In-situ preparation of hierarchical Beta zeolite by steam-assisted crystallization method using meso-macroporous silica

Delong Kong 1*, Hansheng Li 2*, XiaoBo Liu 1, Chunxiao Xu 1, Chen Ding 2, Wei Wang 2, Jiawei Shi 3

1 Aerospace institute of advanced materials & progressing technology, Beijing, 100074, P.R. China
2 State key laboratory of fluorinated functional membrane materials, Zibo, 256400, P.R. China
3 Huantai Science and Technology Association, Zibo, 256400, P.R. China
*Corresponding author’s e-mail: hsli@dongyuechem.com

Abstract: In this paper, a series of meso-macroporous silica (MMS) were prepared by phase separation, then mic-meso-macroporous Beta zeolite was prepared by steam-assisted crystallization (SAC) method using the meso-macroporous silica as substrate. The factors such as the amount of water, crystallization time, aluminum source, amount of template agent during the SAC method were investigated. Various characterization methods such as BET, XRD, SEM were used to investigate the physical and chemical properties of the prepared materials. The results showed that the meso-macroporous silica could be transformed into Beta zeolite through the SAC method while the macroporous structure was still maintained.

1. Introduction
Beta zeolite is widely used in the chemical industry, especially in the field of heterogeneous catalysis because of its regular pore structure, excellent shape-selective catalytic performance, and good hydrothermal stability [1]. However, the microporous structure is not conducive to mass transfer, which limits its application [2]. In order to solve this problem, hierarchical zeolite has been developed, which has good mass transfer properties and accessibility to acid sites [3-4].

Many methods have been developed for the preparation of mic-mesoporous zeolite such as soft template and hard template method [5]. However, the mesoporous structure still cannot solve the problem of internal diffusion limitation for large pellet catalysts (larger than 3 mm) [6-7]. Macroporous structure has been proven to effectively eliminate the problem of internal diffusion limitation in large particle catalysts [8]. However, there are relatively few preparation methods to construct the zeolite with macroporous structure. Researchers have prepared macroporous zeolite by hard template method, which is very complicated and the synthesis cost is very high [9-10]. Therefore, it is necessary to develop a simple and efficient method for preparing macroporous zeolite.

In recent years, the method of steam-assisted crystallization has attracted more and more attention [11]. This method can avoid strong alkali and high temperature aqueous solution environment in the process of preparing zeolite. In the present work, MMS was used as substrate, and the crystallization rate was controlled by a SAC method. While good macroporous structure was maintained, part of the silica was crystallized into Beta crystallite.
2. Preparation of hierarchical Beta zeolite
The MMS was prepared by accurately controlling the relative speed of phase separation and sol-gel. The specific preparation process is detailed in the reference [8].

The preparation process of hierarchical Beta zeolite is as follows: Aluminium nitrate and NaOH were dissolved in a certain amount of tetraethylammonium hydroxide solution. Then the MMS was immersed in the above solution, and sonicated for 10 minutes, dried at room temperature for 24 hours. Put a small amount of water on the bottom of the autoclave. The prepared dry-gel was then subsequently transferred into a Teflon-lined stainless-steel autoclave, and placed on the upper side of the autoclave with a special net in order to separate from water. It was then crystallized at 150 °C. The obtained samples were dried at 60 °C, and then calcined at 550 °C for 6 hours. Then the obtained hierarchical Beta zeolite was subjected to ion exchange and noted as MMMB. Alumina-modified MMS was recorded as MMSA for comparison.

3. Characterization
The phase structures of the samples were detected by XRD using a PANalytical Empyrean X’pert powder diffractometer. Nitrogen sorption was measured by a MicroActive ASAP 2460 2.01 instrument at liquid nitrogen temperature. The pore sizes were obtained by the Horvath–Kawazoe (HK) method and BJH formalism respectively. JSM-7001F scanning electron microscope (SEM) was employed to test the morphology of the samples operating at 5.0–15.0 kV. The Pyridine IR of the samples was used to characterize the type of acid in the prepared samples on a Nicolet Magna 550 infrared spectrometer. Hg intrusion isotherms were carried out to measure the pores larger than 50 nm by a MicroActive AutoPore Iv 9510 analyzer.

4. Results and discussions
4.1 Properties of the meso-macroporous silica
As shown in Fig. 1 (a), the prepared MMS has a honeycomb-like structure, and the interconnected macroporous structure is clearly visible. It can be accurately known through the mercury intrusion test (Fig. 1 (d)) that the diameter of the macropore in the silica is about 1000 nm. The isotherms of the silica exhibited classical irreversible IV type adsorption behavior, indicating the existence of mesoporous structure, which is about 8.7 nm (Fig. 1 (b), Fig. 1 (c))[12].
4.2 Effect of preparation conditions on SAC process

Na ions play a role in balancing electrical balance and guiding crystal synthesis during crystallization [13]. Using aluminum nitrate as the aluminum source, when the Na/Si was 0.05, the meso-macroporous silica can be crystallized into zeolite Bea. However, crystallization could not occur under the condition of low Na/Si or without Na. However, with aluminum isopropoxide as the aluminum source, the zeolite Beta was difficult to be formed under different conditions of Si/Al. [13-14]

Many researches have reported that the amount of water played a very important factor during the SAC process [15]. As shown in Fig. 3(a), when 0.5 ml and 9 ml H2O was used, no crystallization occurred; when the amount of water is 1-6ml (dry gel mass is 2g), the amorphous silica could be transformed into zeolite crystals. When the amount of water exceeds 6 ml, vapor-liquid equilibrium will be reached, and the steam will condense on the gel, which would change the synthesis composition and caused the crystallization to fail [15].

As shown in Fig. 3(b), the crystallization time is longer than the previous report time [15], which may be because large particles of 10-20 mesh silica was used as the silicon source during the preparation process, and the contact between silica, aluminum and TEAOH was insufficient.
Literatures reported that TEA⁺ can promote the polymerization of aluminum and silica, the formation of crystal nuclei and accelerate the crystallization rate [20-22]. As shown in Fig. 3(c), when the molar ratio is 0.43 and 0.6 (TEAOH:Si), zeolite Beta can form. However, if TEAOH is excessive, the crystallization is too complete and the macroporous structure is partly destroyed (Fig. 4).

Fig. 3 XRD patterns of the samples under different condition: water volume (a), crystallization time (b), amount of TEAOH (c)

Fig. 4 SEM image of the sample using excess TEAOH
4.3 Properties of the hierarchical Beta zeolite

As shown in Fig. 5(a), the prepared MMMB exhibited both type I and type IV adsorption isotherms indicating the presence of micropores and mesopores[12]. SEM images (Fig. 5(b) and (c)) show that the MMS can be partially crystallized into Beta nanocrystallites inside and outside of the macroporoes by SAC method while retaining the macroporous structure. Through the SAC method, part of the MMS is transformed into Beta grains, but some remain amorphous. In summary, the prepared zeolite Beta exhibited a mic-meso-macroporous structure.

Pyridine infrared is used to test the acid type of the prepared samples. As shown in Fig. 6, MMS does not have any pyridine adsorption peak, indicating no acidic sites. The apparent adsorption peak of MMSA at 1450 cm⁻¹ indicates the presence of abundant Lewis acids [16]. However, MMSA shows very weak peak at 1550 cm⁻¹, indicating very weak Brønsted acid [17]. MMMB has both abundant Lewis acid and Brønsted sites with adsorption peak at 1550 cm⁻¹ and 1450 cm⁻¹. As we all know, Brønsted acid is derived from the positively charged proton to balance the negative charge caused by Al atoms enter the skeleton of silica[18]. Most Al atoms and silicon are surface-contacted in MMSA, so the Brønsted acid is very weak. Through the SAC method, Al atoms mostly enter the silicon skeleton, so MMMB has abundant Brønsted acid sites.

Fig. 5 N₂ physisorption curves of the samples (a), SEM images of the hierarchical Beta (b), (c).
5. Conclusions
In the present work, a hierarchical mic-meso-macroporous zeolite Beta was successfully prepared by the SAC method. Water consumption is critical to the SAC process. When the water consumption is 1-6 ml, the amorphous silicon can be successfully crystallized into Beta crystals. The SAC method has a fast crystallization speed and can form Beta crystals in 36 hours. The more TEAOH used, the easier it is to form zeolite Beta, but excessive TEAOH will destroy the macroporous structure. The prepared zeolite Beta has a good mic-meso-macroporous structure and is rich in Lewis and Brønsted acids, which would be widely used in the field of heterogeneous catalysis.

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