent two-stage pattern. The first stage involves the rapid increase when the ratio increases to 1/9, followed by a plateau with slight changes from 1/9 to 2/9. In the second stage, the amorphous content rapidly decreases, and eventually reaches the minimum. It is because the formations of sodalite and nepheline consume amorphous aluminosilicates, resulting in slow growth or decrease of amorphous content, which is consistent with our observations in Fig. 1a. Therefore, when the ratio is 2/9, the amorphous content reaches the maximum, suggesting the optimal ratio. Instead of Si/Al ratio, the mass ratio of $Al(OH)_3$/CFA was discussed because of the existence of sodalite. As shown in Fig. 1c, the products contain nepheline and sodalite without the addition of Al source, and with increasing $Al(OH)_3$/CFA, the intensities of nepheline peaks decreases but sodalite peaks intensities increases accordingly. These results suggest high $Al(OH)_3$/CFA ratio favors the synthesis of sodalite. Thus, the optimal ratio is 2/5, and the optimal formulation of CFA pellets is 45 g CFA, 10 g NaOH, 18 g $Al(OH)_3$, and 6 g CMC.

The crystallization of sodalite was further studied by tuning the conditions of zeolitization. When NaOH concentration is 1 M, the peak of sodalite is not pronounced, as shown by the bottommost curve in Fig. 1d. Instead, there is a strong peak of cristobalite whose chemical composition is SiO_2, implying amorphous Si is more easily recrystallized than Al source. With increasing NaOH concentration, the characteristic peak of cristobalite disappears, and the intensities of sodalite peaks quickly increase, implying the growth of sodalite. However, there is a negligible change as NaOH concentration is increased to 7 M, which indicates that NaOH is excess. The effect of NaOH concentration on zeolitization is fully consistent with the corresponding SEM. Fig. 2a and c shows the

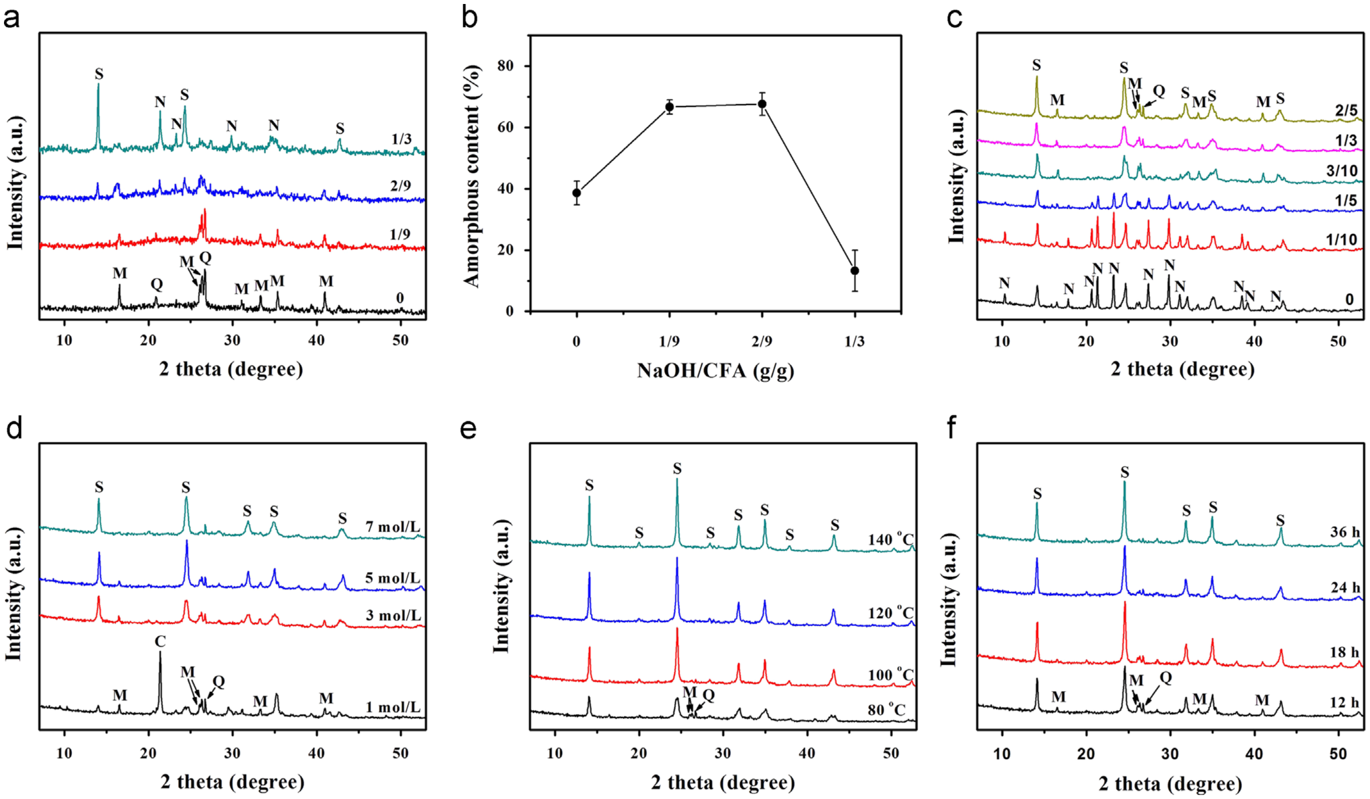

Fig. 1. XRD patterns (a) and amorphous content (b) of CFA pellets synthesized at different NaOH/CFA. (c–f) XRD patterns of zeolitic pellets synthesized at different conditions: (c) the mass ratio of $Al(OH)_3$/CFA, (d) NaOH concentrations, (e) crystallinity temperatures, and (f) crystallinity times. S: sodalite, N: nepheline, M: mullite, and Q: quartz.