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Epoxidation of Propylene with Hydrogen Peroxide Over TS-1 Catalyst Synthesized in the Presence of Polystyrene

**Sunyoung Park · Kyung Min Cho · Min Hye Youn ·
Jeong Gil Seo · Sung-Hyeon Baeck · Tae Jin Kim ·
Young-Min Chung · Seung-Hoon Oh · In Kyu Song**

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Abstract Titanium silicalite-1 (TS-1) catalyst was synthesized in the presence of polystyrene (PS) particles (denoted as TS-1_PS catalyst) for use in the epoxidation of propylene with hydrogen peroxide. For the purpose of comparison, TS-1 catalyst was also synthesized by a conventional method (in the absence of polystyrene particles). In the epoxidation of propylene, the TS-1_PS catalyst showed a higher conversion of hydrogen peroxide and a higher selectivity for propylene oxide (PO) than the TS-1 catalyst. Consequently, the TS-1_PS catalyst showed a higher yield for PO than the TS-1 catalyst. Characterization results showed that the high catalytic performance of TS-1_PS was attributed to the enhanced hydrophobic property of the catalyst and the suppressed formation of anatase TiO_2 in the catalyst.

Keywords Titanium silicalite-1 · Polystyrene · Propylene oxide · Propylene epoxidation

S. Park · K. M. Cho · M. H. Youn · J. G. Seo · I. K. Song (✉)
School of Chemical and Biological Engineering,
Institute of Chemical Processes, Seoul National University,
Shinlim-dong, Kwanak-ku, Seoul 151-744, South Korea
e-mail: inksong@snu.ac.kr

S.-H. Baeck
Department of Chemical Engineering, Inha university,
Inchon 402-751, South Korea

T. J. Kim · Y.-M. Chung · S.-H. Oh
SK Energy Corporation, Yuseong-ku, Daejeon 305-712,
South Korea

1 Introduction

Epoxidation of propylene has attracted much attention as a promising process for producing propylene oxide (PO) [1, 2], which is an important chemical intermediate in the petrochemical industries. Propylene oxide is currently produced in the industries through a chlorohydrin process and a hydroperoxide process. However, these processes use environmentally hazardous chemicals as oxidants and produce a large number of by-products [3]. Therefore, the epoxidation of propylene with hydrogen peroxide has been recognized as an environmentally benign chemical process [1, 2, 4–6].

Various catalysts have been investigated in the epoxidation of propylene with molecular oxygen. These examples include titanium-containing mesoporous materials [7–9] and noble metals supported on titanium-containing zeolites [10–14]. Although the epoxidation of propylene with molecular oxygen over these catalysts has economical and environmental advantages, the yield for PO is found to be very low [7–14]. Therefore, the epoxidation of propylene with hydrogen peroxide has been widely investigated.

Titanium-containing zeolite catalysts such as titanium silicalite-1 (TS-1) [1, 2, 4–6] and Ti-MCM-22 [15] have been widely investigated as efficient catalysts for propylene epoxidation with hydrogen peroxide. In particular, it was reported that the selectivity for PO over Ti-MCM-22 was almost 100%. However, the commercialization of propylene epoxidation using Ti-MCM-22 has been restricted, because the synthesis procedure of Ti-MCM-22 catalyst is very complicated [15]. Therefore, TS-1 has been widely investigated as an alternative and promising catalyst for the epoxidation of propylene due to its simple synthesis route.

TS-1 is a silicalite zeolite with a MFI structure, and has a three-dimensional pore system consisting of straight 10-membered ring channels and intersecting sinusoidal 10-membered ring channels [16]. TS-1 has also been used as a selective catalyst in the low-temperature oxidation reactions such as hydroxylation of phenol [17] and ammoxidation of cyclohexanone [18].

Extraframework Ti in the form of anatase TiO_2 is produced, when Ti content of TS-1 is higher than the upper limit of framework Ti [19, 20]. It is known that tetrahedral Ti isolated in the hydrophobic silica matrix is catalytically active whereas anatase TiO_2 phase is inactive for the epoxidation of propylene [15, 19, 20]. Furthermore, it has been reported that a high catalytic activity of TS-1 in the epoxidation of propylene is attributed to its hydrophobic property [1, 2, 21]. Therefore, it is expected that a highly hydrophobic TS-1 catalyst with no anatase TiO_2 phase would show an excellent catalytic performance in the epoxidation of propylene with hydrogen peroxide.

In this work, TS-1 catalyst was synthesized by a hydrothermal method in the presence of polystyrene (PS) particles (denoted as TS-1_PS catalyst) with an aim of increasing hydrophobicity of the catalyst, and was applied to the epoxidation of propylene with hydrogen peroxide. For the purpose of comparison, TS-1 was also synthesized by a conventional hydrothermal method (in the absence of polystyrene particles). The effect of PS employed in the preparation of TS-1_PS catalyst on the catalytic performance of TS-1_PS in the epoxidation of propylene was investigated.

2 Experimental

2.1 Catalyst Preparation

TS-1 catalyst was prepared according to the method reported in the literature [22]. An aliquot of 0.5 mL titanium butoxide (Sigma-Aldrich) was added to 20 mL of tetraethylorthosilicate (TEOS, Sigma-Aldrich) under a flow of N_2. An aliquot of 45 mL of a 20% aqueous solution of tetrapropylammonium hydroxide (TPAOH, Alfa Aesar) was then slowly added to the mixed solution under vigorous stirring. After maintaining the solution at 65 °C for 3 h, 60 mL of distilled water was added to the solution. Final composition of the resulting solution was $SiO_2/TiO_2/TPAOH/H_2O = 1:0.017:0.45:35$. The mixed solution was crystallized in an autoclave at 175 °C for 96 h. After cooling the autoclave to room temperature, a solid product was filtered and washed with distilled water. The solid product was dried overnight at 100 °C, and it was then calcined at 550 °C for 6 h to yield the TS-1 catalyst.

Polystyrene was prepared by a copolymerization of styrene (Sigma-Aldrich) with divinyl benzene (Fluka), according to the reported method [23]. The preparation method for TS-1 in the presence of PS particles was almost identical to that for TS-1, except that PS particles were added to the mixed solution of TEOS, titanium butoxide, and TPAOH. After maintaining the solution with dispersed PS particles at 65 °C for 3 h, 60 mL of distilled water was added to the solution. The solution was crystallized in an autoclave at 175 °C for 96 h. After cooling the autoclave to room temperature, a solid product was filtered and washed with distilled water. The resulting solid was dried overnight at 100 °C, and it was then calcined at 550 °C for 6 h to yield the TS-1_PS catalyst. During the calcination step, PS particles were totally removed from the catalyst.

2.2 Characterization

Ti content of the prepared catalysts was determined by ICP-AES (Shimadz, ICP-1000IV) analyses. UV-visible spectroscopy (Perkin–Elmer, Lambda-35) measurements were conducted to detect Ti species in the catalysts. Surface areas of the catalysts were measured using a BET apparatus (Micromeritics, ASAP 2010).

NH_3-TPD (temperature-programmed desorption) experiments were carried out to determine the hydrophobic property of the catalysts. 0.2 g of each catalyst was charged into a quartz reactor of the TPD apparatus, and then it was pretreated at 200 °C for 1 h with a stream of helium (20 mL/min). After the catalyst was cooled to room temperature, NH_3 (20 mL) was pulsed into the reactor every minute under a flow of helium (5 mL/min) until the hydrophobic sites were saturated with NH_3. Unlike the conventional TPD measurements, no evacuation was done for the measurement of NH_3 physisorbed on the hydrophobic sites of the catalysts. The furnace temperature was increased from room temperature to 500 °C at a rate of 5 °C/min under a flow of helium (10 mL/min). The desorbed NH_3 was detected using a GC-MSD (Agilent, MSD-6890N GC).

Water sorption capacity of the catalysts was also measured by TGA analyses (TA Instruments, Q-5000 IR) in order to investigate the hydrophobic property of the catalysts. Before the TGA measurements, the catalysts were immersed in distilled water for 12 h, and they were then dried at room temperature for 2 days. 10 mg of each catalyst was placed in an alumina crucible. It was heated from 25 °C to 250 °C at a rate of 5 °C/min in a stream of argon, and the amount of water loss was measured.

2.3 Epoxidation of Propylene

Epoxidation of propylene was carried out in an autoclave reactor. 0.5 g of each catalyst, 80 mL of methanol, and

5.2 mL of 30% hydrogen peroxide were charged into the reactor. After the solution was heated at 40 °C with vigorous stirring (700 rpm), propylene was fed into the reactor at constant pressure (7 atm) to initiate the reaction. The reaction products were periodically sampled and analyzed with a gas chromatograph (HP 5890II) equipped with a FID. The amount of hydrogen peroxide was measured by an iodometric titration method [24]. Conversion of hydrogen peroxide (H_2O_2) and selectivity for PO were calculated as follows. Yield for PO was calculated by multiplying conversion of hydrogen peroxide and selectivity for PO.

$$\text{Conversion of hydrogen peroxide} = \frac{\text{molesofhydrogenperoxidereacted}}{\text{moles of hydrogen peroxide supplied}}$$

$$\text{Selectivity for propylene oxide} = \frac{\text{molesofpropyleneoxideformed}}{\text{total moles of products formed}}$$

3 Results and Discussion

3.1 Catalyst Characterization

Chemical compositions of the catalysts determined by ICP-AES analyses are listed in Table 1. Ti content of TS-1_PS was almost identical to that of TS-1. Furthermore, BET surface area of TS-1_PS was almost the same as that of TS-1. These results indicate that no changes in Ti content and surface area of TS-1_PS catalyst occurred by PS particles employed during the catalyst preparation step.

Figure 1 shows the UV-visible spectra of TS-1 and TS-1_PS catalysts. It has been reported that Ti atoms in the TS-1 can exist in the form of tetrahedral Ti, octahedral Ti, and anatase TiO_2. In the UV-visible spectra, a band at around 230 nm is attributed to the tetrahedral Ti, which is active for the epoxidation of propylene. Absorption bands at around 270 and 340 nm are attributed to the octahedral Ti and the anatase TiO_2, respectively, which are inactive for the epoxidation of propylene [15, 25]. It is noteworthy that no band at around 270 nm was observed in both catalysts, indicating that no octahedral Ti was formed in both TS-1 and TS-1_PS catalysts. The TS-1 catalyst showed the absorption bands at around 230 and 340 nm. This indicates that Ti atoms in the TS-1 catalyst exist in the form of tetrahedral Ti and anatase TiO_2. The TS-1_PS catalyst also showed an absorption band at around 230 nm, indicative of the presence of tetrahedral Ti. However, no band at around 340 nm was observed in the TS-1_PS catalyst. This indicates that PS particles employed in the crystallization step of TS-1_PS catalyst inhibited the formation of anatase TiO_2, which is inactive for the epoxidation of propylene. Therefore, it can be inferred that the TS-1_PS catalyst may retain more active Ti species than the TS-1 catalyst, judging from the fact that both catalysts have almost identical Ti content (Table 1).

Table 1 Chemical compositions and BET surface areas of the catalysts

Catalyst	Ti/Si molar ratio	BET surface area (m^2/g)
TS-1	0.018	424
TS-1_PS	0.017	437

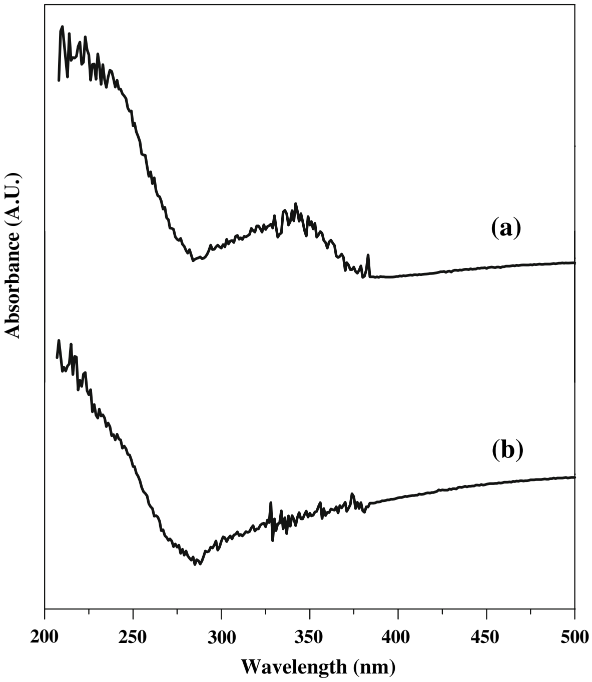

Fig. 1 UV-visible spectra of (a) TS-1 and (b) TS-1_PS catalysts

3.2 Catalytic Performance in the Epoxidation of Propylene

Figure 2 shows the catalytic performance of TS-1 and TS-1_PS in the epoxidation of propylene at 40 °C, plotted as a function of reaction time. Since the epoxidation of propylene was carried out in the autoclave reactor, the conversion of hydrogen peroxide increased with increasing reaction time and kept constant after a 1.5 h-catalytic reaction. In the epoxidation of propylene, small amounts of 1-methoxy-2-propanol, 2-methoxy-1-propanol, and 1,2-propanediol were produced as by-products. These by-products were formed from PO. It is interesting to note that the selectivity for PO decreased after a 1 h-catalytic reaction over TS-1 catalyst, but the selectivity for PO were almost constant over TS-1_PS catalyst. The catalytic

Fig. 2 (**a**) Conversion of hydrogen peroxide (H_2O_2) and (**b**) selectivity for propylene oxide (PO) over TS-1 and TS-1_PS catalysts in the epoxidation of propylene at 40 °C, plotted as a function of reaction time

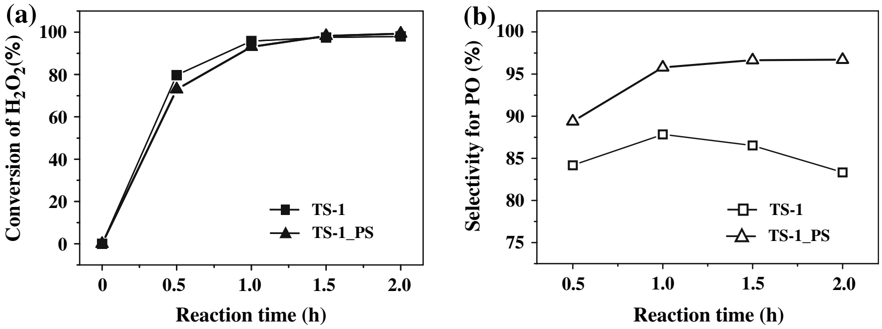

Table 2 Catalytic performance of TS-1 and TS-1_PS after a 1.5-catalytic reaction

Catalyst	Conversion of H_2O_2 (%)	Selectivity for PO (%)	Yield for PO (%)
TS-1	97.5	86.5	84.4
TS-1_PS	98.2	96.7	94.9

performance of TS-1 and TS-1_PS after a 1.5 h-catalytic reaction is summarized in Table 2. The TS-1_PS catalyst showed a higher conversion of hydrogen peroxide and a higher selectivity for PO than the TS-1 catalyst. As a consequence, the TS-1_PS catalyst exhibited a higher yield for PO than the TS-1 catalyst.

3.3 Hydrophobic Property of the Catalysts

In order to elucidate the enhanced catalytic performance of TS-1_PS catalyst, hydrophobic property of the catalysts was measured by NH_3-TPD and TGA analyses [21]. In the conventional TPD measurements, water has been used as an adsorbate for the determination of the hydrophobic property [26]. In our TPD experiments, however, NH_3 instead of water was used as a polar adsorbate molecule, because water was condensed at low temperature.

Figure 3 shows the NH_3-TPD profiles of TS-1 and TS-1_PS catalysts. Solid curves represent the desorption profiles of physicsorbed NH_3, which were obtained from NH_3-TPD measurements without the evacuation step. The desorption peaks of physisorbed NH_3 evolved from TS-1 and TS-1_PS catalysts appeared at around 130 °C and 100 °C, respectively. This result indicates that TS-1_PS catalyst is more hydrophobic than TS-1 catalyst.

For the purpose of comparison, NH_3-TPD measurements were carried out with the evacuation step. Dash curves represent the desorption profiles of chemisorbed NH_3 evolved from TS-1 and TS-1_PS catalysts. Both catalysts showed the desorption peaks of chemisorbed NH_3 at around 190 °C with no difference, indicating that acid strength of TS-1_PS catalyst was almost identical to that of TS-1 catalyst. This result also implies that acid strength of the catalyst is not an important factor determining the catalytic performance in the epoxidation of propylene.

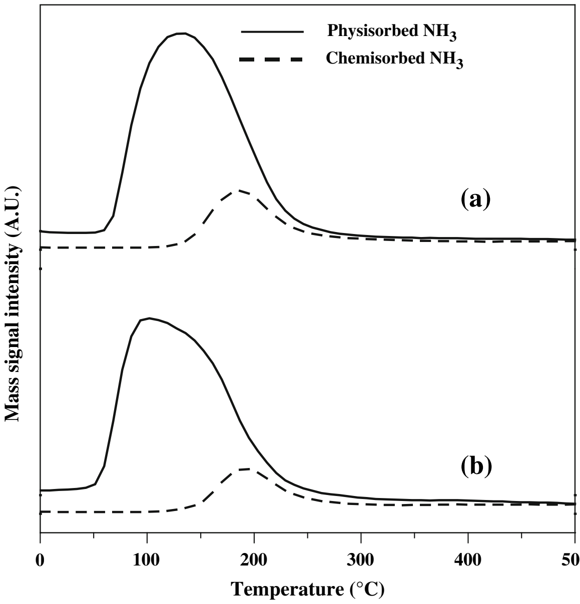

Fig. 3 NH_3-TPD profiles of (a) TS-1 and (b) TS-1_PS catalysts

Figure 4 shows the TGA profiles of water-treated TS-1 and TS-1_PS catalysts. Thermal scanning was done at temperatures ranging from 25 °C to 250 °C. Significant weight loss was observed below 100 °C in both catalysts. The amounts of weight loss of water-treated TS-1 and TS-1_PS catalysts at 100 °C were measured to be 4.7% and 1.7%, respectively. In other words, the amount of water adsorbed on TS-1_PS catalyst was smaller than that on TS-1 catalyst. This result also indicates that TS-1_PS catalyst is more hydrophobic than TS-1 catalyst, as evidenced by the NH_3-TPD measurements.

3.4 Effect of Polystyrene Particles

The results of NH_3-TPD and TGA measurements revealed that TS-1_PS catalyst was more hydrophobic than TS-1

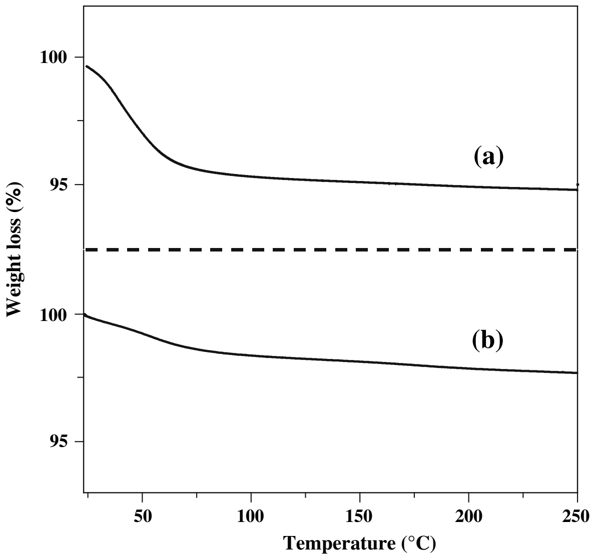

Fig. 4 TGA profiles of water-treated (a) TS-1 and (b) TS-1_PS catalysts

catalyst. Moreover, UV-visible spectroscopy measurements showed that anatase TiO_2 was not formed in the TS-1_PS catalyst. These results indicate that PS particles employed during the hydrothermal synthesis step increased the hydrophobic property of TS-1_PS catalyst and inhibited the formation of anatase TiO_2 in the TS-1_PS catalyst. Therefore, the TS-1_PS catalyst showed a higher yield for PO than the TS-1 catalyst in the epoxidation of propylene. It can be concluded that the high catalytic activity of TS-1_PS was attributed to the enhanced hydrophobic property of the catalyst and the suppressed formation of anatase TiO_2.

4 Conclusions

TS-1_PS catalyst prepared in the PS particles was applied to the epoxidation of propylene with hydrogen peroxide. For the purpose of comparison, TS-1 catalyst was also prepared in the absence of PS particles. It was revealed that PS particles employed during the hydrothermal synthesis step enhanced the hydrophobic property of the catalyst and inhibited the formation of anatase TiO_2 in the catalyst. The TS-1_PS catalyst showed a higher conversion of hydrogen peroxide and a higher selectivity for PO than the TS-1 catalyst. As a consequence, the TS-1_PS catalyst showed a higher yield for PO than the TS-1 catalyst. The enhanced catalytic performance of TS-1_PS was attributed to the increased hydrophobic property of the catalyst and the suppressed formation of anatase TiO_2 in the catalyst.

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