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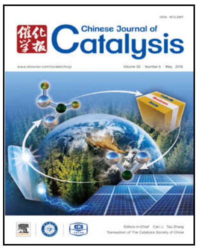

Article

Green and efficient epoxidation of methyl oleate over hierarchical TS-1

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ABSTRACT

The epoxidation of methyl oleate (MO) was conducted in the presence of aqueous H_2O_2 as the oxidant and hierarchical TS-1 (HTS-1) as the catalyst; the catalyst was synthesized using polyquaternium-6 as the mesopore template. The effects of various parameters, i.e., H_2O_2/C=C molar ratio, oxidant concentration, amount of the catalyst, reaction temperature, and time, were systematically studied. Furthermore, response surface methodology (RSM) was used to optimize the conditions to maximize the yield of epoxy MO and to evaluate the significance and interplay of the factors affecting the epoxy MO production. The H_2O_2/C=C molar ratio and catalyst amount were the determining factors for MO epoxidation, wherein the maximum yield of epoxy MO reached 94.9% over HTS-1 under the optimal conditions.

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1. Introduction

In order to address environmental issues, green chemistry-focused researchers typically concentrate on the application of various natural and renewable raw materials for the synthesis of polymeric materials. In particular, the use of vegetable oil-based materials have found numerous applications [1], such as stabilizers and plasticizers of thermoplasts [2,3], lubricants [4], and polymer precursors for the preparation of various polymers (such as polyesters [5], polyamides [6], and polyurethanes [7]). Compared to polymers made from petroleum-based resources, bio-polymers are biodegradable, non-toxic, environmentally friendly, and inexpensive. In general, prior to being suitable polymer precursors, vegetable oils must be modified by converting their double bonds into more reactive functional groups such as, epoxide, acrylate, or hydroxyl groups [8]. Among those groups, epoxides are the most promising candidatesdue to the potential application.

Industrially, the epoxidation of vegetable oils is currently carried out via the Prileshajew reaction [9], in which unsaturated oils react with percarboxylic acid, which is prepared using formic or acetic acid, as well as hydrogen peroxide in the presence of strong mineral acids such as H_2SO_4, HCl, or HNO_3 as catalysts. However, there are various drawbacks for this process, for example, the presence of the strong acid causes side reactions such as oxirane-ring opening, which produces diols, hydroxyesters, and other dimers [10], corrosions, in addition to issues associated with the separation of the water soluble mineral acid, etc. Hence, the exploration of heterogeneous catalysts is significant [11]. In this light, transition metal complexes such as Mo^{IV} [12], W^{VI} [13], Nb^{V} [14], and Ti^{IV} have emerged as catalysts for epoxidation reactions. Among them, Ti-containing materials, e.g., titanium-silica, Ti-MCM-41, and hierarchical TS-1 (HTS-1) [15–18] have been investigated due to their de-

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sirable activities and stabilities in epoxidations in the presence of hydrogen peroxide or organic hydroperoxides.

TS-1 is widely used as a highly selective and environmentally benign catalyst in the presence of H_2O_2 as an oxidant. However, the catalytic oxidation of bulkier substrates is limited due to steric constraints imposed by the 10 MR micropore apertures. Therefore, considerable efforts have been devoted to creating mesopores or macropores in crystalline TS-1 to increase the accessibility of bulky substrates to the internal surface, and consequently, enhance catalytic performance. In order to enhance the performance of HTS-1 in the epoxidation of bulky substrates, several methods such as dealumination, desilication, and other chemical treatments to form defect sites, hard or soft templating methods, have been introduced [19–25]. Recently, a new synthetic approach was developed by our group using low-cost and versatile polyquaternium-6 as a mesoporogen; the obtained materials contained remarkably active, easily accessible tetrahedral Ti sites and showed excellent oxidative desulfurization performance [26].

In general, olefin epoxidation is significantly influenced by the reaction conditions [27], such as the amount and concentration of the oxidant, reaction temperature and time, and amount of catalyst. Herein, in order to gain a deeper understanding of the influence of the aforementioned parameters on the epoxidation of vegetable oil-based unsaturated fatty acid methyl esters (FAMEs), epoxidation reactions were conducted using HTS-1 with polyquaternium-6 as a mesoporogen in the presence of hydrogen peroxide under different conditions. For simplicity, methyl oleate (MO) with only one C=C double bond was chosen as a model unsaturated FAME. Furthermore, three reaction variables, such as H_2O_2/C=C molar ratio, amount of catalyst, and temperature of the epoxidation process of MO were optimized. Response surface methodology (RSM)-based Box-Behnken Design in 17 experimental runs was used for the optimization using Design Expert 8.0.6 software.

2. Experimental

2.1. Catalyst preparation

HTS-1 was synthesized according to a literature procedure [26] using tetrapropylammonium hydroxide (TPAOH, 1.42 mol/L aqueous solution, Shanghai Kairui Chemical Co.) and polyquaternium-6 (39–43 wt.%, Haining Huangshang Chemical Co.) as micropore and mesopore structure-directing agents SDAs, respectively, as well as tetraethylorthosilicate (TEOS, Tianjin Kermel Chemical Co.) and tetrabutyltitanate (TBOT, Tianjin Kermel Chemical Co.) as silica and titanium sources, respectively. Briefly, 16.9 mL of an aqueous solution of TPAOH was added dropwise to 11.2 mL TEOS under vigorous stirring and the mixture was hydrolyzed for 1.5 h at room temperature. In a separate flask, 0.34 mL of TBOT was dissolved in 1.7 mL of isopropyl alcohol (IPA, Tianjin Kermel Chemical Co.), and then mixed with 10.1 mL of the TPAOH solution under stirring for 0.5 h to obtain a clear gel containing Ti. Next, both phases were mixed, stirred for 30 min and the alcohol was removed at 80 °C, followed by the addition of 2.0 g of polyquaternium-6. The resulting mixture was stirred for another 24 h. The molar composition of the synthesized gel was $1SiO_2$:$0.02TiO_2$:0.25TPAOH: 1IPA:$30H_2O$. The synthesized gel was transferred into a Teflon-lined stainless steel autoclave, in which the crystallization was continued at 170 °C for 96 h. Finally, the as-obtained solid was isolated by centrifugation, washed thoroughly with deionized water, dried at 100 °C overnight, and calcined at 550 °C for 8 h to remove the organic templates.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2400 diffractometer using Cu K_α radiation run at 40 kV and 100 mA with a scan speed of 6°/min and a scan step size of 0.02°. The electronic state of Ti in the titanosilicate samples was analyzed using a JASCO UV550 spectrometer with a white broad as the standard. FT-IR spectra were recorded on a Bruker EQUINOX55 spectrometer, using the KBr pellet technique. The titanium content of the samples was determined by elemental analysis via optical emission spectrometry with inductively coupled plasma (ICP-OES, PerkinElmer/Nex ION 300D). The crystal size and morphology were determined by a NOVA NanoSEM 450 scanning electron microscope (SEM) from FEI. N_2 physical adsorption-desorption measurements were carried out at −196 °C using a Quantachrome Autosorb-1MP after degassing the sample under vacuum at 350 °C. The total specific surface area and pore-size distribution were calculated from adsorption data employing the Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) adsorption algorithm, respectively. Total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.99 and the micropore volume was determined by the *t*-plot method.

2.3. Catalytic tests

The catalytic reactions were performed batchwise in a reactor equipped with a reflux condenser using acetonitrile (Tianjin Kermel Chemical Co.) as the solvent, H_2O_2 (50 wt.%, Shanghai HABO Chemical Co.) as the oxidant, and chlorobenzene (99.8%, Tianjin Kermel Chemical Co.) as the internal standard. All catalysts were pretreated at 120 °C in dry air for 2 h prior to use. The typical procedure was as follows: 10 mg of catalyst, 20 μL (58 μmol) of substrate (methyl oleate, 99 wt.%, Aladdin) and 10.5 μL (169 μmol, oxidant/substrate molar ratio = 2.9) of H_2O_2 were added to 5 mL of acetonitrile, followed by the addition of 15 μL chlorobenzene. The reaction mixtures were stirred at 90 °C for 9 h, and the catalyst was recovered by centrifugation.

The reaction products were identified by GC-MS (HP6890/MS5973) with a HP-5 capillary column (0.25 mm × 30.0 m × 0.25 μm). Three types of analysis were performed to quantify the epoxidation reaction results. (i) GC analysis, using an HP6890 GC equipped with an HP-5 capillary column (0.25 mm × 30.0 m × 0.25 μm) and FID detector; conversion was defined as the mass ratio of converted MO to the initial mass of reactant and selectivity was defined as $(\text{mol}_{\text{desired product}})/(\text{mol}_{\text{all}}$

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