



Green and efficient epoxidation of propylene with hydrogen peroxide (HPPO process) catalyzed by hollow TS-1 zeolite: A 1.0 kt/a pilot-scale study

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HIGHLIGHTS

- Hollow TS-1 zeolite is a good catalyst for HPPO process at pilot scale.
- Increasing the solubility of propylene favors fast conversion rate.
- Shortening the residence time of H₂O₂ insider benefits high PO selectivity.
- The lifetime of hollow TS-1 zeolite in HPPO process is very long.

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ABSTRACT

The propylene epoxidation catalyzed by hollow TS-1 zeolite with 30 wt% H₂O₂ solution as oxidant at 1.0 kt/a pilot plant has been examined. Rising reaction temperature is in favor of increasing TOF of H₂O₂ but reduces the selectivity of PO, due to the promotion of major and side reactions at the same time. Enhancing the CH₃OH amount and the WHSV of H₂O₂ is preferential to improving the TOF of H₂O₂ and the selectivity of PO, but increase capital and energy consumption as well. Taking all into consideration, the optimized epoxidation has been confirmed: *T* is 40–50 °C; molar ratio of CH₃OH/H₂O₂ is 5–15, and the WHSV of H₂O₂ is more than 1.2 h⁻¹. When the epoxidation of propylene carried out over 6000 h, the TOF of H₂O₂ is 30.9–32.2 mmol g⁻¹ h⁻¹ and the PO selectivity is 96–99%, respectively. The final PO product from this plant is at 99.97% purity, which has been used as an intermediate to synthesize kinds of chemicals.

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1. Introduction

Propylene oxide (PO) is one of key propylene based chemical intermediates for producing fine chemicals, such as polyurethane plastics, polyglycol esters, unsaturated resins and surfactants [1–3]. As the fast development of material and environmental technologies, the demand of PO is continuously growing in the world, for example, the global PO market is over 7.5 million tons in 2010. Several of synthetic methods have been exploited for producing PO in academic and industrial sections, i.e. chlorohydrin process, styrene monomer propene oxide (PO/SM) process, tert-butyl alcohol (PO/TBA) process, cumene hydroperoxide (CHP) process

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and hydrogen peroxide propene oxide (HPPO) process [4–9]. Compared with other four routes, HPPO route is much more environmental-friendly, without the generation of toxic by-products and wastes. HPPO process is based on titanium silicate (TS-1) zeolite as catalyst, [10–13] low concentration (30–50 wt%) aqueous H₂O₂ solution as oxidant under mild conditions (usually lower than 70 °C) [14,15]. The first commercial HPPO propylene epoxidation plant at 100 kt/a capacity was launched by Evonik and SKC at Korea in 2008 [16]. Then, several more HPPO process units were set up gradually in Belgium by BASF and DOW (300 kt/a, 2009), [17] in China by Evonik and Uhde (230 kt/a, 2013), [18] and in Thailand by DOW (390 kt/a, 2012) [19]. In HPPO process, PO is produced directly from propylene in a one-step reaction, as illustrated in Fig. 1. However, epoxidation is a cascade reaction, and these side products lower the yield of PO via secondary reaction. Among them, propylene glycol monomethyl ethers (MME,

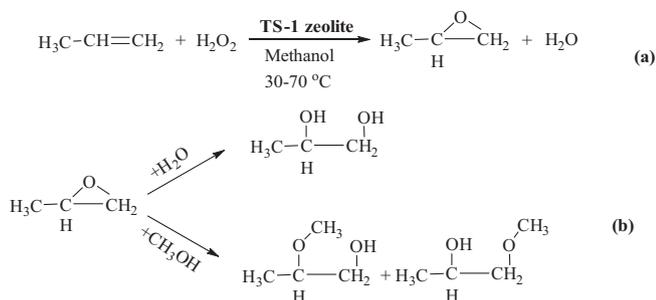


Fig. 1. Major and side reactions involved in the epoxidation of propylene catalyzed by TS-1 zeolite in mild conditions: (1) major reaction of propylene epoxidation; (b) side ring-opening reactions of PO with CH_3OH and H_2O .

with two isomers, as shown in Fig. 1) and 1,2-propylene glycol (PG) are the two main byproducts, which are formed by ring-opening reactions of PO with CH_3OH and H_2O . Thus, it is of ultra-importance to optimize the operating parameters, such as reaction temperature, CH_3OH concentration, and weight hourly space velocity (WHSV) of H_2O_2 , to avoid these side reactions occurred.

However, the conventional TS-1 zeolite usually has poor catalytic activity and reproducibility, due to the mismatch of hydrolysis and crystallization rates between Si and Ti species under hydrothermal conditions [20]. To solve these problems, the hollow TS-1 zeolite was produced by post-synthesis method in the presence of TPAOH solution at high temperature [21–23]. Compared with conventional TS-1, hollow TS-1 zeolite is of abundant intracrystalline cavities and high framework Ti species content. In our previous working, hollow TS-1 zeolite exhibits higher catalytic performances and stability in several oxidation reactions with aqueous H_2O_2 solution as oxidant, such as cyclohexanone ammoxidation, aromatic oxidation, phenol hydroxylation at industrial scale and propylene epoxidation in lab. Herein, the epoxidation of propylene catalyzed by hollow TS-1 zeolite has been carried out at 1.0 kt/a pilot scale. Thus the effects of several major important parameters on epoxidation reaction have been systematically investigated, for obtaining the optimized reaction conditions to support the even larger pilot scale test [24].

2. Experimental

2.1. Synthesis of hollow TS-1 zeolite catalyst

Hollow TS-1 zeolite was synthesized as previously published method [25,26]. In a general procedure, tetrapropylammonium

hydroxide (TPAOH) was selected as organic structure directing agent (OSDA) for synthesis of the TS-1 zeolite, as described in ENI method. The molar ratio of $\text{SiO}_2:\text{TiO}_2:\text{TPAOH}:\text{H}_2\text{O}$ is 1:0.04:0.36:40, the hydrothermal synthesis temperature is 170°C , under the autogenous pressure. Firstly, the tetraethyl orthosilicate (TEOS) and tetrabutyl orthotitanate (TBOT) was dissolved in the aqueous TPAOH solution, and this mixture was heated at 80°C for evaporating the ethanol and butanol molecules. Then, the mixture was transferred to Teflon autoclave and hydrothermally synthesized at high temperature for 3 days. After that, the as made TS-1 zeolite was calcined at 550°C for 3 h. In second step, the calcined TS-1 zeolite was post-synthesized at 170°C for 1 day in the presence of OSDA under autogenous pressure, as illustrated in the literatures [21]. In addition, the calcined hollow TS-1 zeolite was characterized by multiple characterization methods, and sharpened as catalyst for HPPPO process.

2.2. Characterization of hollow TS-1 zeolite

X-ray powder diffraction patterns (XPRD) were collected on a Bruker (Siemens) D5005 diffractometer using nickel filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) under ambient conditions in the 2θ range of $5\text{--}35^\circ$ with a step size of 0.02° and exposure time of 1 s per step. N_2 adsorption/desorption isotherms were collected at 77 K using a Micromeritics ASAP 2010 apparatus. Before the measurement, about 50 mg of the sample was dehydrated under vacuum (10^{-3} Torr) at 300°C overnight. The specific surface areas were determined from the linear part of the BET equation. Transmission electron microscopy (TEM) was carried out on a FEI G2 F20S-TWIN electron microscope. Scanning electron microscopy (SEM) was operated on a FEI Quanta 200F instrument.

2.3. Catalytic testing at 1.0 kt/a scale

The pilot-scale propylene epoxidation reaction was carried out on a fixed bed reactor, and the corresponding schematic diagram is illustrated in Fig. 2. In a typical procedure, hollow TS-1 zeolite was sharpened into about $\varnothing 1\text{--}3$ mm particles, and then they were added into a stainless tube reactor. Then, the mixture of CH_3OH , H_2O_2 (30 wt%), H_2O and propylene was injected into the bottom of reactor, and the reaction temperature was $30\text{--}70^\circ\text{C}$. After the epoxidation of propylene with H_2O_2 , the mixture of solvent, products and reagents went into the C_3^- separation tower for evaporating the remainder propylene, which can be reused as starting material for this process. Moreover, the mixture from the bottom of C_3^- separation tower went into the PO separation tower, for

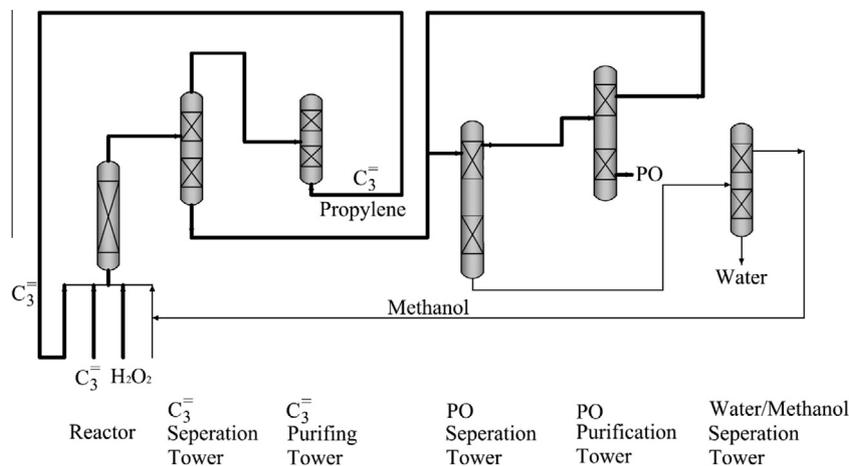


Fig. 2. Schematic process flow diagram of propylene epoxidation at 1.0 kt/a pilot scale.

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