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Single-mode focused microwave synthesis of small crystal NaA zeolite for antibacterial materials

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Small crystal NaA zeolite was synthesized by a single-mode focused microwave approach with sodium silicate as the silica source and sodium meta-aluminate as the aluminum source. The crystallization time, phase composition, and morphology of the NaA zeolite were investigated. To demonstrate the antibacterial capability, Ag^+ was loaded into the NaA zeolite. The amount of silver load in the zeolite was determined by atomic absorption spectrometry. The antibacterial property to Escherichia coli of the Ag-loaded zeolite was analyzed by a spectroturbidity method. Compared to the conventional hydrothermal synthesis of NaA zeolite, the crystallization time was significantly reduced in the single-mode focused microwave synthesis, from 2 hr to 6 min. The size distribution of the NaA zeolite ranges from 300 to 400 nm in the single-mode focused microwave synthesis, more uniform than that of the conventional hydrothermal method. The amount of silver load reached 21.13%, and the minimum inhibitory concentration (MIC) to Escherichia coli was 10.42 ppm in the Ag-loaded zeolite prepared with the carrier of the microwave synthesized NaA zeolite, so the antibacterial ability was significantly improved compared to the Ag-loaded zeolite prepared with the carrier of NaA zeolite by the conventional hydrothermal synthesis.

Key words: single-mode focused microwave synthesis, small crystal NaA zeolite, Ag-loaded zeolite, crystallization time, antibacterial property.

Introduction

NaA zeolite is a three dimensional porous material with cubic lattice structure and pore opening of 0.42 nm. Due to its small pore size, NaA zeolite is useful for the separation of gas or liquid molecules, particularly for the removal of toxic and radioactive species from wastewater [1]. NaA zeolite also finds application for the production of environmentally friendly detergents [1-2]. So far, several well-known methods have been reported to synthesize the NaA zeolite, including hydrothermal synthesis [3-5], confined space synthesis [6], template synthesis [7], and microwave synthesis [8]. Among them, the hydrothermal method [9-11] is the most popular approach. However, the hydrothermal method often requires long synthesis time. Recently, the microwave synthesis has attracted extensive attention for the rapid synthesis of NaA zeolite, which can reduce the crystallization time and increase the crystallinity of the final product, compared to those obtained by the conventional hydrothermal synthesis [12]. Previous reports on microwave-assisted synthesis were carried out in household microwave ovens [13-16]. As a result, the experimental parameters such as microwave power, reaction temperature, and pressure inside the vessel could not be precisely controlled in household microwave ovens. These uncertainties have led to poor control over the synthesis and a lack of reproducibility of the experiments. Therefore, the application of commercially available specially designed microwave reactors with built-in magnetic stirrers, direct temperature and pressure monitoring by various probes and sensors is strongly preferred. In recent years, microwave-assisted synthesis of nanostructured materials such as metal nanostructures [17-18], nanoporous nanomaterials [19-20], inorganic nanomaterials [21], and polymer nanocomposites [22] has been studied. Generally, microwave synthesis takes considerably less time than conventional hydrothermal techniques. The synthesis time can often be reduced by over an order of magnitude. In this work, small crystal NaA zeolite was prepared by the microwave synthesis method, which uses single-mode focused microwave system compared to conventional hydrothermal synthesis. The effect of crystallization time was investigated.

The small crystal NaA zeolite prepared by the single-mode focused microwave synthesis exhibits highly porous structure, large surface area, and high ion exchange capacity. These characteristics of small crystal NaA zeolite are suitable for the carrier of antibacterial materials. In addition, Ag-loaded zeolite was prepared using the microwave synthesized small crystal NaA zeolite as a carrier. The antibacterial property was also estimated.

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Experimental Methods

Raw materials and reagents

Sodium silicate ($Na_2SiO_3 \cdot 9H_2O$, AR), sodium metaaluminate ($NaAlO_2$, CP), sodium hydroxide (AR), NH_4Cl (AR), $AgNO_3$ (AR), NaCl (AR), peptone (BR), yeast extract (BR), and agar powder (BR) were purchased from Sinopharm Chemical Reagent Co. LTD., and used as received without any additional purification.

Synthesis of NaA zeolite

The precursor gel was prepared by adding a solution of silica source to a solution of aluminum source with stirring. The mixture was heated in a water bath of 30 °C with stirring for 30 min, until all components were uniformly distributed. After aging the mixture for 24 hrs at 300 °C, the obtained gel was divided evenly into two parts for the microwave and conventional hydrothermal synthesis. One part of the gel was transferred into a Focused Microwave System (Discover, CEM, America). The sample was heated in oven (10 mL) at 120 °C, with the maximum output power of 150 W for 1, 2, 4, 6, and 8 min, respectively. The other gel was transferred into a Teflon lined stainless steel pressure bomb vessel, and heated in oven at 120 °C for 0.5, 1, 2, and 4 hrs, respectively. After synthesis, the solids were recovered by repeated high-speed centrifugation and re-dispersion in distilled water in an ultrasonic bath until the pH reached around 8. The washed solids were dried at 100 °C, and then cooled to room temperature in a desiccator.

Preparation of Ag-loaded zeolite

A mixed solution of small crystal NaA zeolite and NH_4Cl with solid-liquid mass ratio of 1 : 20 was stirred for 4 hrs under 80 °C, and then washed with distilled water till no white precipitate formed when added $AgNO_3$ solution with a concentration of 0.1 mol/L. The product was dried at 80 °C for 12 hrs. Repeat the previous steps 3 times can fully exchange the NaA zeolite to obtain the NH_4A zeolite. To load Ag^+ into the zeolite, the mixture of NH_4A zeolite and $AgNO_3$ with a molar ratio of 1 : 2 was sintered at 400 °C for 4 hrs. Subsequently, the Ag-loaded zeolite was obtained by washing the above mixture 3 times with dilute nitric acid followed by drying at 300 °C for 2 hrs.

Characterizations

X-ray diffraction (XRD) patterns of the samples were recorded using a D8 Advance diffractometer with Cu-kα radiation. The data collection was carried out in the 2θ range of 3-60 °, with a step size of 0.02 ° s^{-1}. The particle size and the morphology of the final product were measured by scanning electron microscopy (SEM, FEI, Sirion 200). The amount of silver load (m_{Ag}%) of the Ag-loaded zeolite was measured by atomic absorption spectrometry (AAS). MIC of the Ag-loaded zeolite to Escherichia coli was determined by a spectroturbidity method (National standard GB15979).

Results and Discussion

Preparation of small crystal NaA zeolite

Fig. 1 shows the XRD patterns of the small crystal NaA zeolite sample synthesized at 120 °C in single-mode focused microwave system, with the maximum output power of 150 W for 1, 2, 4, 6, and 8 min, respectively. With crystallization time of 1 min, the XRD pattern presents dispersive peaks, which is due to the existence of undefined phase composition. This means the zeolite crystals did not grow in the first minute. With the crystallization time increased, the XRD peaks can be attributed to the NaA zeolite (JCPDS39-0222), and the peaks become sharper and stronger. The intensity of the peaks saturates when the

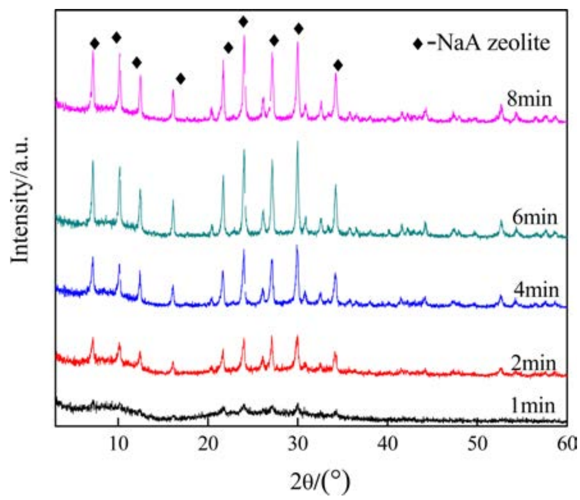

Fig. 1. XRD patterns of the NaA zeolite sample synthesized with different crystallization time by single-mode focused microwave synthesis.

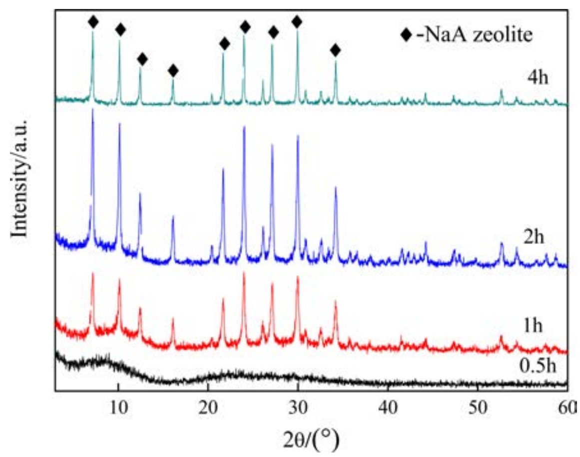

Fig. 2. XRD patterns of the NaA zeolite sample synthesized with different crystallization time by conventional hydrothermal synthesis.

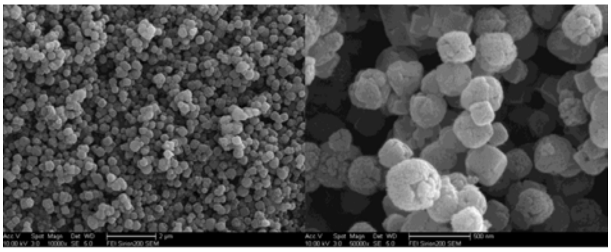

Fig. 3. SEM images of the NaA zeolite synthesized by single-mode focused microwave synthesis.

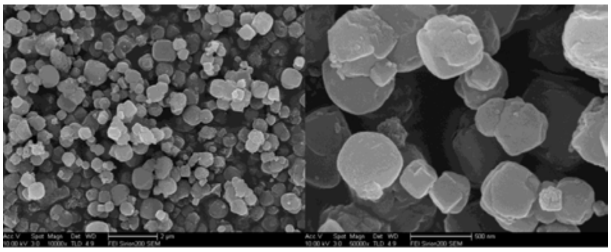

Fig. 4. SEM images of the NaA zeolite synthesized by conventional hydrothermal synthesis.

crystallization time reaches 6 min, which shows that the optimum crystallization time of the small crystal NaA zeolite is 6 min in the single-mode focused microwave synthesis. Fig. 2 shows the XRD patterns of the NaA zeolite sample synthesized by the conventional hydrothermal synthesis at 120 °C for 0.5, 1, 2, and 4 hrs, respectively. As shown in Fig. 2, the sample with 2 hrs crystallization time presents the highest peak, indicating the synthesized zeolite has good crystallinity. This result shows that the optimum crystallization time of the NaA zeolite is 2 hrs in the conventional hydrothermal synthesis. Fig. 3 shows the SEM images of the small crystal NaA zeolite synthesized at 120 °C for 6 min by single-mode focused microwave synthesis. The crystal size of the small crystal NaA zeolite ranges between 300 and 400 nm, and the particle size distribution is visually uniform. Fig. 4 shows the SEM images of the NaA zeolite synthesized at 120 °C for 2 hrs by the conventional hydrothermal synthesis. The majority crystal size is 200 ~ 600 nm, and the particle size distribution is broader than those obtained by the microwave synthesis.

Compared to the conventional hydrothermal synthesis, the crystallization time of the small crystal NaA zeolite synthesized by the microwave synthesis method is significantly reduced, and the particle size distribution is more uniform. The reason is that the single-mode focused microwave irradiation can produce efficient internal heating, which increases the temperature of the whole volume simultaneously and uniformly. On the other hand, conventional hydrothermal synthesis is carried out by conductive heating with an external heat source such as laboratory furnace. This heating procedure is slow and rather inefficient, as it depends on the convection current and the thermal conductivity of the raw materials. As a result, the temperature of the reaction vessel is often considerably higher than that of the reaction mixture.

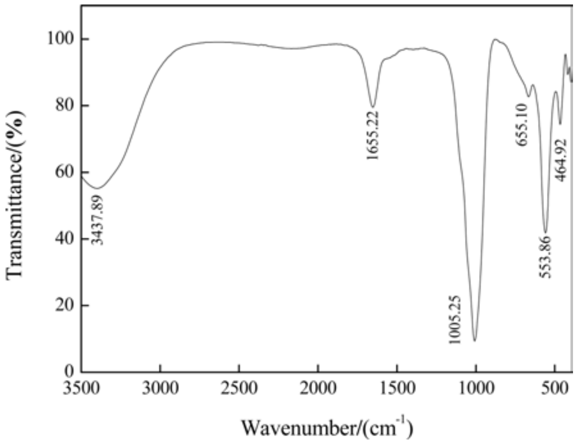

Fig. 5. FTIR spectrum of the NaA zeolite synthesized at 120 °C for 6 min by single-mode focused microwave synthesis.

Analysis of infrared spectrum

Fig. 5 shows the FTIR spectrum of the small crystal NaA zeolite synthesized at 120 °C for 6 min by single-mode focused microwave synthesis. Four characteristic peaks of the small crystal NaA zeolite appear in the infrared spectrum. The broad absorption peak at 464.92 cm^{-1} is attributed to the bending vibrations absorption peak of T-O (T represented Al and Si). The absorption peak at 553.86 cm^{-1} is the double four-member ring vibration absorption peak. The presence this peak is further confirmed by the T-O weakly symmetric stretching vibration peak which appears at 655.10 cm^{-1}. The absorption peak at 1005.25 cm^{-1} is the strong antisymmetric stretching vibration peak. The characteristic band at 3437.89 cm^{-1} corresponds to the absorption peak of structural water. The absorption peak at 1655.22 cm^{-1} is the absorption peak of surface adsorbed water with the H-O-H bending vibration. This peak is relatively weak, because the remaining residual water is reduced after drying. The framework bending and stretching vibration of the NaA zeolite have been proved by infrared spectrum. Therefore, the skeleton of the sample was confirmed to be NaA zeolite.

Analysis of single-mode focused microwave effect

The microwave energy can improve the heating rate of the synthetic mixture in the preparation of the small crystal NaA zeolite by the single-mode focused microwave synthesis, which makes the heating of the synthetic mixture more uniform to reduce the apparent activation energy of the crystallization reaction [23-25]. Fig. 6 shows the reaction temperature and power profile of the synthesized small crystal NaA zeolite at 120 °C by single-mode focused microwave synthesis. From Fig. 6, the single-mode focused microwave synthesis enables the mixture to reach the desired

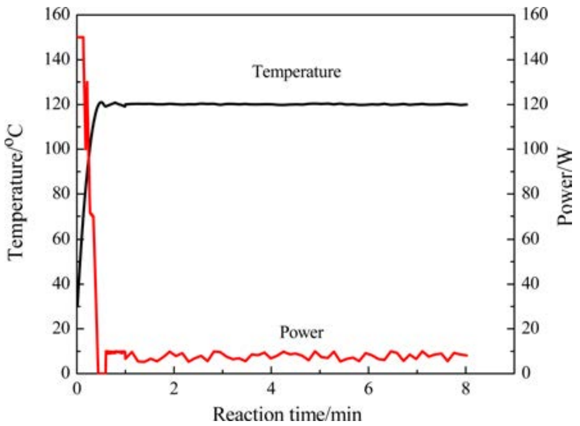

Fig. 6. Reaction temperature and power profile of the synthesis of NaA zeolite at 120 °C by single-mode focused microwave synthesis.

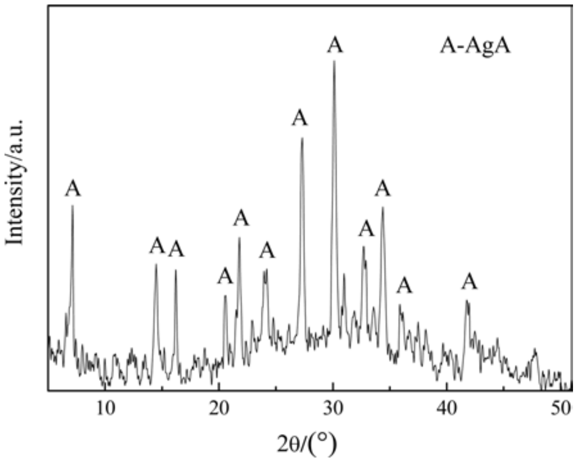

Fig. 7. XRD patterns of the Ag-loaded zeolite prepared with the carrier of NaA zeolite by single-mode focused microwave synthesis.

Table 1. The amount of silver load and MIC of Ag-loaded zeolite.

Ag-loaded zeolite sample	The amount of silver load /%	MIC/ppm
Ag-loaded zeolite (microwave synthesis)	21.13	10.42
Ag-loaded zeolite (hydrothermal synthesis)	5.60	15.60

synthesis temperature within 30 seconds, whereas the conventional hydrothermal synthesis can take over 30 min to reach the same temperature. Microwave irradiation also influences the reaction processes. It can enhance the rate of the gel formation, the formation of structural domains, the nucleation of crystals, and the growth of crystals to the final product.

Antibacterial ability of Ag-loaded zeolite

Fig. 7 shows the XRD pattern of the Ag-loaded zeolite prepared with the carrier of small crystal NaA zeolite by single-mode focused microwave synthesis. The diffraction peak of the product is consistent with the standard card (JCPDS 86-1597). It can be seen that the silver in the Ag-loaded zeolite is presented in the zeolite channel with the state of Ag^+.

Compared to the conventional hydrothermal synthesis of NaA zeolite, the amount of silver load and antibacterial property to Escherichia coli of the Ag-loaded zeolite prepared with the carrier of NaA zeolite by single-mode focused microwave synthesis were determined. The results shows (Table 1) that the amount of silver load is 21.13%, and MIC to Escherichia coli is 10.42 ppm in the Ag-loaded zeolite prepared with the carrier of small crystal NaA zeolite by the single-mode focused microwave synthesis. Meanwhile, the amount of silver load is 5.60%, and MIC to Escherichia coli is 15.60 ppm in the Ag-loaded zeolite prepared with the carrier of NaA zeolite by the hydrothermal synthesis [26]. The antibacterial ability of the Ag-loaded zeolite depends on the amount of silver load. With the increase of silver content, the antibacterial ability is significantly improved. The amount of silver load depends on the type of the Ag-loaded zeolite and the particle size of the NaA zeolite. The particle size of the small crystal NaA zeolite prepared by single-mode focused microwave synthesis is about 300 ~ 400 nm, while the size of the NaA zeolite obtained by traditional hydrothermal synthesis is about 500 nm. The amount of the active center within the NaA zeolite is larger, which is due to its smaller particle size and the shorter channel length. At the same time, the adsorption capacity of the zeolite is improved, and the diffusion resistance of the internal surface in the zeolite is reduced. The inter-diffuse speed for the molecules of reactants or product to get in and out through the pores is also increased. Hence, the amount of silver load of the Ag-loaded zeolite is improved, and the antibacterial ability is enhanced. The main antibacterial effect of the Ag-loaded zeolite is that the catalytic active centers of the Ag^+ can make the oxygen in the air or water activate to produce reactive oxygen ions and hydroxyl radicals. At the same time, the connection of Ag^+ and bacteria destroys or hinders the biological activity to kill or inhibit bacteria.

Conclusions

Small crystal NaA zeolite was successfully synthesized by the single-mode focused microwave synthesis. The crystallization time of the NaA zeolite was investigated. Compared to the conventional hydrothermal synthesis, owing to a fast heating time to the target temperature, the crystallization time of the small crystal NaA zeolite was reduced about 20 times by the single-mode focused microwave synthesis, which only needs 6 min. The particle size distribution of the NaA zeolite was visually uniform ranging between 300 and 400 nm. Therefore, the single-mode focused microwave synthesis is a breakthrough technology for preparation of the NaA zeolite, and the method may have a dramatic impact on the world of zeolite. Furthermore, the amount of silver load was 21.13%, and MIC to Escherichia coli was 10.42 ppm of the Ag-loaded zeolite prepared with the carrier of small crystal NaA zeolite by the single-mode focused microwave synthesis. Compared to the Ag-loaded zeolite that was prepared with the carrier of NaA zeolite by the conventional hydrothermal synthesis, the antibacterial ability was significantly improved.

Acknowledgments

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