



Direct epoxidation of propylene with hydrogen peroxide over TS-1 catalysts: Effect of hydrophobicity of the catalysts

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ABSTRACT

TS-1 (titanium silicalite-1) catalysts were hydrothermally synthesized in the presence of polymethylmethacrylate bead (denoted as TS-1_PMMA) and polystyrene bead (denoted as TS-1_PS) for use in the direct epoxidation of propylene with hydrogen peroxide. TS-1 catalyst was also synthesized by a hydrothermal method in the absence of polymer bead. It was revealed that TS-1_PMMA and TS-1_PS catalysts showed a better catalytic performance than TS-1 catalyst in terms of conversion of hydrogen peroxide, selectivity for propylene oxide, and yield for propylene oxide, due to their enhanced hydrophobicity. Among three catalysts, TS-1_PS with the highest hydrophobicity showed the best catalytic performance.

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1. Introduction

Direct epoxidation of propylene has attracted much attention as a promising process for producing propylene oxide, an important raw material in the petrochemical industries. Propylene oxide currently available in the market is mostly produced through chlorohydrin process and hydroperoxide process. However, the chlorohydrin process uses environmentally hazardous chlorine and the hydroperoxide process produces a large number of by-products [1]. Therefore, the direct epoxidation of propylene with hydrogen peroxide has been recognized as an environmentally benign process [2,3].

Various catalysts have been investigated in the direct epoxidation of propylene with hydrogen peroxide, including heteropolyacids [4,5] and titanium-containing zeolites such as titanium silicalite-1 (TS-1) [2,3,6–8] and Ti-MCM-22 [9]. It has been reported that TS-1 and Ti-MCM-22 showed a high catalytic activity under mild reaction conditions. In particular, selectivity for propylene oxide over Ti-MCM-22 was reported to be almost 100%. However, the commercialization of propylene epoxidation utilizing Ti-MCM-22 has been restricted, because of the complicated preparation method for Ti-MCM-22 [9]. For this reason, TS-1 has been

widely investigated as an alternative and promising catalyst for the direct epoxidation of propylene.

TS-1 is a typical zeolite in which tetrahedral TiO₄ and SiO₄ units are arranged in a MFI structure [10–12]. It has been reported that the high catalytic activity of TS-1 in the direct epoxidation of propylene was attributed to its hydrophobic property [13]. If the hydrophobic property of TS-1 catalyst can be enhanced, therefore, the catalyst will show an excellent performance in the direct epoxidation of propylene with hydrogen peroxide.

In this work, TS-1 catalysts were synthesized by a hydrothermal method in the presence of polymethylmethacrylate bead (denoted as TS-1_PMMA) and polystyrene bead (denoted as TS-1_PS) with an aim of increasing hydrophobic property of the catalysts. They were applied to the direct epoxidation of propylene with hydrogen peroxide. For comparison, TS-1 catalyst was also synthesized by a conventional hydrothermal method in the absence of polymer bead. The effect of hydrophobicity of the catalysts on the catalytic performance in the direct epoxidation of propylene was investigated.

2. Experimental

2.1. Catalyst preparation

TS-1 catalyst was prepared according to the method reported in the literature [14]. 0.5 ml of titanium butoxide (Sigma-Aldrich) was added to 20 ml of tetraethylorthosilicate (TEOS,

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Sigma–Aldrich) under a flow of nitrogen. 45 ml of 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 SiO₂/TiO₂/TPAOH/H₂O = 1:0.017:0.45:35. The mixed solution was crystallized in an autoclave at 175 °C for 96 h. After filtering and washing a solid product with distilled water, the solid product was dried overnight at 100 °C, and finally, it was calcined at 550 °C for 6 h to obtain TS-1 catalyst.

Polymethylmethacrylate (PMMA) bead was prepared according to the reported method [15]. Polystyrene (PS) bead was prepared by copolymerizing styrene (Sigma–Aldrich) with divinylbenzene (Fluka), according to the reported method [16]. The preparation method for TS-1 catalysts in the presence of PMMA bead and PS bead was almost identical to that for TS-1 catalyst, except that 0.5 g of each polymer bead was added to the mixed solution composed of TEOS, titanium butoxide, and TPAOH. TS-1 catalysts prepared in the presence of PMMA bead and PS bead were denoted as TS-1_PMMA and TS-1_PS, respectively.

2.2. Characterization

Ti content of the catalyst was determined by ICP-AES analysis (Shimadzu, ICP-1000IV). Carbon content of the catalyst was determined by CHNS elemental analyzer (Leco, CHNS-932). Surface area of the catalyst was measured using a BET apparatus (Micromeritics, ASAP 2010). Crystal size and morphology of the catalyst were examined by SEM (Jeol, JSM-6700F).

NH₃-TPD (temperature-programmed desorption) experiment was conducted to determine the hydrophobic property of the catalyst. 0.2 g of catalyst was charged into a quartz reactor of the TPD apparatus, and it was pretreated at 200 °C for 1 h with a stream of helium (20 ml/min). After cooling the catalyst to room temperature, NH₃ (20 ml) was pulsed into the reactor every minute under a flow of helium (5 ml/min) until the hydrophobic sites were saturated with NH₃. Unlike the conventional TPD measurement, no evacuation was done for the measurement of NH₃ physisorbed on the hydrophobic sites of the catalyst. The furnace temperature was increased from room temperature to 500 °C at a heating rate of 5 °C/min under a flow of helium (10 ml/min). The desorbed NH₃ was detected using a GC-MSD (Agilent, MSD-6890N).

Water sorption capacity of the catalyst was measured by TGA analysis (TA Instruments, Q-5000 IR) for further investigation of the hydrophobic property of the catalyst. Before the TGA measurement, the catalyst was immersed in distilled water for 12 h, and it was then dried at room temperature for two days. Ten milligrams of catalyst was placed in an alumina crucible. It was heated from room temperature to 250 °C at a heating rate of 5 °C/min under a flow of argon (100 ml/min), and the amount of water loss from the catalyst 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 heating the mixed solution to 40 °C with vigorous stirring (700 rpm), propylene was fed into the reactor at 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 [17]. Conversion of hydrogen peroxide (H₂O₂) and selectivity for propylene oxide (PO) were calculated according to the following equations. Yield for PO was calculated by multiplying conversion of hydrogen peroxide and selectivity for PO.

Conversion of hydrogen peroxide

$$= \frac{\text{moles of hydrogen peroxide reacted}}{\text{moles of hydrogen peroxide supplied}} \quad (1)$$

Selectivity for propylene oxide

$$= \frac{\text{moles of propylene oxide formed}}{\text{total moles of products formed}} \quad (2)$$

3. Results and discussion

3.1. Catalyst characterization

Chemical composition, carbon content, and BET surface area of the catalyst are summarized in Table 1. Ti content of TS-1_PMMA and TS-1_PS was almost identical to that of TS-1. BET surface area of TS-1_PMMA and TS-1_PS was also almost the same as that of TS-1 catalyst. These results indicate that no changes in Ti content and surface area of TS-1_PMMA and TS-1_PS catalysts occurred by the introduction of PMMA and PS beads during the catalyst preparation step. Furthermore, carbon content of TS-1_PMMA and TS-1_PS was very low, and was similar to that of TS-1. This implies that PMMA and PS beads employed during the catalyst preparation step were completely removed through the calcination process.

Fig. 1 shows the SEM images of TS-1, TS-1_PMMA, and TS-1_PS catalysts. The images clearly show the formation of cubes with an average size of ca. 200 nm in all the catalysts with no considerable difference. This result indicates that no changes in crystal size and morphology of TS-1_PMMA and TS-1_PS catalysts occurred in spite of the introduction of polymer beads during the crystallization process of the catalysts. It can be summarized that PMMA and PS beads introduced during the catalyst preparation step showed no considerable effect on the chemical composition, surface area, crystal size, and crystal morphology of the catalysts.

3.2. Catalytic performance in the epoxidation of propylene

Fig. 2 shows the catalytic performance of TS-1, TS-1_PMMA, and TS-1_PS catalysts in the epoxidation of propylene with hydrogen peroxide, plotted as a function of reaction time. Since the epoxidation of propylene was carried out in the autoclave reactor, conversion of hydrogen peroxide increased with increasing reaction time and was almost constant after a 1.5 h reaction. In this reaction, small amounts of by-products such as 1-methoxy-2-propanol, 2-methoxy-1-propanol, and 1,2-propanediol were produced from propylene oxide. It is interesting to note that selectivity for PO over TS-1 catalyst decreased after a 1 h reaction, while selectivity for PO over TS-1_PMMA and TS-1_PS catalysts was almost constant after a 1 h reaction.

Fig. 3 shows the catalytic performance of TS-1, TS-1_PMMA, and TS-1_PS catalysts at 40 °C after a 1.5 h reaction. Conversion of hydrogen peroxide and selectivity for PO over TS-1_PMMA and TS-1_PS catalysts were higher than those over TS-1 catalyst, and consequently, yield for PO over TS-1_PMMA and TS-1_PS catalysts was higher than that over TS-1 catalyst. The catalytic performance was decreased in the order of TS-1_PS > TS-1_PMMA > TS-1.

Table 1
Chemical composition, carbon content, and BET surface area of the catalyst

Catalyst	Ti content (wt.%)	Carbon content (wt.%)	BET surface area (m ² /g)
TS-1	1.4	0.070	424
TS-1_PMMA	1.5	0.068	400
TS-1_PS	1.4	0.090	437

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