



Selective Oxidation of Cyclohexene with H₂O₂ Catalyzed by Resin Supported Peroxo Phosphotungstic Acid Under Mild Conditions

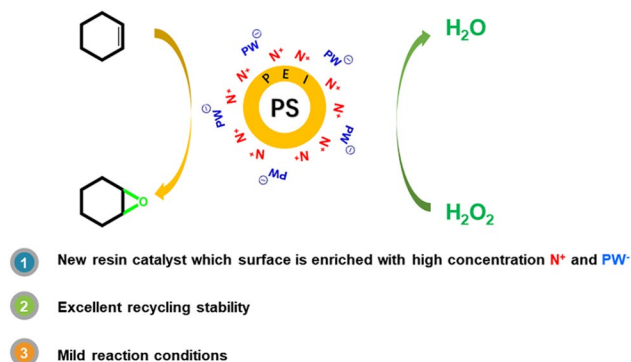
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Abstract

A series of modified chloromethyl polystyrene resins loaded with peroxo phosphotungstic acid catalysts were synthesized for the selective oxidation of cyclohexene. The surface of resin was enriched with high concentration quaternary ammonium salt, and grafted with a large amount of peroxo PW-anion through ion exchange. The novel resin catalyst showed excellent cyclohexene conversion and epoxide selectivity using 30% H₂O₂ as oxidant at ambient temperature. Furthermore, the resin catalyst exhibited excellent recycling stability, which can be reused by a simple filtration and the peroxo phosphotungstic acid did not leach into the solvent after reaction.

Graphic Abstract



Keywords Resin · Oxidation · Cyclohexene · H₂O₂ · Recyclable

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1 Introduction

Cyclohexene oxide is one of the most essential chemical feedstocks for producing polymers, pharmaceuticals, fine chemicals and biological materials. The development of effective industrial production for the epoxidation of cyclohexene has drawn much attention over the last few years. The two main traditional methods for producing epoxides are the hydroperoxides process and the chlorohydrin process. However, these processes produce a large number of low-value by-products and cause severe environmental pollution. As a replacement for traditional method, environmentally benign oxidants, such as hydrogen peroxide [1–5] and molecular oxygen [6–11] have been used for

the epoxidation of alkenes. It has been reported that a high selectivity of epoxides could be obtained from the epoxidation of cyclohexene using hydrogen peroxide as an oxidant. Many catalysts were developed for this process, including heteropoly acid [12, 13], TS-1 [14–16], Schiff base complex [17], non-heme iron [18], and metal porphyrin [19]. Phosphotungstic heteropoly acid is a very active catalyst for the epoxidation of alkene by aqueous H_2O_2 [13, 20]. The activity of this epoxidation system is due to the formation of metal peroxo species in situ, which are the real active oxidants [13]. Most of the phosphotungstic acid catalysts reported are liquid biphasic and homogeneous system, with a quaternary ammonium cation playing the role of phase transfer of peroxo phosphotungstic acid between aqueous and organic layer [20–24]. However, this system suffers from the problem of poor catalytic reactivity in the recycling processes.

From the view of industrial manufacture and green chemistry, heterogeneous catalysts are desirable because of their separability, high stability, long lifetime and recyclability [25]. In 1999, Aida et al. reported a reusable resin-supported catalyst (PW-Amberlite) [26]. Although high yields were obtained with PW-Amberlite for the epoxidation of terpenes with H_2O_2 , the catalytic performance for the selective oxidation of cyclic olefins was weak [27]. In 2016, Peng et al. reported a powdered anion-exchange resin D201 supported peroxo PW-anion (D201-PWAR(4)), D201-PWAR(4) exhibited high activity in the cyclohexene epoxidation using 30% H_2O_2 at 323 K, 92.4% cyclohexene conversion and 98.1% epoxy cyclohexane selectivity were obtained [28].

In the present work, we developed a series of active catalysts based on chloromethyl polystyrene resin (PS-Cl). By surface modification with polyethyleneimine (PEI), a large amount of quaternary ammonium salt was grafted onto the surface of resin. Through ion exchange of peroxo phosphotungstic acid with modified resin, an active heterogeneous catalyst was obtained, which showed excellent catalytic performance for the selective oxidation of cyclohexene with 30% H_2O_2 under mild conditions (308 K). This catalyst has a millimetre-level particle diameter, which is easy to be separated and reused, showing potential for industrial application.

2 Experimental

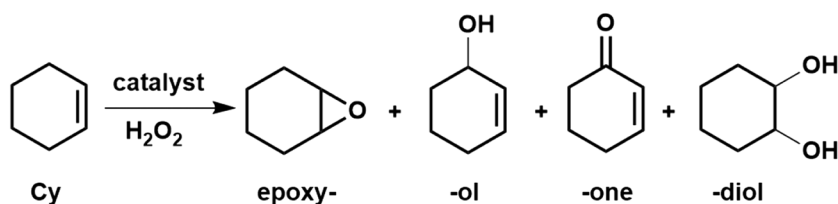
2.1 Catalyst Preparation

The chloromethyl polystyrene resin (PS-Cl) used here is a commercial product (Cross-linked with 1% DVB, Particle size: 100–200 mesh, chloromethyl content: 3.0 mmol/g), the cyclohexene (no stabilizer added) was purchased from TCI, PEI (*M.W.* 600, branched) was purchased from Adamas. The mixture of 10 g PS-Cl resin, 0.8 g PEI and 40 mL DMF were stirred at 303 K for 4 h (Scheme 1). The resulting PS/PEI was filtered off and purified in a soxhlet extraction ($\text{Et}_2\text{O}-\text{CH}_2\text{Cl}_2$ (1:1)) to remove the excess PEI. Next, the PS/PEI support was dried at 353 K for 12 h. The dried support, 50 mmol 1-chlorooctadecane and 25 mL 2-propanol were added into a 100 mL round bottom flask (reflux, 353 K, 6 h). Then, it was cooled down to 323 K. After that, 100 mmol 1-chlorobutane was added and the mixture was refluxed at 323 K for 5 h. The resulting PS/PEI- C_{18} was filtered off and purified in a soxhlet extraction, then dried at 353 K for 12 h. Peroxo phosphotungstic acid compounds $\text{H}_2[\text{PO}_3(\text{OH})][\text{WO}(\text{O}_2)_2]_2$ (H_2PW_2), $\text{H}_3[\text{PO}_4(\text{WO}(\text{O}_2)_2)_4]$ (H_3PW_4) and $\text{H}_2(\text{PhPO}_4)[\text{WO}(\text{O}_2)_2]_2$ (H_2PhPW_2) were prepared according to the methods reported in the literatures [29–31]. The catalysts with different peroxo PW-anions were prepared through ion exchange treatment of 5 g PS/PEI- C_{18} with excessive aqueous solution of different peroxo phosphotungstic acid compounds (5 mmol PW-anion), and named as PS/PEI- C_{18} - PW_2 , PS/PEI- C_{18} - PW_4 , PS/PEI- C_{18} - PhPW_2 (Scheme S1(A)). Finally, the solution was removed by filtration, and the resin catalysts were washed consecutively with deionized water and acetone, then dried at 353 K for 6 h. Using a similar method, the PS- C_{18} - PW_2 was prepared through ion exchange treatment of 5 g PS- C_{18} with 5 mmol H_2PW_2 (Scheme S1(B)).

2.2 Catalyst Characterization

Fourier transform infrared (FT-IR) spectra of samples were determined by Nicolet NEXUS 870 spectrometer using KBr as background atmospheric conditions. Elemental contents of C and N were measured by Elementar Vario ELII. Content of P and W elements were performed in a PE Optima 5300DV elemental analyzer (ICP-AES). X-ray photoelectron

Scheme 1 Catalytic oxidation of cyclohexene



spectroscopy (XPS) was carried out by using a PHI 5000 VersaProbe spectrometer equipped with an Al K α X-ray source in ultrahigh vacuum (10–10 Torr). The SEM images were observed by Hitachi S-3400 N. The N₂ adsorption isotherm was measured by Micromeritics ASAP 2020 at 77 K. The surface area was observed from the BET plot, and the pore volume was performed by the BJH method. Thermogravimetric analysis (TGA) was performed on Netzche STA449F3 at a heating rate of 10 K/min from 298 to 1073 K under N₂ flowing.

2.3 Catalyst Testing

The selective oxidation of cyclohexene was carried out in a round bottom flask (25 mL) equipped with a reflux condenser (263 K ethanediol as a cooling medium for the condensing to prevent the evaporation of cyclohexene and solvent) (Scheme 1). Typically, 500 mg catalyst, 10 mmol of cyclohexene, 20 mmol of H₂O₂ (30 wt% solution in water), 5 mL of CH₃CN were added into the flask. The mixture was heated in an oil bath and stirred by a magneton. After the reaction, the resin catalyst was filtered off and washed consecutively with deionized water and acetone, then dried at 353 K overnight for reuse. The substrates and products were analyzed by Shimadzu GC 2014C with a capillary column WondaCAP-5 (30 m \times 0.32 mm \times 0.25 μ m) and a flame ionization detector. The cyclohexene and products were determined by comparing the responsive peak areas of sample products against standard curves prepared with known authentic compounds using internal standard decane. The conversion of cyclohexene and the selectivity of epoxy cyclohexane were calculated by Eqs. (1) and (2), respectively.

The conversion of cyclohexene (mol%)

$$= \frac{\text{total moles of products}}{\text{total moles of products} + \text{moles of remaining cyclohexene}}$$

The selectivity of epoxy cyclohexane (%) = moles of epoxy cyclohexane/total moles of products

3 Results and Discussion

3.1 Catalyst Characterization

The SEM pictures of resin surface morphology in different stages are shown in Fig. S1. The shape and size of PS/PEI are similar to PS-Cl (50–100 μ m), the surface of PS/PEI is rougher than that of PS-Cl. As shown in Table 1, after grafted with PEI, the mass percentage of N in PS/PEI is 2.5%, the total pore volume and surface area of the resin is 0.27 cm³ g^{−1} and 27.7 m² g^{−1}. The mass percentage of N, P and W in PS/PEI-C₁₈-PW₂ are much greater than that of PS-C₁₈-PW₂. This means that more quaternary ammonium

Table 1 Characteristics of support and catalysts

Support and ctalalysts	C%	N%	P%	W%	S_{BET} ; V_{BJH}
PS/PEI	80.6	2.5	–	–	27.7; 0.27
PS/PEI-C ₁₈ -PW ₂	66.3	1.8	1.2	14.3	17.8; 0.12
PS/PEI-C ₁₈ -PW ₄	52.5	1.4	1.7	34.5	–
PS/PEI-C ₁₈ -PhPW ₂	67.1	1.7	1.2	14.2	–
PS-C ₁₈ -PW ₂	76.8	0.2	0.1	1.7	22.2; 0.22

Chemical composition of support and catalysts, weight%; specific surface area, S_{BET} , m² g^{−1}; pore volume, V_{BJH} , cm³ g^{−1}

can be enriched on the resin through surface modification by PEI, and more peroxo PW-anion can be grafted onto the surface of the resin. As showing in Fig. S2, the TGA curves of different stages of the resin show high thermal stability of resin at temperatures below 400 K. According to the IR spectrum (Fig. S3), the PS-Cl is characterized by the following IR bands (in cm^{−1}): 2920 (antisymmetric vibration of C–H); 2850 (symmetric vibration of C–H); 1500 and 1600 (benzene skeleton vibration); 680 (stretching vibration of C–Cl). In the spectrum of the PS/PEI, the absorption peak $\nu(\text{C–Cl})$ at 680 cm^{−1} reduced significantly, at the same time, the $\nu(\text{C–N})$ peak appears at 1361 cm^{−1}, which shows that the C–Cl bond replaced by the C–N bond and the PEI had been grafted onto the PS-Cl. New peaks ($\nu(\text{P=O})$ at 1070 cm^{−1}, $\nu(\text{W=O})$ at 940 cm^{−1}, $\nu(\text{W(O}_2\text{)})$ at 540 cm^{−1}, and $\nu(\text{O–O})$ at 820 cm^{−1}) are observed in the spectrum of PS/PEI-C₁₈-PW₂ [20, 32–34]. These results suggest that the PW₂ anion had been immobilized on the surface of resin. The IR spectra of PS-C₁₈-PW₂, PS/PEI-C₁₈-PW₄ and PS/PEI-C₁₈-PhPW₂ are similar to the PS/PEI-C₁₈-PW₂.

(1)

(2)

The elemental compositions of resin surface were analyzed by XPS. Figure S4(A) shows the presence of Cl 2p (BE = 200 eV), C 1s (BE = 285 eV), O 1s (BE = 531 eV), this is consistent with the chemical composition of PS-Cl. Figure S5(a) shows the Cl 2p core-level spectrum with Cl 2p_{3/2} located at 199.6 eV and Cl 2p_{1/2} located at 200.8 eV, which are characteristic peaks of C–Cl [35]. A new characteristic peak of N 1s appears at 399.1 eV (Fig. S4(B)) [36]. The Cl 2p core-level spectrum of PS/PEI with Cl 2p_{3/2} at 197.3 eV and Cl 2p_{1/2} at 198.8 eV (Fig. S5(b)), which are characteristic peaks of free chloride ion [37]. The peak area of C–N⁺ of PS/PEI-C₁₈-PW₂ is obviously increased compared to PS/PEI (Figs. S5(c), S5(d)), indicating that

Table 2 Effect of various catalysts on the epoxidation of cyclohexene

Catalysts	n(PW-anion) /(mmol)	Conv (mol%)	Sel.(%)		
			epoxy-	-diol	others
PS/PEI-C ₁₈	0	0	—	—	—
PS/PEI-C ₁₈ -PW ₂	0.200	73.2	98.2	1.5	0.3
PS/PEI-C ₁₈ -PW ₄	0.282	84.2	87.9	10.1	2.0
PS/PEI-C ₁₈ -PhPW ₂	0.202	74.2	91.3	5.3	3.4
PS-C ₁₈ -PW ₂	0.018	9.1	100	0	0

Reaction conditions: catalyst (500 mg), CH₃CN (5 mL), cyclohexene (10 mmol), H₂O₂ (20 mmol, 30 wt% solution in water), rpm (600), 308 K, 180 min

quaternization reaction has occurred on the surface of PS/PEI. A strong W 4f peak (35.0 eV) and O 1s peak (530.1 eV) appear, and the peak of Cl 2p is weakened (Fig. S4(C)), because the peroxy PW-anion has replaced the chloride ion (on the surface of resin) by ion exchange. The W 4f core-level spectrum of PS/PEI-C₁₈-PW₂ with W 4f_{7/2} at 35.6 eV and W 4f_{5/2} at 37.6 eV (Fig. S5(e)), W 4f_{7/2} belongs to PW₂. Figure S5(f) shows the O 1s core-level spectrum, 530.1 eV is ascribed to W–O band, 531.2 and 532.6 eV can be assigned to the W–O–W and W–O–P bands in PW₂ [28, 32, 38].

3.2 Catalyst Performance Evaluation

As shown in Table 2, resin catalysts supported with various phosphotungstic acids were investigated for catalytic activity. The cyclohexene conversion was 0% when PS/PEI-C₁₈ was used, indicating that the support has no catalytic activity. Only 9.1% cyclohexene conversion was obtained with 100% selectivity of epoxy cyclohexane in the presence of PS-C₁₈-PW₂ (The amount of PW-anion is only 0.018 mmol). In contrast, catalysts grafted with PEI presented an excellent catalytic activity with more than 70% conversion, which was remarkably higher than that of PS-C₁₈-PW₂. Because the contents of PW-anion in catalysts modified by PEI are much higher than that of the catalyst not modified by PEI. In addition, phosphotungstic acid catalysts with various structures showed different conversions and selectivities. Based on the above results, PS/PEI-C₁₈ was considered to be better catalyst support than PS-C₁₈, and PS/PEI-C₁₈-PW₂ was selected as the most suitable catalyst because of its highest epoxy cyclohexane selectivity (98.2%).

Figure 1 shows the performance of PS/PEI-C₁₈-PW₂ for the epoxidation of cyclohexene with H₂O₂. The conversion of cyclohexene can arrive 95.9% in 360 min and the selectivity of epoxy cyclohexane was almost 100% in the first two hours. Then, the selectivity of epoxy cyclohexane decreased to 92.1 and 65.5% in 180 min and 360 min, respectively. The decrease in epoxy cyclohexane selectivity is due to the enriched polar species in solution (e.g., water, epoxide), the

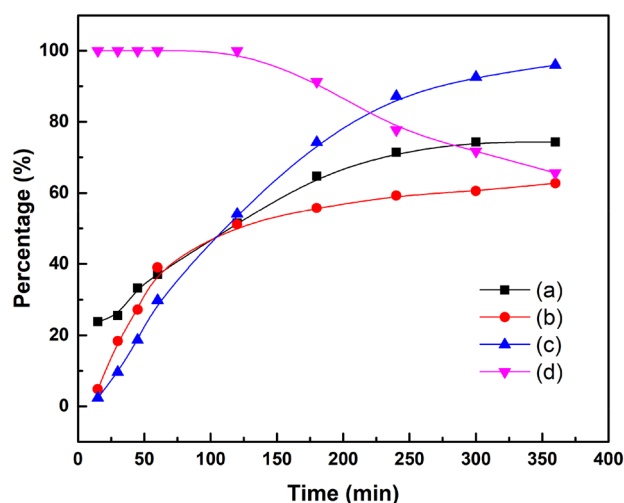
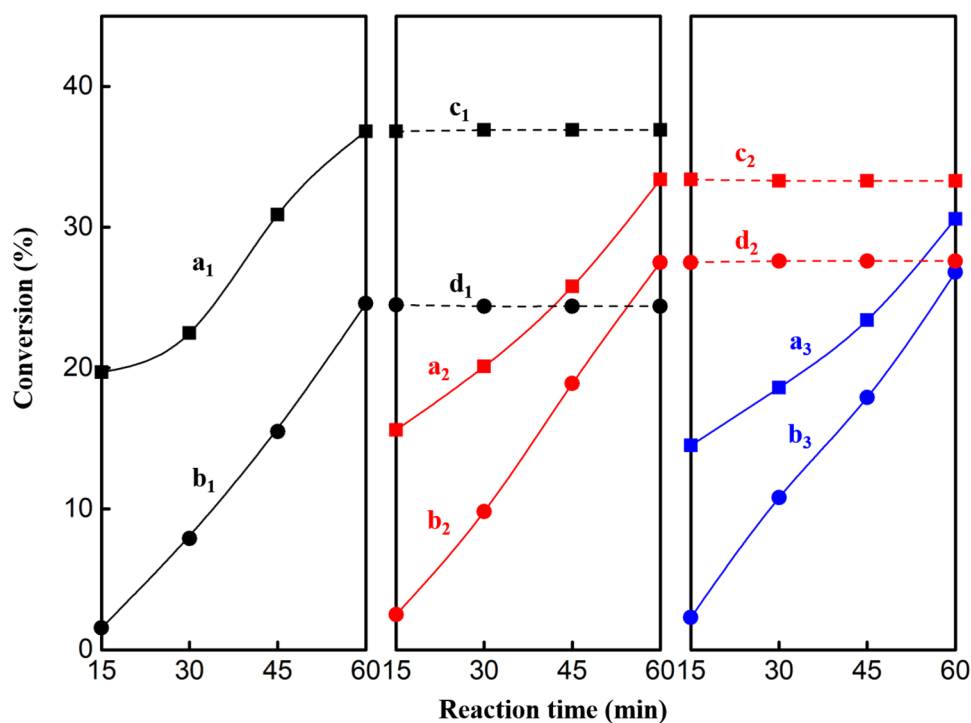


Fig. 1 Cyclohexene epoxidation at normal operating conditions: conversion of H₂O₂ (a); utilization of H₂O₂ (b); conversion of cyclohexene (c); selectivity of epoxy cyclohexene (d). Reaction conditions: PS/PEI-C₁₈-PW₂ (500 mg), CH₃CN (5 mL), H₂O₂ (20 mmol, 30 wt.% solution in water), cyclohexene (10 mmol), rpm (600), 308 K

increase of solution polarity will promote the hydrolysis of epoxy cyclohexene to 1,2-cyclohexanediol. The utilization coefficient of H₂O₂ increased from 4.8 to 62.7%, with an increase in reaction time. Hydrogen peroxide reacts with phosphotungstic acid to form tungsten peroxy species, and the tungsten peroxy species can catalyze the epoxidation of cyclohexene as real active oxidants. The reaction rate of forming tungsten peroxy species is much higher than the speed of epoxidation of cyclohexene, so the utilization coefficient of H₂O₂ was only 4.8% at the beginning of the reaction (detection method of the concentrations of hydrogen peroxide is mentioned in supporting information).

Furthermore, we designed the control experiment to confirm the stability of catalyst PS/PEI-C₁₈-PW₂. As shown in Fig. 2, PS/PEI-C₁₈-PW₂ was used to catalyze the cyclohexene oxidation at 308 K for 60 min (the first run), then the catalyst was filtrated and was put into another glass flask filled with the same reactant, and the reaction was also carried at 308 K for 60 min (the second run). The filtered solution after the first run was transferred to an empty glass flask and reacted at 308 K for 60 min. The conversions of H₂O₂ and cyclohexene reached 36.8 and 24.6% respectively in 60 min for the first run (Fig. 2a₁, b₁). In contrast, the conversions of H₂O₂ and cyclohexene of the reaction of the filtered solution were almost unchanged (Fig. 2c₁, d₁). On the other hand, for the PS/PEI-C₁₈-PW₂ catalyst that used for the second time (Fig. 2a₂, b₂), no reduction of the catalytic activity was found compared to the first time. The same results could be obtained by repeating all the above operations (Fig. 2c₂, d₂, a₃, b₃). These results indicated that the PS/PEI-C₁₈-PW₂ catalyst could be reused by a simple filtration, and the peroxy

Fig. 2 Stability of PS/PEI-C₁₈-PW₂ catalyst: conversion of H₂O₂ for catalyst first/second/third run (a₁/a₂/a₃); conversion of cyclohexene for catalyst first/second/third run (b₁/b₂/b₃); conversion of H₂O₂ of the reaction of the filtered solution after the first/second run (c₁/c₂); conversion of cyclohexene of the reaction of the filtered solution after the first/second run (d₁/d₂). Reaction conditions: catalyst (500 mg), CH₃CN (5 mL), H₂O₂ (20 mmol, 30 wt% solution in water), cyclohexene (10 mmol), rpm (600), 308 K



phosphotungstic acid did not leach into the solvent in this reaction conditions.

The effects of different solvents on the cyclohexene epoxidation have been studied (Table S1). A higher cyclohexene conversion could be obtained in water-miscible solvents, such as CH₃CN (73.2%), EtOH (74.6%), MeOH (68.2%) and acetone (63.1%). Aprotic solvents offered higher epoxy cyclohexane selectivity (CH₃CN (98.2%), acetone (98.8%)) as compared to protic solvents (EtOH (85.4%), MeOH (59.2%)). Therefore, CH₃CN is the most suitable solvent for cyclohexene epoxidation, which is both water-miscible and aprotic. The effect of the catalyst amount as illustrated in Fig. S6. The cyclohexene conversion increased from 28.6 to 73.2%, and the epoxy cyclohexane selectivity increased from 88.5 to 98.2% with increasing the amount of PS/PEI-C₁₈-PW₂ 125 to 500 mg at 180 min. This may be because the resin's pores can adsorb water, which reduced the polarity of the solution and suppressed the hydrolysis of epoxy cyclohexane. Figure S7 described the effect of H₂O₂ by varying the H₂O₂/cyclohexene molar ratio from 0.5 to 2.0, the cyclohexene conversion increased from 13.0 to 96.3%, still, the epoxy cyclohexane selectivity decreased from 99.8 to 64.8% at 360 min, ascribable to the hydrolysis of epoxy cyclohexane in the presence of excess H₂O. The optimal reaction temperature on the epoxidation of cyclohexene was screened out by evaluating the catalytic performance in temperature range from 298 to 308 K (Fig. S8). The cyclohexene conversion increased from 45.0 to 73.2%, and the epoxy cyclohexane selectivity was maintained above

98.0% in 180 min, as the reaction temperature rose from 298 to 308 K. As the reaction temperature rose to 313 K, the cyclohexene conversion increased from 73.2 to 84.2% and the epoxy cyclohexane selectivity sharply decreased from 99.2 to 87.8% in 3 h, attributed to the hydrolysis of epoxy cyclohexane to 1,2-cyclohexanediol at higher reaction temperature.

Based on the standard reaction conditions for the selective oxidation of cyclohexene, the reaction scale was increased by 100 times (Fig. S9). To eliminate the exothermic effect of hydrogen peroxide decomposition, hydrogen peroxide was dripped at a rate of 3 mL/min by a peristaltic pump in the experiment of 100 times expansion. Since hydrogen peroxide was added slowly to the reaction solution, the temperature of the reaction system was stably controlled at 308 K, and the water content was reduced in the initial stage of the reaction, 89.0% cyclohexene conversion and 94.3% epoxy cyclohexane selectivity were obtained at 360 min. The results showed that the catalytic system performed well after enlarging the reaction scale, and the selectivity of epoxy cyclohexane was improved significantly by controlling the drop rate of hydrogen peroxide.

The activity of the PS/PEI-C₁₈-PW₂ was still maintained at a high level after eight cycles (Table 3). As shown in Figs. S3(G) and S4(D), the IR and XPS spectra of the recovered catalyst were consistent with the fresh catalyst. These results indicated that the catalyst could keep high recyclable stability and has hopefully application foreground in industrial production.

Table 3 Recycling of catalyst PS/PEI-C₁₈-PW₂ for the epoxidation of cyclohexene

Catalyst	Conversion (%)	Selectivity (%)
Fresh	73.2	98.2
Cycle1	74.2	91.3
Cycle2	76.5	94.5
Cycle3	72.5	96.5
Cycle4	76.0	96.1
Cycle5	72.1	98.7
Cycle6	73.4	97.6
Cycle7	69.7	98.4
Cycle8	71.3	96.4

Reaction condition: PS/PEI-C₁₈-PW₂ (500 mg), CH₃CN (5 mL), cyclohexene (10 mmol), H₂O₂ (20 mmol), rpm (600), 308 K, 180 min

4 Conclusions

A series of modified chloromethyl polystyrene resin loaded with various phosphotungstic heteropoly acid catalysts can be synthesized by a simple method, and the PS/PEI-C₁₈-PW₂ exhibits excellent catalytic performance in cyclohexene epoxidation using CH₃CN as solvent and 30 wt% H₂O₂ as oxidant. 73.2% cyclohexene conversion and 98.2% epoxide selectivity were obtained under mild conditions in 180 min. 89.0% cyclohexene conversion and 94.3% epoxide selectivity can also be achieved by controlling the dropping rate of H₂O₂ after enlarging the reaction scale 100 times (in 360 min). This catalyst has a good recovery, stability performance and a millimeter-sized particle size, which is quite close to the industrial design requirement.

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Compliance with Ethical Standards

Conflict of interest There are no conflicts to declare.

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