



# Synthesis and crystallization mechanism of nano-sized zeolite beta aggregates via aerosol-assisted method



Guang Xiong\*, Xiyan Liu, Ruixue Zhao, Jiaxu Liu, Jinpeng Yin, Qingrun Meng, Zhendong Guo, Liping Liu

State Key Laboratory of Fine Chemistry, School of Chemical Engineering, Dalian University of Technology, Dalian, 116024, China

## ARTICLE INFO

### Article history:

Received 16 February 2017

Received in revised form

24 April 2017

Accepted 25 April 2017

Available online 27 April 2017

### Keywords:

Zeolite beta

Aerosol-assisted method

Nano-agglomerates

Cracking of 1,3,5-TIPB

## ABSTRACT

Nano-sized zeolite Beta aggregates with interparticle mesopores were synthesized by the aerosol-assisted method. The amorphous powders in the  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  system, which was obtained from an aerosol drying process, were used as the precursor. The zeolite was crystallized in a high concentration system with high alkalinity. This can not only improve the autoclave utilization and the crystallization rate, but also reduce the amount of both template and waste water. The obtained zeolite Beta is spherical nano-aggregates with interparticle mesopores. It shows high BET surface area and good Al species distribution. The study on crystallization process indicated that the precursor gradually dissolved under the strong alkaline condition and the nano-sized zeolite crystals were formed in the liquid phase as time prolonged. Therefore, the transformation mechanism mainly followed the liquid-phase mechanism. More importantly, the zeolite beta synthesized by aerosol-assisted method exhibited good catalytic activity and stability in the cracking reaction of 1,3,5-TIPB.

© 2017 Elsevier Inc. All rights reserved.

## 1. Introduction

Zeolite beta with a three-dimensional structural system composed of 12-membered ring channels is one of the most industrially important zeolites used in petroleum refining, petrochemical industry and fine chemistry as catalysts, sorbents or ion-exchangers [1–3]. It was generally synthesized by conventional hydrothermal method, which needs plenty of water as solvent [4]. This leads to several issues such as: (1) high autogenous pressure at relatively high temperature and consequent issues with equipment safety; (2) low utilization efficiency of the autoclaves and consequent low solid yields; (3) pollution from large amounts of waste water [5]. Tetraethylammonium hydroxide (TEAOH) as an organic structure directing agent (OSDA) is considered to be crucial for the formation of the zeolite beta framework [6]. However, the cost of zeolite beta is increased due to the high price of TEAOH. Therefore, it is very urgent to synthesize zeolite beta with less template and solvent. For this purpose, Cooper et al. [7] reported an ionothermal synthesis of zeolite in the presence of ionic liquid ([EMIm]Br), which is used as template and solvent. This method can be carried

out at atmospheric pressure, but used to synthesis of silica-based zeolites are very scarcely for the dissolution of silicon-containing reagents in ionic liquid. Xiao et al. [8–11] reported a solvent or OSDA free method to synthesize zeolite beta. This method is low-cost and environmental friendly by avoiding the production of waste water and TEAOH. Mao et al. [12] used a seeding-steam-assisted dry gel conversion method to synthesize zeolite beta with a small quantity of water ( $\text{H}_2\text{O}/\text{SiO}_2 = 9.4$ ), seed (1%) and template ( $\text{TEAOH}/\text{SiO}_2 = 0.15$ ). Recently, Dou et al. [13] also adopted dry gel method to synthesize zeolite beta with  $\text{TEAOH}/\text{SiO}_2 = 0.06$ . Aerosol-assisted method is a simple and adaptable route which was generally used to synthesize mesoporous and macroporous materials with the size from nanometer to submicrometer [14–21]. In a previous communication we reported a aerosol-assisted method to synthesize microporous zeolites [22]. The method includes two steps: (1) The precursor solutions were prepared by mixing raw materials. With an aerosol-dry apparatus, the precursor solutions were quickly transformed into amorphous powder. (2) The amorphous powder and a given amount of TEAOH were loaded into a Teflon-lined autoclave and crystallized under autogenous pressure. No extra water except TEAOH aqueous solution was added, which maintained a high concentration of crystallization system. For this reason, aerosol-assisted method possesses the following

\* Corresponding author.

E-mail address: [gxiong@dlut.edu.cn](mailto:gxiong@dlut.edu.cn) (G. Xiong).

superiority: (1) less consumption of TEOAH; (2) less sewage emission; (3) Improved utilization of the autoclave volume.

The previous communication mainly discussed the results of TS-1 as a model study. The raw materials of TS-1 were hydrolyzed under acidic condition. The final products were single crystals with the size of 350–800 nm. The aim of this study is to explore a route to synthesize the nanosized Beta zeolite in a extremely dense system without the addition of seeds. The crystallization is carried out under the supersaturation system with high alkalinity (provided by Na<sub>2</sub>O and TEOAH), which may promote the formation of nanosized Beta zeolite. The physical-chemical properties were investigated by various techniques. In particular, the crystallization mechanism was studied in detail. Finally, the catalytic performances were evaluated by the cracking of 1,3,5-TIPB.

## 2. Experimental

### 2.1. Materials

All chemicals were used as received without any further purification. The chemicals were alkaline silica sol (30wt%, Qingdao Cheng Yu Chemical Co.,Ltd), sodium aluminate (Al<sub>2</sub>O<sub>3</sub> ≥ 41.0%, Sinopharm Chemical Reagent Co. Ltd), and tetraethylammonium hydroxide (TEAOH, 25wt% in water, Tianjin Guangfu Fine Chemical Research Institute). A commercial Q50 (H-β) zeolite manufactured by Dalian Ligong Qiwangda Chemical Technology (Dalian, China) was used as a reference.

### 2.2. Zeolite synthesis

A50 sample was synthesized by the aerosol-assisted method. In a typical run, the synthesis started by dissolving alkaline silica sol in a sodium aluminate aqueous solution. The mixture was stirred for 30 min at room temperature. The molar composition of the solution was 0.021Na<sub>2</sub>O: SiO<sub>2</sub>: 0.02Al<sub>2</sub>O<sub>3</sub>: 0.042OH<sup>-</sup>: 25H<sub>2</sub>O. After that the solution was sprayed via an aerosol apparatus (BILON-6000Y, Shanghai BILON Instrument Co.,Ltd.) to generate the aerosol particles at 230 °C. Then the particles were quickly dried to form SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O amorphous powder at 110 °C. In the second step, 1g amorphous powder and 1.3963g TEOAH aqueous solution with a composition of 0.021Na<sub>2</sub>O: SiO<sub>2</sub>: 0.15TEAOH: 0.02Al<sub>2</sub>O<sub>3</sub>: 0.192OH<sup>-</sup>: 3.68H<sub>2</sub>O were loaded into Teflon-lined autoclave and crystallized at 130 °C for 48 h under autogenous pressure. The as-synthesized product was obtained by washing with distilled water and centrifuging. Then the product was dried at 100 °C and calcined at 540 °C for 10 h to remove the template. Ion exchange of the calcined product with 1M aqueous solution of NH<sub>4</sub>NO<sub>3</sub> at 80 °C for 2 h was repeated twice. The final product was converted to H-form Beta zeolite by calcination at 550 °C for 6 h.

### 2.3. Characterization

XRD patterns were recorded by a Rigaku Corporation D/MAX-2400 instrument with CuKα radiation. Data was collected in 2θ range from 5° to 50° with a step size of 0.02° and a step time of 0.15s. The SEM images were obtained on Nova NanoSEM 450. Elemental analyses were performed on inductively coupled plasma-optical emission spectrometer (ICP, Optima2000DV). FT-IR spectra were characterized on a Bruker EQUINOX55 spectrometer. Prior to the FT-IR measurement, the sample was degassed at 300 °C for 1 h under vacuum condition in order to remove adsorbed water. Framework-IR was recorded by using the dried KBr disk technique in the range of 400 to 4000 cm<sup>-1</sup>. Pyridine-IR was performed at 150 °C, 300 °C and 450 °C to study the acidic strength. After dehydration at 400 °C for 35 min, pyridine was exposed to the

sample for 5 min. Nitrogen sorption measurements were performed at liquid nitrogen temperature on a Quantachrome AUTO-SORB-1-MP physical sorption apparatus. Surface area and pore volume were calculated according to the BET and BJH methods, respectively. The t-plot was used for the analysis of the surface area. The total acidity and acidic strength distributions of the catalyst were determined by calorimetric measurement of differential adsorption of NH<sub>3</sub> at 60 °C and subsequent TPD of the adsorbed NH<sub>3</sub> with a ramp of 10 °C min<sup>-1</sup> up to 650 °C (Quantachrome CHEMBET 3000, USA). All NMR spectra were recorded on an Agilent DD2-500 MHz spectrometer. <sup>27</sup>Al MAS NMR experiments were carried out at 130.2 MHz using a 4 mm MAS NMR probe with a spinning rate of 14 kHz. The spectra were accumulated for 120 scans with 2s recycle delay. The chemical shifts were referenced to 1% Al(NO<sub>3</sub>)<sub>3</sub> aqueous solution.

### 2.4. Catalytic test

Zeolites beta were applied to the cracking of 1,3,5-triisopropylbenzene (1,3,5-TIPB) in order to evaluate their catalytic performances. 0.3 μL 1,3,5-TIPB (95wt%, aladdin) was injected directly into a pulse micro-reactor equipped with a U-shape stainless tube (inner diameter was 4 mm). The center zone was filled with 0.1g catalyst (20–40 mesh). An online GC-7890T equipped with TCD detector was used to analyse the catalytic products. The temperatures of injection port and detector at chromatogram were both 270 °C. Besides, the reaction temperature was 400 °C and the pressure of nitrogen carrier gas was 0.1 MPa. Before the catalytic reaction, the H-Beta catalyst was activated at 400 °C for 3 h. The conversion of 1,3,5-TIPB and the selectivity of products were calculated by the following formula:  $C_{TIPB} = (X - X_i)/X$ ;  $S_m = S_i/S_t$ ;  $X_i$  and  $X$  denote the chromatographic peak areas of unreacted 1,3,5-TIPB and initial 1,3,5-TIPB, respectively.  $S_i$  and  $S_t$  represent the chromatographic peak areas of product (m) and total products, respectively.

## 3. Results and discussion

### 3.1. The physical-chemical properties of the zeolite beta synthesized by aerosol-assisted method

Fig. 1a and b shows the XRD pattern and SEM image of the A50 sample. XRD pattern exhibits the characteristic peaks at  $2\theta = 7.8^\circ$  and  $22.4^\circ$ , which are typical for BEA topology [23]. Since no extra water was added in the crystallization step, a relatively low amount of the TEOAH is sufficient for the construction of zeolite beta with a high crystallinity in a dense synthesis system. As shown in the SEM image, the morphology of A50 sample exhibits spherical nano-agglomerates with the size of 200–500 nm. Clearly, there might be intercrystal pores between the nanosized crystals, which was further confirmed by N<sub>2</sub> sorption analysis.

The N<sub>2</sub> sorption isotherm curve and the pore size distribution of A50 sample are given in Fig. 1c and d. The sample shows the type IV isotherm, which exhibits a remarkable uptake at the very low pressure and a hysteresis loop from  $P/P_0 = 0.4$ , indicating the adsorptions in micropores and mesopores of the sample [24]. According to the BJH adsorption pore size distribution of A50, a mesopore distribution in the range of 2–10 nm can be clearly observed. The mesopore should be formed by the aggregation of the nanosized crystals. The BET surface area and mesopore volume are 714m<sup>2</sup>/g and 0.22 cm<sup>3</sup>/g, respectively. These results also confirm that the A50 sample contains mesopores.

Table 1 lists texture properties of A50 and Q50 samples. The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of A50 is almost consistent with that of the raw material. Usually, the synthesis of zeolite under hydrothermal

Download English Version:

<https://daneshyari.com/en/article/6456597>

Download Persian Version:

<https://daneshyari.com/article/6456597>

[Daneshyari.com](https://daneshyari.com)