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# Epoxidation of propylene to propylene oxide catalyzed by large-grain TS-1 in supercritical $CO_2$

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ABSTRACT

Large-grain titanium silicalite (TS-1, 3.0 μm long), which is a low-cost catalyst that can easily be separated from the product and exhibits an efficient catalyst recovery, was synthesized using tetrapropylammonium bromide (TPABr) as the template. However, it exhibited very poor catalytic activity in the traditional organic solvent compared with small-grain TS-1. The epoxidation of propylene to propylene oxide (PO) using the large-grain TS-1 as the catalyst and $H_2O_2$ as the oxidant in a supercritical $CO_2$ ($scCO_2$) medium was then investigated. The effects of the $CO_2$ pressure, reaction temperature, propylene pressure, cosolvent (methanol) concentration, and reaction time on the epoxidation reaction in $scCO_2$ were investigated and compared with those of the reaction in methanol. The use of $scCO_2$ as the reaction medium significantly improved the catalytic activity of the large-grain TS-1 and increased the PO yield from 50.1 to 83.5%. The effect of alkaline components [NaOH, $NaHCO_3$, urea, and $(NH_4)_2CO_3$] on the epoxidation reaction in $scCO_2$ was also investigated. The addition of alkaline components had a positive effect on the selectivity to PO as well as to $H_2O_2$ utilization. The addition of $(NH_4)_2CO_3$ yielded the best results, with the $H_2O_2$ conversion, PO selectivity, $H_2O_2$ utilization, and PO yield reaching 98.7%, 95.2%, 94.3%, and 88.6%, respectively. Therefore, a novel approach to PO production is introduced, which provides a basis as well as technical parameters for its further industrialization.

## 1. Introduction

More than four million tons of propylene oxide (PO), an important raw material in petrochemical industries, is globally produced every year. Two traditional methods of manufacturing PO are the chlorohydrin and cooxidation processes [1]. However, the chlorohydrin process produces environmentally hazardous chloric compounds, whereas the co-oxidation process produces a large number of by-products [2]. Consequently, developing a novel, clean process for producing PO is needed to replace the currently used industrial processes.

The discovery of titanium silicalite (TS-1), synthesized using tetrapropylammonium hydroxide (TPAOH) as the template, by Taramasso [3,4] opened up an environmentally benign catalytic process for propylene epoxidation using TS-1 as the catalyst, hydrogen peroxide ($H_2O_2$) as the oxidant and methanol ($CH_3OH$) as the solvent [5–9]. Compared with conventional routes, this innovative process, which generates a higher PO yield, is more environmentally friendly and requires significantly milder reaction conditions [5,6]. The epoxidation reaction is considered the most promising method of PO production and has become one of the new research areas in green chemistry. However, the high cost of the raw materials (mainly TPAOH) and the difficult separation of the catalyst from the catalyzed products have largely restricted the industrial application of this reaction.

By contrast, the large-grain TS-1 (3.0 μm in length), which is synthesized using tetrapropylammonium bromide (TPABr) as the template and silica sol–gel as the silicon resource [10], has notable advantages, namely, easy separation from the catalyzed products and lower cost. The price of TPABr is only about one-eighth that of TPAOH. However, the catalytic activity of the large-grain TS-1 in the direct oxidation of propylene to PO in the presence of $H_2O_2$ in a $CH_3OH$ medium is poor compared with that of the small grains [11]. PO cannot rapidly transfer from zeolite because of its poor diffusion in the traditional solvent ($CH_3OH$), which results from the nearly 10-fold longer pore channel in the large grains. This phenomenon results in the occurrence of a number of side reactions (also catalyzed by TS-1) between PO and the conventional $CH_3OH$ solvent. These by-products can combine to form larger molecules, which can then cover the active sites of TS-1 and deactivate the catalyst

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[12]. Therefore, given the obvious advantages of using large-grain TS-1, the improvement in its catalytic activity will be highly beneficial to the industrial production of PO.

Recently, the use of supercritical $CO_2$ ($scCO_2$: $T_c = 31.06\,^\circ C$, $P_c = 7.38$ MPa [13]) as a reaction medium has received considerable attention because of its numerous advantages, including innocuousness, inertness, low cost, high solubility, and excellent diffusion [14]. For example, the excellent diffusion of $scCO_2$ has extracted the product from molecular sieve catalysts [15], which reduces the side reactions and maintains the catalytic activity. For these reasons, the use of $scCO_2$ could resolve some of the difficulties currently being encountered with the use of large-grain TS-1 in PO synthesis.

Danciu [1], Jenzer [16], and Beckman [17,18] reported on the synthesis of PO using $scCO_2$ as the solvent, and their results showed the benefits of $scCO_2$ use. For example, transport limitations across liquid and gas phases were avoided because of the good solubility of propylene in $scCO_2$, and the side-reaction products were obviously decreased because of the chemical inertness of $scCO_2$. However, these previous studies focused on the noble metal-promoted, small-grain TS-1 (such as Pd-Pt/TS-1) and the production of $H_2O_2$ in situ by $H_2$ and $O_2$, which were then directly used as an oxidant for propylene epoxidation. Published data involving solely large-grain TS-1 as the catalyst and $H_2O_2$ as the oxidant in a $scCO_2$ medium are not available.

In the current study, we report on the use of large-grain TS-1 to catalyze the epoxidation of propylene in $scCO_2$. The effects of several parameters, such as $CO_2$ pressure, propylene pressure, reaction temperature, reaction time, and the alkaline components [NaOH, $NaHCO_3$, urea, and $(NH_4)_2CO_3$], were examined to improve the PO yield in this system. The results of the epoxidation reactions in $scCO_2$ catalyzed by large- and small-grain TS-1 were then compared with those in a traditional organic solvent.

## 2. Experimental

### 2.1. Catalyst preparation and characterization

Small-grain TS-1 was prepared according to a previously reported method [19]. Large-grain TS-1 was synthesized under previously reported conditions [11]. X-ray diffraction (XRD) patterns were obtained using a D/MAX-rA diffractometer with a Cu Kα radiation, a 30 mA electric current, and a 30 kV voltage. Scanning electron microscope (SEM) images were obtained using a JSM-6490LV (JEOL Ltd.) and a HITACHI S-4500 electron microscope.

### 2.2. Phase behavior

The phase behavior of the reaction system was determined in an 80 mL self-made high-pressure reactor with viewing windows placed in a super thermostat water bath. Opalescence was observed at the critical temperature and pressure. A specific amount of $CH_3OH$ or of another component (like propylene) was added. The system was pressurized with $CO_2$ and the mixture was stirred. The phase behavior was observed with the naked eyes through the viewing windows. The reactor was heated when the phase interface disappeared, and then slowly cooled down until the opalescence reappeared. The pressure and temperature at this point were recorded as the critical pressure and temperature, respectively. The phase behaviors of a series of different components were examined to determine the range of critical pressure and critical temperature in this reaction. The values recorded for the pressure and the temperature were accurate to 0.01 MPa and 0.1 K, respectively.

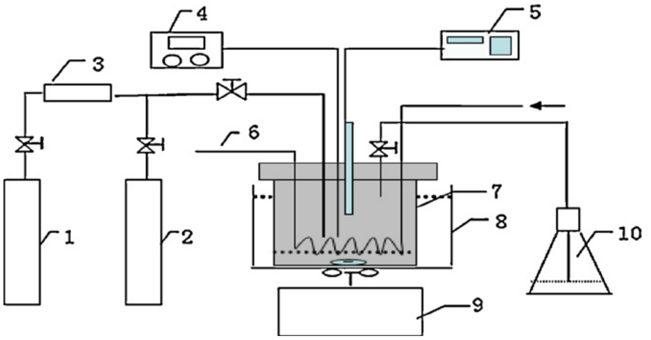

**Fig. 1.** Experimental apparatus for the catalytic reaction in supercritical $CO_2$ ($scCO_2$).

### 2.3. Propylene epoxidation

The epoxidation reaction of propylene in $scCO_2$ was performed in a 165 mL customized, high-pressure, stainless supercritical catalytic reactor (Fig. 1). TS-1 (0.40 wt%), aqueous $H_2O_2$ (3.00 wt%), and the cosolvent ($CH_3OH$, 4.84 wt%) were then added to the reactor. The reactor was sealed and flushed with $CO_2$ three times and then heated to the desired temperature in the water bath. When the required temperature was reached, propylene and $CO_2$ were sequentially introduced into the reactor to initiate the reaction. The vessel was in a state of agitation during the reaction. When the reaction was completed, the reactor was rapidly cooled in an ice bath to terminate the reaction. The gas was then released, and the pressure was slowly decreased. The mixture in the reactor was removed and separated from the catalyst via centrifugation. The amount of $H_2O_2$ was analyzed via an iodometric titration method [20], and PO was analyzed using a GC-7890, gas chromatograph (Shanghai Tianmei Technologies Co. Ltd., China) with a flame ionization detector (FID) and a stainless steel capillary column (2 m × Ø2 mm I.D., Propark Q). Propylene glycol (PG) and its monomethyl ethers (MME) were the by-products and analyzed using the same analytic method used on PO. In the current paper, the $H_2O_2$ conversion ($X_{H_2O_2}$, %), selectivity to PO ($S_{PO}$, %), $H_2O_2$ utilization ($U_{H_2O_2}$, %), and PO yield ($Y_{PO}$, %) were defined as follows:

$$X_{H_2O_2}(\%) = \frac{n^0_{H_2O_2} - n^i_{H_2O_2}}{n^0_{H_2O_2}} \times 100$$

$$S_{PO}(\%) = \frac{n_{PO}}{n_{PO} + n_{MME} + n_{PG}} \times 100$$

$$U_{H_2O_2}(\%) = \frac{n_{PO} + n_{MME} + n_{PG}}{n^0_{H_2O_2} x_{H_2O_2}} \times 100$$

$$Y_{PO}(\%) = \frac{n_{PO}}{n^0_{H_2O_2}} \times 100$$

where $n^0_{H_2O_2}$ is the number of moles of $H_2O_2$ before the reaction and $n^i_{H_2O_2}$, $n_{PO}$, $n_{MME}$, and $n_{PG}$ are the number of moles of $H_2O_2$, PO, MME, and PG after the reaction, respectively.

## 3. Results and discussion

### 3.1. Phase behavior of the reaction system

The critical point data of the reaction system at different molar ratios of the mixtures, as well as the effects of the different components and molar ratios on the phase behavior are indicated in Table 1.