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A rapid synthesis route for Sn-Beta zeolites by steam-assisted conversion and their catalytic performance in Baeyer–Villiger oxidation

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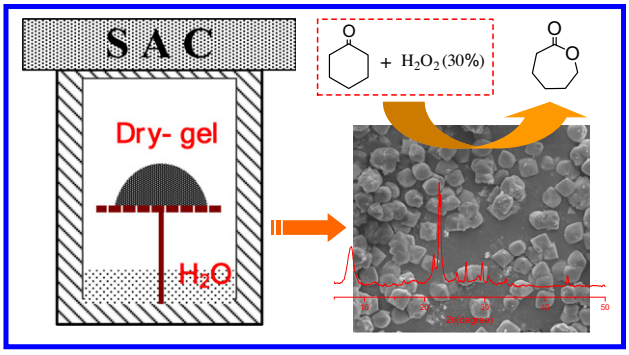
HIGHLIGHTS

- A steam-assisted conversion (SAC) method is used to rapidly synthesize Sn-Beta zeolites.
- Sn-Beta zeolites with high crystallinity and BEA topology could successfully be synthesized by SAC method.
- The Sn-Beta by SAC method can demonstrate good catalytic activity for cyclohexanone oxidation with 30% H_2O_2.

GRAPHICAL ABSTRACT

A steam-assisted conversion (SAC) method was used to rapidly synthesize Sn-Beta zeolites with high crystallinity and yield. The Sn-Beta zeolites could exhibit good catalytic activity for Baeyer–Villiger (B–V) oxidation reaction of cyclohexanone to ε-caprolactone using aqueous H_2O_2 (30%) as oxidant.



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ABSTRACT

Sn-Beta zeolites were prepared by a rapid and clean steam-assisted conversion (SAC) method from dry stannosilicate gel. The amorphous gel was converted to highly crystalline Sn-Beta within 5 h at mild reaction temperature of 453 K. The properties of the as-prepared samples were characterized by XRD, SEM, FT-IR, UV–Vis, UV-Raman, ICP and N_2 adsorption. A high gel conversion to BEA can be obtained with Sn^{4+} inserted in the zeolite framework. The SAC method was successfully used to produce pure silica Beta zeolite (Si/Sn = ∞) to Sn-Beta zeolite with 3.8 wt.% SnO_2 (i.e., Si/Sn = 83). The Sn-Beta prepared by SAC method is an efficient catalyst for Baeyer–Villiger (B–V) reaction of cyclohexanone to ε-caprolactone.

1. Introduction

Tin-containing zeolites are of considerable interest due to their unique chemistry and applications [1–4]. The Sn-Beta zeolite having large 3D pore structure is shown to be very active and chemoselective catalyst for many important organic reactions [5], such as Baeyer–Villiger (B–V) oxidation [6], Meerwein–Ponndorf–Verley (MPV) reduction [7], Oppenauer oxidations [8] as well as sugar conversion to lactic acid derivatives [9], isomerization of glucose to fructose [10] and conversion of carbohydrates to 5-(hydroxymethyl)-furfural (HMF) [11]. The conventional

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preparation of Sn-Beta is via hydrothermal synthesis in fluoride system [6–11]. Seeds are often required and are prepared by dealumination of nano-sized Al-Beta zeolites with concentrated nitric acid. Besides the lengthy synthesis time, the use of hydrofluoric acid as mineralizer produces unwanted pollutions and hazards. Furthermore, it is often difficult to adjust the H_2O/SiO_2 ratio when silicon alkoxides are used as the removal of alcohol also evaporates water that often leads to poor synthesis reproducibility [12–16]. Thus, the process is energy intensive and difficult to scale-up. Recently, Li et al. [17] have reported an alternative route for preparing of Sn-Beta zeolite by a solid–gas reaction of dealuminated Al-Beta zeolite at high temperature. The process although attractive is complex as well as very energy intensive.

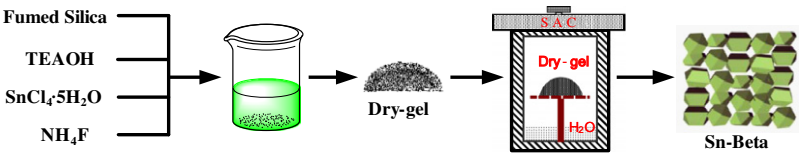
This work explores the possibility of preparing Sn-Beta zeolites by steam-assisted conversion (SAC) method. This method transforms a precursor gel into porous crystalline zeolites [18–20], molecular sieves [21–25] and metal organic frameworks (MOFs) [26] using steam. SAC method is characterized by rapid synthesis [18,27,28] at milder conditions of pH and temperature, while requiring less SDA and thus generating less waste than the conventional hydrothermal synthesis route. There is no prior report on the preparation Sn-Beta by SAC method, and this work aims to investigate the synthesis of active Sn-Beta catalyst for Baeyer–Villiger (B–V) oxidation of cyclohexanone to ε-caprolactone.

2. Experimental

2.1. Synthesis

Sn-Beta zeolites were prepared according to Scheme 1. A wet gel was first prepared from fumed silica powder (SiO_2, 99.8%, Shenyang Chemical Co. Ltd.), $SnCl_4{\cdot}5H_2O$ (98%, Tianjin Kermel Chemical Reagent Co. Ltd.), tetraethylammonium hydroxide (TEAOH, 40%, Zhejiang Kente Chemical Co., Ltd.) and NH_4F (98%, Tianjin Kermel Chemical Reagent Co. Ltd.). Following careful drying at 333 K for 6 h, a dry gel with a composition of 1 SiO_2: 0.27 $(TEA)_2$: 0.002–0.012 SnO_2: 0.54 NH_4F: 7.5 H_2O was obtained. The 2 g dry stannosilicate gel was ground into powder and placed in a homemade autoclave that prevents water condensation on the dry gel during the steam-assisted conversion process. This precaution allows reproducible gel composition to be obtained. 1.5 mL water was added to the autoclave and the steam was generated at 453 K. Products were obtained following 3–6 h of treatment and were washed and dried at 383 K for 8 h prior air calcination at 823 K for 6 h to remove the organic template.

Sn-Beta zeolite with Si/Sn = 120 was prepared by conventional method according to the procedure reported by Corma et al. [6]. The synthesis was carried out in a fluoride system using TEOS (98%, Tianjin Kermel Chemical Reagent Co. Ltd.) as



Scheme 1. Illustration of the Sn-Beta zeolite preparation by SAC method.

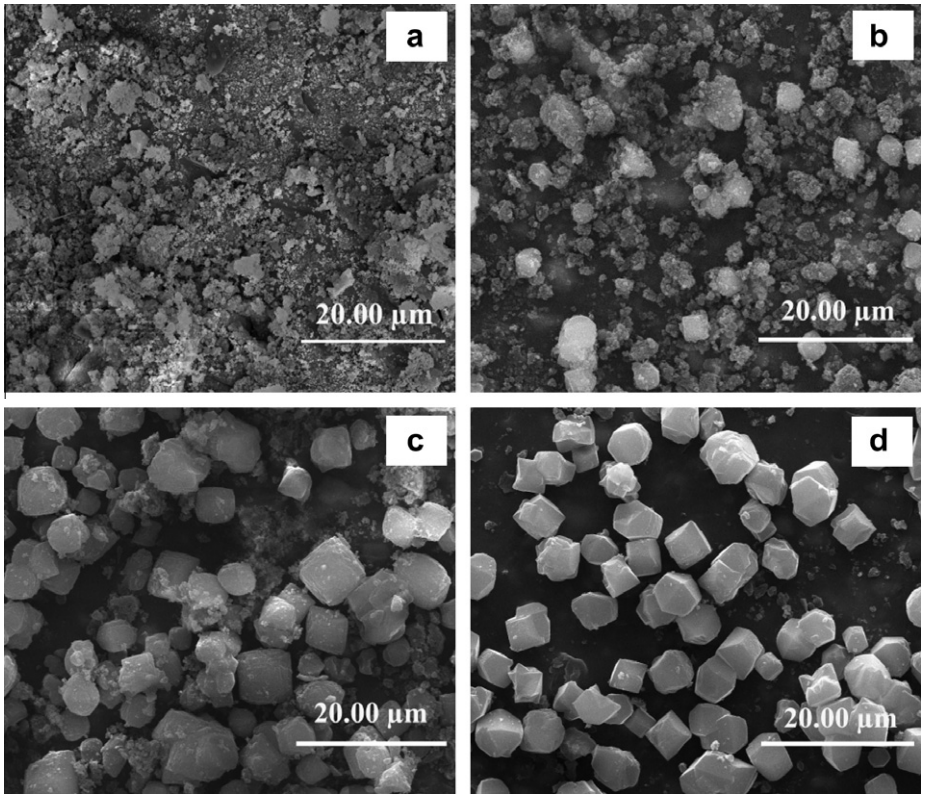


Fig. 1. SEM images of as-synthesized Sn-Beta (125) samples at different crystallization time: (a) 0 h, (b) 2 h, (c) 4 h, and (d) 6 h.