



Sn-Beta zeolite hydrothermally synthesized via interzeolite transformation as efficient Lewis acid catalyst



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ARTICLE INFO

Article history:

Received 26 January 2017

Revised 21 April 2017

Accepted 27 April 2017

Available online 23 May 2017

Keywords:

Interzeolite transformation

Sn-Beta zeolite

MWW zeolite

Lewis acid catalysis

Baeyer–Villiger oxidation

ABSTRACT

An innovative hydrothermal synthesis strategy of heteroatom-containing zeolite, in this case Sn-Beta, via interzeolite transformation is reported in present study. To the best of our knowledge, this prepared Sn-Beta zeolite possesses the highest isolated Sn contents (3.03 wt% or Si/Sn molar ratio of 63) in comparison to other hydrothermally synthesized ones. The success of this synthesis strategy to Sn-Beta synthesized from MWW silica is mainly due to its nucleating and growing readily compared with those prepared from amorphous silica source. The introduction of Beta seeds and the structural similarity between the parent zeolite (MWW) and the targeted zeolite (^βBEA) are found to be indispensable factors in the crystallization of Sn-Beta zeolite. The obtained Sn-Beta zeolites possess isolated tetrahedral Sn⁴⁺ in the framework and high hydrophobicity. Additionally, lowering the molar ratio of H₂O₂ to cyclohexanone and moderately reducing reaction time are proved to be effective methods to improve the selectivity of ε-caprolactone in the Baeyer–Villiger oxidation of cyclohexanone with H₂O₂ using Sn-Beta as Lewis catalyst. Thus, the prepared Sn-Beta zeolite demonstrated promising catalytic properties, especially for the desired products selectivity, in the Baeyer–Villiger oxidation of ketones as well as the isomerization–esterification reaction of dihydroxyacetone in ethanol, far outperforming the conventional Sn-Beta-F catalyst, which were attributed mainly to its high Sn content in the framework and excellent diffusion properties resulting from the relatively small crystal size.

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1. Introduction

Zeolite materials with crystallized structures, high surface areas, and uniform pore channels have attracted great interest, as they are widely used in various fields, especially in the petrochemical industry [1–8]. They are typically synthesized by hydrothermal treatment of gels with the assistant of organic structure-directing agents (OSDAs), which favors nucleation and growth in the light of kinetics [9]. Apart from classical strategy, interzeolite transformations, which are prone to construct targeted zeolites with smaller pores, higher framework density, and a more negative enthalpy, have gained much attention as they provide a strategy for the selective synthesis of specific zeolite structures in a short synthetic time, in some cases, even without OSDAs [10–15].

The outcome of such transformations is highly susceptible on the nature and composition of the parent zeolite as well as other conditions, such as, treatment temperature, treatment time, the

composition of the reacting solution, etc. [14,15]. The zeolites framework undergoes dissolution to release monomers and/or aluminosilicates fragments at a rapid rate initially. This stage doesn't stop until the synthesis solution is saturated in the corresponding oligomer composition. Subsequently, nucleation and growth of a new phase may occur at the cost of oligomer consumption, which in turn likely contributes to continued dissolution of the parent phase. The composition of the solid and liquid phase is altered continuously during the process of dissolution–recrystallization, thereby affecting the conditions for nucleation and recrystallization [13]. A typical approach is “composite building unit (CBU) Hypothesis” proposed by Okubo and coworkers [13], which relies on the presence of at least one common CBU between the parent and targeted zeolites to overcome kinetic and thermodynamic hurdles. Otherwise, it requires OSDAs or target seeds to accomplish the transformations. Subsequently, a series of targeted zeolites have been synthesized using this transformation method, for example, in the preparation of RUT-, ^βBEA-, CHA-, MTN-, LEV-, MFI-, and OFF-type zeolites using FAU-type zeolite as the starting material [14–18], the transformation of B-^βBEA to B-SSZ-24, B-SSZ-31 and the transformation of B-SSZ-33 [19], LTA to GIS

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[20]. Note that the successful transformation of FAU-type zeolite into β BEA-type zeolite with the aid of seed crystals results from the presence of a common four-membered ring (4R) between the CBUs *d6r* and *bea*, which may act as the common structural unit [21]. Coincidentally, the *d6r* unit is also observed in the MWW-type structure; namely, there is a common 4R unit between the MWW and β BEA-type structure, suggesting that the MWW-type zeolite is a potential candidate for transformation into β BEA-type zeolites via recrystallization in an alkaline medium under hydrothermal conditions in short synthetic periods.

A typical representative of the stannosilicates, Sn-Beta, with the β BEA topology and tetrahedrally coordinated Sn^{4+} in the framework, shows great potential for various industrially-relevant reactions mainly because of its Lewis acidic behavior even in the presence of water. Hence, Sn-Beta is capable to catalyze the Baeyer–Villiger (B–V) oxidation reaction [1], the Meerwein–Pon dorf–Verley–Oppenauer (MPVO) reaction [22], the Diels–Alder reaction [23], the conversion of xylose to xylulose [24], the transformation of glyceraldehydes (GLA) or dihydroxyacetone (DHA) into alkyl lactates [25], and the isomerization of glucose to fructose [26–28].

Nevertheless, the traditional synthetic route for Sn-Beta with a limited Sn content (Si/Sn ratio > 100) is time-consuming (requiring more than 20 d) due to slow nucleation and crystallization process [1]. Additionally, involving a large amount of Sn (Si/Sn ratio < 100) in the stannosilicate gels would further inhibit the nucleation of Sn-Beta zeolite [29,30]. Significant efforts, including hydrothermal synthesis and post-synthesis methods, have been made to address the challenge of synthesizing Sn-Beta [29–32]. Kang et al. synthesized Sn-Beta with the Si/Sn of 64 by steam-assisted conversion with a rapid crystallization rate. However, the amorphous phase was found as a concomitant in the final products [29]. Takayuki et al. also demonstrated that an incorporated Sn content of up to 3.17 wt % (Si/Sn = 60) could be realized by utilizing a Sn–Si mixed oxide composite as the precursor for the crystallization of Sn-Beta zeolite. Unfortunately, impurity atoms (i.e., Al and Y) were also inevitably incorporated into the products owing to limitations of the method [30]. On the other hand, post-synthesis methods have the disadvantages of requiring multiple steps, yielding poor hydrophobicity, forming extra-framework Sn species, leading to poor catalytic performances in some reactions, and requiring dangerous operations for the preparation of Sn-Beta [33–35]. Therefore, further exploration of innovative synthesis strategy to Sn-Beta zeolite with a high framework Sn content and short crystallization time is an urgent need but still a significant challenge.

Interzeolite transformations may provide a general and efficient route for the incorporation of a large amount of Sn into β BEA-type zeolite framework with short synthetic periods. This manuscript reports a well-crystallized Sn-Beta zeolite with a high Sn content (3.03 wt% or Si/Sn molar ratio of 63) is synthesized via dissolution of all-silica MWW crystals and seed-assisted recrystallization of degraded silicate species in a short crystallization time of 3 d. The crystallization mechanism and physicochemical properties (i.e., Sn^{4+} coordination state and hydrophilicity/hydrophobicity) of the prepared Sn-Beta zeolite are investigated in detail by various characterization techniques. The catalytic performance of this Sn-Beta is assessed by comparing with Sn-Beta-F prepared by the conventional approach in the Baeyer–Villiger oxidation of ketones as well as isomerization–esterification reaction of dihydroxyacetone in ethanol. Additionally, we also propose an effective strategy to improve the selectivity of ϵ -caprolactone in the Baeyer–Villiger oxidation of cyclohexanone with H_2O_2 using Sn-Beta as Lewis catalyst.

2. Experimental section

2.1. Preparation of ITQ-1 zeolite and Beta seeds

ITQ-1 zeolite (all-silica MWW-type zeolite) was hydrothermally synthesized using *N,N,N*-trimethyl-1-adamantammonium hydroxide (TMAdaOH) and hexamethylenimine (HMI) as co-structure-directing agents from a silicate gel with following chemical composition: SiO_2 : 0.25 TMAdaOH: 0.31 HMI: 44 H_2O . The ITQ-1 zeolite typically crystallized after the gel was heated at 150 °C for 3 d. Then, it was calcined at 823 K for 6 h and used as the silica source for Sn-Beta synthesis. The synthesis is described in more detail elsewhere [36].

The Beta seeds were prepared by acid treatment of commercially available H-Beta (Si/Al = ca. 11, Shanghai Xinnian Petrochemical Additives Co., Ltd.). First, the parent H-Beta was calcined in air at 873 K for 6 h, and then it was refluxed in 6 M HNO_3 solution at a solid-to-liquid ratio of 1 g: 50 mL for 24 h to remove Al atoms in the zeolite. The product was collected by centrifugation and washed repeatedly with deionized water until the pH was around 7. Finally, the dried product acted as the seeds for synthesizing Sn-Beta zeolite.

2.2. Synthesis of Sn-Beta by interzeolite conversion

Sn-Beta zeolite with a high Sn content was synthesized utilizing the calcined ITQ-1 zeolite as the silica source. In a typical synthesis, the ITQ-1 silicate, $\text{SnCl}_4 \cdot 5 \text{H}_2\text{O}$, and dealuminated Beta seeds (10 wt% with respect to ITQ-1) were added into an aqueous solution of tetraethylammonium hydroxide (TEAOH) (25 wt%) under stirring at room temperature for 15 min. The ammonium fluoride (NH_4F) was then blended with the mixture. The final molar composition of the mixture was SiO_2 : $x \text{SnO}_2$: 0.4 TEAOH: 7.5 H_2O : 0.6 NH_4F , where x represents the Sn/Si ratio in the synthetic gel. Subsequently, the mixture was transferred into an autoclave and further crystallized at 413 K for a certain time under static conditions. The product was recovered by filtration, dried at 353 K for 10 h, and then calcined at the temperature of 873 K for 6 h. The obtained Sn-Beta zeolite is denoted as Sn-Beta-Trans- n , where n represents the Si/Sn ratio in the synthetic gels.

For the control experiment, Sn-Beta-F- y , where y represents the Si/Sn in the synthetic gel, was also prepared in our laboratory according to well-established procedures reported in the literature [1]. It is worth mentioning that Sn-Beta-F was synthesized in the presence of the Beta seeds (10 wt% with respect to added Si source) utilizing ammonium fluoride as the fluorine source. The as-synthesized catalyst was washed three times with deionized water, dried at 353 K for 10 h, and then calcined at the temperature of 823 K for 6 h.

2.3. Characterizations

The X-ray diffraction (XRD) patterns were obtained using a Rigaku Ultima IV X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$) at 35 kV and 25 mA. UV-Raman spectroscopy with an excitation line at 210 nm was carried out on the UV Raman spectrograph utilizing a Jobin-Yvon T6400 triple-stage spectrograph with a spectral resolution of 2 cm^{-1} . Transmission electron microscopes (TEM) were taken on a JEOL-JEM-2100 microscope and scanning electron micrographs (SEM) were collected from Hitachi S-4800 microscopy. The adsorption isotherms of N_2 and water were measured on a BELSORP-MAX instrument equipped with a precise sensor for low-pressure measurement at 77 K for N_2 and 298 K for water after activating the samples at 573 K at least for 5 h under vacuum conditions. The Si and Sn contents were

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