Catalytic performance of Ti-SBA-15 prepared by chemical vapor deposition for propylene epoxidation: The effects of SBA-15 support and silylation

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ABSTRACT

Ti-SBA-15 catalysts were prepared by the chemical vapor deposition (CVD) method using $TiCl_4$ as titanium source and characterized by XRD, N_2 desorption, FT-IR and UV–vis spectroscopies, and TG analysis. The effects of SBA-15 support and silylation on the catalytic performances of Ti-SBA-15 catalysts for the propylene epoxidation using cumene hydroperoxide (CHP) as the oxidant were investigated. The results show that SBA-15 supports prepared with different methods have different surface properties, leading to the difference on the amount and the status of Ti deposited on the SBA-15 surface and different catalytic performances. On the other hand, the silylated Ti-SBA-15 catalysts exhibit higher activities than the unsilylated Ti-SBA-15 catalyst due to the increase of the hydrophobicity of the catalyst, which originates from the impact of methyl groups anchored on the surface of Ti-SBA-15 catalysts. The silylated Ti-SBA-15 catalyst prepared with reflux for 6 h exhibits the best epoxidation performances, over which CHP conversion of 90.3% and PO selectivity to CHP of 96.2% can be obtained.

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1. Introduction

Propylene oxide (PO) is an important chemical raw material and intermediate for the production of polyurethanes, unsaturated polyesters and surfactants [1]. The chlorohydrin process and indirect oxidation process are two conversional methods for producing propylene oxide [2–4]. The former need use chlorine and produces hypochlorous acid in situ by the reaction between water and chlorine, leading to the environmental pollution. The indirect oxidation involving tert-butyl hydroperoxide or ethylbenzene hydroperoxide as the oxidant, mainly produce co-products such as tert-butyl alcohol or styrene, greatly restricting the economic benefit. However, when using cumene hydroperoxide (CHP) as the oxidant, the indirect oxidation processes can overcome the production of co-products, because the co-product of cumyl alcohol can be converted to CHP through hydrolysis and oxidation, resulting in the decrease of the cost. Therefore, the indirect oxidation using CHP as the oxidant has been attracting more attentions.

Although titanium silicalite zeolite (TS-1) is an excellent catalyst for the epoxidation of olefins [5], it exhibits very low catalytic performances for the epoxidation of bulky molecules due to its small pore diameter (less than 0.55 nm). Fortunately, the invention of titanium-containing mesoporous materials, such as Ti-MCM-41

[6], Ti-MCM-48 [7], Ti-HMS [8], Ti-MSU [9], can overcome this barrier. However, the loading amount and the dispersity of Ti greatly affect its reactivity. Among the methods to load Ti on the support, chemical vapor deposition (CVD) is a useful method for the preparation of highly dispersed Ti-containing catalyst, through the reaction of the active sites such as silanol groups (Si–OH) on catalyst surface with vaporous metal compounds [10]. For instance, the Ti supported MCM-41 catalysts have been prepared by CVD method and show high activity for the epoxidation of propylene [11,12]. We have also prepared the titanium modified SBA-15 catalysts by CVD method and investigated the effect of the method for removing the surfactant of SBA-15, the temperature and time of $TiCl_4$ deposition on the Ti content and catalytic performances of Ti-SBA-15 for the epoxidation of propylene with CHP [13]. Compared with the Ti-SBA-15 catalysts prepared by the hydrothermal synthesis and the impregnation method, the Ti-SBA-15 catalysts prepared by the CVD method show more excellent activity for the epoxidation of propylene. In this paper, a series of SBA-15 supports have been prepared by hydrothermal method and the effect of SBA-15 support on the catalytic performances of Ti-SBA-15 for the propylene epoxidation has been studied.

On the other hand, it has been proposed that the catalytic performances of mesoporous molecular sieves for the epoxidation of olefins can be improved significantly by the surface modification [14–16]. Among these methods, silylation is the most common way to modify the physical and chemical properties of the

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molecular sieves surface. For example, the silylated Ti-TUD-1 catalyst shows better activity than unsilylated Ti-TUD-1 catalyst [17] in the epoxidation of olefins with organic hydroperoxides as oxidants. Similarly, the silylated Ti-HMS catalyst exhibits better activity in the epoxidation of propylene than unsilylated Ti-HMS catalyst due to the decrease of remaining surface silanol groups [18]. To the best of our knowledge, no work on the epoxidation of propylene with CHP as the oxidant over methyl-grafted Ti-SBA-15 prepared by the CVD method has reported yet. In this paper, methyl-grafted Ti-SBA-15 catalysts were prepared and the effect of the silylation on the catalytic performances of Ti-SBA-15 for the propylene epoxidation was studied.

2. Experimental

2.1. Preparation of mesoporous SBA-15

Different mesoporous SBA-15 samples were prepared by the similar methods with the reference [19]. The typical synthesis procedure of the first kind of SBA-15 sample was as follows: 1.8 g of P123 ($EO_{20}PO_{70}EO_{20}$, M_{av} = 5800, Aldrich) and 1.8 g of glycerol were dissolved in 69 g of 1 M HCl aqueous solution. Then 3.9 g of tetraethyl orthosilicate (TEOS) was added to the above solution under vigorous stirring. A typical reaction composition was 1.8 g P_{123}: 30 g H_2O: 1.8 g glycerol: 69 g 1 M HCl: 3.9 g TEOS. After kept at 40 °C for 20 h without stirring, the synthesis gel was transferred into a Teflon-lined autoclave and heated to 100 °C for 24 h. The solid particles produced were collected by filtration, dried at 100 °C, and calcined at 550 °C for 6 h in air to remove the template. The sample prepared was denoted as SBA-15-st.

The second kind of mesoporous SBA-15 sample was prepared according to above procedure except that dimethylformamide (DMF) was used as a cosolvent and the synthesis gel was stirred at 40 °C for 20 h before transferred into Teflon-lined autoclave. A typical reaction composition was 2.0 g P123: 30 g H_2O: 15 g DMF: 30 g 4 M HCl: 4.4 g TEOS. The sample prepared was denoted as SBA-15-nd.

The third kind of mesoporous SBA-15 sample was synthesized by using a cationic surfactant, cetyltrimethylammonium bromide (CTAB), as a cosurfactant according to above procedure. The typical reaction composition was 2.0 g P123: 0.2 g CTAB: 15 g H_2O: 45 g 2 M HCl: 5.8 g TEOS. The mixture was stirred at 40 °C for 20 h before transferred into Teflon-lined autoclave. The sample prepared was denoted as SBA-15-rd.

The fourth kind of mesoporous SBA-15 sample was synthesized by prehydrolyzing TEOS in ethanol (EtOH) solution to obtain an oligomeric silica sol [20,21]. Then the silica sol was added to the mixture of P123 and inorganic salts in water and ethanol. After being stirred at 40 °C for 20 h, the solution was transferred into Teflon-lined autoclave. The final composition of the mixture was 2.0 g P123: 14.7 g EtOH: 1.4 g $MgSO_4$: 13.44 g H_2O: 2.4 g TEOS. The sample prepared was denoted as SBA-15-th.

2.2. Preparation of Ti-SBA-15 by CVD

The CVD process was carried out on a quartz tube reactor [11]. 3 g of SBA-15 was put into the quartz tube and pretreated in nitrogen (150 ml/min) at 200 °C for 1 h. After the CVD reactor was heated rapidly to the 700 °C at the rate of 10 °C/min, a gaseous feed of $TiCl_4$ vapor in nitrogen was introduced into the reactor with a flow rate of 150 ml/min for 1.5 h. Finally, the reactor was blown with the nitrogen (150 ml/min) at 400 °C for 2 h. The samples using SBA-15-st, SBA-15-nd, SBA-15-rd and SBA-15-th as the silica matrix were denoted as Ti-SBA-15-st, Ti-SBA-15-nd, Ti-SBA-15-rd and Ti-SBA-15-th, respectively.

2.3. Silylation of Ti-SBA-15

The silylated Ti-SBA-15-rd catalysts were prepared according to the literature [18]. 1 g of Ti-SBA-15-rd was mixed with the mixture of 1 g of hexamethyldisilazane (HMDSZ) and 30 ml of cumene, and then was refluxed at 160 °C for 4–12 h. Finally, the sample was collected by filtration and dried at 100 °C overnight. The sample prepared was denoted as Ti-SBA-15-rd-(x), where x was the reflux time at 160 °C.

2.4. Characterization of samples

The X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max2550VB/PC diffractometer with Cu Kα radiation (λ = 1.5496 Å) at 40 kV and 40 mA. N_2 adsorption–desorption isotherms were measured at −196 °C on a Micromeritics ASAP 2020 M apparatus. Before the measurement, the sample was outgassed at 180 °C for 12 h. The specific surface area of sample was assessed by the Brunauer–Emmett–Teller (BET) method. The pore size distribution curve was calculated from the desorption branch by using the Barrett–Joyner–Halenda (BJH) method. The Fourier Transform Infrared (FT-IR) spectra were carried out on a Nicolet NEXUS 670 FT-IR spectrometer, and the sample was ground with KBr and pressed into thin wafer. In order to detect the amount of hydroxyl groups on SBA-15 surface, a little of liquid paraffin was mixed with SBA-15 sample and then was grinded to a paste. The FT-IR spectra were carried out by coating the paste on salt slice. The UV–vis spectra were recorded on a Varian Cary 500 spectrophotometer using the diffuse reflectance technique in the range of 200–800 nm with $BaSO_4$ as the reference. TG analysis was carried out on a Pyris Diamond TG/DTA instrument at a heating rate of 20 °C/min in air. The titanium content of the catalyst was determined with an inductively coupled argon plasma (ICP, TJA IRIS 1000) after the sample was solved in the solution of HF-$HClO_4$. The content of total methyl groups in the silylated MCM-41 was determined by the CHN elemental analysis, which was performed on a vario EL III elemental analyzer.

2.5. Epoxidation of propylene

The catalytic performances of the samples for the epoxidation of propylene with cumene hydroperoxide (CHP) as the oxidant were tested as follows. The mixture of 0.3 g of catalyst, 10 ml of CHP (48%, industrial) and 20 ml of *tert*-butyl alcohol were placed into the autoclave, and then propylene was charged to 0.55 MPa at 5 °C. This mixture was heated to 80 °C under magnetic stirring and kept at 80 °C for 4 h, in which the pressure increased from 0.55 MPa at 5 °C to 2.4 MPa at 80 °C. After the end of the reaction, the autoclave was cooled immediately in an ice-bath before opening the reactor, and the liquid phase at about 0 °C was analyzed by a PerkinEimer Claus 500 Gas Chromatograph equipped with a flame ionization detector (FID) and AE.PEG-20 M separation column (30 m × 0.32 mm), and toluene was used as an internal standard. The conversion of CHP was determined by an iodometric analysis. The conversion of CHP (X_{CHP}), the selectivity to PO (S_{PO}) for CHP and the yield of PO (Y_{PO}) were calculated as follows:

$$X_{CHP} (\%) = \frac{n^i_{CHP} - n^t_{CHP}}{n^i_{CHP}} \times 100$$

$$S_{PO} (\%) = \frac{n_{PO}}{n^i_{CHP} - n^t_{CHP}} \times 100$$

$$Y_{PO} (\%) = (S_{CHP} \times X_{CHP}) \times 100$$