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Original article

Preparation of high purity 1,2-diols by catalytic oxidation of linear terminal alkenes with H_2O_2 in the presence of carboxylic acids under solvent-free conditions



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ABSTRACT

The oxidation of terminal alkenes was smoothly catalyzed by a recyclable and environmentally friendly catalytic system: $[(C_{18}H_{37})_2N(CH_3)_2]_3[PW_4O_{16}]/H_2O_2/formic acid. This new catalytic system is not only capable of catalyzing oxidation of terminal alkenes with a phase-transfer character, but also under solvent-free conditions, avoiding the use of chlorinated solvents. Many different kinds of terminal alkenes could be converted to the corresponding 1,2-diols of high purity in high yields. The catalyst could be easily separated and reused after reaction. Both fresh and used <math>[(C_{18}H_{37})_2N(CH_3)_2]_3[PW_4O_{16}]$ catalyst was characterized by Raman and FTIR.

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1. Introduction

1,2-Diols are important chemical raw materials for a wide variety of chemicals such as polyesters, surfactants, pharmaceutical raw materials and so on. The preparation of straight-chain 1,2-diols is mostly carried out by the epoxidation of olefins followed by the hydrolysis of the epoxides. The oxidation of olefins is the most significant step in preparing 1,2-diols, so it has attracted more and more attention in recent years [1,2].

In the past decades, an extensively studied epoxidation system relevant to heteropolytungstophosphates was the Venturllo–Ishii system, but drawbacks of the Venturello–Ishii epoxidation are the use of chlorocarbons solvents and catalyst deactivation, causing difficulties in a catalyst cycle [3]. In order to solve this problem, heterogenization of such catalysts has been studied in many ways [4–12]. Recently, Xi reported a reaction-controlled phase-transfer catalysis for the epoxidation of olefins with H₂O₂ generated in situ or commercially available 30% H₂O₂ as the oxidant [13], Chen reported the nature of reaction-controlled phase transfer catalysts for the epoxidation of olefins using ³¹P NMR technique [14]. Hua reported [π -C₅H₅N(CH₂)₁₅CH₃]₃ [PMoW₃O₂₄], an efficient and recyclable heteropolyoxomolybdotungstate catalyst for the epoxidation of 1-octene with 30% H₂O₂ using environmentally friendly

solvent [15]. However, the oxidation of olefins using H_2O_2 in the presence of carboxylic acids was scarcely studied, because peracids that was produced by the reaction of carboxylic acids and hydrogen peroxide (HP) are difficult to handle, but they are vital in the process. Formic acid (FA) can ionize under reaction conditions and the formation of performic acid (PFA) is fast enough even without the presence of mineral acids, a phenomena known as formic acid-autocatalyzed [16] preparation of PFA. PFA was generated by the reaction between FA and HP in aqueous phase and then quickly consumed in the epoxidation reaction in organic phase.

In this paper, we report our initial results on the research in which a tungsten-based polyoxometalate, $[(C_{18}H_{37})_2N(CH_3)_2]_3$ [PW₄O₁₆] (abbreviated as Cat. I) was synthesized and used as a phase-transfer catalyst for the oxidation of terminal alkenes with H₂O₂ in the presence of carboxylic acids under solvent-free conditions. This system can be used for the catalytic oxidation of olefins and exhibits high conversion and yield. After reaction, the catalyst can be precipitated from the reaction medium and reused as a heterogeneous catalyst. Therefore, this catalytic system possesses the advantages of both heterogeneous and homogeneous catalysts.

2. Experimental

* Corresponding author. E-mail address: libindong@mail.njust.edu.cn (B.-D. Li). All solvents and chemicals were of analytical grade, commercially available and used without further purifications unless mentioned otherwise.

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2.1. Preparation of catalysts

The catalyst $[(C_{18}H_{37})_2N(CH_3)_2]_3[PW_4O_{16}]$ (Cat. I) was prepared according to the literature [17]. A suspension of tungstic acid (5.0 g, 20 mmol) in 16.5 mL of 30% aqueous H_2O_2 was heated at 60 °C for 15 min. H_3PO_4 (40%, 1.24 mL, 5.0 mmol) was added to the obtained colorless solution at room temperature and the whole solution was diluted with another 40 mL of water and then stirred for 30 min. To the resulted solution, 6.0 g of dioctadecyl dimethyl ammonium chloride (10 mmol) in dichloromethane (80 mL) was added dropwise with stirring. After the solution was stirred continuously for 30 min, the organic phase was separated, dried over anhydrous Na₂SO₄, filtered and then the solvent was removed at 60 °C under atmospheric pressure. A yellow dry powder was obtained by further evaporating under reduced pressure.

The catalysts with different quaternary ammonium cations were similarly prepared using cetylpyridinium chloride (π -C₅H₅NC₁₆H₃₃Cl), hexadecyl trimethyl ammonium chloride (C₁₆H₃₃N(CH₃)₃Cl) and tetrabutylammonium hydrogen sulfate (Bu₄NHSO₄), denoted as Cat. II, Cat. III and Cat. IV, respectively.

2.2. Characterization techniques

The laser Raman experiments were performed using a Jobin Yvon ARAMIS, Raman spectrometer equipped with a CCD (Te RAMAN-1024 \times 256-OPEN-SYN) detector and the spectrum resolution of 1 cm⁻¹ using a laser at 532 nm as the excitation source. The infrared spectra were recorded on a Nicolet IS10 FT-IR spectrometer.

2.3. Catalytic oxidation of terminal alkenes to 1,2-diol

The catalytic reactions were performed in a 50 mL four-necked round-bottomed flask equipped with a reflux condenser. The assembly was kept in an isothermal water bath at a constant known temperature and mechanically agitated with an electric motor. The oxidation was carried out as follows: catalyst (0.12 mmol), terminal alkenes (30 mmol), H₂O₂ (30% ag., 40 mmol) and FA (60 mmol) were charged in the reaction flask. The catalyst/ olefin ratio was 1:250 for all the reactions. When the oxidation reaction was over, the catalyst was precipitated from the reaction medium for further use when acetone was subsequently added to the solution, the precipitate was removed by centrifugation and filtration, and the filtrate extracted with CH_2Cl_2 (50 mL \times 3); the organic layer was collected and dried under anhydrous Na₂SO₄. After the evaporation of the solvent under reduced pressure, a solution of sodium hydroxide was added dropwise to the organic product to give high purity 1,2-diols. The organic product was analyzed by GC9600 using an internal standard method. Typical GC-MS analysis was also conducted to identify the products.

3. Results and discussion

3.1. Catalysts with different cations

The oxidation of terminal olefins is the more difficult but important step in the alkene/diol transformation. In our catalytic system, the oxidation of terminal olefins generates some byproducts that can be transformed to the corresponding 1,2-diol in high yield (Scheme 1).

Chen *et al.* [14] have reported that cations played a significant role in phase-transfer catalytic oxidation. It was found that the choice of proper cations is crucial for the precipitation of heteropoly species from the reaction media. Three more catalysts with different cations, $[\pi$ -C₅H₅NC₁₆H₃₃]⁺, $[C_{16}H_{33}N(CH_3)_3]^+$ and $(Bu_4N)^+$, were synthesized.



Scheme 1. The process of phase-transfer catalysis for preparation of 1,2-diol.



Fig. 1. IR spectra of the catalysts with different cations. (A) $[(C_{18}H_{37})_2N(CH_3)_2]^*$; (B) $[Bu_4N]^*$; (C) $[C_{16}H_{33}N(CH_3)_3]^*$; (D) $[\pi$ - $C_5H_5NC_{16}H_{33}]^*$.

For catalyst Cat. I, its IR spectrum (Fig. 1A) gives a strong peak at 840 cm⁻¹, which indicates that the catalyst still contain active oxygen. For catalyst Cat. II, its IR spectrum (Fig. 1D) indicates it is a mixture of $[PW_{11}O_{39}]^{7-}$ and $[PW_{12}O_{40}]^{3-}$, as demonstrated by the following resonances: $\nu(PO_4)$ 1077 cm⁻¹; $\nu(W=O)$ 967 cm⁻¹; $\nu(W-O_b-W)$ 880 cm⁻¹. The IR spectra of fresh catalysts showed almost no active oxygen (Fig. 1B and C). So the nature of quaternary ammonium cation affects the composition of the catalyst, and bigger cation can more efficiently stabilize active oxygen.

The oxidation of 1-octene catalyzed by a series of catalysts was conducted in the H_2O_2 /formic acid system, and the results are summarized in Table 1. Cat. I showed the highest activity (entry 1) and a 91.2% yield of 1,2-octanediol was obtained. The activity of Cat. II was similar to that of Cat. I and a 80.4% yield of 1,2-octanediol was obtained. The activity of Cat. IV was not as good as that of Cat. I and the yields of 1,2-octanediol were 73.1%

Table 1
Oxidation of 1-octene catalyzed by various catalyst. ^a

Entry	Catalyst	Conversion ^b (mol%)	Yield ^c (mol%)
1	Cat. I	98	91.2
2	Cat. II	88	80.4
3	Cat. III	81	73.1
4	Cat. IV	67	60.6
5	1	58	51.9

 $^a\,$ Reaction conditions: olefin (30 mmol); H_2O_2 (40 mmol); catalyst (0.12 mmol); FA (60 mmol).

^b Conversion was determined by gas chromatography using an internal standard technique and was based on 1-octene.

^c Yield was also based on olefin, yield (%) = 1,2-diol (mol)/1-octene (mol) × 100%.

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