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Synthesis of hierarchical zeolite Beta with low organic template content via the steam-assisted conversion method

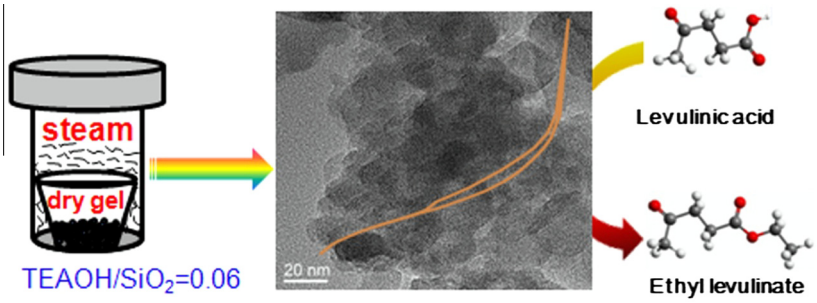
Junliang Zhang, Peng Cao, Huiyan Yan, Zhijie Wu *, Tao Dou *

State Key Laboratory of Heavy Oil Processing and the Key Laboratory of Catalysis of CNPC, China University of Petroleum, Beijing 102249, China

HIGHLIGHTS

- The steam-assisted conversion method led to highly crystalline zeolite Beta.
- The amount of organic template content (TEAOH/SiO_2 ratio = 0.06) was reduced.
- As-prepared zeolites possessed large external surface areas and mesoporous volumes.
- Zeolite Beta showed high activity and reusability in levulinic acid esterification.

GRAPHICAL ABSTRACT



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ABSTRACT

We report the synthesis of hierarchical zeolite Beta with low organic template (tetraethylammonium hydroxide, TEAOH) content by the steam-assisted conversion (SAC) method. Neither zeolite seeds nor the secondary mesoporogen were required. Only a bit amount of organic template (denoted as TEAOH/SiO_2 ratio = 0.06) was used to obtain highly crystalline zeolite Beta, which was remarkably lower than the reported lowest value (0.10). Physicochemical properties of the resulting samples were investigated by comprehensive characterizations including X-ray diffraction, scanning electron microscopy, transmission electron microscopy, solid state ^{27}Al MAS NMR spectra, nitrogen adsorption–desorption, X-ray fluorescence, temperature-programmed desorption of ammonia and infrared spectra of pyridine adsorption. These characterization results showed that the SAC method led to hierarchical crystalline zeolite Beta aggregates assembled by 20–40 nm nanosized crystals with controllable SiO_2/Al_2O_3 ratios among 29–47 by varying the compositions of synthetic gels with the Na_2O/SiO_2 ratio of 0.12 and the H_2O/dry gel ratios at 0.20–0.30. These zeolite Beta aggregates possessed large external surface area (158–180 m^2/g) and mesoporous volume (0.27–0.30 cm^3/g) resulted from the formation of intercrystalline mesopores and of the small zeolite crystal sizes. The obtained hierarchical zeolite Beta showed 41.2% conversion in the esterification reaction of levulinic acid with ethanol and four catalytic runs without obvious decrease in conversion, which were better than those on the zeolite Beta samples from the conventional hydrothermal synthesis. This was due to the promotion of the accessibility of reactants to the acid sites distributed on the external surface of zeolite nanocrystals and of the prominent diffusion in intercrystalline mesopores.

* Corresponding authors. Tel.: +86 10 8973 3235; fax: +86 10 8973 4979.
E-mail addresses: zhijiewu@cup.edu.cn (Z. Wu), doutao@cup.edu.cn (T. Dou).

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1. Introduction

Zeolite Beta possesses intriguing pore system featuring three-dimensional and intersectional channels with 12-ring apertures and has been served as efficient catalysts or supports in the oil refining, the abatement of NO_X emissions, and the conversion of biomass to biofuels and chemicals [1–3]. Especially, zeolite Beta shows excellent performance in the fluid catalytic cracking (FCC) process as catalyst additive [4]. However, the industrial application of zeolite Beta in FCC is rarely reported because of the huge consumption and the high price of zeolites. Generally, large amount of organic template (i.e., TEAOH) is required in the synthesis of zeolite Beta using the conventional hydrothermal synthesis ($TEAOH/SiO_2$ = 0.20–0.50) and the expense of TEAOH is the main constitution of the production cost of zeolite Beta. Moreover, indispensable calcination treatment results in completely decomposition of organic template (TEA^+) occluded in the micropores of zeolite Beta and then in a heavy pollution-emission problem [5]. Therefore, reduction even elimination of TEAOH in the synthesis of zeolite Beta is very desirable.

Xie et al. reported a hydrothermal synthetic route without using any organic template via the assistance of calcined zeolite Beta as crystallization seeds [6]. Majano et al. used zeolite Beta containing TEAOH as crystallization seeds to prepared low silica zeolite Beta [7], and it was found that a low product yield of this route. These resulting zeolite Beta showed large crystal size (>500 nm) and high framework polarity with low SiO_2/Al_2O_3 ratios (<15) [7–11]. In contrast, the TEAOH is still essential for the synthesis of high silica zeolite Beta, and hence the development of new synthetic strategy for the high silica zeolite Beta with using low amount of TEAOH is still a great challenge.

Borade et al. employed a dense synthetic gel to prepare high silica zeolite Beta (SiO_2/Al_2O_3 = 14–32) with a low $TEAOH/SiO_2$ ratio of 0.17 [12], and this ratio could be reduced to 0.11 in the synthesis of zeolite Beta (SiO_2/Al_2O_3 = 21–29) by changing the crystallization conditions [13]. Besides, the steam-assisted conversion (SAC) method has been regarded to be another effective approach to reduce the $TEAOH/SiO_2$ ratio (0.15–0.50, typically 0.37) [14,15]. The SAC method was one of the dry gel conversion method proposed by the report of Xu et al. [16]. It is typically carried out in a reactor where the dry gel containing organic templates is never in contact with the liquid but reacts under the assistance of its vapor at autogenous pressure. The SAC method has received much attention not only because it needs less organic template but also this method can be used to prepare zeolite membranes with different topological structure, such as MFI and MOR [17,18]. Recently, Cheng et al. succeed in the use of the SAC method to prepare zeolite Beta with the lowest $TEAOH/SiO_2$ ratio (0.10) with the aid of zeolite Beta as crystallization seeds [19]. In our view, it is significant to investigate the limit of the organic template required for the synthesis of high silica zeolite Beta. Here, high silica (SiO_2/Al_2O_3 = 29–47) zeolite Beta aggregates were synthesized with a much lower $TEAOH/SiO_2$ ratio (as low as 0.06) without any aid of crystallization seeds by the SAC method. To the best of our knowledge, it's the lowest value utilized for the synthesis of high silica zeolite Beta. The effects of expressive synthetic parameters, such as the alkalinity of the synthetic gel and the steam pressure on the phase purity, morphology and size of zeolite Beta were studied and optimized.

In addition to the expensive cost of zeolite synthesis, the diffusion limitation imposed by the sole presence of microporous channel system is another challenge restricting the catalytic performance of zeolite Beta [20]. Generally, the alkaline treatment is used to generate intracrystalline mesopores to alleviate the diffusion limitation [21]. Interestingly, the SAC method could fabricate zeolite Beta aggregates from the assembly of zeolite nanocrystals, and hence the formation of large intercrystalline mesoporosity without complicated post-synthetic steps or secondary mesoporogen. On the other hand, the esterification of levulinic acid (LA) with ethanol conducted in the presence of zeolite Beta under the benign condition can produce value-added ethyl levulinate (EL) that was reported as potential blending component in gasoline or diesel for transportation fuels [22,23], and the textural properties and accessibility of active sites have been regarded as the key factors governing the activity. Therefore, this reaction was used to evaluate the catalytic performance of hierarchical zeolite Beta samples from the SAC method and another series of counterparts from the conventional hydrothermal synthesis was used for comparison.

2. Experimental section

2.1. Chemicals

Silica gel (SiO_2, 98%, Qingdao Haiyang Chemical Co., Ltd), sodium aluminate ($NaAlO_2$, C.P., Tianjin Jinke Fine Chemical Institute), tetraethylammonium hydroxide (TEAOH, 25 wt.% aqueous solution, Hangzhou Yanshan Chemical Co., Ltd.), and sodium hydroxide (NaOH, A.R., 96 wt.%, Beijing Chemical Works) were used in the preparation of zeolite Beta. Levulinic acid ($CH_3COCH_2CH_2COOH$, LA, 98%, Alfa) and ethanol (CH_3CH_2OH, 99.5%, Acros) were used in the catalytic reaction. The commercial zeolite Beta for hydrocracking was obtained from China National Petroleum Corporation (CNPC). All the reagents were invoked as purchased without any further purification.

2.2. Synthesis of zeolite Beta

A typical procedure of the SAC method was described as followed. Firstly, 0.75 g NaOH and 2.92 g TEAOH were dissolved in 11.71 g distilled H_2O, and stirred until the formation of a clear solution. Next, 0.27 g $NaAlO_2$ was added and stirred for about 30 min in order to dissolve aluminum source. Then, 5.0 g solid silica was added to the clear solution and the resulting mixture was stirred vigorously for 2 h at room temperature to form a gel with the molar composition of SiO_2:$0.014Al_2O_3$:$0.125Na_2O$:0.06 TEAOH:$15H_2O$. The gel was heated at 60 °C for 12 h to form a dry gel. Finally, 5.0 g of obtained dry gel was weighed, coarsely crushed and transferred into a 40 mL Teflon cup. The charged Teflon cup was placed into a 180 mL Teflon-lined stainless-steel autoclave, and then 1.0 g distilled water was added into the bottom of Teflon liner without contacting the dry gel. Crystallization of zeolite was conducted in a preheated oven at 140 °C for 48 h under static condition. The solid product was collected and washed with distilled water by centrifugation at 7000 rpm and dried at 100 °C overnight. When the samples with different SiO_2/Al_2O_3 ratios were synthesized, only the $NaAlO_2$ was altered and other parameters kept constant.

A series of zeolite Beta with different SiO_2/Al_2O_3 ratios were prepared by the conventional hydrothermal synthesis method using the same starting materials. A typical gel with the molar composition of SiO_2:$0.014Al_2O_3$:$0.032Na_2O$:0.20TEAOH:$7.50H_2O$ was prepared. Specifically, 0.15 g NaOH, 0.27 g $NaAlO_2$ and 9.60 g TEAOH were mixed with 3.83 g distilled H_2O and stirred until the formation of a clear solution. Subsequently, 5.0 g solid silica gel was added and the mixture was stirred vigorously for 2 h, then the resulting alumino-silicate gel was transferred into a Teflon-lined stainless autoclave and subjected to hydrothermal synthesis at 140 °C for 48 h under static condition. The resulting products were collected by filtration, washed thoroughly with distilled water and dried at 100 °C overnight. Similarly, zeolite Beta with