Epoxidation of Allyl Chloride with H₂O₂ Catalyzed by Three Structurally Related Quaternary Ammonium Modified Polyoxophosphotungstates

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Epoxidation of Allyl Chloride with H₂O₂ Catalyzed by Three Structurally Related Quaternary Ammonium Modified Polyoxophosphotungstates

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Graphical Abstract



Highlights

- The catalyst of polyoxophosphotungstate was synthesized by green method.
- The epoxidation of allyl chloride was achieved under real solvent-free condition.
- The catalysts exhibited excellent catalytic performance and reusability.
- The catalytic mechanism was explored by FT-IR spectroscopy.
- The catalytic activity is related to the structure of cations.

Abstract

The one-step epoxidation of allyl chloride has always been a great challenge for the industrial production. The key of this technology is to find efficient and friendly catalyst. In this paper, three structurally related quaternary ammonium modified polyoxophosphotungstates were synthesized by green and facile method. Among them, $[C_{16}H_{33}(CH_3)_3N]_3PW_4O_{24}$ and $[\pi-C_5H_5NC_{16}H_{33}]_3PW_4O_{24}$ are reaction-controlled phase transfer catalyst (RPTC) and $[(C_{18}H_{37})_2(CH_3)_2N]_3PW_4O_{24}$ is temperature-controlled phase transfer catalyst (TPTC). All three catalysts could achieve the epoxidation of allyl chloride with equimolar H₂O₂ under solvent-free and mild conditions. Moreover, the catalysts exhibited excellent catalytic performance and reusability. The catalytic mechanism was explored by FT-IR spectroscopy. The results of kinetic experiments show that the chain length of alkanes and heterocyclic structure of cations have a great influence on the catalytic activity of the catalysts.

Keywords

Catalytic activity; Epoxidation; Epichlorohydrin; Phase transfer catalyst;

1. Introduction

Epoxidation has been the subject of extensive research interest for a long time because epoxides are often used as starting materials or intermediates in chemical or pharmaceutical industry.[1] As an important chemical raw material, epichlorohydrin (ECH) has large demand in the whole world, which is widely used in the preparation of glycerol, epoxy resin, chlorohydrin rubber and polyether polyols.[2] Up to now, chlorohydrin method remains dominant in the industrial production. However, the chlorohydrin method showed inevitable shortcomings such as low yield, high energy consumption, many by-products, and environmental pollution.[3] Therefore, it is urgent to develop an eco-friendly and cost-effective method for ECH production.

In recent years, various catalysts have been reported for the epoxidation of olefins with H₂O₂ such as nano materials,[4-10] metal complex,[11-18] silicates,[19-25] hydrotalcites[26-29] and polyoxometalates.[30-36] Catalysts play an indispensable role in epoxidation reaction. The traditional homogeneous and heterogeneous catalysts have the intrinsic advantages and limitations. Homogeneous catalysts dissolve in reactants and exhibit high reactivity but have difficulty in separation and reuse. On the contrary, heterogeneous catalysts are beneficial to facile separation and recycling but always show poor activity compared with homogeneous counterparts in most catalytic processes.[37-39] In order to combine the advantages of homogeneous and heterogeneous catalysts, many efforts have been devoted to develop phase transfer catalysts.[40-43] The derived reaction-controlled phase transfer catalyst and temperature-controlled phase transfer catalyst possess the superiorities of both homogeneous and heterogeneous catalysts, which have been applied to the epoxidation of olefins.[44-47]

The one-step epoxidation of allyl chloride with environmentally friendly H_2O_2 is an ideal production route, which could reduce side reactions and improve atomic utilization. However, a few of catalysts were reported for the epoxidation of allyl chloride. Venturello group first reported a catalyst based on polyoxophosphotungstate, $[(C_8H_{17})_3NCH_3]_3[PO_4[W(O)(O_2)_2]_4]$, which could be used for the epoxidation of allyl chloride with H₂O₂ using excess allyl chloride and benzene solvent.[48] Clerici group reported that the titanium silicalite (TS-1) catalyzed the epoxidation of allyl chloride with H₂O₂ using excess allyl chloride and methanol solvent.[49] Sun group testified allyl chloride could be epoxidized into ECH catalyzed by $[\pi-C_5H_5NC_{16}H_{33}]_3[PW_4O_{16}]$ in toluene and tributylphosphate solution.[50] Jun Li group reported a reversible supported catalyst (RSC), [C₁₆H₃₃N(CH₃)₃]₃PW₄O₁₆ supported on silanized silica gel, epoxidizing allyl chloride to ECH with H₂O₂ under excess allyl chloride.[51] All the reported catalysts achieved the epoxidation of allyl chloride in organic solvents or excess allyl chloride, which made subsequent separation and purification difficult and did not meet the requirements of green chemistry. Therefore, it is significant to exploit a series of catalysts to achieve the epoxidation of allyl chloride with equimolar H₂O₂ in the absence of any solvent. It can be seen from previous studies that polyoxophosphotungstate has a very good catalytic potential for epoxidation of allyl chloride. However, a traditional synthesis method of polyoxophosphotungstate involved carcinogenic chlorinated solvents, and the synthesized catalyst could not achieve the desired effect for the epoxidation of allyl chloride. Moreover, the influence

of cation structure on the catalytic activity of polyoxophosphotungstates has not been reported yet.

In present work, three phase transfer catalysts based on polyoxophosphotungstate were synthesized by green and facile method. Due to the difference of cations, the three catalysts showed the properties of reaction-controlled and temperature-controlled phase transfer catalysts respectively. Three structurally related quaternary ammonium modified polyoxophosphotungstates showed excellent catalytic performance for the epoxidation of allyl chloride with equimolar H₂O₂. First, the catalytic performance of three catalysts were investigated and compared. Then, the catalytic mechanism was studied by FT-IR spectroscopy. To further study and compare the catalytic activity of three catalysts, the turnover frequency and activation energy of the epoxidation reaction catalyzed by different catalysts were studied.

2. Experimental

2.1 Reagents and Characterization

All the chemicals used in this study are as follows: Phosphotungstic acid $(H_3PW_{12}O_{40}\cdot xH_2O, \ge 99.0\%, Sinopharm Chemical Reagent Co. Ltd.), hydrogen peroxide <math>(H_2O_2, 30\%, Sinopharm Chemical Reagent Co. Ltd.),$ hexadecyltrimethylammonium chloride $(C_{16}H_{33})(CH_3)_3NCl, 98.0\%, Sinopharm Chemical Reagent Co. Ltd.),$ hexadecylpyridinium chloride monohydrate $[\pi$ -C₅H₅NC₁₆H₃₃]Cl·H₂O, 98.0\%, Sinopharm Chemical Reagent Co. Ltd.), dimethyl dioctadecyl ammonium chloride $(C_{18}H_{37})_2(CH_3)_2NCl, 97.0\%, Sinopharm Chemical$

Reagent Co. Ltd.), absolute ethanol (CH₃CH₂OH, \geq 99.7%, Sinopharm Chemical Reagent Co. Ltd.), allyl chloride (CH₂=CHCH₂Cl, 97.0%, Sinopharm Chemical Reagent Co. Ltd.), and deionized water was used throughout the experiments. All chemicals were analytical in grade, commercially available and used without further purification.

The functional groups of the catalyst were characterized by fourier transform infrared spectroscopy (FT-IR, VERTEX 70, Bruker, USA) using 2–4% (w/w) KBr pellets prepared by manual grinding. The catalysts were pretreated by microwave digestion equipment (MARS6, CEM), and then the content of P and W was measured by inductively coupled plasma emission spectrometer (iCAP6300, Thermo Fisher Scientific). The content of C, H, N atoms was measured by elemental analyzer (vario EL cube, Elementar). ³¹P NMR spectroscopy was detected by Bruker AVANCE NEO600. The concentration of ECH was analyzed by gas chromatography (GC, GC-2030ATF, SHIMADZU, Japan) with a flame-ionization detector and a TM-1701 column (35 m×0.32 mm, film: 0.5 mm). The temperature of injector, detector and oven was 160 °C, 230 °C, 100 °C, respectively. High purity nitrogen was used as the carrier gas.

2.2 Preparation of Catalysts

 $[C_{16}H_{33}(CH_3)_3N]_3PW_4O_{24}$: Firstly, phosphotungstic acid 2.88 g (1 mmol) was dissolved in 20 mL aqueous H₂O₂ (30%) and stirred at room temperature for 2 h. Secondly, the suspension of hexadecyltrimethylammonium chloride 1.01 g (3.1 mmol) in 20 mL

anhydrous ethanol was heated to 40 °C to obtain light yellow solution. Then the oxidic phosphotungstic acid aqueous solution was added dropwise into the resultant ethanol solution at 40 °C, the white precipitate was appeared and the suspended solution was stirred for another 2.5 h. After the reaction, the white precipitate was filtered and washed with water (100 mL×2) and anhydrous ethanol (20 mL) respectively. Finally, the white precipitate was dried in vacuum at 30 °C for 12 h to obtain white powder 1.76 g. (Yield 72.3%, based on P atoms). FT-IR spectrum (KBr, cm⁻¹): $\vec{v} = 1091$ (s), 1058 (s) (P-O), $\vec{v} = 964$ (s) (W=O), $\vec{v} = 845$ (s) (O-O), $\vec{v} = 773$ (w), 721 (m) (C-C) , $\vec{v} =$ 652 (m) (Figure S1). Elemental analysis: found C 35.01%, N 2.14%, H 6.66%, P 1.27%, W 34.3%. Calculated for [C₁₆H₃₃(CH₃)₃N]₃PW₄O₂₄: C 34.6%, N 2.10%, H 6.34%, P 1.55%, W 36.7%.

 $[\pi$ -C₅H₅NC₁₆H₃₃]₃PW₄O₂₄: The catalyst of $[\pi$ -C₅H₅NC₁₆H₃₃]₃PW₄O₂₄ was synthesized using the similar method with $[C_{16}H_{33}(CH_3)_3N]_3PW_4O_{24}$. The difference is that hexadecylpyridinium chloride dissolved in water was added dropwise into oxidic phosphotungstic acid aqueous solution at 40 °C. (Yield 73.6%, based on P atoms). FT-IR spectrum (KBr, cm⁻¹): $\vec{v} = 1091$ (s), 1058 (s) (P-O), $\vec{v} = 983$ (m) (W=O), $\vec{v} = 846$ (s) (O-O), $\vec{v} = 773$ (w), 721(w) (C-C), $\vec{v} = 685$ (m). (Figure S2). Elemental analysis: found C 37.53%, N 2.09%, H 5.67%, P 1.37%, W 32.9%. Calculated for $[\pi$ -C₅H₅NC₁₆H₃₃]₃PW₄O₂₄: C 36.66%, N 2.04%, H 5.57%, P 1.50%, W 35.63%.

 $[(C_{18}H_{37})_2(CH_3)_2N]_3PW_4O_{24}$: The catalyst of $[(C_{18}H_{37})_2(CH_3)_2N]_3PW_4O_{24}$ was synthesized using the similar method with $[C_{16}H_{33}(CH_3)_3N]_3PW_4O_{24}$. (Yield 73.5%, based on P atoms). FT-IR spectrum (KBr, cm⁻¹): $\tilde{v} = 1088$ (s), 1058 (s) (P-O), $\tilde{v} = 978$ (m) (W=O), $\tilde{v} = 848$ (m) (O-O), $\tilde{v} = 789$ (w), 719 (w) (C-C) , $\tilde{v} = 650$ (w) (Figure S3). Elemental analysis: found C 50.05%, N 1.62%, H 8.99%, P 0.86%, W 22.7%. Calculated for $[(C_{18}H_{37})_2(CH_3)_2N]_3PW_4O_{24}$: C 48.84%, N 1.50%, H 8.63%, P 1.10%, W 26.23%.

2.3 Catalytic Reaction

2.3.1 Catalyst Content

Allyl chloride (6.12 g, 0.08 mol), 30% H_2O_2 (9.07 g, 0.08 mol), different amounts of catalyst (allyl chloride: catalyst (mol: mol) =1:100, 1:200, 1:300, 1:400, 1:500) were put into a number of single-neck flasks respectively. The flasks were heated in an oil bath with a reflux condenser and stirred at 45 °C for 6.5 h.

2.3.2 Temperature

Allyl chloride (6.12 g, 0.08 mol), 30% H₂O₂ (9.07 g, 0.08 mol), catalyst $[C_{16}H_{33}(CH_3)_3N]_3PW_4O_{24}$ (1.60 g, 0.8 mmol) were put into single-neck flask. The mixture was prepared in quintuplicate and then reacted at 25 °C, 35 °C, 45 °C, 55 °C respectively. Similarly, catalyst $[\pi$ -C₅H₅NC₁₆H₃₃]_3PW_4O_{24} (1.65 g, 0.8 mmol) and $[(C_{18}H_{37})_2(CH_3)_2N]_3PW_4O_{24}$ (1.12 g, 0.4 mmol) were performed the above reaction. 2.3.3 Recycling

A single-neck flask was charged with catalyst $[C_{16}H_{33}(CH_3)_3N]_3PW_4O_{24}$ (1.60 g, 0.8 mmol), 30% H₂O₂ (9.07 g, 0.08 mol) and allyl chloride (6.12 g, 0.08 mol) in a molar ratio of 1/100/100. The flask was heated in an oil bath with a reflux condenser and stirred at 55 °C for 4 h. After the reaction, the mixture was cooled to room temperature and catalyst was filtered out. Then, the catalyst was washed with ethanol and dried in

vacuum for next use. The recovery percent for one cycle was 92.6%. The catalyst was recycled for five times and properly replenished in each cycle. Similarly, catalyst [π -C₅H₅NC₁₆H₃₃]₃PW₄O₂₄ (1.65 g, 0.8 mmol) and [(C₁₈H₃₇)₂(CH₃)₂N]₃PW₄O₂₄ (1.12 g, 0.4 mmol) were performed the above reaction.

For all catalytic reactions, the mixture was cooled to room temperature after the reaction for $[C_{16}H_{33}(CH_3)_3N]_3PW_4O_{24}$ and $[\pi$ -C₅H₅NC₁₆H₃₃]_3PW_4O_{24} system. But the mixture was cooled to 15 °C after the reaction for $[(C_{18}H_{37})_2(CH_3)_2N]_3PW_4O_{24}$ system. Then catalyst was filtered out. The mixture was allowed to separate into layers and then the content of ECH in organic phase was analyzed by GC.

2.4 Kinetic Experiment

To investigate the catalytic activity of three phase transfer catalysts, the following experiments were carried out for the calculation of turnover frequency (TOF) and activation energy (E_a). Catalyst (1.60 g [C₁₆H₃₃(CH₃)₃N]₃PW₄O₂₄), 30% H₂O₂ (9.07 g) and allyl chloride (6.12 g) in a molar ratio of 1/100/100 were mixed in a two-neck flask, adding 10mL chloroform as solvent. Similarly, catalyst (1.65)[πg $C_5H_5NC_{16}H_{33}$]₃PW₄O₂₄), 30% H₂O₂ (9.07 g) and allyl chloride (6.12 g) in a molar ratio of 1/100/100 were mixed in a single-neck flask, adding 10mL chloroform as solvent. Catalyst $(1.12 \text{ g} [(C_{18}H_{37})_2(CH_3)_2N]_3PW_4O_{24})$, 30% H₂O₂ (9.07 g) and allyl chloride (6.12 g) in a molar ratio of 1/200/200 were mixed in a single-neck flask, adding 10mL chloroform as solvent. The above three reaction systems were heated in an oil bath with a reflux condenser and stirred at 25 °C, 35 °C, 40 °C, 45 °C, 55 °C respectively. The products were sampled at different time and detected by GC.

The turnover frequency (TOF) were calculated according to equations (1).

$$TOF = \frac{mol \ of \ ECH}{2 \times mol \ of \ W \times time} \tag{1}$$

The concentration changes of ECH with time at different temperature was fitted by Exponential decay equation (2). The reaction rate equation (3) was obtained by derivation of equation (2).

$$y = y_0 + A_1 e^{\left(\frac{-t}{B_1}\right)} + A_2 e^{\left(\frac{-t}{B_2}\right)}$$
(2)
$$y' = -\frac{A_1}{B_1} e^{\left(\frac{-t}{B_1}\right)} - \frac{A_2}{B_2} e^{\left(\frac{-t}{B_2}\right)}$$
(3)

y is the concentration of ECH. t is time. y' is differential coefficient for y. Other parameters are constants.

Arrhenius equation (4) and kinetic equation (5) are used for calculating activation energy.[52, 53] Equation (6) is derived from equations (4) and (5).

Arrhenius equation:

$$k = k_0 \times e^{\left(-\frac{E_a}{RT}\right)} \tag{4}$$

Kinetic equation:

$$r = k \times C_A \times C_B \tag{5}$$

$$lnr = -\frac{E_a}{RT} + \ln(k_0 \times C_A \times C_B)$$
(6)

k is reaction rate constant. E_a is activation energy. T is temperature. r is reaction rate. C_A and C_B are the concentration of allyl chloride and H₂O₂ respectively.

3. Results and Discussion

3.1 Characterization of the fresh catalysts

The ³¹P NMR spectroscopy of three catalysts are shown in Fig. S4 - S6. There is a

peak at 6.69 ppm and a smaller peak at -10.77 ppm in the spectrum of $[C_{16}H_{33}$ (CH₃)₃N]₃PW₄O₂₄ (Fig. S4), which illustrates the catalyst is not a single component. In Fig. S5, a broad peak from -15 to 8 ppm could be ascribed to many components with different P/W ratio. [55] Ten independent peaks in Fig. S6 demonstrates that there are many active components in $[(C_{18}H_{37})_2(CH_3)_2N]_3PW_4O_{24}$. The significant difference in the composition of the three catalysts may be attributed to the different forces between the quaternary ammonium cations and peroxotungstates anions during the reaction. The result of elemental analysis shows that the W/P ratio of three catalysts are 4.54, 4.35, 4.44 respectively. Similar values of W/P ratio indicate that the active sites of three catalysts are similar in number. [56]

3.2 Catalytic Performance

The catalytic performance of three catalysts for the epoxidation of allyl chloride was studied separately. First of all, the effect of catalyst content on conversion and selectivity of allyl chloride was investigated. Allyl chloride was allowed to react with equimolar H_2O_2 at 45 °C for 6.5 h in the presence of different catalysts. The molar ratio between catalysts and allyl chloride was set as 1:100, 1:150, 1:200, 1:300, 1:400 and 1:500 respectively. As shown in Fig. 1A, the conversion of allyl chloride was improved gradually and exceeded 94% with the increase in catalysts ratio from 1:500 to 1:100, and the selectivity was found higher than 99% (Fig. 1B). Compared with the previous reported catalysts, the catalysts synthesized in this paper all showed excellent catalytic performance for the epoxidation of allyl chloride (Table 1). For the catalyst of

 $[(C_{18}H_{37})_2(CH_3)_2N]_3PW_4O_{24}$, the conversion approached maximum when catalyst ratio increased to 1:200. Therefore, the catalytic content of $[(C_{18}H_{37})_2(CH_3)_2N]_3PW_4O_{24}$ was set as 1:200 in the following experiments.

Catalyst	Solvent	Conversion%	Selectivity%	Yield%	Ref.
$[(C_8H_{17})_3NCH_3]_3[PO_4[W(O)(O_2)_2]_4]$	Benzene	96 ^a	/	80 ^a	[48]
TS-1	Methanol	98 ^a	92 ^a		[49]
$[\pi - C_3 H_5 N C_{16} H_{33}]_3 [PW_4 O_{16}]$	Toluene and tributylphosphate	93.5 ^b	1	80.5 ^b	[50]
RSC	Excess allyl chloride	90.6 ^a	94.4 °	1	[51]
$[C_{16}H_{33}(CH_3)_3N]_3PW_4O_{24}$	None	94.8 °	> 99 °	/	This work
$[\pi\text{-}C_{5}H_{5}NC_{16}H_{33}]_{3}PW_{4}O_{24}$	None	94.5 °	> 99 °	/	This work
$[(C_{18}H_{37})_2(CH_3)_2N]_3PW_4O_{24}$	None	94.1 °	> 99°	/	This work

Table 1. The epoxidation of allyl	chloride with H_2O_2 b	y different catal	ysts
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a The conversion and selectivity are based on H_2O_2 .

b The conversion and yield are based on EAHQ.

c The conversion and selectivity are based on allyl chloride.

In the experimental process, it has been found that $[C_{16}H_{33}(CH_3)_3N]_3PW_4O_{24}$ and $[\pi-C_5H_5NC_{16}H_{33}]_3PW_4O_{24}$ are reaction-controlled phase transfer catalyst, and $[(C_{18}H_{37})_2(CH_3)_2N]_3PW_4O_{24}$ is temperature-controlled phase transfer catalyst.[57, 58] The reaction-controlled phase transfer catalysts emulsified the two phases during the reaction and then precipitated out with the end of the reaction. The temperature-controlled phase transfer catalyst emulsified the two phases during the reaction and then precipitated out with the end of the reaction. The temperature-controlled phase transfer catalyst emulsified the two phases during the reaction and dissolved in ECH absolutely above 15 °C after the reaction, which precipitated out by

cooling to 10 °C. In order to observe the state of reaction system more intuitively before and after the reaction and the formation of emulsification during the reaction, the corresponding photos were shown in Fig. S7 & S8. This phenomenon demonstrates that the kind of quaternary ammonium salt cations determines the solubility of the catalysts. Since the liquid-liquid two-phase reaction takes place at the interface, as a promoter of the reaction, the catalyst must play a role in the interface. Therefore, the structure of the catalyst influences the reaction. The prepared catalysts have amphiphilic structure, the cations with alkyl groups have lipophilicity, and the phosphotungstic acid anions have hydrophilicity. The surfactant-like structure makes the catalysts aggregate at the interface, and the increase of lipophilic group chain length can increase the tendency of aggregation at the interface.[60] Therefore, the catalytic performance of $[(C_{18}H_{37})_2(CH_3)_2N]_3PW_4O_{24}$ is the best among the three and the other two also show good efficiency under the similar condition.



Figure 1. (A) Effect of different catalyst amount on conversion of allyl chloride. (B) Effect of different catalyst amount on selectivity of allyl chloride. Experimental condition: allyl chloride: H_2O_2 (mol: mol) = 1:1, 45 °C, 6.5 h.

To evaluate the reusability of the catalysts, recycling experiments were carried out as shown in Fig. 2. Allyl chloride reacted with equimolar H_2O_2 at 45 °C for 6.5 h

catalyzed by different catalysts. After five cycles, the conversion of allyl chloride was no less than 85% and selectivity was still more than 99%, which indicated three catalysts possessed good catalytic activity and stability. The decrease of conversion rate may be attributed to the leaching of W after each catalytic run. [45] In order to further explore the stability of the catalysts, the IR spectra of the catalysts before and after the reaction were compared. The results showed that the band of v(O-O) band disappeared and v(W-Oc-W) and v(W-Ob-W) appeared (Fig. S4-Fig. S6), which demonstrated that the hydrogen peroxide had been consumed completely and the catalysts transferred the oxygen of themselves to allyl chloride.[52] The other bands did not change obviously, testifying that the structures of catalysts were relatively stable after the reaction.

Temperature plays an important role on catalytic reaction. Herein, the effect of temperature on conversion rate and selectivity was investigated keeping the molar ratio between catalysts and allyl chloride as 1:100,1:100,1:200 for [C₁₆H₃₃(CH₃)₃N]₃PW₄O₂₄, [π-C₅H₅NC₁₆H₃₃]₃PW₄O₂₄ and [(C₁₈H₃₇)₂(CH₃)₂N]₃PW₄O₂₄, respectively. Allyl chloride reacted with equimolar H₂O₂ in the presence of catalysts for 6.5 h at 25 °C, 35 °C, 40 °C, 45 °C, 55 °C respectively. The conversion of allyl chloride in three catalytic systems enhanced with the increase in the temperature and the maximum value was more than 97% at 55 °C. What is worth mentioning is that the selectivity keeps above 99% under different reaction temperature (Fig. 3), which shows the feasibility of reaction with raising temperature.



Figure 2. (A)The effect of cycle test on conversion of allyl chloride. (B) The effect of cycle test on selectivity of allyl chloride.



Figure 3. (A) The effect of temperature on conversion of allyl chloride in the presence of different catalysts. (B) The effect of temperature on selectivity of allyl chloride in the presence of different catalysts.

3.3 Catalytic Mechanism

To explore the catalytic mechanism, the catalytic process of the reaction was tracked by infrared spectroscopy. When the catalyst $[C_{16}H_{33}(CH_3)_3N]_3PW_4O_{24}$ reacted with allyl chloride at 55 °C for 1min, 5 min, 15 min, respectively, the v(O-O) band at 845 cm⁻¹ disappeared gradually (Fig. 4). At the same time, two new bands at 883 cm⁻¹ and 804 cm⁻¹ assigned to v(W-Oc-W) and v(W-Ob-W) appeared respectively, which indicated that the catalyst transferred the oxygen atom to allyl chloride.[52] Then, the system was treated with 30% H₂O₂ for additional 1 min, 5 min, 15 min at 55 °C. The v(O-O) band appeared again and shift to 832 cm⁻¹, while the band of v(W-Oc-W) and v(W-Ob-W) disappeared. The phenomenon illustrated active oxygen was transferred from hydrogen peroxide to catalyst. The slight shift of spectrum may be attributed to the changes of catalyst structure after adding hydrogen peroxide. The catalyst could degrade into smaller species after the reaction with hydrogen peroxide.[57] Meanwhile, the similar results were obtained from the catalytic system of $[\pi$ -C₃H₅NC₁₆H₃₃]₃PW₄O₂₄

catalysts acted as oxygen carrier during the reaction and obtained the oxygen from hydrogen peroxide, then transferred the oxygen to allyl chloride. In our previous work, it has been testified the catalyst exhibited obvious interfacial activity and aggregated at the interface.[59] Therefore, the catalytic process takes place at the interface of the two phases, as shown in Scheme 1.



Figure 4. FT-IR spectrum of the catalyst $[C_{16}H_{33}(CH_3)_3N]_3PW_4O_{24}$ under reaction condition (a) fresh catalyst (b) catalyst treated with allyl chloride for 1 min at 55 °C (c) catalyst treated with allyl chloride for 5 min at 55 °C (d) catalyst treated with allyl chloride for 15 min at 55 °C (e) **d** system treated with 30% H₂O₂ for additional 1 min at 55 °C (f) **d** system treated with 30% H₂O₂ for additional 10 min at 55 °C (g) **d** system treated with 30% H₂O₂ for additional 25 min at 55 °C.



Scheme 1. The catalytic process of catalysts at two-phase interface.

3.4 Kinetic Study

Turnover frequency (TOF) is a common parameter to evaluate the catalytic activity. [61] The reaction could reach to equilibrium in three hours at 55 °C. Therefore, the turnover frequency of three catalysts was calculated under 55 °C (Fig. 6). As the reactant concentration decreased with the progress of the reaction, the contacting probability between the reactant and catalyst decreased, so the TOF value on the whole showed a downward trend. For $[C_{16}H_{33}(CH_3)_3N]_3PW_4O_{24}$, the TOF value first decreased with time and then showed a small recovery and then fell. The brief rebound of 80-120 minutes may attribute to a better emulsion state of the reactant. For $[\pi$ -C₅H₅NC₁₆H₃₃]₃PW₄O₂₄, the TOF value went down to almost the same value as $[C_{16}H_{33}(CH_3)_3N]_3PW_4O_{24}$, (TOF= 4.37 h⁻¹ for $[C_{16}H_{33}(CH_3)_3N]_3PW_4O_{24}$, TOF= 4.46 h⁻¹ for $[\pi$ -C₅H₅NC₁₆H₃₃]₃PW₄O₂₄), which illustrated the similar catalytic activity. For $[(C_{18}H_{37})_2(CH_3)_2N]_3PW_4O_{24}$, there was a slow decline in TOF value and it still kept a

high value when the reaction reached equilibrium (TOF= 9.29 h⁻¹), which showed that the catalytic activity of $[(C_{18}H_{37})_2(CH_3)_2N]_3PW_4O_{24}$ is much higher than that of the other two. The order of catalytic activity is $[(C_{18}H_{37})_2(CH_3)_2N]_3PW_4O_{24} >$ $[C_{16}H_{33}(CH_3)_3N]_3PW_4O_{24} \approx [\pi-C_5H_5NC_{16}H_{33}]_3PW_4O_{24}.$

The catalytic activity of catalyst in heterogeneous reaction is not only related to the activation energy but also to the interfacial properties. In order to further explore the relationship between catalytic activity and catalyst structure, the reaction activation energy of allyl chloride catalyzed by different catalysts was studied. First of all, the concentration changes of generated ECH with time was explored at different temperatures. As shown in Fig. 5, allyl chloride reacted with equimolar H₂O₂ catalyzed by [C₁₆H₃₃(CH₃)₃N]₃PW₄O₂₄ at 25 °C, 35 °C, 40 °C, 45 °C and 55 °C respectively. The concentration of ECH increased gradually and reached to maximum value during the reaction time at different temperatures. With the temperature increased, the equilibrium time for the reaction gradually decreased. The experimental data were fitted with equation (2) to further explore the effect of temperature on the reaction rate. Relevant fitting parameters were shown in Table S1. The initial reaction rates at different temperature were calculated by equation (3), and there was good linear relationship between reaction rate and temperature. The calculated activation energy of allyl chloride in catalyst [C₁₆H₃₃(CH₃)₃N]₃PW₄O₂₄ system was 64.05 kJ/mol. The similar experiments carried $[\pi - C_5 H_5 N C_{16} H_{33}]_3 P W_4 O_{24}$ were out in and [(C₁₈H₃₇)₂(CH₃)₂N]₃PW₄O₂₄ catalytic system. The activation energy was 62.58 kJ/mol and 68.90 kJ/mol respectively (Fig. S9-Fig. S10). The order of activation energy values

[(C₁₈H₃₇)₂(CH₃)₂N]₃PW₄O₂₄ [C₁₆H₃₃(CH₃)₃N]₃PW₄O₂₄ is >[π-C₅H₅NC₁₆H₃₃]₃PW₄O₂₄. Considering the catalytic activity, the results of activation energy demonstrate that the order of interfacial activity is $[(C_{18}H_{37})_2(CH_3)_2N]_3PW_4O_{24} > [C_{16}H_{33}(CH_3)_3N]_3PW_4O_{24} > [\pi - C_5H_5NC_{16}H_{33}]_3PW_4O_{24}.$ The interface aggregation of catalyst can promote the interface reaction, that is, the mass transfer between hydrogen peroxide and catalyst, and then affect the whole reaction rate.

There is a significant correlation between catalytic activity and interfacial activity. [62] During the reaction in this study, as an oxygen carrier, the interface location of polyoxophosphotungstic acid anions directly determines the interfacial activity of the catalysts, while the interface position of anions is closely related to the structure of lipophilic cations. The above results prove that the chain length of alkanes and heterocyclic structure in quaternary ammonium cations have a great influence on the catalytic activity of such catalysts. The results also provide a new idea for the subsequent study and industrial application of this kind of catalysts.



Figure 5. (A) The concentration changes of ECH over time catalyzed by [C₁₆H₃₃(CH₃)₃N]₃PW₄O₂₄

at different temperatures. (B) The relationship between reaction rate and temperature. Experimental condition: catalyst: allyl chloride: $H_2O_2(mol: mol: mol) = 1:100:100$.



Figure 6. The changes of turnover frequency with time of three catalysts under 55 °C.

4. Conclusions

In summary, three structure related quaternary ammonium modified polyoxophosphotungstates, $[C_{16}H_{33}(CH_3)_3N]_3PW_4O_{24}$, $[\pi$ -C₅H₅NC₁₆H₃₃]_3PW_4O_{24} and $[(C_{18}H_{37})_2(CH_3)_2N]_3PW_4O_{24}$, were synthesized by a simple way. These catalysts present excellent catalytic performances for the epoxidation of allyl chloride because they combine the advantages of both homogeneous and heterogeneous catalysis. The experimental results indicate the maximum conversion rate of allyl chloride is more than 97% and selectivity is higher than 99%. Moreover, three catalysts are easily recycled for several times without significant loss of activity. The results of kinetic experiments show the catalytic activity of the catalysts is related to the chain length of alkanes and heterocyclic structure in quaternary ammonium cations. This study lays a foundation for further study of the influence of cations in phase transfer catalysts on catalytic activity and has a strong industrial application value.

Credit Author Statement

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