One-pot synthesis of ethylene glycol by oxidative hydration of ethylene with hydrogen peroxide over titanosilicate catalysts

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ABSTRACT

The oxidative hydration of ethylene with aqueous hydrogen peroxide was investigated over various titanosilicate catalysts for the purpose of one-pot synthesis of ethylene glycol (EG). The effect of titanosilicate topology (Ti-MWW, TS-1, Ti-MCM-68 and Ti-MOR), solvent, Ti content, catalyst amount, H_2O/H_2O_2 ratio, reaction temperature and time on the EG production have been studied in detail. The Ti-MWW/H_2O_2/H_2O catalytic system showed the highest EG yield together with high H_2O_2 conversion and utilization efficiency for the oxidative hydration of ethylene. The mechanism for the titanosilicate-catalyzed hydration of ethylene oxide (EO) has also been considered, which then shed light on the active sites for the second step in the oxidative hydration of ethylene. The catalyst deactivation could be ascribed to that the target product of EG and other heavy by-products with high boiling points were deposited inside the channels. The used Ti-MWW can be reusable when subjected to the regeneration by high-temperature calcination. Amine-assisted structural rearrangement of Ti-MWW not only enhanced the catalytic activity but also improved its stability in the oxidative hydration of ethylene.

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1. Introduction

Ethylene glycol (EG) as the simplest diol is widely used as engine coolants, antifreezes as well as raw material for the manufacture of polyesters, cosmetics, and other down-stream products [1]. The global demand for EG had reached 25 million tons in 2014 and continues to grow at an annual increasing rate of around 5% [2]. The non-catalytic hydration of ethylene oxide (EO) to EG at elevated temperatures (423–493 K) still accounts for the major market share, since it was developed in 1937 by Union Carbide Corporation (UCC) [3,4]. However, large excess of water is required in most cases to inhibit the generation of the by-products of di-ethylene glycol (DEG) and tri-ethylene glycol (TEG) that are produced from self-condensation of EG, even though various homogeneous or heterogeneous catalysts have been developed over the past few decades for the selective hydration of EO, such as quaternary phosphonium halides [5], macrocyclic chelating compounds [6], polymeric organosilane ammonium salts [7], cation- and anion-exchange resins [8–11], supported metal oxides [12–15], and zeolites [12]. Recently, Yang et al. made a breakthrough in developing an efficient immobilized homogeneous catalyst with

high activity and EG selectivity for the hydration of EO at almost a stoichiometric H_2O/EO molar ratio (as low as 2) and mild reaction temperature (313 K), wherein Co^{III} (salen) was encapsulated in FDU-12 mesosilica-based nanoreactors [13]. Additionally, Li et al. also designed a nanoreactor with active Sn sites confined in Chabazite cages using SSZ-13 zeolite as the EO hydration catalyst [14], which exhibited similar catalytic performance with FDU-12-$[Co^{III}(salen)]$ catalyst.

Tandem catalysis, that enables multistep reactions to take place in one-pot, holds great potential for increasing the efficiency of chemical synthesis [15]. The direct synthesis of EG from ethylene and H_2O_2 through oxidative hydration, which formally involves a combination of ethylene epoxidation and subsequent EO hydration, could be a more economically viable process because it operates with the low-cost and easily available feedstock of alkenes, and requires no separation of epoxide after the first step. Titanosilicate containing tetrahedral Ti species in the framework is well known as efficient heterogeneous catalysts in the epoxidation of various alkenes [16–18]. It is a general phenomenon that the alkene epoxidation is accompanied with the ring-opening of epoxide in the presence of a protic solvent (methanol or water, etc.), due to the acidity related to titanosilicates and/or from catalytic systems [16,17,19–21]. Although some reports have made the attempts at direct synthesis of EG from ethylene and H_2O_2 over titanosilicates like TS-1 and Al-TS-1 [21], no substantial progress

has been made due to the difficulty of meeting the demand of high EG selectivity and H_2O_2 utilization simultaneously. Hence, it is highly desirable to develop a more suitable titanosilicate for clean production of EG through oxidative hydration of ethylene.

Recently, we reported that MWW-type titanosilicate (Ti-MWW) was a more effective catalyst for the selective oxidation of ethylene to EO with H_2O_2 in comparison to other titanosilicates (TS-1, Ti-MOR and Ti-Beta) [16]. Moreover, Ti-MWW showed superior reactivity and selectivity in various oxidation reactions [18], including alkene epoxidation, ketones or aldehydes ammoximation, amines and sulfides oxidation. With the special lamellar structure, Ti-MWW reactivity could be improved by structural modifications including swelling [22], delamination [22,23], pillaring and silylation [24–26]. Additionally, it has been demonstrated that the reactivity of Ti-MWW in the alkenes epoxidation can be further enhanced by the fluorination treatment [17,27,28], or structural rearrangement [29,30]. Ti-MWW is thus considered to be a suitable candidate for the oxidative hydration of ethylene to ethylene glycol.

In this present study, we applied Ti-MWW to the oxidative hydration of ethylene with the aim of producing EG efficiently and selectively. The effect of solvent on the oxidative hydration of ethylene has been investigated in detail by comparing Ti-MWW with conventional TS-1. The catalytic performance of other titanosilicates was also evaluated and compared with Ti-MWW. The effect of the reaction conditions on the oxidative hydration of ethylene over Ti-MWW were investigated in detail. In addition, the Ti-MWW catalyst was modified by structural rearrangement with the purpose to enhance the catalytic performance in oxidative hydration of ethylene.

2. Experimental

2.1. Catalyst preparation

According to the procedures reported previously [31], Ti-containing MWW precursors with different Si/Ti ratios were hydrothermally synthesized, wherein boric acid and piperidine (PI) were used as crystallization-supporting agent and structure-directing agent (SDA), respectively. The synthetic gels with molar compositions of 1.0 SiO_2: 0.01–0.04 TiO_2: 1.4 PI: 0.67 B_2O_3: 19 H_2O were crystallized at 443 K for 7 days in a Teflon-lined stainless-steel autoclave under tumbling conditions. After crystallization, the obtained precursor was refluxed in 2 M HNO_3 solution with the purpose of removing extra-framework Ti species as well as part of framework boron. The acid-treated products were filtered, washed with deionized water and dried at 353 K overnight. Subsequently, the sample was calcined in static air at 823 K for 6 h with a ramp rate of 1 K min^{-1}, denoted as [Ti, B]-MWW. B-MWW was prepared in the same way as Ti-MWW lamellar precursors without the introduction of tetrabutyl orthotitanate (TBOT). In order to remove the framework B^{3+} ions, both [Ti, B]-MWW and B-MWW zeolites were then subjected to hydrothermal treatment in H_2O at 373 K for 8 h and subsequent calcination in static air at 823 K for 6 h with a ramp rate of 1 K min^{-1}. The obtained products almost free of B were denoted as Ti-MWW and deB-MWW, respectively. For control experiments, MWW-type all silica ITQ-1 (Si/Al = ∞) [32], H-MCM-22 aluminosilicate (Si/Al = 18) [33], and other titanosilicates of Ti-MCM-68 [34], TS-1 [35], and Ti-MOR [36], were also prepared according to the established literature.

In order to adjust the solid acidity of Ti-MWW, sodium ion-exchange was performed in 1 M aqueous $NaNO_3$ or NaOAc solution with a solid-to-liquid weight ratio of 1:100 at room temperature for 24 h. Then, the obtained sample was filtered, washed with deionized water until the Na^+ amount in the filtrate is lower than

10 ppm, and dried at 353 K overnight to get the corresponding sample of $NaNO_3$-Ti-MWW or NaOAc-Ti-MWW. The structural rearrangement treatment for Ti-MWW was performed with the composition of SiO_2: 0.4 PI: 10 H_2O at 443 K for 1 day under rotation condition (10 rpm) [29,30]. The treated product was washed with deionized water, dried at 393 K overnight, and calcined in static air at 823 K for 6 h with a ramp rate of 1 K min^{-1}, denoted as Re-Ti-MWW.

The adsorption of EG was carried out by vigorous stirring the mixture of 0.5 g of Ti-MWW or H-MCM-22 and 50 g of 1 M EG aqueous solution at 303 K for 24 h. The EG absorbed samples were separated from the above-mentioned mixture and dried at 353 K for 12 h, denoted as EG/Ti-MWW and EG/H-MCM-22, respectively.

2.2. Characterization methods

The crystalline structures of various titanosilicates were confirmed by X-ray diffraction (XRD) on a Rigaku Ultima IV diffractometer using Ni-filtered Cu Kα radiation. Scanning electron microscopy (SEM) images were collected on a Hitachi S-4800 microscope to show the crystal morphologies. The amounts of Na, Si, Ti, Al and B were determined by inductively coupled plasma (ICP) on a Thermo IRIS Intrepid II XSP after the samples were dissolved in aqueous HF solution. The coordination states of Ti species were examined by UV–visible spectroscopy on a Shimadzu 2700PC spectrophotometer using $BaSO_4$ as a reference. Infrared spectra were collected by a Nicolet Nexus 670 FT-IR spectrometer at a resolution of 2 cm^{-1}. The spectra were obtained using self-supported wafers with a diameter of 2 cm (10 mg cm^{-2} thickness), except that the spectra in the region of framework vibration (500–1300 cm^{-1}) were recorded using a KBr pellet technique (3 wt% diluted in KBr). In order to avoid the influence of absorbed water, the self-supported wafer or the KBr diluted wafer placed in a quartz IR cell sealed with CaF_2 or KBr windows, respectively, was evacuated at 723 K for 2 h before measurement. For pyridine spectra measurement, the pretreated self-supported wafer was exposed to a pyridine vapor at 298 K for 20 min, and then the physisorbed and chemisorbed pyridine was then removed by evacuation at different temperature (323–523 K) for 0.5 h. In addition, the in-situ IR analysis of EG/Ti-MWW or EG/H-MCM-22 was carried out by evacuation at different temperature (373–473 K) for 5 min. Thermogravimetric (TG) analysis was carried out in a Netzsch Sta 4049 F3 apparatus in air with a heating rate of 10 K min^{-1} in the temperature range of 300–1073 K.

2.3. Catalytic reactions

The oxidative hydration of ethylene to EG with hydrogen peroxide was carried out under vigorous stirring in an autoclave reactor equipped with a telfon-inner. In a typical run, 0.1 g titanosilicate, 10 g H_2O, and 10 mmol H_2O_2 (30 wt%) were added into the reactor, and then ethylene was charged into the autoclave to replace the air inside three times, reaching a constant reaction pressure at of 2.5 MPa at 313 K. For the hydration of EO, it was also proceeded in the above-mentioned autoclave reactor. A mixture of catalyst, EO, H_2O and H_2O_2 (if added) was vigorously stirred at 313 K under N_2 pressure of 1.5 MPa. After specified reaction time, the reactor was cooled down with ice water to stop the reaction and depressurized slowly before opening.

The amount of unconverted H_2O_2 was determined by standard titration method with 0.05 M $Ce(SO_4)_2$ solution. The products were separated from the reaction mixture by centrifugation and determined by a gas chromatograph (Shimadzu 2014) equipped with an Rtx®-Wax capillary column (30 m × 0.25 mm × 0.25 μm) and FID detector using isopropanol as internal standard. The products formed were identified by a GC-MS (Agilent 6890 series GC system,