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Selective synthesis of propylene oxide through liquid-phase epoxidation of propylene with H_2O_2 over formed Ti-MWW catalyst

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ABSTRACT

The liquid-phase epoxidation of propylene to propylene oxide (PO) over formed titanosilicate catalysts was investigated in a fixed-bed reactor. The effects of reaction temperature, $n(C_3^=)/n(H_2O_2)$ molar ratio, and weight hourly space velocity (WHSV) of H_2O_2 or solvent on the catalytic performance of the formed Ti-MWW catalyst have been extensively studied. Adding an appropriate amount of ammonia to the reaction mixture prolonged the catalyst lifetime effectively. The main byproduct of propylene glycol (PG) and other heavy byproducts with high boiling points were deposited inside zeolite micropores, which corresponded to the main reason for the catalyst deactivation. The high-temperature calcination in air recovered readily the reactivity of the deactivated catalyst. Fluorine implantation remarkably enhanced the reactivity and lifetime of the catalyst in the hydrogen peroxide propylene oxide (HPPO) process, exhibiting a PO selectivity of >99%.

1. Introduction

Propylene oxide (PO) is one of the most important epoxide chemicals, useful for the manufacture of polyether polyols, propylene glycols, and propylene glycol ethers [1]. PO production capacity reached approximately 10 million metric tons in 2012 and continues growing at an annual rate of about 5% [2,3]. The current commercial routes for PO production are the classic chlorohydrin process and variations of the hydroperoxide process, including the propylene oxide/styrene monomer process (PO/SM), the propylene oxide/*t*-butyl alcohol process (PO/TBA), the cumene hydroperoxide-based process (CHPO), and the titanosilicate-based hydrogen peroxide propylene oxide process (HPPO).

The chlorohydrin process was first developed by Wurtz for the synthesis of ethylene oxide (EO) and PO in 1859. This route has played a critical role for many decades and it is even currently widely employed in the production of PO. However, it suffers serious problems of equipment corrosion and environmental pollution. Thus, it has been gradually replaced by more environmentally benign processes using hydroperoxides as oxidants. For co-production processes such as the PO/SM and PO/TBA techniques, the demand and pricing of the co-products styrene monomer (SM) or *t*-butyl alcohol (TBA) may not economically match those of PO well, making the process optimization difficult. Moreover, in the past few years, the fairly stagnant styrene monomer market and the increasing limitation of methyl *t*-butyl ether (MTBE) in gasoline [4] restricted the further development of such PO processes. In 2006, Sumitomo Chemical Co. Ltd. developed an innovative process free of co-product using cumene hydroperoxide as an oxidant, in which the intermediate cumyl alcohol was reduced to cumene with costly hydrogen for recycling. The CHPO process exhibits an obvious advantage in terms of avoiding a co-product, but it requires energy-consuming multiple steps including cumene oxidation, propylene epoxidation, and reduction of alcohol intermediate.

The HPPO process is a more ecoefficient method for selective production of PO, in which the catalytic epoxidation of propylene hydrogen peroxide is carried out on titanosilicate catalysts under mild reaction conditions (313–323 K and 2–3 MPa), giving water as the main byproduct. The development of the HPPO process dates back to 1983, when ENI patented a titanosilicate (TS-1) as a useful catalyst for this process [5]. Subsequently, there have been many fundamental researches focusing on the synthesis of TS-1 catalysts [6–13] and the investigation of propylene epoxidation with different reaction conditions [14–16], reactors [3,17,18], and additives [19,20], as well as the reaction mechanism and kinetics of this process [1,14,21–23]. Based on deep understanding of the

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HPPO process, Evonik and SKC launched a commercial plant in South Korea in 2008 with a capacity of 100 Kton/yr, and this plant is operated continuously at maximum capacity [24]. The next year BASF and DOW Chemical launched a similar plant based on HPPO technology in Belgium, with a higher capacity of 300 Kton/yr [25]. Later, the HPPO plants were widely used for the production of PO and they have been launched around the world [26,27]. However, all the commercial HPPO processes adopt without exception the catalytic system TS-1/H_2O_2/methanol. With methanol as the optimized solvent, the separation of PO from the reaction system has high energy consumption due to the zeotropic problem of methanol and PO. Moreover, the solvolysis of PO with the protic methanol solvent would inevitably decrease the PO selectivity. In addition, the manufacturing cost of TS-1 is always an obstacle to its industrial application, because extremely expensive tetrapropylammonium hydroxide (TPAOH) is required as the structure-directing agent (SDA) for the crystallization of TS-1. Hence, it is desirable to develop a more suitable titanosilicate for the HPPO process.

In our earlier work [28], we conducted a HPPO batch reactor process over Ti-MWW, which preferred an aprotic solvent of acetonitrile and showed superior performance to TS-1. Benefiting from the weak basicity of acetonitrile, the solvolysis of PO was effectively suppressed to make the PO selectivity high level 99%. A certainly cheaper SDA of piperidine (PI) or hexamethyleneimine (HMI) is used for the synthesis of Ti-MWW [29]. On the other hand, possessing a special lamellar structure different from that of the conventional three-dimensional zeolites with rigid structures, Ti-MWW is readily structurally modifiable by swelling [30], full delamination [30], partial delamination [31], pillaring [32], and silylation [33,34]. Moreover, the structural rearrangement [35,36] or fluorination treatment [37,38] was effective to enhance the reactivity of Ti-MWW.

In the present study, we investigated the HPPO process in the fixed-bed reactor-formed Ti-MWW catalysts. The effects of reaction temperature, the molar ratio of propylene to H_2O_2, the concentration of ammonia, and the weight hourly space velocity (WHSV) of H_2O_2 or solvent on this HPPO process were systematically studied. We have studied the causes of catalyst deactivation as well as the optimized reaction conditions for prolonging the catalyst lifetime. Additionally, the formed Ti-MWW catalyst was chemically modified to enhance its HPPO catalytic performance by structural rearrangement or fluorination.

2. Experimental

2.1. Catalyst preparation

2.1.1. Synthesis of the active component of Ti-MWW zeolite powder

The Ti-MWW powder was hydrothermally synthesized using boric acid as a crystallization-supporting agent and PI as a SDA in two steps as follows: the synthetic gels with molar composition 1.0 SiO_2:0.05 TiO_2:1.4 PI:0.67 B_2O_3:19 H_2O were hydrothermally crystallized at 443 K for 7 days, and then the obtained powder was refluxed in a 2 M HNO_3 aqueous solution to remove extra-framework Ti species and part of framework boron as well [29]. Finally, the acid-washed product was filtered, washed with deionized water to pH 7, dried at 393 K overnight, and calcined at 823 K for 6 h (denoted as Ti-MWW powder).

2.1.2. Preparation of formed Ti-MWW catalyst

The catalyst shaping was performed by an extrusion procedure from a homogeneous paste of zeolite active component, silica binder, and pore generator. A solution of 66.7 g silica sol (30 wt.%) was added dropwise into a mixture of 80 g Ti-MWW powder and 5 g Sesbania cannabina Pers powder under grinding. Then a certain amount of deionized water was added to the mixture to adjust the hardness of the paste. Finally, the paste was extruded into ∅ 1.8 mm strips, dried at 393 K overnight, and calcined at 823 K for 6 h (denoted as formed Ti-MWW).

2.1.3. Preparation of chemically modified Ti-MWW catalyst

Two different modification methods were employed to enhance the performance of the catalyst. First, the extrudates were subjected to hydrothermal structural rearrangement treatment in an aqueous PI solution according to the procedures adopted previously for the Ti-MWW powder [35,36]. The treatment was carried out under rotation (10 rpm) at 443 K for 1 day at a PI/SiO_2 molar ratio of 0.4 and a H_2O/SiO_2 molar ratio of 10. The treated product was washed with deionized water, dried at 393 K overnight, and calcined at 823 K for 6 h, and was denoted as formed Re-Ti-MWW. Second, following previously reported fluorination for the titanosilicate powder [39], we conducted the treatment of the extruded catalysts in a solution of methanol and NH_4F at 443 K for 1 day at an NH_4F/SiO_2 molar ratio of 0.05 and a MeOH/SiO_2 molar ratio of 20. The product was then dried at 393 K overnight and calcined at 823 K for 6 h (denoted as formed F-Ti-MWW).

2.2. Characterization methods

The X-ray diffraction (XRD) pattern was recorded on a Rigaku Ultima IV diffractometer using Ni-filtered Cu$K\alpha$ radiation ($\lambda = 0.1541$ nm) in a scanning range of 5–35° at a scanning rate of 10° min^{-1} to confirm the structure and crystallinity of the catalysts. The voltage and current were 35 kV and 25 mA, respectively. The morphologies and crystal sizes were examined by a Hitachi S-4800 scanning electron microscope. The UV–visible spectra were collected on a PerkinElmer UV–vis Lambda 35 spectrophotometer using $BaSO_4$ as a reference. The IR spectra of hydroxyl stretching and pyridine adsorption were collected by a Nicolet Nexus 670 FT-IR spectrometer at a resolution of 2 cm^{-1}. In order to avoid the influence of absorbed water, a self-supported wafer that was placed in a quartz IR cell sealed with CaF_2 windows was evacuated at 723 K for 2 h; then the spectra in the hydroxyl stretching region were collected at room temperature. For pyridine spectra measurement, the pretreated wafer was exposed to a pyridine vapor at 298 K for 20 min, and then the absorbed pyridine was evacuated at 423 K for 0.5 h. In addition, the IR spectra in the region of organic functional group vibration were measured using a KBr technique. All the spectra were collected at room temperature. ^{29}Si MAS NMR spectra were recorded on a VARIAN VNMRS-400 MB NMR spectrometer. The content of titanium and boron was determined by ICP-AES on an IRIS Intrepid II XSP after the samples were dissolved in HF solution. The textural properties of the catalysts were determined by N_2 adsorption at 77 K using a BEL SORP instrument. Prior to the adsorption measurements, the samples were degassed in vacuum at 573 K for 6 h. The microporous volume was derived from the *t*-plot method [40]. According to the reported method [17], the mechanical strength of the formed catalysts was determined under different weights until the extrudates were crushed. Thermogravimetric (TG) analysis was carried out in a Netzsch Sta 4049 F3 apparatus in air with a heating rate of 10 K min^{-1} to 1073 K.

2.3. Liquid-phase epoxidation of propylene

2.3.1. Continuous reaction

As shown in Scheme 1, the continuous epoxidation of propylene was carried out in a fixed-bed reactor (11 cm length, 1 cm internal