



# Postsynthesis of FAU-type stannosilicate as efficient heterogeneous catalyst for Baeyer-Villiger oxidation

Zhiguo Zhu, Hao Xu, Jingang Jiang, Xue Liu, Jianghong Ding, Peng Wu\*

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, North Zhongshan Rd. 3663, Shanghai 200062, PR China

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## ABSTRACT

Sn-Y zeolite with hierarchical pore system was prepared using the atom-planting method from properly dealuminated USY zeolite and SnCl<sub>4</sub> vapor. Sn ions were tetrahedrally incorporated into the zeolite framework by the reaction between the SnCl<sub>4</sub> molecules and the “silanol nests” generated by steaming and acid treatment. The amount of incorporated Sn depended closely on the dealumination degree, in which the maximum Sn content of 2.6 wt.% was achieved when the parent USY zeolite was treated by precisely controlled acid treatment. Compared with Sn-MFI, Sn-MWW, Sn-MCM-41, hydrothermally synthesized or postsynthesized Sn-Beta, thus prepared Sn-Y zeolite showed excellent catalytic properties in the Baeyer-Villiger oxidation of 2-adamantanone using hydrogen peroxide or *tert*-butyl hydroperoxide as oxidant, which was mainly attributed to the open pore system contributed by 3-dimensional 12-membered ring channels and dealumination-derived intracrystal mesoporosity.

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## 1. Introduction

Zeolites materials, with crystalline structures, uniform pore channels and high surface area, have aroused great interests as they are widely used in various fields including catalysis, separation and ionic exchange [1–3]. Tetrahedral framework Al ions endow traditional zeolites with Brønsted acidity, making them active in catalytic reactions as solid acid catalysts. In the past three decades, many other metal ions such as Ti [4–8], Ga [9], Fe [10], V [11], Zr [12] and Sn [1] have been introduced into zeolite framework by direct synthesis or post-synthesis method. As one of the successful metallosilicates, titanosilicate TS-1, with tetrahedrally coordinated Ti in framework, shows great potential in catalytic oxidation field rather than the traditional acid catalytic processes. Since its discovery in 1983 [4], TS-1 has been served as catalyst in many industrial processes, such as propylene epoxidation [5] and ammoximation of cyclohexanone [6] with H<sub>2</sub>O<sub>2</sub> as the oxidant, giving the sole byproduct H<sub>2</sub>O. The successes, achieved in developing green oxidation processes by TS-1/H<sub>2</sub>O<sub>2</sub> system, stimulate the invention of other new titanosilicates such as Ti-MWW [7] and Ti-Beta [8] with larger pores than TS-1. On the other hand, it also motivates the researchers to develop other metallosilicates with novel cat-

alytic active sites, for example, Sn-zeolites or stannosilicates with isolated Sn ions in the framework. Corma et al. proved that tetrahedral Sn sites in BEA\* zeolite was highly efficient in activating carbonyl groups and then transforming ketones to corresponding lactones in the Baeyer-Villiger (B-V) oxidation reactions [1]. With Lewis acidity, Sn-zeolites were also capable to catalyze Meerwein-Ponndorf-Verley (MPV) reduction reaction of ketones and aldehydes with alcohols [13]. More recently, Sn-zeolites were found to be active in the clean synthesis of chemicals from biomass, such as converting glyceraldehydes or dihydroxyacetone into alkyl lactates [14,15] and isomerizing glucose to fructose in aqueous media [16–18].

Although many Sn-zeolites such as Sn-MFI [19], Sn-MEL [20], Sn-MWW [21], Sn-BEA-56 [22], Sn-MFI nanosheets [23] and Sn-MCM-41 [24] have been reported, Sn-Beta zeolite is still the most widely studied mainly because of its relative stable and open framework structure with 3-dimensional (3D) 12-membered ring (MR) channels.

Nevertheless, the disadvantages of the traditional hydrothermal synthesis method for Sn-Beta zeolite are time consuming and limited Sn content (generally Si/Sn ratio > 100). An additional drawback is the utilization of hazardous F<sup>-</sup> ions in synthesis, which not only cause environment problem but also lead to large crystals [1]. Significant efforts have been made to improve the synthesis process of Sn-Beta, such as using less toxic NH<sub>4</sub>F instead of HF [25], shortening the crystallization time by seeding method [26]

\* Corresponding author.

E-mail address: [pwu@chem.ecnu.edu.cn](mailto:pwu@chem.ecnu.edu.cn) (P. Wu).

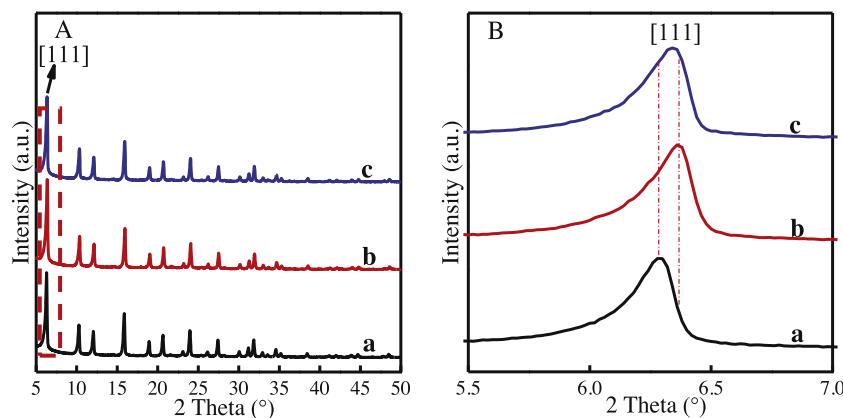


Fig. 1. Wide angle XRD patterns (A) and enlarged [111] reflections (B) of USY (a), USY-AT-1 (b) and Sn-Y-1 (c).

and even synthesis in a fluoride-free system by dry gel conversion method [27]. We once put forward a post-synthesis method to prepare Sn-Beta zeolite with a relatively high Sn content as well as a nanocrystal size [28]. The aluminosilicate Beta was constructed in advance and then Al ions were removed by  $\text{HNO}_3$  treatment followed by an atom-planting process to introduce the Sn ions into the defect sites generated by dealumination. Thus prepared Sn-Beta zeolite was more active than that hydrothermally synthesized in the fluoride medium in the B-V oxidation reaction. Dijkmans et al. synthesized Sn-Beta by grafting  $\text{Sn}^{4+}$  into dealuminated Beta framework in isopropanol solution under reflux condition [29]. Hermans et al. also showed that it was possible to insert Sn ions into the vacant tetrahedral sites of BEA\* zeolite by solid-state ion-exchange method [30]. However, the intergrowth of polymorphs A and B in BEA\* structure generates numerous defects in the structure, which then make the structure easily attacked by water molecules [31–33]. Moreover, Sn-Beta still possesses a serious diffusion problem when processing large substrates like biomass although it is demonstrated to be an excellent catalyst [16–18,34].

As a result, it is necessary to explore novel stannosilicate zeolites with more open pore channels and higher hydrophobicity. Y zeolite, with the FAU topology and 3-dimensional 12-MR channels as well as supercages, was firstly used as commercial solid acid catalyst in the fluid catalytic cracking (FCC) industrial process by Mobile, which was perhaps the biggest revolution in oil refining industry in 1960s [35]. Nevertheless, the synthesis system involving alkaline metals and extremely high Al content made it impossible to obtain heteroatom-containing Y zeolite directly. Besides, the high Al content also affects the catalytic performance of the material in practical reactions.

Inspired by the post-synthesis approaches used to synthesize metallosilicates mentioned above [28–30], a novel FAU-type stannosilicate zeolite with high hydrophobicity and hierarchical pore systems was successfully prepared from properly dealuminated USY zeolite using atom-planting technique. The physicochemical properties of the obtained Sn-containing USY zeolite and the Sn ions incorporation mechanism were investigated by various characterization techniques. The catalytic performances of Sn-Y were evaluated in detail by comparing to other Sn-zeolites in the B-V oxidation reaction.

## 2. Experimental

### 2.1. Synthesis of catalysts

Sn-Y was post-synthesized following the similar procedures previously adopted for Ti-MOR [36] and Sn-Beta-PS [28]. The

preparation strategy consists of controlled dealumination of USY and incorporation of Sn ions into the defect sites as graphically described in Scheme 1. A commercially available H-USY with a Si/Al molar ratio of ca. 6, purchased from Shanghai Xinnian Petrochemical Additives Co., Ltd, was used as the parent material for preparing different dealuminated H-USY zeolites. Firstly, the parent H-USY was calcined in air at 873 K for 6 h and then it was refluxed in 6 M  $\text{HNO}_3$  solution at a liquid-to-solid of 1 g: 50 mL for different time (0–18 h). The dealuminated products were denoted as USY-AT-X where X represents the acid treatment time. For a typical run of  $\text{SnCl}_4$  vapor treatment, 1 g dealuminated H-USY powder sample was placed in a vertical quartz tubular reactor and pretreated at 773 K for 2 h under a stream of dry  $\text{N}_2$ . Then, keeping the reactor temperature at 773 K, the dry  $\text{N}_2$  stream was switched to go through an anhydrous  $\text{SnCl}_4$  liquid in a glass bubbler which was maintained at room temperature. The  $\text{SnCl}_4$  vapor was delivered into the reactor by  $\text{N}_2$  flow to contact the zeolite bed for 2 h. After the treatment, the sample was purged with pure dry  $\text{N}_2$  stream at the same treatment temperature for 1 h to remove any residual  $\text{SnCl}_4$ . After cooling to room temperature in  $\text{N}_2$  stream, the treated zeolite was washed with deionized water until the chloride ions were not detected in the filtrate by  $\text{AgNO}_3$  solution. After drying in air at 373 K overnight, the stannosilicate samples were obtained, denoted as Sn-Y-X where X also represents the acid-treatment time in the first stage.

For control experiments, Sn-Beta-PS [28], Sn-Beta-F [1], Sn-MWW [22], Sn-MFI [19], Sn-MCM-41 [24] and Sn-impregnated USY [20] catalysts were also prepared in our laboratory strictly following the procedures reported in literatures. It should be noted that the synthesis of Sn-Beta-F was performed using  $\text{NH}_4\text{F}$  as the fluorine source instead of HF. All the as-synthesized catalysts were washed with deionized water repeatedly, dried at 373 K overnight and calcined at 823 K for 6 h.

### 2.2. Characterization methods

The X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV X-ray diffractometer using  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ) at 35 kV and 25 mA to check the structure and crystallinity of the zeolites. To determine the morphology, scanning electron micrographs (SEM) were performed on a Hitachi S-4800 microscopy, while the TEM images were taken on a JEOL-JEM-2100 microscope. The nitrogen adsorption isotherms were performed at 77 K on a BELSORP-MAX instrument after activating the samples at 573 K under vacuum at least for 5 h. The Brunauer-Emmett-Teller (BET) analysis was carried out using the data in the relative pressure region of  $P/P_0 = 0.05\text{--}0.25$ , which provided the specific surface area.

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