

Amphiphilic phosphotungstate-paired ionic copolymer as a highly efficient catalyst for triphase epoxidation of alkenes with H₂O₂†

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A novel amphiphilic POM-paired ionic copolymer was prepared by the anion-exchange of a newly task-specific designed functionalized-ionic liquid copolymer with H₃PW₄O₁₆, and characterized by FT-IR, SEM, TG, ¹H NMR, and elemental analysis. This catalyst was not only capable of catalyzing the epoxidation of alkenes in a liquid–liquid–solid triphase reaction system, showing high catalytic conversions and selectivity, but also avoids the use of chlorinated solvents. After reaction, the catalyst can be conveniently recovered and steadily reused without the change of catalyst structure. The unique amphiphilic catalyst structure is revealed to be responsible for the catalyst's excellent performances in the epoxidation of alkenes with H₂O₂ by accelerating the mass transfer.

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1. Introduction

Polyoxometalates (POMs), a well-known class of anionic oxide nanoclusters of transition metals–oxygen-based materials, have achieved wide applications in catalysis, materials science, optics, biology, and magnetism.^{1,2} They have been shown to be efficient Brønsted acid catalysts and highly selective oxidation catalysts for a host of commercially important transformations.^{3–6} Nonetheless, the pure POMs are soluble in many polar solvents, which causes difficulty in separation and recycling of the catalysts; therefore, a number of strategies have been developed for the heterogenisation of POM catalysts including supporting to the silica-based materials^{7,8} or electrostatic anchoring to organic counter cations.^{9,10} However, the design and fabrication of active and recyclable heterogeneous catalysts is still a challenging topic, since most POM-based solid catalysts often suffer from leaching of the active components and the severe mass transfer limitation while using them in liquid-phase selective oxidation.

The transformation of alkenes to corresponding epoxides is both an important industrial technology and a useful synthetic method for a wide range of products including

pharmaceuticals and agrochemicals, for which metal oxides,^{11,12} organometallic complexes,^{13,14} heteroatomic molecular sieves,¹⁵ POMs,^{16,17} and so on, have been investigated as the catalysts. H₂O₂ is regarded as a green oxidant because of its high availability, nontoxic by-product and mild reaction conditions for oxidation reactions.¹⁸ Anyway, when (hydrophilic) aqueous H₂O₂ was used as the oxidant in the epoxidation of lipophilic alkenes which is catalyzed by a solid POM catalyst, the liquid–liquid–solid “triphase” catalysis often occurs, which leads to low catalytic activity due to the poor interfacial interaction. To overcome this disadvantage, phase transfer agents (like tetra(*n*-butyl)ammonium chloride, cetylpyridinium chloride, quaternary ammonium cations) and cationic surfactants are often used to replace the counterions of POMs, leading to the phase-transfer catalysts or emulsion catalysts.^{19,20} These catalysts favor lower interfacial resistance to accelerate the mass transfer to some extent, but often complicates the recovery of the catalyst, and the usage of toxic organic solvents (such as halogen solvent) which largely defeated the significant environmental and economic advantages of using H₂O₂ as the oxidant. Accordingly, there is a significant interest in constructing an amphiphilic substructure for a POM-based recyclable solid catalyst, which can be used in aqueous/oil biphasic systems to balance the desire for improved activity and selectivity.^{21–23}

Recently, poly(ionic liquids) (PILs) resulting from the combination of ionic liquid (IL) monomers were shown to constitute an interesting system to develop amphiphilic materials.^{24,25} By varying the cations and/or anions with specific functions that constitute IL's structure, it is possible to design abundant PILs with required functionalities.^{26,27} Indeed, POM-anions have been used as the counter anions for preparing “task-specific”

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ionic hybrids,^{28,29} and several IL-POMs have been reported as efficient homogeneous, heterogeneous, or phase-separation catalysts for epoxidation reactions.^{16,30–33} Very recently, we have also prepared a series of POM-paired ionic hybrids for organic transformations.^{34–36} Although the emergence of POM-based IL hybrids will endow the POMs with huge diversity in catalytic properties and with more space for organic synthesis, to the best of our knowledge, no amphiphilic POM-paired ionic polymer-based heterogeneous epoxidation system has appeared as yet.

Herein, a new PIL containing dodecyl imidazole IL (DIM) and carboxylic acid-functionalized imidazole IL (CIM) units, is designed to fabricate an amphiphilic POM-paired ionic copolymer through ion exchange with the $[\text{PO}_4(\text{WO}_3)_4]^{3-}$ species. The hydrophobic alkyl chains ($-\text{C}_{12}\text{H}_{25}$) and hydrophilic carboxyl groups ($-\text{COOH}$) were introduced to supply a unique interfacial amphiphilic microenvironment for H_2O_2 -based epoxidation of alkenes, which would accelerate the mass transfer in the liquid–liquid–solid media. Catalytic tests for the epoxidation of alkenes, along with comparisons to various counterparts, well demonstrate that this newly designed catalyst exhibits high activity and selectivity, coupled with easy recovery and steady reuse.

2. Experimental section

2.1 Materials and methods

All chemicals were analytical grade and used as received. FT-IR spectra were recorded on a Nicolet 360 FT-IR instrument (KBr discs) in the 4000–400 cm^{-1} region. $^1\text{H-NMR}$ spectra were measured with a Bruker DPX 300 spectrometer at ambient temperature in D_2O or CDCl_3 using TMS as internal reference. The CHN elemental analysis was performed on an elemental analyzer Vario EL cube. SEM image was performed on a HITACHI S-4800 field-emission scanning electron microscope. TG analysis was carried out with a STA409 instrument in dry air at a heating rate of 10 $^\circ\text{C min}^{-1}$. The amount of leached tungsten species in the filtrate was measured using a Jarrell-Ash 1100 ICP-AES spectrometer. The molecular weight (M_w) and polydispersity (PDI) were measured on a Water 1515 Gel permeation chromatography (GPC).

2.2 Catalyst preparation

Preparation of IL monomers DIM and CIM

[3-Dodecyl-1-vinylimidazolium]Br (DIM). The dodecyl-containing IL monomer DIM was prepared as follows: *N*-vinylimidazole (9.42 g, 0.10 mol) and bromododecane (25.0 g, 0.10 mol) were dissolved in ethanol (50 mL) at 80 $^\circ\text{C}$ for 48 h under nitrogen atmosphere with stirring. On completion, the liquid was removed by distillation, and the solid was washed with anhydrous acetone three times to remove the unreacted starting materials. After drying under vacuum, DIM was obtained. $^1\text{H NMR}$ (300 MHz, CDCl_3 , TMS) δ (ppm) = 0.97 (s, 3H, $-\text{CH}_3$), 1.28 (m, 18H, $-\text{CH}_2$), 1.87 (m, 2H, $-\text{CH}_2$), 3.32 (m, 2H, $-\text{CH}_2$), 5.48 (d, 1H, $-\text{CH}$), 5.95 (d, 2H, $-\text{CH}_2$), 7.15 (d, 2H, $-\text{CH}$), 7.68 (d, 1H, $-\text{CH}$) (Fig. S1 in ESI[†]).

[3-Propionic acid-1-vinylimidazolium]Br (CIM). CIM was prepared as follows: *N*-vinylimidazole (9.42 g, 0.10 mol) and 3-bromopropionic acid (15.30 g, 0.10 mol) were dissolved in ethanol (50 mL) at 80 $^\circ\text{C}$ for 24 h under nitrogen atmosphere. On completion, the white solid of CIM was obtained after the removing of solvent and washing with acetonitrile. $^1\text{H NMR}$ (300 MHz, D_2O , TMS) for CIM δ (ppm) = 3.01 (t, 2H, $-\text{CH}_2$), 4.72 (t, 2H, $-\text{CH}_2$), 5.45 (d, 1H, $-\text{CH}$), 5.81 (d, 1H, $-\text{CH}$), 7.17 (m, 1H, $-\text{CH}$), 7.63 (s, 1H, $-\text{CH}$), 7.79 (s, 1H, $-\text{CH}$), 9.12 (s, 1H, $-\text{CH}$) (Fig. S2 in ESI[†]).

Preparation of IL copolymer DIM–CIM. The IL copolymer (DIM–CIM) was prepared according to the literature.³⁷ In detail, the obtained IL monomers DIM (2.0 g), CIM (1.0 g), and azobisisobutyronitrile (AIBN) (0.05 g) were dissolved in methanol (20 mL) under nitrogen, and the mixture was refluxed at 75 $^\circ\text{C}$ for 16 h with stirring. Then the solvent was removed by distillation, and the residue was washed with ethyl acetate to give a solid product DIM–CIM. The IL polymers of DIM and CIM were prepared accordingly. The content of $-\text{COOH}$ groups in the copolymer DIM–CIM is determined by KOH titration with phenolphthalein as indicator. According to the amount of KOH consumed in the neutralization of COOH in the CIM, the composition of the ionic copolymer DIM–CIM can be calculated to be DIM_{1.5}–CIM.

Preparation of the POM-paired ionic copolymer DIM–CIM–PW. POM-paired ionic copolymer DIM–CIM–PW was prepared according to the methods reported in literatures.³⁸ A solution of H_3PO_4 (0.25 g, 2.5 mmol) in water (5 mL) was added to a solution of 2.5 g H_2WO_4 (10 mmol) in water (15 mL) and 30 wt.% H_2O_2 (7 mL) at 70 $^\circ\text{C}$, then a solution of DIM–CIM (2.20 g) in chloroform (15 mL) was added drop wise to the above solution over a period of 2 min. The biphasic mixture was stirred vigorously at room temperature for 2 h. Then, the solid product DIM–CIM–PW was filtered, washed with small amounts of water and ethanol, and dried. The polymers DIM–PW and CIM–PW were prepared accordingly. DIM–CIM–PW_{12O₄₀} was prepared by adding a chloroform solution (20 mL) of DIM–CIM (1.90 g) to an aqueous solution (15 mL) of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (5.76 g). After stirred vigorously at room temperature for 2 h, the solid product was treated in a similar manner to that for DIM–CIM–PW.

2.3 Catalytic tests

Cyclooctene (10 mmol), ethyl acetate (10 mL), and DIM–CIM–PW (0.06 mmol) were added to a 25 mL flask. The reaction started after the addition of aqueous H_2O_2 (30 wt.%, 12 mmol) at 60 $^\circ\text{C}$ within 10 min under vigorous stirring. After reaction, the product mixture was analyzed by gas chromatography (GC), and the byproducts were determined by GC-MS. Other alkene substrates were tested accordingly. For a three-run operation of the epoxidation of cyclooctene to test the catalytic stability of DIM–CIM–PW, the catalyst was recovered by a filtration or centrifugation after reaction, followed with washing with ethanol and vacuum drying.

3. Results and discussion

The synthesis of DIM-CIM-PW is illustrated in Fig. 1. The IL monomers DIM and CIM were first prepared and characterized by ^1H NMR. The IL copolymer (DIM-CIM) was synthesized by the free radical copolymerization of DIM and CIM using AIBN as the initiator. The final catalyst DIM-CIM-PW was obtained by the anion-exchange of DIM-CIM with the previously prepared $\text{H}_3[\text{PO}_4(\text{WO}_3)_4]$ (abbreviate as PW) in aqueous solution, and was fully characterized by TG, FT-IR, SEM, and CHN elemental analysis.

3.1 Catalyst characterization

Fig. 2 shows the FTIR spectra of the DIM-CIM and DIM-CIM-PW. The FTIR spectrum of DIM-CIM (Fig. 2, curve a) clearly shows the characteristic bands at 1735, 1570, 1161, 2923, and 2852 cm^{-1} that are attributed C=O, C=N, C-N, and CH_2 stretching vibrations, respectively. The strong and broad peak at 3450 cm^{-1} is assigned to the stretching vibration of O-H in -COOH groups. After the combination of DIM-CIM with PW (Fig. 2, curve b), the position of the peaks assigned to the organic moiety in DIM-CIM-PW is almost consistent with that of the IR spectrum for individual DIM-CIM. Moreover, the characteristic bands for the PW species appeared at 1080, 949, 883 and 821 cm^{-1} , assignable to vibrations of P-O_a, W=O_d, W-O_b-W and W-O_c-W, respectively, which are in reasonable agreement with those of the IR spectra for $[\text{PO}_4(\text{WO}_3)_4]^{3-}$ in previous literatures.^{20,39-42}

The DIM-CIM-PW was characterized by thermogravimetric analysis (TG). The TG curve in Fig. 3 indicates a thermally stable structure for DIM-CIM-PW up to 200 °C. The small weight loss of before 200 °C resulted from the release of adsorption water, whereas the drastic weight loss in the range 200–600 °C was assigned to the decomposition of the organic PILs moiety DIM-CIM plus the complete collapse of the inorganic PW anions with the formation of P_2O_5 and WO_3 . The total weight loss obtained from the thermal analysis was

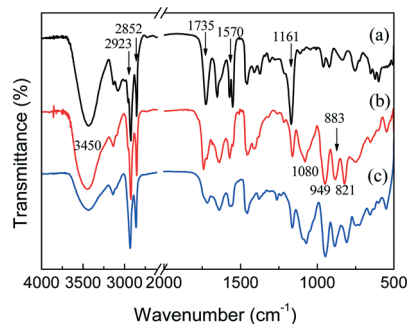


Fig. 2 FTIR spectra of (a) DIM-CIM, (b) fresh DIM-CIM-PW, and (c) recovered DIM-CIM-PW.

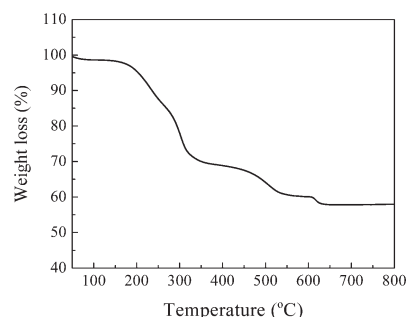


Fig. 3 TG pattern of DIM-CIM-PW.

about 40 wt.%. The composition of DIM-CIM-PW was further examined by CHN elemental analysis, and the result showed 27.24 wt.% for the weight percentage of C, 4.87 wt.% for N, and 3.92 wt.% for H, which was very near to the theoretical values of C: 26.45 wt.%, N: 4.6 wt.%, and H: 3.81 wt.%.

SEM images of the catalysts DIM-CIM-PW, DIM-PW, and CIM-PW are illustrated in Fig. 4. It is very clear from the SEM pictures that the synthesized ionic copolymer DIM-CIM-PW was of nearly spherical shape with the sizes in the range of 200–800 nm (Fig. 4, a). However, structures of catalysts had large changes for the ionic polymer without

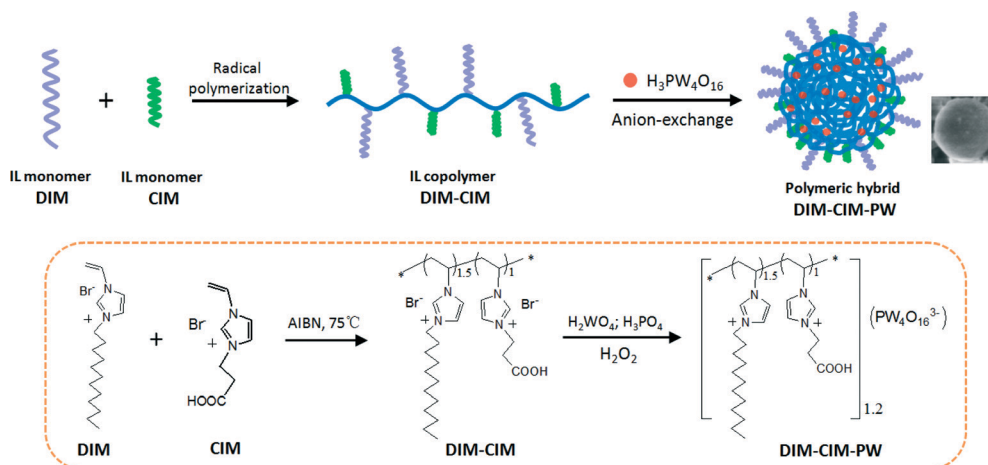


Fig. 1 Schematic illustration outlining the preparation and structure of the catalyst DIM-CIM-PW.

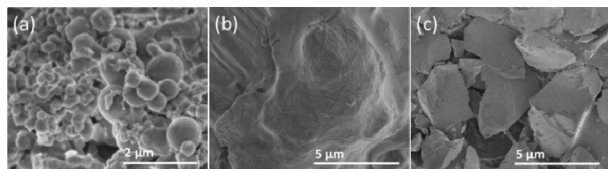


Fig. 4 SEM images of (a) DIM-CIM-PW, (b) DIM-PW, and (c) CIM-PW.

bearing CIM or DIM units in the polymeric cations. The SEM image in Fig. 4 (b) illustrates amorphous structure for DIM-PW, and in the case of CIM-PW, the morphology changed to angular blocks (Fig. 4, c). These phenomena indicate that the balance between the DIM with hydrophobic alkyl chains $-C_{12}H_{25}$ and the CIM with hydrophilic carboxyl groups $-COOH$ is very important in forming the spherical particles. Amphiphilic block copolymers are well-known to self-assemble in aqueous media into robust nanostructures, including spherical micelles, rods, and vesicles.^{43–45} In the present case, the copolymer DIM-CIM containing hydrophobic DIM and hydrophilic CIM units showed a similar good self-assembly manner. It is proposed that when DIM-CIM was anion-exchanged with PW in ethanol solution, hydrophilic groups tended to aggregate together by the chain segment movement, and hydrophobic groups were located in the exterior of hydrophobic groups facing the outside. Thus, spherical particles formed. Furthermore, the molecular weights (M_w) of DIM-CIM, DIM, and CIM determined by gel permeation chromatography (GPC, Fig. S3 in ESI[†]) were measured to be 7168 Da (polydispersity (PDI) = 1.25), 9740 Da (PDI = 1.07), and 8100 Da (PDI = 1.12), respectively.

3.2 Catalytic activity in the epoxidation reaction

The catalytic performances of various catalysts were first assessed in the epoxidation of cyclooctene with H_2O_2 as the oxidant and ethyl acetate as the solvent. Because of the immiscibility of ethyl acetate with aqueous H_2O_2 , the reaction process is a liquid-liquid biphasic system. As seen in Table 1, in the absence of catalyst, the reaction did not proceed at all

even after prolonged reaction times (Table 1, entry 1). The newly synthesized catalyst DIM-CIM-PW was insoluble in the oxidation reaction medium, thus leading to a liquid-liquid-solid triphase system and exhibiting a high conversion of 100% and selectivity of 100% (Table 1, entry 2). However, when the POM-paired polymers DIM-PW and CIM-PW were used as the catalysts, they were also insoluble in the reaction system, but showed very low activities, which are lower than 10% (Table 1, entries 3 and 4). For the PW-free polymers, DIM was inactive (Table 1, entry 5), but $-COOH$ -containing polymers CIM and DIM-CIM showed low activities (Table 1, entries 6 and 7). These results suggest that the interaction between $-COOH$ groups in the polymeric catalysts and H_2O_2 may lead to the generation of peroxy-acid species, which may also take part in the epoxidation reaction.

The traditional POM salt of quaternary ammonium cation CTAB-PW obtained by combining the cetyltrimethylammonium cations $[CTAB]^+$ with $[PO_4(WO_3)_4]^{3-}$ gave a conversion of 95% with 96% selectivity, but it dissolved in the reaction medium (Table 1, entry 8), which makes catalyst recovery very difficult. When $CHCl_3$ was used as the solvent, the heterogeneous DIM-CIM-PW also exhibited a higher activity than homogenous CTAB-PW with the same number of active sites (Table 1, entries 9 and 10). The above comparisons strongly suggest that both the DIM and CIM units in polymeric cations are indispensable for the high activity of the target copolymer catalyst DIM-CIM-PW. Meanwhile, the featured structure of the polymeric cations endows the catalyst with the insolubility in the reaction media of epoxidation reactions, which is thus responsible for the liquid-liquid-solid heterogeneous system.

Keggin-type $H_3PW_{12}O_{40}$ is another well-known important POM catalyst with efficient redox capability for oxidation reactions, thus, $PW_{12}O_{40}^{3-}$ -paired counterpart DIM-CIM-PW $_{12}O_{40}$ with the same copolymeric cations to DIM-CIM-PW was also tested for the epoxidation of cyclooctene with H_2O_2 . However, it only offered a very low conversion of 12% (Table 1, entry 11). This result implies that the $[PO_4(WO_3)_4]^{3-}$ anions favor a better catalytic performance than Keggin $PW_{12}O_{40}^{3-}$ anions for epoxidation of alkenes.

Table 1 Catalytic performances of various catalysts for the epoxidation of cyclooctene with H_2O_2 ^a

Entry	Catalyst	Solubility in reaction	Con ^b (%)	Sel ^c (%)
1	—	Homogeneous	—	—
2	DIM-CIM-PW	Heterogeneous	100	100
3	DIM-PW	Heterogeneous	4	100
4	CIM-PW	Heterogeneous	10	100
5	DIM	Homogeneous	—	—
6	DIM-CIM	Homogeneous	1.9	100
7	CIM	Homogeneous	1.7	100
8	CTAB-PW	Homogeneous	95	96
9 ^d	DIM-CIM-PW	Heterogeneous	99	100
10 ^e	CTAB-PW	Homogeneous	100	97
11	DIM-CIM-PW $_{12}O_{40}$	Heterogeneous	12	95

^a Reaction conditions: catalyst (0.06 mmol), cyclooctene (10 mmol), 30 wt.% H_2O_2 (12 mmol), ethyl acetate (10 mL), 60 °C, 6 h. ^b Conversion of the cyclooctene. ^c Selectivity for the epoxide product. Byproducts for entries 8, 10 and 11 are 2-cycloocten-1-ol and 2-cycloocten-1-one. Reaction conditions for ^d and ^e: catalyst (0.06 mmol), cyclooctene (10 mmol), 30 wt.% H_2O_2 (12 mmol), $CHCl_3$ (10 mL), 60 °C, 1 h.

3.3 Epoxidation reactions with various substrates over the DIM-CIM-PW catalyst

Alkene substrates other than cyclooctene such as cyclohexene, *cis*-3-hexenol, and bipentene were also investigated over the copolymer catalyst DIM-CIM-PW (Table 2). Liquid-liquid-solid three-phase reaction systems were observed in the epoxidation of such alkenes, and good to excellent catalytic activities were obtained. For the epoxidation of cyclohexene, 2-cyclohexen-1-ol and 2-cyclohexen-1-one byproducts were formed. Thus, a relatively low selectivity 85% for the epoxidation of cyclohexene should have resulted from the allylic oxidation through the homolytic radical mechanism. Additionally, the inert terminal alkenes such as 1-octene and 1-hexene could be transformed to the corresponding epoxide specifically with 56% and 48% conversions.

3.4 Catalyst reusability

After reaction, the catalyst recovered by filtration was washed with ethanol, dried and reused for the next run without adding any fresh catalyst. The catalytic reusability for DIM-CIM-PW in epoxidations of cyclooctene and 1-octene was measured by two five-run tests in ethyl acetate solvent. The results in Table 3 reveal that the catalyst can be reused with a slight and gradual loss of activity, while the selectivity is preserved. Furthermore, the IR spectrum for the recovered DIM-CIM-PW in Fig. 2 curve (c) was well consistent with that of the fresh one, demonstrating a durable catalyst structure accounting for the steadily catalytic reuse.

In order to test the possible catalysis of the slightly leached species in the reaction solution from the catalyst, a hot-filtration experiment was carried out under the reaction conditions shown in Table 1. Initially, the mixture of catalyst DIM-CIM-PW and H₂O₂ in ethyl acetate was stirred at 60 °C for 2 h. The conversion of 51.2% and selectivity 100% were obtained. Then, the solid catalyst was filtered immediately at the reaction temperature and the reaction proceeded for another 4 h with the homogeneous filtrate, which resulted in almost unchanged conversion 51.8% and selectivity 100%. The result of ICP-AES elemental analysis for the reacted

Table 2 Epoxidation of various alkenes with H₂O₂ catalyzed by DIM-CIM-PW^a

Entry	Substrate	Reaction time (h)	Con ^b (%)	Sel ^c (%)
1	Cyclooctene	6	100	100
2	Cyclohexene	4	96	85
3	<i>Cis</i> -3-hexenol	4	83	95
4	Bipentene	4	94	92
5	1-Octene	6	56	99
6	1-Hexene	8	48	98

^a Reaction conditions: catalyst (0.06 mmol), substrate (10 mmol), 30% H₂O₂ (12 mmol), ethyl acetate (10 mL), 60 °C. ^b Conversion of the substrate. ^c Selectivity for the epoxide product. Byproducts for entry 2: 2-cyclohexen-1-ol (0.93 mmol) and 2-cyclohexen-1-one (0.51 mmol); entry 3: 3,4-epoxyhexane-1-aldehyde; entry 4: 1,2:8,9-diepoxyp-menthane and 1,2-ene-p-menth-8,9-epoxy; entry 5: octylaldehyde; entry 6: 2-hexenone.

Table 3 Catalytic reusability of DIM-CIM-PW for the epoxidations of cyclooctene and 1-octene with H₂O₂^a

Run	Cyclooctene		1-Octene	
	Con (%)	Sel (%)	Con (%)	Sel (%)
1	100	100	56	99
2	100	100	57	99
3	99	100	55	99
4	95	100	53	100
5	88	100	50	100

^a Reaction conditions: catalyst (0.06 mmol), cyclooctene or 1-octene (10 mmol), 30% H₂O₂ (12 mmol), ethyl acetate (10 mL), 60 °C for 6 h.

filtrate shows that less than 1.6 wt.% of the total W in the catalyst leached into the reaction media, and this may be responsible for the gradual decrease in activity observed in the recycling tests.

3.5 Solvent effects in the epoxidation reaction

Fig. 5 shows the catalytic performances of DIM-CIM-PW in the epoxidation of cyclooctene using H₂O₂ in various solvents over the reaction times of 2 h, 4 h, and 6 h, respectively. For chloroform, dichloromethane, acetone, and ethyl acetate, a liquid-liquid-solid triphase reaction system was formed due to the immiscibility of these solvents with aqueous H₂O₂, and a monophasic liquid reaction system was formed by using acetonitrile and methanol as the solvent. During the reaction process, the catalyst DIM-CIM-PW was insoluble in all cases, and exhibited different catalytic activities with satisfying selectivity above 99%. In the 1,2-dichloroethane, dichloromethane, and acetic acid solvents, very high conversions (≥99%) were observed in a short reaction time of 2 h. It is noteworthy that peroxyacids generated from the oxidation of carboxylic acid with H₂O₂ in acetic acid solvent may take part in the epoxidation. For ethyl acetate, acetonitrile, acetone, and methanol solvents, excellent conversions (≥96%) were obtained as well with a slightly longer reaction time of 6 h. Even when cyclohexane was used as the solvent, a considerable conversion of 70% could be achieved. Thus, the present copolymer catalyst DIM-CIM-PW is applicable for the epoxidation of alkenes with H₂O₂ in various solvent

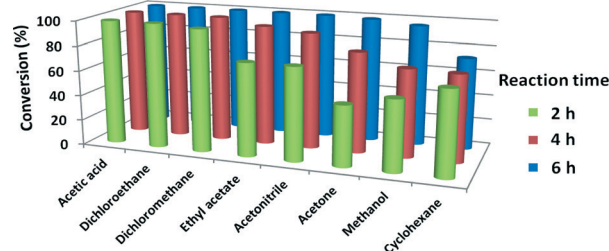


Fig. 5 Catalytic performances of DIM-CIM-PW in the epoxidation of cyclooctene with H₂O₂ in different solvents. Reaction conditions: catalyst (0.1 g), cyclooctene (10 mmol), 30% H₂O₂ (12 mmol), solvent (10 mL), 60 °C.

systems. Nevertheless, the chlorocarbons have environment safety problems such as high toxicity and carcinogenicity. Moreover, the epoxidation process using acetic acid and H_2O_2 may cause severe safety and corrosion problems relative to the peroxyacids. Therefore, ethyl acetate was selected as the organic phase in the epoxidation of alkenes due to its less toxicity and high commonality.

3.6 Understanding of the catalytic behavior of DIM-CIM-PW

It is known that most solid-state heterogeneous catalysts have larger mass transfer resistance than homogeneous or phase-transfer catalysts, and constructing an amphiphilic structure for a solid is one of the most effective solution to form highly reactive systems.^{46,47} We thus suggest that the excellent catalytic activity of DIM-CIM-PW for the epoxidation of cyclooctene in a liquid-liquid-solid triphase system largely arises from its unique amphiphilic catalyst structure. In order to confirm this, the dispersion properties of the catalysts in H_2O_2 /(cyclooctene + ethyl acetate) biphasic media are examined and shown in Fig. 6. For the POM-paired polymers without bearing the CIM or DIM units, DIM-PW was found to highly disperse in the cyclooctene + ethyl acetate layer of the biphasic system, due to the hydrophobic nature of the $-\text{C}_{12}\text{H}_{25}$ moiety in DIM (Fig. 6, a), while CIM-PW was found to suspend in the aqueous H_2O_2 layer due to the hydrophilic nature of the $-\text{COOH}$ moiety in CIM (Fig. 6, b). When the catalyst DIM-CIM-PW was added into this biphasic system, assembling of the hybrid DIM-CIM-PW at the H_2O_2 /(cyclooctene + ethyl acetate) boundary was observed (Fig. 6, c). The phenomena well demonstrate the amphiphilic nature of DIM-CIM-PW, because of the spontaneous change in the hydrophobic long carbon chain of $-\text{C}_{12}\text{H}_{25}$ and hydrophilic $-\text{COOH}$ interfacially oriented on the surface of the copolymer catalyst. For the practical epoxidation system H_2O_2 /(cyclooctene + ethyl acetate), the catalyst DIM-CIM-PW also appeared at the interface of the aqueous and oil phases (Fig. 6, d), which further confirms the amphiphilic nature of DIM-CIM-PW. It is thus proposed that the amphiphilic catalyst structure should have supplied a unique microenvironment for the catalyst to involve both the hydrophobic alkene substrates in oil phase and hydrophilic H_2O_2 molecules

in aqueous phase, which allows PW in the bulk of the catalyst to give full play as catalytic centers. In contrast, the hybrids DIM-PW and CIM-PW were mostly retained in the oil phase or aqueous phase, respectively, thus giving very low conversion and selectivity due to the less accessibility of H_2O_2 or substrate molecules to catalyst's active sites.

More insight into the POM-paired copolymer-catalyzed epoxidation was gained by the IR measurement of the H_2O_2 -treated POM-paired catalysts. On treatment with H_2O_2 , the $\nu(\text{W}-\text{O}-\text{W})$ bands at 883 cm^{-1} shifted to 875 cm^{-1} in the spectrum for DIM-CIM-PW, and a new peak occurred distinctly at 833 cm^{-1} for the peroxy-oxygen band $\nu(\text{O}-\text{O})$ (Fig. 7, b). That new vibration is attributed to the peroxy-oxygen in peroxo-tungsten species $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]^{3-}$, which has been known as the active species for H_2O_2 -based epoxidations.^{16,48-53} It is notable that the $\nu(\text{O}-\text{O})$ band for the H_2O_2 -treated polymeric control samples DIM-PW and CIM-PW also appeared at 833 cm^{-1} (Fig. S4 in ESI[†]), mostly due to the strong ionic interaction between PW-anions and large polymeric cations. Furthermore, after treatment with H_2O_2 , the $\nu(\text{W}-\text{O}_b-\text{W})$ band at 887 cm^{-1} disappeared for $-\text{COOH}$ -free DIM-PW, but still existed for $-\text{COOH}$ -containing CIM-PW (also with a slight shift). These results imply that the existence of the $\nu(\text{W}-\text{O}_b-\text{W})$ band for the H_2O_2 -treated DIM-CIM-PW may result from the presence of $-\text{COOH}$ groups in the catalyst, because the hydrogen-bond interaction between $-\text{COOH}$ groups and PW species may stabilize the hybrid catalyst. The recovered catalyst from the reacted mixture returned to its original structure (Fig. 7, c). Therefore, the presence of tungsten-peroxy species for H_2O_2 -treated DIM-CIM-PW implies a similar mechanism for traditional POM-catalyzed epoxidations.^{39,48,49,54} For the H_2O_2 -treated DIM-CIM-PW₁₂O₄₀, the peroxy-oxygen band at 833 cm^{-1} could not be observed (Fig. S5 in ESI[†]), thus, the low catalytic activity of DIM-CIM-PW₁₂O₄₀ is understandable.

In terms of the above experiment results, a possible reaction model is proposed. As shown in Fig. 8, PW clusters encapsulated by IL copolymer cations with $-\text{COOH}$ groups and $-\text{C}_{12}\text{H}_{25}$ chains result in the formation of an amphiphilic solid PW-paired copolymer catalyst. At the interface of the aqueous/oil system, the H_2O_2 in aqueous phase reacts with

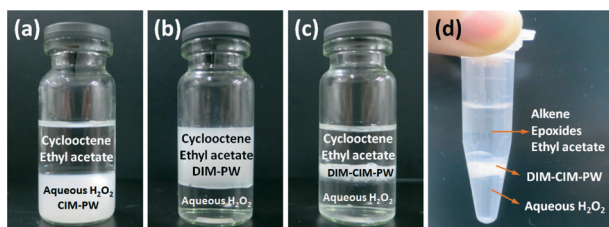


Fig. 6 The illustrations of the catalysts in H_2O_2 /(cyclooctene + ethyl acetate) biphasic system: (a) CIM-PW suspended in aqueous H_2O_2 layer, (b) DIM-PW suspended in (cyclooctene + ethyl acetate) layer, (c) DIM-CIM-PW appeared at the H_2O_2 /(cyclooctene + ethyl acetate) interface, (d) catalyst DIM-CIM-PW appeared at the interface of practical H_2O_2 /(cyclooctene + ethyl acetate) reaction system.

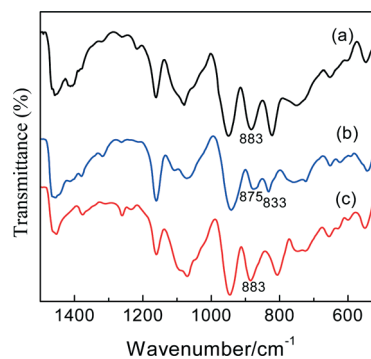


Fig. 7 FTIR spectra of (a) fresh DIM-CIM-PW, (b) H_2O_2 -treated DIM-CIM-PW and (c) recycled DIM-CIM-PW.

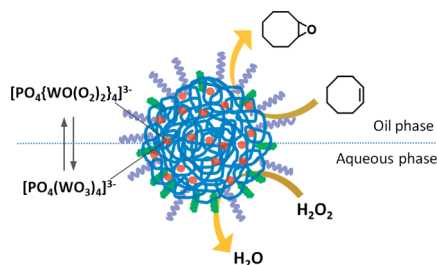


Fig. 8 Proposed mechanism of the epoxidation of alkene with DIM-CIM-PW in liquid-liquid-solid triphase catalytic system.

the W sites of the $[\text{PO}_4(\text{WO}_3)_4]^{3-}$, leading to the generation of the peroxy-tungstate complex $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]^{3-}$ that is supposed to be the active site for epoxidation. Then, the peroxy-tungstate complex is resumed to the original state of $\text{W}=\text{O}$ by inserting its oxygen into the alkene reactant in oil phase to produce an epoxide product. In this liquid-liquid-solid triphase system, the hydrophilic $-\text{COOH}$ groups and hydrophobic $-\text{C}_{12}\text{H}_{25}$ chains on the surface of the catalyst act as “trapping agent” for H_2O_2 and alkene molecules through hydrophilic-hydrophilic or hydrophobic-hydrophobic interactions, respectively, and thus promote the catalytic activity of DIM-CIM-PW. Though the above proposal is able to reasonably explain our reaction results, it is presently tentative and more direct evidence is needed to make it clearer.

4. Conclusion

In summary, we have synthesized a novel amphiphilic POM-paired copolymer catalyst DIM-CIM-PW for the liquid-liquid-solid triphase epoxidation of alkenes with H_2O_2 . The new catalyst exhibits high catalytic activity and selectivity, plus the advantages of convenient recovery and steady reusability. The peroxy-tungstate species in PW anions act as the active centres for epoxidation reactions, while the amphiphilic catalyst structure as a “trapping agent” for both the hydrophobic alkene substrates and the hydrophilic H_2O_2 molecules, and thus the catalytic activity is largely promoted. The design strategy for the present catalyst might be a significant step towards the design of heterogeneous catalysts with integrated and enhanced properties for more catalytic processes.

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