



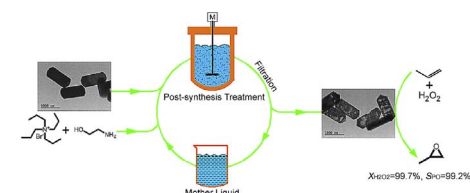
Green and efficient preparation of hollow titanium silicalite-1 by using recycled mother liquid



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GRAPHICAL ABSTRACT



The process can almost eliminate the discharge of waste liquid to achieve a sustainable development

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ABSTRACT

A green and efficient preparation of hollow titanium silicalite-1 (TS-1) has been developed by using recycled mother liquid in the post-synthesis treatment. The parent TS-1 was hydrothermally treated with different bases, and hollows appeared in the crystals, due to the controlled desilication from framework. In the presence of tetrapropylammonium cation (TPA⁺) during post-synthesis treatment, more hollows were generated, and higher concentration of Ti inside crystals was obtained. The reaction substrates could get sufficient contact with the active centers, and this hollow TS-1 exhibited superior catalytic activity in the propylene epoxidation compared to that of parent sample. When the sample was prepared by using ethanolamine and TPABr as desilication medium, the obtained mother liquid can be reused in the next post-synthesis treatment. In the recycling process, the added amount of ethanolamine and TPABr was only 50% and 25% of the amount for the first post-synthesis treatment, respectively. Even the mother liquid was recycled eight times, all obtained hollow TS-1 showed similar catalytic activity in the propylene epoxidation to that of the sample prepared by using TPAOH as desilication medium. This process can almost eliminate the discharge of waste liquid to achieve a sustainable development, and save the cost of hollow TS-1 production.

1. Introduction

Titanium silicalite-1 (TS-1) was first hydrothermally synthesized by Taramasso et al. [1] in 1983. Many green selective oxidation with H₂O₂ as oxidant over TS-1 were studied for decades, such as aromatic hydroxylation [2–4], oxidation of alcohols and alkanes [5–8], ammoxidation of ketone [9–11], and epoxidation of alkenes [12–17]. Recently, the HPPO process, which is direct epoxidation of propylene to

propylene oxide (PO) with hydrogen peroxide using TS-1 as catalyst, has attracted much attention due to its cleanness, high-efficiency, mild operating condition, and low investment [18–20]. However, TS-1 catalyst possess intrinsic micropore of about 0.55 nm in diameter which limits the diffusion of reactants and/or products to and from internal active sites. Many attempts have been made to increase the utilization of active sites and to retain longer catalytic activity by either decreasing TS-1 crystal size to nano-scale [21,22] or creating intra-crystalline

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mesoporosity or macroporosity [23–27]. The synthesis of nanosized TS-1 requires the use of expensive tetrapropylammonium hydroxide (TPAOH) as template, and produced nano-crystals are often difficult to separate [28]. The incorporation of mesoporosity or macroporosity in zeolites offers an alternative strategy to minimize diffusion barriers, and potentially enhance the distribution of active sites during catalyst preparation. Typical synthetic strategies of creating macro-meso-structure are classified as templating methodologies, self-assembly or post-synthesis treatment [29]. Su et al. developed a new type of hierarchical micro-meso-macroporous zeolitic TS-1 architecture by a crystallization process in a quasi-solid-state system [30]. A hierarchical mesoporous TS-1 zeolite had been synthesized by a simple steam-assisted crystallization method [31]. Li and co-workers synthesized hierarchical TS-1 with a well connected network of meso/macropores inside the zeolite crystal by using cheap template caramel that can directly convert to hard template during the same period of heat-treatment of gel [32].

Considering industrial applications, desilication is an efficient methodology to create intracrystalline mesoporosity in MFI-type zeolites, because it is simple to operate and easy to scale up [33,34]. Groen et al. [35] prepared hollow ZSM-5 particles with a well-preserved Al rich exterior by treatment with NaOH solution. Tsai et al. [36] found that TS-1 treated by TPAOH and NaOH could generate mesopores with framework Ti intact, and improve the catalytic performance for phenol hydroxylation. Tuel and co-workers reported the preparation of hollow crystals with large intra-crystalline voids by a post-synthesis treatment of the conventional TS-1 or S-1 zeolite with highly alkaline TPAOH solution [37,38]. Shi et al. prepared a new bi-functional titanosilicate by combining noble-metal sources with modified TS-1 which was obtained by using triethanolamine and TPAOH as desilication medium [39]. Zuo and co-workers treated the small-crystal TS-1 with different organic bases, and found the sample modified with TPAOH exhibited superior catalytic property for the hydroxylation of phenol [40]. Lin et al. reported that the TS-1 sample with hollow structure was prepared by using a variety of organic bases as desilication mediums [41]. Our group had also prepared hollow TS-1 mesocrystals (HTMs) by hydrothermal post-synthesis treatment of normal TS-1 zeolite with TPAOH, and the obtained sample showed high catalytic performance in cyclohexanone ammoxidation [42]. Although the catalytic activity could be improved by the post-synthesis treatment with TPAOH, the obtained mother liquid produced in the treatment process is difficult to recycle due to thermal decomposition of TPAOH which limits the wide application of TS-1 in industrial production [43,44].

Green process is gaining popularity because of the demand from conscientious consumers and strict environmental regulations [45–48]. Pan et al. synthesized ZSM-5 with mother liquid recycling in the absence of organic template [48]. A well-crystalline SUZ-4 was obtained from the synthesis, and the mother liquid was entirely recycled without increasing in amount [49]. Pengthamkeerati et al. found that the synthesis of nanosilicalite-1 could be conducted via a greener approach by using an alternative silica source from biomass fly ash and the synthesis yield was enhanced by recycling the mother liquid [50]. Guo and co-workers analyzed the residual template and organic base in the mother liquid produced by the preparation of TS-1 zeolite, and reused mother liquid in the next preparation of TS-1 [51]. Shi et al. reported that the mother liquid obtained in the preparation of titanosilicate can be used to regenerate the deactivated titanosilicate catalyst, and the regenerated catalyst exhibited similar catalytic activity compared with fresh catalyst [52]. Almost 5–10 tons of mother liquid would be produced and discharged as waste when per ton of TS-1 zeolite was post-treated [53–55], and this mother liquid still retains many reagents. Although the post-synthesis treatment of TS-1 with various bases has been reported [35–42], to date there is no detailed study on recycling the mother liquid in the treatment.

As a result, the using of inexpensive reagents and reduction of waste liquid discharge, is of interest to enhance a green process of post-

synthesis treatment. The aim of the presented work was to develop a green and efficient process for the preparation of hollow TS-1 by using recycled mother liquid in the post-synthesis treatment. Different bases were introduced into the process of post-synthesis treatment to assist in obtaining TS-1 with hollow structure. Furthermore, the mother liquid recycling in the post-synthesis treatment was investigated in detail. The catalytic activity of obtained samples was evaluated in the process of propylene epoxidation to propylene oxide (PO).

2. Experimental

2.1. Preparation of hollow TS-1

Parent TS-1 was prepared according to the method in Ref. [56]. To be brief, molar composition of the prepared sol was 1.0 SiO₂/0.029 TiO₂/0.1 tetrapropylammonium bromide (TPABr)/0.5 ethanalamine/30 H₂O, and the sol was transferred to a Teflon lined autoclave and crystallized for 24 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 parent TS-1 was hydrothermally treated in different solutions, and the ratio of TS-1 zeolite to the solution was 1 g: 7.2 mL. In a typical synthesis, a certain desilication medium was first dissolved in deionized water under stirring, then the parent TS-1 was added into the above solution. Finally, the obtained mixture was transferred to a Teflon lined autoclave and kept at 443 K under stirring for 48 h. Afterward, the product was filtered, washed with distilled water, dried at 393 K, and calcined at 823 K for 6 h to obtain the hollow TS-1. The mother liquid produced in the post-synthesis treatment was kept for using in the next treatment. The detailed post-synthesis treatment conditions were listed in Table S1.

2.2. Analysis of mother liquid

The concentration of ethanalamine in the mother liquid obtained from post-synthesis treatment was analyzed by using a GC 9790 plus gas chromatograph equipped with a flame ionization detector (FID) and a KB-624 capillary column (60 m × 0.25 mm × 0.33 μm). The concentrations of TPABr and TPAOH in mother liquid were analyzed by using an Agilent 1200 HPLC equipped with an ultraviolet detector (λ = 210 nm) and a ZORBAX SB-CN column (4.5 μm, 150 mm × 4.6 mm). The mother liquid produced from the post-synthesis treatment with TPAOH was extracted by dichloromethane and analyzed using a Thermo Fisher Scientific DSQ II series gas chromatograph and mass spectrometer system (GC–MS).

2.3. Propylene epoxidation

The epoxidation of propylene was carried out in a 200 mL stainless steel reactor. In a typical run, designated amount of TS-1 catalyst, 3 mL of 27.5 wt% of H₂O₂, and 24 mL of methanol were fed into the reactor, and the pH of mixture was adjusted with ammonium hydroxide. The mixture was stirred and warmed to 318 K, and then, propylene was charged to reach 0.6 MPa. Under stirring, the reaction system was kept for 60 min.

The initial and residual H₂O₂ was checked by iodometric titration. The products were analyzed by using a GC 9790 plus gas chromatograph equipped with a flame ionization detector (FID) and a KB-624 capillary column (60 m × 0.25 mm × 0.33 μm). Propylene oxide (PO) was the main product, and propylene glycol monomethyl ethers (MME) and propylene glycol (PG) were byproducts. The conversion of H₂O₂ ($X_{\text{H}_2\text{O}_2}$), selectivity to PO (S_{PO}), utilization of H₂O₂ ($U_{\text{H}_2\text{O}_2}$), and yield of PO (Y_{PO}) were calculated as follows:

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

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