

# Heterocycle-modified 12-tungstophosphoric acid as heterogeneous catalyst for epoxidation of propylene with hydrogen peroxide



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## ABSTRACT

12-Phosphotungstic acid (PWA)-based complex catalysts for propylene epoxidation were prepared by modification with nitrogen-containing heterocycles such as imidazole, pyrazole and 1,2,4-triazole. Heterocycles played an important role in promotion of the catalytic activity and selectivity to propylene oxide, mostly due to the strong electronic interactions between heterocycles and terminal tungsten-oxygen on PWA. Propylene epoxidation over the complex catalyst seriously depended on the pressure and the temperature, favoring high pressure and low temperature for improved conversion and yields, respectively. The complex catalysts maintained good thermal stability up to 450 °C as well as recycling performance for 5 reaction runs without any significant loss of catalyst, suggesting that they are promising heterogeneous catalysts on propylene epoxidation.

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## 1. Introduction

Owing to wide usage of epoxides as raw material for some resins, paints, surfactants and intermediates in organic synthesis, propylene epoxidation is regarded as one of the important reaction in the field of chemical industry producing propylene oxide over 4.5 million tons annually [1]. In general, there are two classical processes of propylene epoxidation, chlorohydrin process and hydroperoxide process. The chlorohydrin process is fairly simple, requiring only two reaction steps, but it causes to serious environmental problem producing large outputs of chloride-laden sewage [2–5]. The recently built plants adopted the latter, considering environmental aspect. Since they utilize hydroperoxide having high content of active oxygen species as oxidants, the environment-friendly by-products such as H<sub>2</sub>O are produced. This process usually adopts transition-metal catalysts including titanosilicates, zeolite supported metal catalysts [6]. Lately, in several industrial processes, heteropoly acids (HPAs) with Keggin structure such as H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> has been paid attention as a substitute for traditional transition-metal catalyst. Due to its strong acidity, uniform acidic sites, and

unique redox property, HPAs are more active than the conventional solid acid catalysts in selective oxidation and hydroxylation [7]. Even though the mechanism of HPAs-catalyzed reaction is not yet fully understood, it has been suggested that phosphotungstic acid reacts with hydrogen peroxide to produce small peroxotungstophosphates formed on polynuclear sites such as {PO<sub>4</sub>[WO(O<sub>2</sub>)<sub>2</sub>]<sub>4</sub>}<sup>3-</sup>, which catalyze oxidation [8]. However, one of the major disadvantages is the selectivity to propylene oxide; large amount of co-products yields 2–4 times higher than that of propylene oxide [6]. Furthermore, since these reaction systems are homogeneous catalysis, there are several problems that should overcome for application: low thermal sustainability and high solubility of HPA in polar solvents is a major obstacle to catalyst/product separation and catalyst recycling.

Several groups have conducted research in order to compensate these inherent defects of HPA catalysts. It was reported that partial or total substitution of proton to other cations in Keggin polyoxometalates could enhance thermal stability of HPA without any structural change of primary Keggin backbone in heteropoly anion [9,10]. Organic-modified polyoxometalates were also extensively highlighted as heterogeneous hybrid catalysts. As the redox properties of the inorganic cluster of HPA were modified by organic  $\pi$ -electron, high yield of product could be achieved by applying tetrabutylammonium-modified or pyridine-modified HPA catalysts in epoxidation of olefins or benzene hydroxylation, respectively [1,11]. However, it is still ambiguous how the organic

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$\pi$ -bond affects the catalytic activity and what factor should be considered in choosing hetero-compound for the modified complex catalyst.

In this work, we attempt to modify heteropoly acids with two or three nitrogen atoms-containing heterocycles and apply them as the heterogeneous catalyst for epoxidation of propylene. In preparation of catalysts, imidazole, pyrazole or 1,2,4-triazole were utilized for modification of 12-phosphotungstic acids in order to investigate the effect of heterocycles on the complex catalysts. Furthermore, the potential of the complex catalyst was assessed as the heterogeneous catalyst for propylene epoxidation by focusing on regioselectivity in various reaction conditions, thermal stabilities and recyclabilities.

## 2. Experimental

### 2.1. Catalyst preparation and characterization

12-Phosphotungstic acid (PWA,  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ , >98.0%; Kanto Chemical) was used as heteropoly acids in this study. The heterocycle-modified PWA composite catalysts were prepared by ion-exchange with nitrogen containing heterocycle compound such as imidazole (>98.0%, TCI Chemical), pyrazole (>98.0%, TCI Chemical) and 1,2,4-triazole (>98.0%, TCI Chemical). 5 M of aqueous solution of heterocycle was added dropwise to 0.1 M aqueous solution of PWA with designated volumetric ratios. The mixture was stirred for 24 h and then was centrifuged at 1200 rpm to separate the precipitates from solution. The precipitate was washed with deionized water thrice and dried at 100 °C overnight. The obtained samples were denoted as ([Heterocycle]<sub>x</sub>/PWA), where *x* is the molar ratio of heterocycle to PWA. In order to investigate the thermal stability of the catalyst, the catalyst was placed into the oven and oven was slowly heated up to the designated temperature (200–500 °C) with a heating rate of 2 °C/min.

X-ray diffractometer (XRD, Rigaku D/MAX-II A) with monochromated Cu-K $\alpha$  radiation source at 30 kV and 30 mA were used to investigate the crystal structure change by addition of heterocycles. X-ray diffraction patterns were obtained in a scan range of  $2\theta = 5\text{--}60^\circ$  with a scan rate of 4°/min. In order to clarify the interaction between PWA and heterocycles, infrared spectra were obtained from Fourier transformed infra red spectroscopy (FT-IR, Digilab Excalibur series) at universal attenuated total reflection (ATR) mode in the range of 550–4000  $\text{cm}^{-1}$ . The thermogravimetric analysis (TGA, Rigaku Thermo plus TG8120) was conducted under air atmosphere with a heating rate of 2 °C/min in the range of 25–800 °C.

### 2.2. Catalytic reaction

Epoxidation of propylene was carried out in a micro-batch reactor. 30 mg of the catalyst, 0.2 mL of hydrogen peroxide (35% in  $\text{H}_2\text{O}$ , Aldrich) and 0.3 mL of methanol as medium were introduced into the stainless steel reactor having 10 mL of inner volume and then the reactor was charged with the 0.5 MPa of propylene. The reactor was vertically positioned and agitated by the temperature controllable shaker for 8 h of the reaction. To minimize the loss of product samples (gases and liquids), the quenching (1 °C water bath) has been performed after reaction. When the temperature of reactor reached at 5 °C, gas phases have been collected in PVDF bag (0.1 L) through degassing line attached to reactor. The conversion of feed and products (gases and liquids) were determined by analysis of gas chromatography (GC; Hewlett-Packard 6890, USA) equipped with flame ionization detector (FID) and DB 1701 capillary column (J&W Science).  $\text{CO}_2$  in the gases has been specially analyzed by using methanizer-FID with Carboxene 1006 column, which can convert

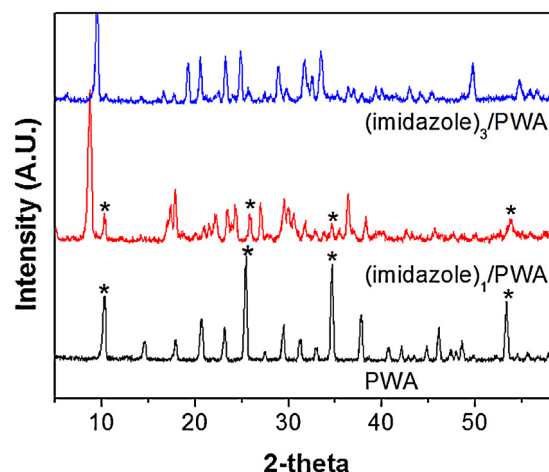


Fig. 1. XRD patterns of raw PWA and imidazole-modified PWA by varying imidazole contents.

$\text{CO}_2$  into methane and detect in FID with the detection limit of several ppm level. GC calibration for propylene and  $\text{CO}_2$  were performed using mass flow controllers (MKS) with the balanced in He gas. PO, acetone, IPA and propanol were calibrated by vaporizing known quantities of liquids in a heated, evacuated 2000  $\text{cm}^3$  stainless steel tank and using He as a carrier gas. All calibration data showed linear 5-point plots ( $R^2$  of at least 0.996) with peak area as the basis for determining the conversion and yields.

The conversion and selectivity was calculated from the propylene oxide data as shown below.

$$\text{Conversion (\%)} = \frac{1 - X_{\text{C}_3\text{H}_8}}{X_{0,\text{C}_3\text{H}_8}} \times 100$$

$$\text{Selectivity (\%)} = \frac{X_{\text{PO}}}{\sum X_{\text{product}}} \times 100$$

where  $X_{0,\text{C}_3\text{H}_8}$ ,  $X_{\text{C}_3\text{H}_8}$ ,  $X_{\text{PO}}$  and  $X_{\text{product}}$  are the moles of initial  $\text{C}_3\text{H}_8$ , remaining  $\text{C}_3\text{H}_8$  after reaction, propylene oxide and each product, respectively.

The catalyst recycle test was performed to observe the thermal and chemical stability of complex catalysts. After each cycle, the spent catalyst was collected, washed by acetone, dried under vacuum and then weighed to check the loss of the catalyst during reaction and separation of the catalyst from product. There was no change in the weight of the used catalyst, indicating that the prepared catalyst was stable under the reaction conditions.

## 3. Results and discussion

### 3.1. Characterization of heterocycles-modified heteropoly acid catalysts

Fig. 1 shows the comparison of XRD patterns among the raw PWA and imidazole-modified PWAs as a function of the ratio of imidazole to PWA ( $x = 1$  and 3). From the XRD pattern, it was confirmed that the raw PWA is the hexahydrated form, the characteristic peaks of the body centered cubic structure [12]. It was found that the crystal structures of imidazole-modified PWA depended on the contents of imidazole. The XRD pattern of (imidazole)<sub>3</sub>/PWA exhibit totally different from that of the raw PWA, while (imidazole)<sub>1</sub>/PWA contains both patterns of the raw PWA and (imidazole)<sub>3</sub>/PWA. It can be deduced that the imidazole content at (imidazole)<sub>1</sub>/PWA was not enough to change the crystal structure of PWA, but at (imidazole)<sub>3</sub>/PWA, the surface was entirely modified by imidazole addition.

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