



# Low-cost synthesis of size-controlled TS-1 by using suspended seeds: From screening to scale-up



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## ABSTRACT

The synthesis of TS-1 zeolite with controllable crystal sizes has been successfully scaled up by using the suspension of nanosized S-1 as seed in a TPABr-template hydrothermal system. Even under poor stirring condition, the suspended seeds can be easily dispersed in the mixture of zeolite precursor. Therefore the synthesis shows a very good reproducibility when scaled up from 2 L to 500 L, and the crystal size of TS-1 zeolite can be exactly controlled and changed in a wide range by only changing seed amount. Using this TS-1 zeolite through large-scale synthesis as material, the catalyst was prepared by modification and used in propylene epoxidation. The yield of propylene oxide based on H<sub>2</sub>O<sub>2</sub> and propylene reaches 96.5% and 64.3%, respectively, which is superior to that of nanosized TS-1. Though the TS-1 samples synthesized with dried nanosized S-1 seed are similar to the samples synthesized with suspended seeds on the lab scale, the synthesis process using dried seeds shows a low reproducibility on the large scale. This research also implies the low cost and high energy efficiency of the production of TS-1 by using suspended seeds in large-scale process.

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## 1. Introduction

All chemical processes need to be scaled up from laboratory to large scale before their industrialization implementation [1–3]. The scale-up effect has been a major hurdle in the successful process development of new chemical technologies [4], especially for the hydrothermal synthesis of zeolites. Due to the transformation from homogeneous to heterogeneous in crystallization process [5], the scale-up synthesis of zeolites involves not only chemical reactions, but also mass transfer, heat transfer, momentum transfer, phase transition and other complicated chemical and physical changes, and there often are a great many unexpected problems [4,6].

Since the titanium silicalite-1 (TS-1) was first hydrothermally synthesized by Taramasso et al. [7] in 1983, it has attracted much research attention due to its remarkable catalytic properties. By classical synthesis method, TS-1 with very small particle size (100–200 nm) was obtained from organic reactants using tetrapropylammonium hydroxide (TPAOH) as template [7]. TS-1 nanoparticles have exhibited good catalytic activity in many green selective oxidation with H<sub>2</sub>O<sub>2</sub>, such as aromatic hydroxylation [8], oxidation of alcohols and alkanes [9], ammoximation of ketone [10],

and epoxidation of alkenes [11–13]. However, the expensive high-purity template and difficult separation of nanoparticles increase the cost of TS-1 and limit its wide application in industrial production [14].

In recent years, there are many researches about the low-cost synthesis of TS-1 by using inexpensive tetrapropylammonium bromide (TPABr) as template and colloidal silica as silicon sources [15–17]. TS-1 synthesized from cheap reactant system always possesses a crystal size over 1 μm. Large TS-1 crystals are always not suitable for industrial application due to the slow diffusion at low reaction temperature, and deactivation has been shown to proceed quicker on larger crystals due to their smaller specific external areas [18]. Consequently, some synthesis methods yielding small TS-1 crystals from cheap reactant system have been desired to be developed. It has been reported that addition of seed can decrease the crystal size, promote the nucleation and enhance the crystallization rate of zeolites [19–22]. Cundy et al. [23] have synthesized size-controllable S-1 and TS-1 using the nanocrystalline as seed. Small-crystal TS-1 was synthesized in a TPABr-ethylamine system using the mother liquid of nanosized TS-1 or S-1 as the crystal seed [24–27]. Our group also found that the addition of powdered nanosized S-1 as the crystal seed could directly provide crystal nucleus and significantly enhance crystallization rate, and size-controllably synthesized TS-1 submicrocrystals (SMCs) with the size of 0.81 × 0.33 × 0.15 μm [28].

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The crystallization of TS-1 zeolites occurs via the sequential steps of nucleation of the phase, or phases, dictated by the composition of solution, followed by growth of the nuclei to larger sizes by incorporation of material from solution. Even though the formula composition and crystallization condition in large-scale synthesis are completely consistent with those in lab-scale synthesis, the crystal size of zeolites obtained from large-scale reactor is difficult to be controlled and always larger than that obtained from laboratory. Many lab-scale synthesis (especially “micro-synthesis”) experiments are almost carried out without stirring, while stirring is essential for all large-scale synthesis but extreme cases [6]. Stirring plays a significantly important role in the zeolite synthesis for affecting the diffusion efficiency, and poor stirring would lead to a low reproducibility in large-scale synthesis. Implemented catalysts not only need excellent catalytic activity but also must be reproducibly manufactured on a large scale [4,6]. Up to date, there are few detail studies on the scale-up synthesis of small-crystal TS-1 from cheap reactant system.

In this work, an improved method for the size-controlled synthesis of TS-1 crystals has been scaled up. This synthesis method involves zeolite crystallization in the presence of highly dispersed seed. Even under poor stirring condition, it is easy to tailor-make the crystal size distribution of TS-1 in a large-scale reactor by only changing seed amount. The obtained TS-1 zeolite can be processed into high-performance catalyst for propylene epoxidation to propylene oxide (PO).

## 2. Experimental

### 2.1. Preparation of seeds

#### 2.1.1. Preparation of S-1 precursor sol (denoted as S-1-U)

The S-1 precursor sol was prepared by using tetraethoxysilane (TEOS) as the silicon source, and TPAOH as the template. TEOS was hydrolyzed in an aqueous solution of TPAOH at 343 K, and a clear solution with a molar composition of  $\text{SiO}_2/\text{TPAOH}/\text{H}_2\text{O} = 1:0.256:30$  was obtained.

#### 2.1.2. Preparation of suspended S-1 (denoted as S-1-S)

The precursor sol (S-1-U) was transferred to an autoclave and heated at 448 K for 24 h, then the suspension containing S-1 zeolite was obtained.

#### 2.1.3. Preparation of dried S-1 zeolite (denoted as S-1-D)

The solids obtained from S-1-S suspension were filtered and washed with distilled water, then dried at 393 K and calcined at 823 K for 6 h in air.

The fumed silica and microsized ZSM-5 ( $n(\text{Si}/\text{Al}) = 25$ ) were purchased from China Silicon Corporation Ltd. and the Catalyst Plant of Nankai University, respectively.

### 2.2. Synthesis of TS-1

TS-1 was synthesized in a hydrothermal system by using colloidal silica and tetrabutyl titanate (TBOT) as silicon and titanium sources, respectively. TPABr was spent as the template and ethanolamine as base. Molar composition of the sol was  $1.0 \text{ SiO}_2/0.02 \text{ TiO}_2/0.1 \text{ TPABr}/0.5 \text{ ethanolamine}/30\text{H}_2\text{O}$ . S-1-U, S-1-S, S-1-D, fumed silica and microsized ZSM-5 were used as crystal seeds in the synthesis of TS-1.

A typical synthesis of TS-1 was as follows: ethanolamine and TPABr were dissolved in deionized water under stirring, followed by addition to colloidal silica, and then, TBOT-isopropanol solution was added dropwise under vigorous stirring. Finally, the seed was added into the above mixture, and the obtained sol was aging under stirring for 24 h at room temperature. The amount of seed added

corresponded to a proportion of 0–8.0 wt% (dry basis) of silica relative to the total amount of silica in the sol. Then the final sol was transferred to various size autoclaves, and crystallized under stirring for 72 h at 448 K. Afterward, the product was filtered, washed with distilled water, dried at 393 K and calcined at 823 K for 6 h. The obtained samples were denoted as X-M-R-V, while the X stands for the seed (U, S, D, Z and F for S-1-U, S-1-S, S-1-D, ZSM-5 and fumed silica, respectively), the M for weight ratio of seed to  $\text{SiO}_2$  in precursor sol (2, 4, 6 and 8 for 2, 4, 6 and 8 wt%, respectively), the R for the stirring speed during crystallization (100, 260 and 900 for 100, 260 and 900 rpm, respectively) and the V for the volume of autoclave (2 L and 0.5 M for 2 L and  $0.5 \text{ m}^3$ , respectively). For example, the sample synthesized with S-1-S seed under the weight ratio of seed to  $\text{SiO}_2$  in precursor sol ( $m(\text{seed}/\text{SiO}_2)$ ) of 4 wt% in a 2 L autoclave at the stirring speed of 900 rpm was denoted as S-4-900-2 L. The parameters of the two reactors are listed in Table S1. TS-1 sample synthesized without seed was denoted as TS-1-Null.

The catalyst was prepared by alkaline posttreatment [16] of S-6-100-0.5 M and denoted as TS-1H.

The catalyst sample of nanosized TS-1 (denoted as TS-1N) was synthesized using the improved conventional method [29] for comparison.

### 2.3. Propylene epoxidation

The propylene epoxidation was carried out in a 200 mL stainless-steel reactor. In a typical run, a certain amount of TS-1 catalyst, 24 mL methanol and 3 mL  $\text{H}_2\text{O}_2$  (27.5 wt%) were added to the reactor, and the pH of mixture was adjusted with ammonium hydroxide. After heating the mixture to 318 K, the propylene was charged to reach 0.6 MPa, and the mole ratio of propylene to  $\text{H}_2\text{O}_2$  was 1.5. Under stirring, the reaction system was kept for 60 min.

The residual  $\text{H}_2\text{O}_2$  was checked by iodometric titration. The products were analyzed on a GC 7890 II gas chromatograph with a flame ionization detector and a capillary column ( $30 \text{ m} \times 0.32 \text{ mm} \times 0.5 \mu\text{m}$ ). Propylene glycol monomethyl ethers (MME) and propylene glycol (PG) were the byproducts. The conversion of  $\text{H}_2\text{O}_2$  ( $X_{\text{H}_2\text{O}_2}$ ), selectivity to PO ( $S_{\text{PO}}$ ), utilization of  $\text{H}_2\text{O}_2$  ( $U_{\text{H}_2\text{O}_2}$ ), yield of PO based on  $\text{H}_2\text{O}_2$  ( $Y_{\text{H}}$ ), and yield of PO based on propylene ( $Y_{\text{P}}$ ) were calculated as follows:

$$X_{\text{H}_2\text{O}_2} = (n_0(\text{H}_2\text{O}_2) - n(\text{H}_2\text{O}_2))/n_0(\text{H}_2\text{O}_2) \times 100\%$$

$$S_{\text{PO}} = n(\text{PO})/(n(\text{PO}) + n(\text{MME}) + n(\text{PG})) \times 100\%$$

$$U_{\text{H}_2\text{O}_2} = (n(\text{PO}) + n(\text{MME}) + n(\text{PG}))/n_0(\text{H}_2\text{O}_2) \times X_{\text{H}_2\text{O}_2} \times 100\%$$

$$Y_{\text{H}} = n(\text{PO})/n_0(\text{H}_2\text{O}_2) \times 100\%$$

$$Y_{\text{P}} = n(\text{PO})/n_0(\text{C}_3\text{H}_6) \times 100\%$$

The  $n_0(\text{H}_2\text{O}_2)$  and  $n_0(\text{C}_3\text{H}_6)$  represent the initial molar amounts of  $\text{H}_2\text{O}_2$  and propylene, respectively. The  $n(\text{H}_2\text{O}_2)$  represent the final molar amount of  $\text{H}_2\text{O}_2$ . The  $n(\text{PO})$ ,  $n(\text{MME})$  and  $n(\text{PG})$  stand for the mole amounts of PO, MME, and PG, respectively.

### 2.4. Characterizations

The X-ray diffraction (XRD) patterns were generated on a Panalytical X'pert PRO Diffractometer instrument using  $\text{Cu K}\alpha$  radiation. The relative crystallinity (RC) was calculated from total integrated intensities of the reflections at  $2\theta = 7.8^\circ$ ,  $8.8^\circ$ ,  $23.0^\circ$ ,  $23.9^\circ$  and  $24.4^\circ$  based on those of TS-1-Null which was considered to be 100% [30].

Fourier-transform infrared (FT-IR) spectra was recorded from 4000 to  $400 \text{ cm}^{-1}$  on a Nicolet Nexus 470 FT-IR spectrometer, and the KBr pellet technique was adopted. Ultraviolet–visible diffuse

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