



Highly efficient epoxidation of cyclohexene with aqueous H₂O₂ over powdered anion-resin supported solid catalysts

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ABSTRACT

Resin supported solid acid catalysts have extended the application of conventional solid acid catalysts in the field of selective oxidations. The present work describes selectively catalytic epoxidation of cyclohexene with aqueous 30% H₂O₂ over powdered anion-resin supported peroxo phosphotungstic acid heterogeneous catalysts prepared through a simple anion-exchange from powdered chloride-form anion resin without any special pre-exchanged treatment. Among these powdered solid catalysts, anion-exchanged resin D201 supported peroxo phosphotungstic acid exhibits the best activity for the titled reaction to obtain 92.4 mol% conversion and 98.1% selectivity of epoxide, for which D201-PWAR(4) behaves as a truly heterogeneous catalyst. Some factors such as various peroxo phosphotungstic acid concentrations, the oxidants, the solvents, the molar ratios of H₂O₂/cyclohexene, the catalyst amount, the reaction temperature and time play important roles in controlling the epoxidation.

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1. Introduction

The epoxidation reaction of olefins is one of the most important catalytic oxidation processes, the epoxy products of which as intermediates can be used in the synthesis of polymers, pharmaceuticals, fine chemicals and biological materials [1–3]. Epoxy compounds can be converted to a series of chiral compounds through ring-opening reaction, therefore receiving much attention [4].

Traditionally, the production of epoxy compounds is mainly conducted in the presence of organic peroxides [5] and inorganic hypochlorite [6]. However, these systems will generate a lot of low-value by-products and hazardous wastes to increase the cost. In order to overcome these disadvantages, hydrogen peroxide (H₂O₂) and molecular oxygen/air have been used as the oxidizing agents for the epoxidation of alkenes [7,8]. Among these oxygen donors, H₂O₂ is an important oxidant with respect to environmentally

cleanness and economic consideration [9]. So far, the epoxidation reactions have involved in the use of Schiff base complexes, metal phthalocyanine, metal porphyrins, heteropoly acids and Ti-containing zeolites as the catalysts [1,10–12].

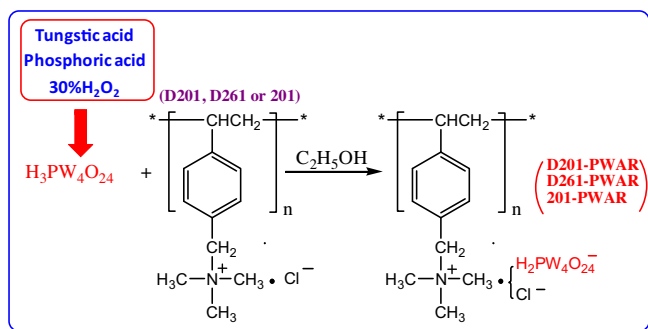
Anion resin is commonly used for water treatment, so as to improve the water quality [13,14]. The modified anion resin as the catalyst in recent years has been widely used in the synthesis of nitrile and ether [15,16], alkylation, aldol condensation, olefin hydration, elimination, rearrangement, and so on [17–19].

Currently, rhenium- and tungsten-based homogeneous compounds are the most active catalyst for the epoxidation using aqueous H₂O₂ [20]. In the case of tungsten chemistry, the most significant developments were made in the 1980s by Venturello et al. [21] and Ishii et al. [22], who used phosphotungsten-based catalysts in biphasic reaction media for the epoxidation of apolar olefins. Most of the tungsten catalysis reported is homogeneous and liquid biphasic system, with a quaternary ammonium compound enhancing phase transfer of peroxo W compound from aqueous to the organic layer [23–27]. In 1999 and 2000, PW-Amberlite catalyst, was prepared by ion-exchange of a peroxo PW-anion onto a specially-preformed nitrate form of a commercial macroreticular resin Amberlite IRA-900, in the presence of H₂O₂ [28,29]. However, the preparation process is slightly complicated since anion resin must be transferred into a special nitrate form prior to the ion-

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Scheme 1. Preparation route of the catalysts.

exchange, and the catalytic activity of the resulting catalyst for the epoxidation of cyclohexene is poor. In 2015, $PW_4-Zn(x)/SnO_2$ was prepared by using zinc-modified SnO_2 as the support, which could act as an efficient and reusable heterogeneous catalyst for selective oxidation with aqueous H_2O_2 oxidant [30]. The catalytic performance of $PW_4-Zn(0.8)/SnO_2$ was much superior to those of the corresponding homogeneous analogue THA_3PW_4 and the previously reported tungstate-based heterogeneous catalysts; however, no any report has approached its use in the epoxidation of cyclohexene.

In the present work, a simple synthesis route of peroxo phosphotungstic acid anion-exchanged resin (PWAR) heterogeneous catalysts is firstly developed. Through a simple anion-exchange of only chloride-form powdered anion-resin with peroxo phosphotungstic acid, an active solid catalyst is achieved, which has shown a very good catalytic activity for the epoxidation of cyclohexene with 30% H_2O_2 to obtain of 92.4 mol% conversion of cyclohexene and 98.1% selectivity of epoxide.

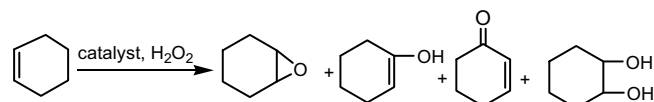
2. Experimental

2.1. Materials

Chloride-form anion resins (D201, D261, 201) are commercial products and ground into fine powder from ball before use. Note that three resins are styrene-divinylbenzene type ones containing exchangeable chloride anions. D201 and D261 are macroporous anion resins similar to Amberlite IRA-900, and 201 is gelatinous resin similar to Amberlite IRA-400, for which the compositions and anion-exchange capacities of these anion resins are shown in Scheme 1 and Table 2. Various alkenes and solvents underwent re-distillation treatment prior to use, inclusive of cyclohexene, cyclooctene, 1-hexene, styrene, 1-dodecene, allyl alcohol, chloropropene, α -pinene, acetonitrile (CH_3CN), ethyl alcohol (EtOH), ethyl acetate, acetone, methylbenzene, N,N' -dimethyl formamide (DMF), 1,4-dioxane, cyclohexane and dichloroethane. All other reagents were used as received without further purification, including hydrogen peroxide (30%, H_2O_2), tungstic acid (H_3WO_4), phosphoric acid (85%, H_3PO_4), aqueous *tert*-butyl hydroperoxide (65%, TBHP), sodium hypochlorite (NaClO) and cumyl hydroperoxide (>70%, CHP).

2.2. Preparation of catalysts

Anion resins that had been ground into fine powders required one pretreatment for the removal of impurities prior to use [31]. In a 100-ml 3-necked flask, the mixture of 2.5 g anion resin powder and 50 ml ethanol was refluxed at 80 °C for 24 h. Then, the solid powder was recovered by filtration and washed thoroughly with deionized water. Note that above-said two steps were repeated once. The recovered powder resin was washed by acetone, and then dried at



Scheme 2. Catalytic oxidation of cyclohexene with H_2O_2 .

80 °C for 2 h. In the meantime, 7.80 mmol tungstic acid, 1.95 mmol phosphoric acid, and 15 ml 30% H_2O_2 , and 40 ml water were added into a 100-ml 3-necked flask to obtain a mixture solution, which was stirred at 60 °C overnight. Subsequently, the powdered anion resin was added into a solution of preformed peroxo phosphoric acid and aged at 60 °C for 1 h under shaking, which was then heated to 80 °C for the anion-exchange treatment for 5 h. Finally, the powder resin catalyst was recovered by filtration, washed with deionized water until neutral, and then washed by acetone, followed by drying at 60 °C for 2 h. Besides, D201-PWAR catalysts with different P contents (0.70, 0.78, 0.84, 0.99 and 1.23 wt%) were prepared through above-said anion-exchange treatment of anion resin D201 with aqueous solutions of different P concentrations, and named as D201-PWAR(1), D201-PWAR(2), D201-PWAR(3), D201-PWAR(4) and D201-PWAR(5) (Scheme 1). Other anion resins (D261 and 201) underwent the same anion-exchange procedure to obtain the catalysts D206-PWAR and 201-PWAR.

2.3. Characterization

X-ray diffraction (XRD) patterns of samples were recorded on a Rigaku D/MAX-IIIC diffractometer with $Cu\ K\alpha$ radiation ($\lambda = 1.54184\text{ \AA}$) operating at 30 kV and 25 mA. The average crystal sizes were estimated from SEM images, which were observed using a JEOL JSM 6500 F scanning electron microscope (SEM) operating at an accelerating voltage of 25 kV and a tube current of 100 μA under vacuum at 10^{-6} mbar, where the setup was coupled to an Energy Dispersive Spectrometer (EDS) for micro-analysis. UV-vis spectra of samples was determined on a Shimadzu UV-2550 spectrometer. The Kubelka–Munk function was used to convert reflectance measurements into equivalent absorption spectra using the reflectance of $BaSO_4$ as a reference, and to obtain absorption edge energies directly from the curves. Thermogravimetric analysis (TGA) of the catalysts was performed on a Mettler Toledo TGA/SDTA851e under N_2 flowing of 60 ml/min at heating rate of 20 °C/min up to 800 °C.

2.4. Epoxidation of cyclohexene

The catalytic epoxidation of cyclohexene (Scheme 2) was carried out in a 25-ml single-necked round-bottom glass flask equipped with a cryogenic-liquid condenser under atmospheric pressure. Typically, 10.0 mmol of cyclohexene, 12.0 mmol of H_2O_2 , 5.0 g of acetonitrile and 350 mg of the catalyst were added into the reactor. Note that H_2O_2 was added by four times and each time lasted ten minutes. The mixture was vigorously stirred by a magnetic stirrer and heated to desired temperature in a water bath. After the completion of the reaction, the solid powder catalyst was recovered by filtration and washed thoroughly with acetone and ethanol, and dried at 60 °C overnight for the next use. The liquid filtrate was analyzed by a gas chromatograph equipped with a capillary column (SE-30, 30 m \times 0.25 mm \times 0.25 μm) and an FID detector, in which chlorobenzene was used as an internal standard to quantify all the components. The cyclohexene conversion and the epoxide selectivity were calculated by using Eqs. (1) and (2).

$$\text{Cyclohexene conversion(mol\%)} = \frac{\text{moles of cyclohexene reacted}}{\text{total moles of cyclohexene}} \times 100 \quad (1)$$

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