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$_2$O$_2$ 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$_4$)$_2$CO$_3$] 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$_2$O$_2$ utilization. The addition of (NH$_4$)$_2$CO$_3$ yielded the best results, with the H$_2$O$_2$ conversion, PO selectivity, H$_2$O$_2$ 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.

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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$_2$O$_2$) as the oxidant and methanol (CH$_3$OH) 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$_2$O$_2$ in a CH$_3$OH 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$_3$OH), 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$_3$OH 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 °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$_4$)$_2$CO$_3$], 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$_3$OH 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.
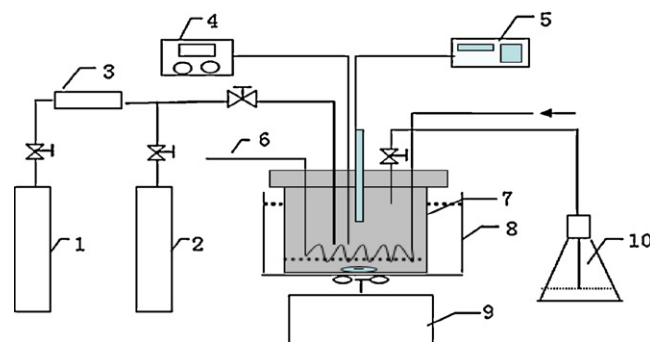

Fig. 1. Experimental apparatus for the catalytic reaction in supercritical CO_2 (scCO$_2$).

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$_3$OH, 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.

Table 1
Effect of different components and molar ratios on phase behavior.

Number	Components	Molar ratio (mol%)				T_c (°C)	P_c (MPa)
1	CO_2	100%				31.3	7.33
2	$CO_2 + CH_3OH$	CO_2 95.44	CH_3OH 4.56			33.0	7.45
3	$CO_2 + CH_3OH + H_2O_2 + H_2O$	CO_2	CH_3OH	H_2O_2	H_2O		
		92.2	2.3	1.0	4.3	33.4	7.50
		91.3	4.0	0.9	3.8	33.7	7.58
4	$CO_2 + CH_3OH + H_2O_2 + H_2O + C_3H_6$	CO_2	CH_3OH	$H_2O_2 + H_2O$	C_3H_6		
		89.8	4.0	5.0	1.2	33.8	7.45
		89.0	4.2	5.1	1.7	33.3	7.34
5	Reaction system (m_{TS-1} = 0.2 g)	CO_2	CH_3OH	$H_2O_2 + H_2O$	C_3H_6		
		89.2	2.5	6.5	1.8		
				React start		34.4	7.75
				2 h later		33.0	7.50

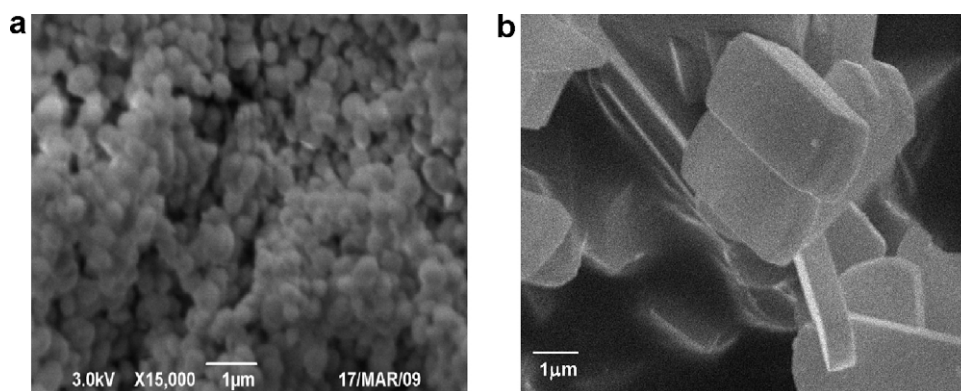**Fig. 2.** SEM images of (a) small-grain and (b) large-grain TS-1.

As seen in Table 1, when the liquid components such as CH_3OH or $CH_3OH + H_2O_2 + H_2O$ were introduced into the one-component CO_2, the critical temperature and critical pressure in the system slightly increased. This result may be due to the low solubility of hydrous H_2O_2, CH_3OH, and water in the $scCO_2$ medium. When propylene was added to the system, the critical pressure decreased because of the high solubility of propylene in the $scCO_2$ medium. The interactive forces between propylene and CO_2 are greater than that between the CO_2 molecules. After the introduction of TS-1 in the system and the reaction was allowed to continue, the critical temperature and critical pressure presented a downward trend. A possible reason is that H_2O_2 is insoluble in supercritical CO_2, whereas PO is partially soluble, and that the intermolecular forces between PO and the CO_2 molecules are strong, which results in a decrease in the system critical pressure with the generation of PO.

3.2. Catalyst characterization

The SEM images of the catalysts are shown in Fig. 2a shows the small-grain TS-1 (BET surface area, 384.56 m²/g; Ti content of the final product, 2.14%) at less than 0.3 μm in length. Fig. 2b shows a larger TS-1 grain (SiO_2/TiO_2 ratio, 35; BET surface area, 350.00 m²/g) with a particle dimension of 0.7 μm × 1.5 μm × 3.0 μm. Fig. 3 shows the XRD patterns of the TS-1 samples. The characteristic peaks of a mordenite framework inverted structure indicate that both samples are highly crystalline.

3.3. Propylene epoxidation catalyzed by TS-1

3.3.1. Propylene epoxidation in CH_3OH catalyzed by TS-1 with different grain-sizes

This stage of the investigation was conducted under the optimal reaction conditions. In brief, 0.2 g TS-1, 2 g aqueous H_2O_2, and 60 g CH_3OH were added to the reactor. The propylene pressure was 0.65 MPa. CO_2 was introduced into the reactor until the pressure reached 7.65 MPa at 35 °C.

Fig. 4 shows the results of the reaction in CH_3OH catalyzed by TS-1 with different grain sizes. Fig. 4a shows the reaction catalyzed by small-grain TS-1 in CH_3OH. The conversion of H_2O_2 increased as time was extended, whereas the reaction rate gradually decreased. At the same time, the selectivity to PO decreased because of the ring-opening reaction of PO. As the reaction rate decreased with the drop in H_2O_2 concentration, H_2O_2 decomposition increased, and the utilization of H_2O_2 reached its peak before decreasing. Thus, the maximum PO yield was obtained during the entire reaction.
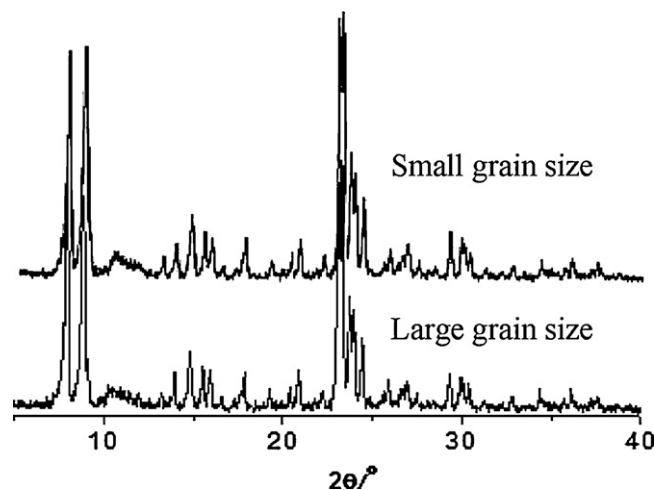

Fig. 3. XRD patterns of the small- and large-grain TS-1.
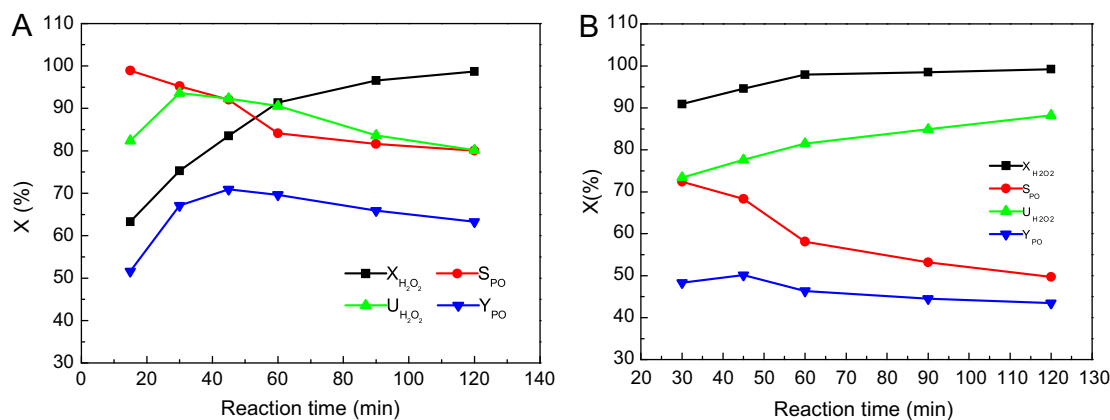
Fig. 4. Results of propylene epoxidation catalyzed by different-sized TS-1 in methanol.

The best results for the H_2O_2 conversion, selectivity to PO, H_2O_2 utilization, and PO yield in CH_3OH were 83.5%, 92.1%, 92.3%, and 70.9%, respectively. Fig. 4b shows the reaction catalyzed by the large-grain TS-1 in CH_3OH. Although the increase over time, utilization, and conversion of H_2O_2 were constantly increasing, the yield and selectivity to PO exhibited a downward trend. The catalytic properties of the large-grain TS-1 in CH_3OH was significantly lower than those of the small-grain TS-1. To improve the catalytic performance of the large-grain TS-1, the reaction solvent should be changed. Therefore, $scCO_2$ was introduced into the reaction system.

3.3.2. Effect of the reaction temperature on the epoxidation reaction in $scCO_2$ catalyzed by large-grain TS-1

The reaction temperature plays an important role in the catalytic process. The effect of temperature on the epoxidation reaction

catalyzed by large-grain TS-1 in $scCO_2$ around the supercritical temperature was investigated by maintaining constant amounts of the reactants, CO_2, and cosolvents. Several studies on this reaction were conducted either in $scCO_2$ or in CH_3OH, and the optimal reaction conditions were chosen for the subsequent comparison of the catalytic performance. The results are shown in Fig. 5.

The H_2O_2 conversion, selectivity to PO, H_2O_2 utilization, and PO yield in $scCO_2$ were higher than those in CH_3OH. The conversion of H_2O_2 in the $scCO_2$ reaction system was almost 100% at temperatures between 40 °C and 60 °C, improving by 12.9% compared with that in CH_3OH at 60 °C. The selectivity to PO obviously decreased in the process. This result may be due to the solvolysis of PO, which increased with the rise in temperature. The utilization of H_2O_2 in $scCO_2$ decreased when the temperature increased from 40 to 60 °C, although it was still higher than that in CH_3OH.
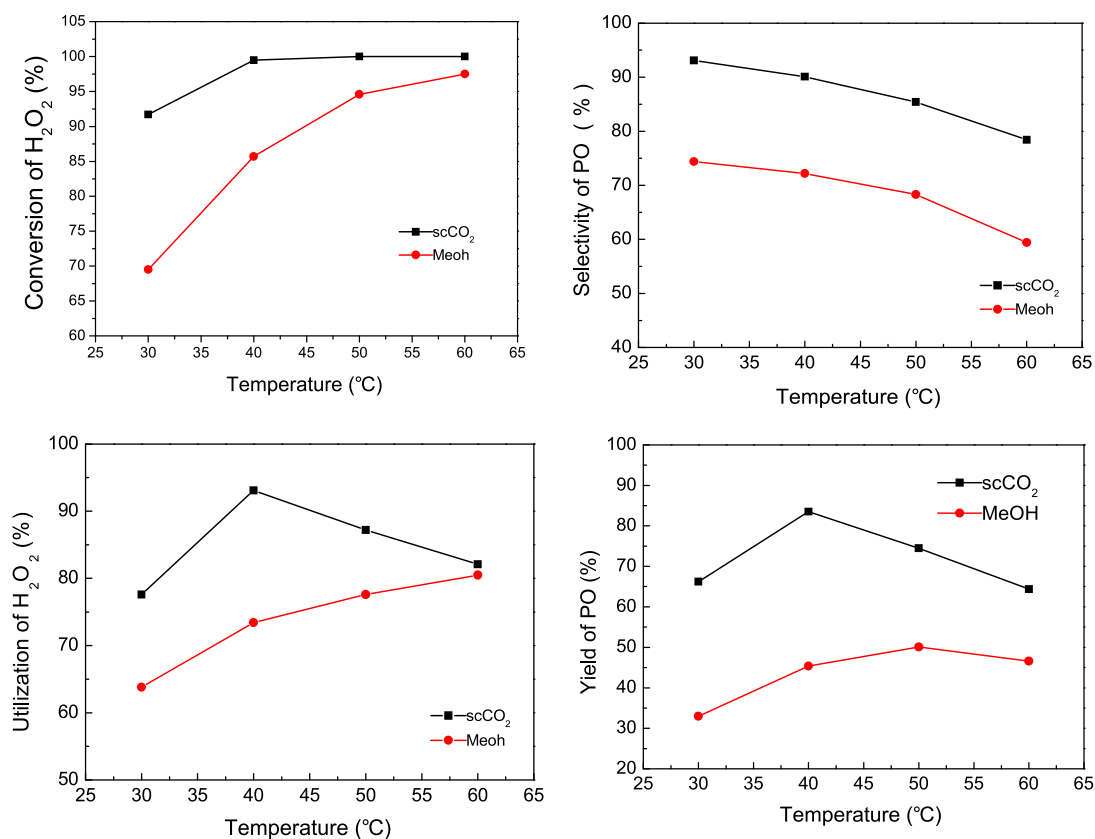

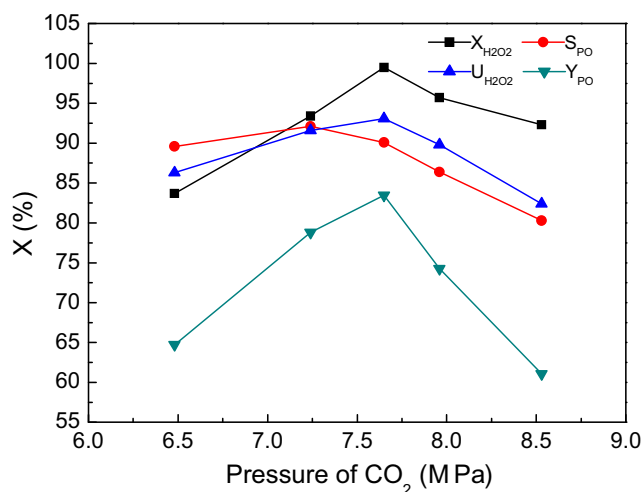**Fig. 5.** Effect of the reaction temperature on epoxidation.

Fig. 6. Effect of CO_2 pressure on epoxidation.

Fig. 7. Effect of the TS-1 amount on epoxidation.

The epoxidation reaction was accelerated because the diffusion in $scCO_2$ is faster than that of CH_3OH. However, the decomposition rate of H_2O_2 increased with the increase in the reaction temperature, which led to the decrease in H_2O_2 utilization. The highest PO yield was obtained at 40 °C; hence, the reaction temperature in $scCO_2$ should be close to 40 °C.

3.3.3. Effect of CO_2 pressure on the epoxidation reaction in $scCO_2$ catalyzed by large-grain TS-1

CO₂ pressure is also an important parameter in epoxidation. The pressure changes are obtained by adjusting the amount of CO_2. The optimal reaction conditions were also chosen as the actual condition for the subsequent comparison of the catalytic performance. Fig. 6 shows the effect of the CO_2 pressure on the catalytic performance in propylene epoxidation. The CO_2 pressure exhibited a significant effect on this reaction. The performance of the reaction was gradually enhanced until the critical pressure was reached (7.65 MPa), which may be due to the increase in the diffusivity of the reactants and the solubility of propylene. On the other hand, H_2O_2 reacts with aqueous bicarbonate to form percarbonate (HCO_4^-), which epoxidizes hydrophilic alkenes [21,22]. However, further increasing the CO_2 amount in the reaction system clearly reduced the reaction rate, the conversion and utilization of H_2O_2, the selectivity to PO, and the PO yield. The experimental results simply illustrate the effect of dilution by CO_2, as excess CO_2 can lower the mole ratio of the reactants. Therefore, the addition of CO_2 from subcritical pressures up to the critical pressure (7.6–7.7 MPa) would enhance the diffusivity and control the effect of the diluents at an acceptable level.

3.3.4. Effect of the TS-1 amount on the epoxidation reaction in $scCO_2$ catalyzed by large-grain TS-1

Different amounts of TS-1 (0.2 wt%, 0.3 wt%, 0.4 wt%, and 0.6 wt%) were used in the reaction to investigate the effect of TS-1 concentration on propylene epoxidation (Fig. 7). The conversion and utilization of H_2O_2 significantly increased with the increase in TS-1. This result is due to the increased number of active catalytic sites, which enhanced the surface reactions. As the amount of TS-1 was further increased, the increase in the reaction rate slowed down because of the gas–liquid mass-transfer effect. On the other hand, the selectivity to PO gradually declined as the reaction progressed. The increase in the number of Lewis acid sites on the TS-1 catalyst, which further increased the side reactions between PO, H_2O, and CH_3OH to form propylene glycol and its monomethyl ethers, may have been responsible for the reduction
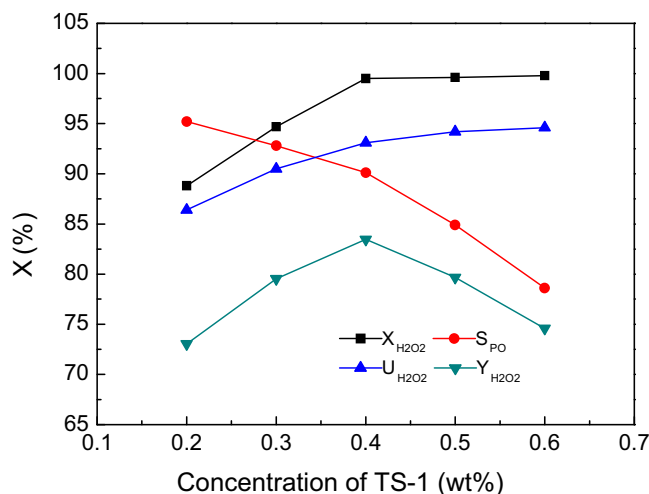
in selectivity. Based on these results, 0.4 wt% was the optimum TS-1 concentration.

3.3.5. Effect of propylene pressure

Fig. 8 shows the results of propylene epoxidation in $scCO_2$ and CH_3OH at different propylene pressures. The conversion and utilization of H_2O_2 markedly increased with increasing propylene pressure in both media; however, the improvement in $scCO_2$ is greater than that in CH_3OH. As the propylene pressure in the epoxidation reaction was increased, a higher amount of propylene dissolved in the reaction medium, which then accelerated the reaction rate. In the traditional solvent, the primary inhibitor to transport in gas-liquid reaction systems is the low solubility of the reactant gases in the liquid phase and the low diffusion across the interface [20]. Although more propylene can dissolve in CH_3OH as the propylene pressure is increased, it cannot diffuse to the active sites reacting with H_2O_2 because of its poor diffusion in CH_3OH. Thus, the selectivity to PO in CH_3OH decreased as the pressure increased. Used as a solvent, $scCO_2$ has excellent properties that facilitate the dissolution and diffusion of propylene to active sites. Consequently, the selectivity to PO in $scCO_2$ increased with the increase in propylene pressure. A greater effect of the variation in the propylene pressure on the reaction was observed in $scCO_2$ compared with that in CH_3OH because of the significant increase in propylene solubility and diffusion in $scCO_2$.

3.3.6. Effect of the solvent and cosolvent

The cosolvent plays a very important role in adjusting the properties of supercritical fluids, including the kinetic and thermodynamic properties of the reactions. In the present work, the use of CH_3OH as a cosolvent in the epoxidation reaction in $scCO_2$ was investigated. The solvent effect on the propylene epoxidation with H_2O_2 over large-grain TS-1 was investigated. The results show that the cosolvent concentration had a significant effect on the epoxidation reaction (Fig. 9). The H_2O_2 conversion and utilization greatly increased when the CH_3OH content was increased. The epoxidation of propylene was enhanced because of the strong interaction between CH_3OH and the Ti center, which stabilized the complex through hydrogen bonds to form a five-membered ring [23]. This kind of structure is stable and suitable for epoxidation; hence, CH_3OH as a cosolvent in the $scCO_2$ system can significantly enhance the epoxidation activity of the TS-1 catalyst. However, when the CH_3OH content was greater than 4.84 wt%, the selectivity to PO decreased, which may be due to the occurrence of side reactions such as ring-opening between PO and CH_3OH, or
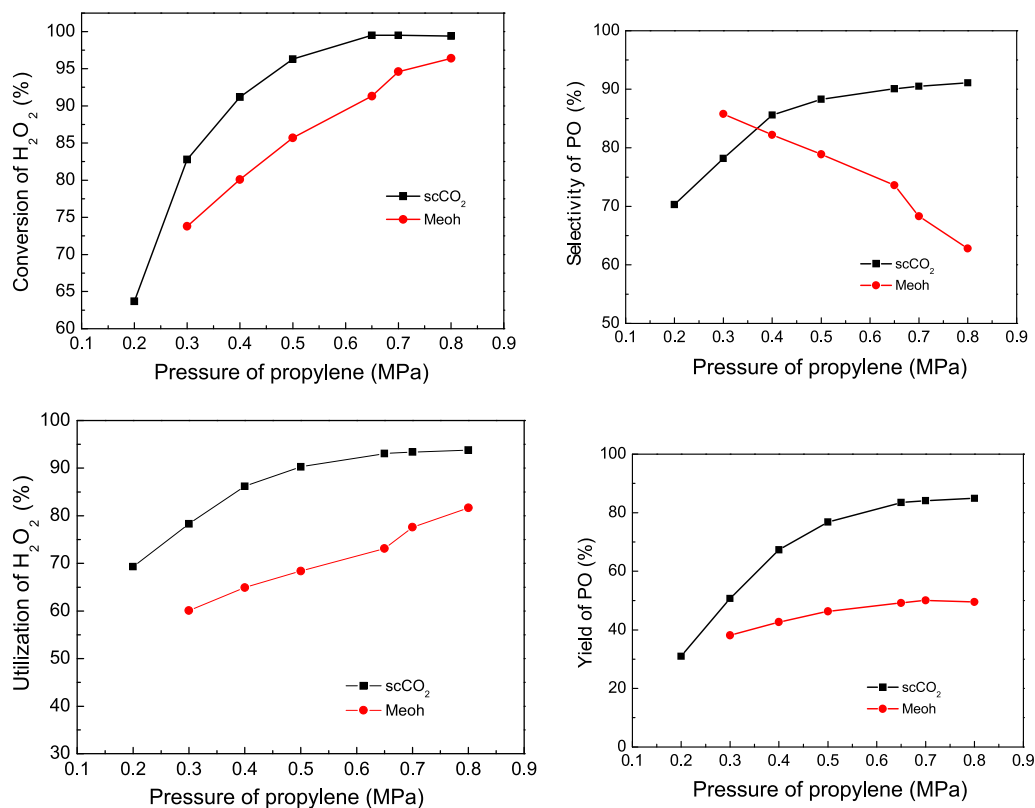
Fig. 8. Effect of propylene pressure on epoxidation.

polymerization reactions between PO and the initial CO_2. A high PO yield was maintained when the CH_3OH content was in the 4.5 wt% to 6.5 wt% range.

3.3.7. Effect of the reaction time on the epoxidation reaction in scCO2 catalyzed by large-grain TS-1

The catalytic activities at different reaction times are shown in Fig. 10. H_2O_2 conversion increased when the reaction time was extended, and the reaction rate was faster in $scCO_2$ than in CH_3OH. H_2O_2 conversion in $scCO_2$ reached 95% within 60 min, whereas the conversion in CH_3OH took 120 min. The use of $scCO_2$ as the reaction medium entirely eliminated the gas–liquid interface, thereby enhancing the epoxidation rate.
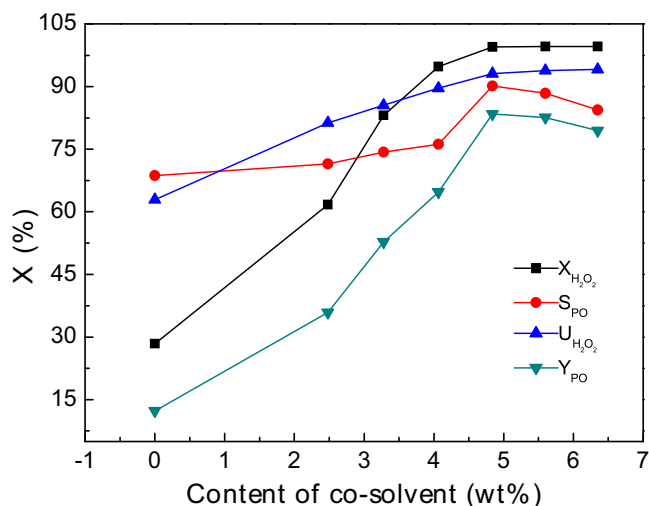

Fig. 9. Effect of the cosolvent on epoxidation.

The selectivity to PO in $scCO_2$ clearly decreased within 45 min. However, as the reaction time was extended to 60 min or longer, the selectivity to PO gradually increased and then remained constant. This behavior is attributed to the pore channel of the large-grain TS-1 (10-fold longer than that of the small-grain TS-1), which prevented the diffusion of the product out of the channel in time. The products required more time to diffuse out of the channel; hence, after 60 min, the selectivity to PO began to again increase, reaching its highest value at 120 min. On the other hand, the selectivity to PO in CH_3OH consistently decreased because of the poor diffusion of PO in CH_3OH, resulting in the occurrence of more side reactions. The optimal reaction time for $scCO_2$ was 120 min. The PO yield in the $scCO_2$ reaction system was maintained at approximately 83.5%, which is higher than that in CH_3OH.

3.3.8. Effect of the alkaline component on the epoxidation reaction in scCO2 catalyzed by large-grain TS-1

Propylene epoxidation in $scCO_2$ catalyzed by TS-1 can obtain a higher PO yield if the H_2O_2 utilization and selectivity to PO can be improved. Laha [23,24] reported that the introduction of urea to the epoxidation of styrene can greatly reduce the decomposition of H_2O_2. Li [7] also found out that both the selectivity to PO and the utilization of H_2O_2 in propylene epoxidation can be increased when urea is used. Clerici [5] reported that a small amount of an alkaline component such as Na_2CO_3 or $KHCO_3$ can inhibit the side reactions of epoxidation. The current paper investigated the effect of several alkaline components [NaOH, $NaHCO_3$, urea, and $(NH_4)_2CO_3$] on the epoxidation of propylene in $scCO_2$.

Fig. 11 shows the effect of the alkaline components on the reaction. The four alkaline components significantly increased the PO selectivity to 90%. However, NaOH and $NaHCO_3$ enhanced the decomposition of H_2O_2. By comparison, urea and $(NH_4)_2CO_3$ increased the selectivity but decreased the decomposition of H_2O_2.
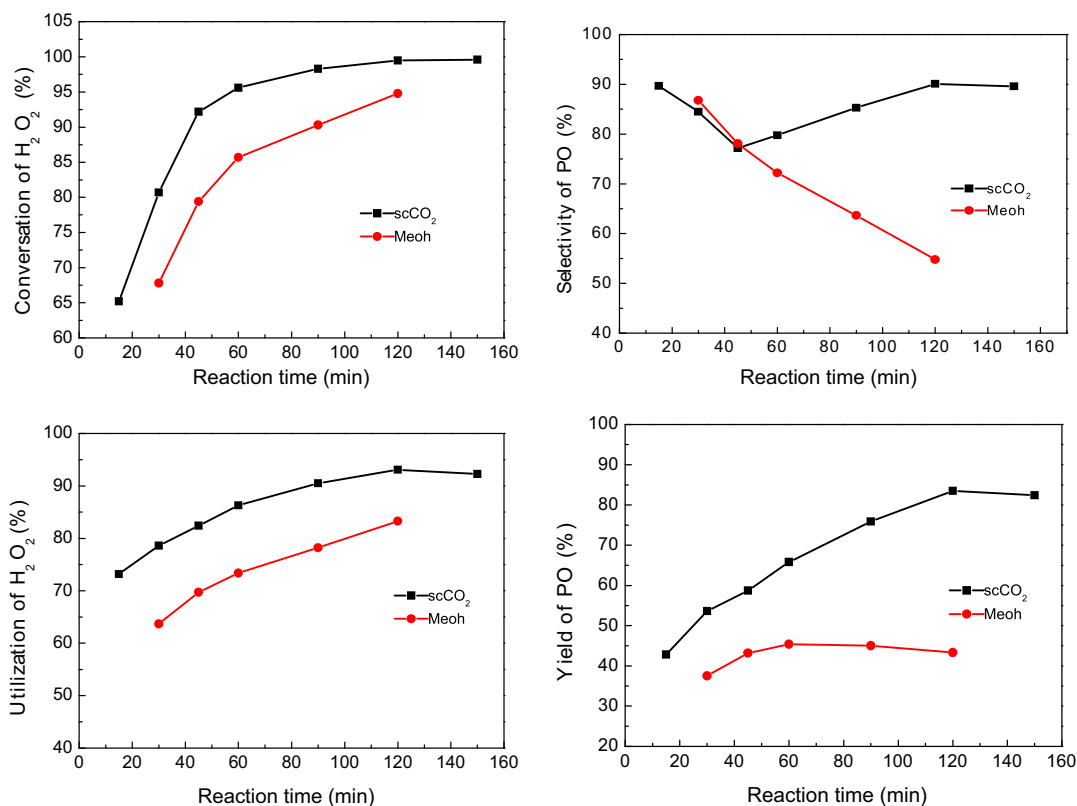
Fig. 10. Effect of the reaction time on epoxidation.

$(NH_4)_2CO_3$ yielded the best result among the four alkaline components.

A similar mechanism underlies the reaction between the large- and small-particle TS-1. The mechanism behind the excellent catalytic performance of the large-grain TS-1 can be explained using Scheme 1, as reported by Clerici [5]. In the TS-1 system, equilibrium exists between the alcohol solvent and the hydrogen peroxide. TS-1 reportedly develops acid centers in the presence of H_2O_2 in alcoholic or aqueous solutions. The Ti-OOH species, which is formed by the interaction between the Ti atom framework and the H_2O_2 molecule, can form a stable five-membered cyclic structure with a donor hydroxyl moiety coordinated on Ti (species II) [23]. The

Fig. 11. Effect of the alkaline components on epoxidation in $scCO_2$.

acid strength in the charge-separated species may increase because of increased hydrogen bonding. In addition, the acid centers can catalyze the epoxide ring opening. If an excess amount of a basic compound is added, the equilibrium shifts and the active species II in propylene epoxidation is converted into either species III or IV. Species IV is inert, and TS-1 loses its catalytic activity in propylene epoxidation. The catalytic activity of the large-grain TS-1 in the direct oxidation of propylene to PO in CH_3OH is poor compared with that of the small-grain TS-1. However, the introduction of $scCO_2$ to the reaction system resulted in an excellent diffusion because of the nearly 10-fold longer pore channel in the large grains, which facilitated the rapid transfer of PO from the zeolite. In turn, this diffusion remarkably improved the catalytic activity of the large-grain TS-1. This improvement will be of great benefit to the industrial production of PO. The mechanism behind the decreased H_2O_2 utilization rate with the addition of NaOH and NaHCO_3, while these parameters increased with the addition of urea and $(NH_4)_2CO_3$, is currently being investigated.

The addition of $(NH_4)_2CO_3$ increased the H_2O_2 conversion, selectivity to PO, H_2O_2 utilization, and PO yield to 98.7%, 95.2%, 94.3%, and 88.6%, respectively. The selectivity to and yield of PO increased to 4.3% and 5.1%, respectively, compared with that in $scCO_2$ without alkaline components. Although the use of $scCO_2$ can increase the acidity of the reaction medium, it cannot lower the selectivity to PO because $scCO_2$ facilitates the diffusion of the produced PO from the TS-1 active site, resulting in the decline of the ring-opening reaction of PO. In addition, the introduction of alkaline substances to the reaction resulted in a decrease in the acidity and an improvement in the reaction selectivity to PO.

Table 2 summarizes the optimum results of the epoxidation reaction catalyzed by small- and large-grain TS-1 in CH_3OH and in $scCO_2$. In the CH_3OH system, the catalysis by the small grain TS-1 produced better results compared with that by the large-grain TS-1. This observation may be attributed to the shorter pore canal
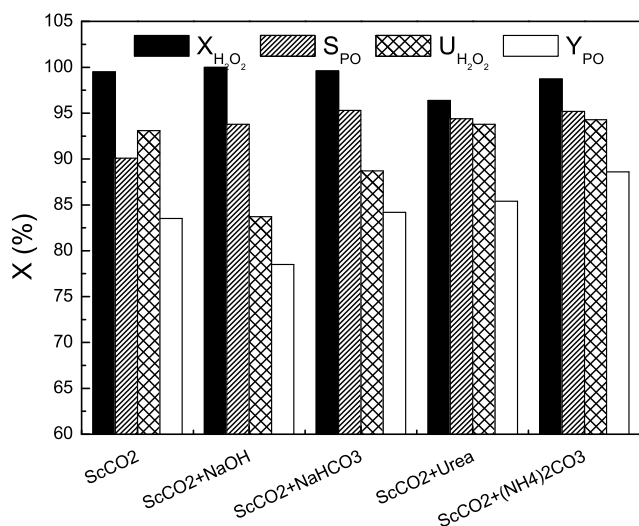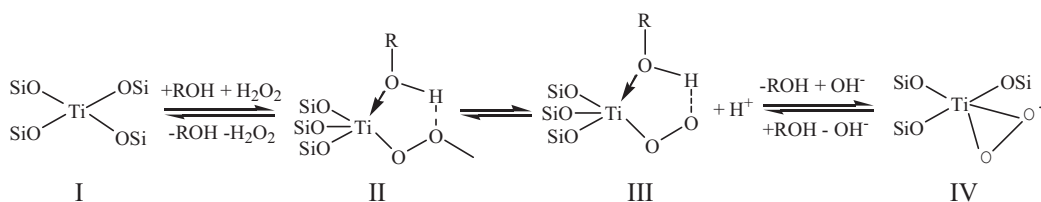
Scheme 1. Equilibrium of the active species.

Table 2
Optimum results under different reaction conditions.

Solvent and TS-1	$X_{H_2O_2}$ (%)	S_{PO} (%)	$U_{H_2O_2}$ (%)	Y_{PO} (%)
Small TS-1 + MeOH	83.5	92.0	92.3	70.9
Large TS-1 + MeOH	94.6	68.3	77.6	50.1
Large TS-1 + scCO$_2$	99.5	90.1	93.1	83.5
Large TS-1 + scCO$_2$ + (NH$_4$)$_2$CO$_3$	98.7	95.2	94.3	88.6

and larger specific surface area of the small-grain TS-1 compared to the large-grain TS-1. When scCO$_2$ was introduced to the reaction system, the reaction performance significantly improved because of the excellent transport and solubility properties of scCO$_2$. In addition, the alkaline component positively affected the H$_2$O$_2$ conversion, selectivity to PO, H$_2$O$_2$ utilization, and PO yield.

Several studies on the current topic have been published. Clerici [5] reported the synthesis of PO from propylene using CH$_3$OH or CH$_3$OH/water mixtures as the solvent and small-grain TS-1 as the catalyst. The current study is different from that of Clerici in that the solvent is CH$_3$OH and the catalyst used is small-grain TS-1. Li [7] reported on the effect of sodium ions on propylene epoxidation catalyzed by large-grain TS-1 using CH$_3$OH as the solvent. In the present study, the results of the epoxidation of PO in scCO$_2$ using large-grain TS-1 as the catalyst were obtained. No published results involving solely large-grain TS-1 as the catalyst and H$_2$O$_2$ as the oxidant in a scCO$_2$ medium are found. The H$_2$O$_2$ conversion, selectivity to PO, and utilization of H$_2$O$_2$ in scCO$_2$ using the large-grain TS-1 as the catalyst in the presence of an alkaline component were 98.7%, 95.2%, and 94.3%, respectively. These results are higher compared with those reported in literature [7]. When scCO$_2$ was introduced to the reaction system, the catalytic activity of the large-grain TS-1 was remarkably improved, which will be of great benefit to the industrial production of PO.

4. Conclusions

The synthesis of PO from propylene epoxidation catalyzed by large-grain TS-1 using H$_2$O$_2$ as the oxidant and scCO$_2$ as the reaction medium was investigated. When the large-grain TS-1 was used as the catalyst in the scCO$_2$ system, the H$_2$O$_2$ conversion, selectivity to PO, H$_2$O$_2$ utilization, and PO yield were 98.7%, 95.2%, 94.3%, and 88.6%, respectively. When alkaline components were added, the results improved by 4.1%, 26.9%, 16.7%, and 38.5%, respectively. The use of scCO$_2$ as the reaction medium can eliminate the transport limitations and enhance the reaction because propylene is highly soluble in scCO$_2$, which contributes to the excellent diffusivity of the reactants and products. The H$_2$O$_2$ conversion,

selectivity to PO, H$_2$O$_2$ utilization, and PO yield improved by 15.2%, 3.2%, 2.0%, and 17.7%, respectively, compared with the results of the reaction catalyzed by the small-grain TS-1 in CH$_3$OH. ScCO$_2$ enhanced the catalytic performance of the large-grain TS-1 to a level comparable to that of the more expensive small-grain catalysts, thereby making the use of large-grain TS-1 feasible in the synthesis of PO from propylene on a large scale. The reaction mechanisms of the large- and small-grain TS-1 activities are similar, and the exceptional mass-transfer and diffusion performance of scCO$_2$ significantly improved the catalytic performance of TS-1, especially that of the large-grain TS-1. The current study presents a potentially novel approach to the production of PO using a low-cost, easily separated catalyst and provides a basis as well as technical parameters for the further industrialization of this process.

Acknowledgements

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