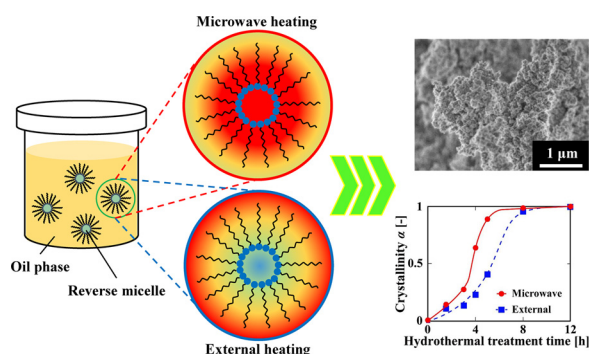# Synthesis of potassium-type zeolites by the reverse-micelle method with microwave heating

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G R A P H I C A L   A B S T R A C T

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Potassium-type zeolites (K-zeolites) containing a chabazite phase were synthesized using the reverse-micelle method with microwave heating. The reverse micelle acts as a space-confining reactor, and treatment by microwave irradiation provides fast, homogeneous, and preferential heating of the aqueous phase where the zeolites are synthesized. As control experiments, K-zeolites were also synthesized using the reverse-micelle method with external oil bath heating, the conventional method with microwave heating, and the conventional method with external heating. Based on dynamic light scattering and scanning electron microscopy analyses, we confirmed that small zeolite crystals could be successfully prepared using the reverse-micelle method. We also found that the crystallization rate of zeolites obtained using the reverse-micelle microwave heating method was larger than those obtained using other methods. Furthermore, we evaluated the adsorption performance of the synthesized zeolites via ammonium adsorption experiments. The rates of ammonium adsorption and the maximum adsorption capacities of the zeolites obtained by the reverse-micelle method were larger than those of the zeolites obtained by the conventional method.

1. Introduction

Zeolites are crystals consisting of aluminate and silicate frameworks and have the ability to act as adsorbents and catalysts. As such, zeolites have many potential applications in gas purification [1,2], water purification [3,4], radioactive waste immobilization [5], fertilizer [6], and petrochemical reactions [7], with a reduction in the zeolite size being expected to further improve zeolite performances in these applications [8].

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In this context, the microemulsion-microwave synthesis of zeolites has been previously employed to control zeolite crystal morphologies and size [9–13]. In addition, Chen et al. reported the preparation of small uniform zeolite crystals in a reverse micelle under microwave heating [14]. These reverse micelles consist of aqueous domains dispersed in a continuous oil phase, and in this system, the small aqueous domains can be viewed as nanoreactors for the synthesis of zeolite crystals [15,16]. Furthermore, compared with external heating methods, microwave heating allows shorter reaction times [17], and so the combination of reverse micelle and microwave heating results in the direct, selective, and rapid heating of the aqueous domains, as the oil phase in the reverse micelle system is transparent to microwaves. In contrast, in conventional external heating methods, heat is transferred from the oil phase to the aqueous domains through conduction, and so a temperature gradient is expected.

The reverse-micelle microwave synthetic route successfully produced smaller zeolite crystals, which are expected to have better adsorption performance due to their small size. However, to date, the adsorption performances and comparison with other synthetic routes have not been evaluated and investigated in detail. Investigation of the adsorption performance of the prepared zeolites is indispensable for applications. In addition, evaluation of the crystallization rates by the reverse-micelle microwave synthetic route has not yet been carried out. Improvement of the synthesis rate can contribute to further advancement of the zeolite synthesis process.

Thus, we herein report the synthesis of potassium-type zeolites using the reverse-micelle microwave heating method and subsequent investigation of the effect of this method on the zeolite crystal size, crystallization rate, and adsorption performance. The rate of zeolite crystal synthesis achieved using this method was compared with that of other synthetic methods via empirical equations. Finally, the adsorption performance of the synthesized zeolites was investigated via ammonium adsorption experiments.

2. Experimental methods

2.1. Materials

Aluminum hydroxide (> 98%, Sigma Aldrich) and colloidal silica (Ludox HS-40, 40 wt% suspension in H_2O, Sigma Aldrich) were used as the sources of alumina and silica for the zeolite framework. Biomass incineration ash, which had a potassium concentration of 25.8 mass%, was employed for preparation of the alkaline solution (see Section 2.2 below) [17–20]. This ash was collected from a bag filter dust collector following the combustion of dry sawdust, bark, and wood chips of Douglas fir and Japanese cedar using a fluidized bed furnace in the Chugoku Mokuzai woody biomass power plant in Hiroshima, Japan. The surfactant employed herein was sodium bis(2-ethylhexyl)sulfosuccinate (AOT, Nacalai Tesque). Ammonium chloride was purchased from Sigma Aldrich. These reagents were of analytical grade and used without further purification.

2.2. Preparation of the precursor gel for zeolite synthesis using the extracted solution obtained from the biomass incineration ash

The typical preparation procedure for the alkaline solution is described elsewhere [17,18]. More specifically, a portion of the biomass incineration ash (18.0 g) was added to deionized water (100 mL) and stirred for 15 min at room temperature (298 ± 2 K), after which the extracted solution was obtained by filtration. Finally, the desired alkaline solution was obtained by adding potassium hydroxide (2.8 g, > 85%, Sigma Aldrich) to the extracted solution.

Aluminum hydroxide (2.0 g) and colloidal silica (3.85 mL) were added separately to Teflon pressure vessels along with portions of the alkaline solution (50 mL). The resulting mixtures were then stirred at 400 K for 6 h to give clear aluminate and silicate solutions. After cooling

both solutions to room temperature (298 ± 2 K), the aluminate solution was added slowly to the silicate solution under stirring at 600 rpm to obtain the precursor gel required for zeolite synthesis. The precursor gel was then stirred continuously for 24 h prior to crystallization.

2.3. Preparation of the reverse micellar solution

The above-prepared precursor gel was added slowly to n-decane (100 mL, > 99%, Nacalai Tesque) containing AOT (8.92 g) under stirring at 600 rpm to give the clear reverse micellar solution.

2.4. Crystallization of the zeolite by reverse-micelle synthesis under microwave heating

The prepared reverse micellar solution was subjected to microwave irradiation (2.45 GHz), and the solution temperature (controlled by varying the output of the microwaves with a proportional-integral-derivative (PID) controller) was held at 393 K A hydrothermal treatment time of 1–12 h was employed and the rotational speed of the stirrer was set to 300 rpm. Following hydrothermal treatment, the product was cooled to room temperature, washed several times with deionized water by centrifugation, then collected by centrifugation. We herein refer to this synthetic method as the reverse-micelle microwave heating method.

To investigate the effect of the heating method on zeolite crystallization, the prepared reverse micellar solution was treated hydrothermally under external heating (referred to as the reverse-micelle external heating method). External heating was carried out using an oil bath (OHB-1000 G, EYELA, Japan) at 393 K with constant stirring at 300 rpm (RCX-1000D, EYELA, Japan). In addition, to confirm the effectiveness of the reverse micelle route in reducing the zeolite crystal size, conventional synthetic methods involving the direct hydrothermal treatment of the precursor gel using microwave heating (the conventional microwave heating method) or external heating (the conventional external heating method) were employed.

2.5. Analytical methods

The crystalline phases of products were identified by X-ray diffraction (XRD, RINT-2000, Rigaku, Japan) and the corresponding hydrodynamic diameters were evaluated by dynamic light scattering (DLS, LB-550, HORIBA, Japan) using dilute aqueous suspensions of the products. The surface morphologies were observed by field emission-scanning electron microscopy (FE-SEM, S-5200, Hitachi, Japan).

Zeolites are crystalline hydrated aluminosilicates. The trivalent aluminum in the structure generates a negative charge in the framework that imparts the ion exchange properties. In K-zeolite, ion exchange occurs between the potassium ions adsorbed on the zeolite and other cations. In this study, ammonium ions were used as the other cation. The ammonium adsorption rate and performance of the products were evaluated as described below, and the concentration of ammonium ions was measured using an ion meter (F-53, Horiba, Japan).

(i) Ammonium adsorption rate: The powdered product (0.2 g) was added into an aqueous NH_4Cl solution (50 ppm, 100 mL) and the resulting mixture was stirred at 200 rpm for 1–180 min at room temperature (298 ± 2 K). After the desired time, the supernatant was isolated by centrifugation. The ammonium adsorption ratio, *R,* calculated from the mass concentration of ammonium ions in the supernatant $C(t)$ was defined as:

$$R = \frac{C_0 - C(t)}{C_0} \times 100$$

(1)

where C_0 is the initial mass concentration of ammonium ions.

(ii) Equilibrium adsorption: The powdered product (0.2 g) was added to an aqueous NH_4Cl solution (1–1000 ppm, 100 mL) and the