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A novel heteropolyanion-based amino-containing cross-linked ionic copolymer catalyst for epoxidation of alkenes with H_2O_2

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ABSTRACT

A heteropolyanion-based cross-linked ionic copolymer was prepared by the anion-exchange of a newly task-specific designed amino-containing ionic copolymer with a Keggin heteropolyacid, and characterized by FT-IR, SEM, TG, XRD, UV–vis, ESR, ^{1}H NMR, and elemental analysis. Its catalytic activity was evaluated in the epoxidation of alkenes with aqueous H_2O_2. The resultant heteropolyanion-based ionic copolymer is revealed to be a highly efficient heterogeneous catalyst for epoxidation of alkenes with H_2O_2, adding the advantages of convenient recovery and steady reuse.

1. Introduction

Epoxidation of alkenes with H_2O_2 has been extensively investigated over the catalysts of heteroatomic molecular sieves [1], transition metal compounds [2], organometallic complexes [3], and polyoxometalates (POMs) [4,5]. Heterpolyacids (HPAs) are a family of POMs, and the tungsten-containing HPAs, typically the Venturello-Ishii $\{PO_4[WO(O_2)_2]_4\}^{3-}$ species, have attracted much attention for a long time as the effective catalysts for the H_2O_2-based epoxidation of alkenes [6]. However, HPAs always cause homogeneous reactions because of their good solubility in polar/oxidative media, resulting in the difficulty of catalyst isolation. Thus, heterogeneous HPA catalysts are a promising option, and various strategies, including attaching HPAs to porous supports [7–9], biphasic technology and phase-transfer catalysis [10,11], have been developed. Though good activity was achieved in those cases, most of them still bear some drawbacks like the slow reaction speed, leaching of active species, low catalyst recovery rate, or high cost. A new strategy for catalyst preparation to overcome the above problems is therefore highly desirable.

The organic–HPA hybrids, obtained by the modification of HPAs with organic blocks, have attracted great research interest due to their diverse chemical structures and improved catalytic behaviors [12,13]. A topic of recent interest in this context is the design and application of HPA-based ionic liquid (IL) hybrids as the catalysts for organic syntheses [14], and some thermal/solvent-responsive HPA-based IL hybrids have been reported [15,16]. We recently prepared a series of HPA-based ionic hybrids by combining organic IL cations with Keggin heteropolyanions, and the resulting ionic solids turned out to be effective and recyclable catalysts for acid-catalyzed or oxidative organic transformations [17,18].

More recent studies have shown that ionic copolymers containing IL units are capable of acting the bifunctions of both ILs and polymers [19–21]. Moreover, owing to the features of high thermal stability, easily shaping, corrosion resistance, and the variety of structures available, polymer matrices are excellent supports to entrap POMs for applications in heterogeneous catalysis [22]. For example, poly(nisopropylacrylamide) polymer with a quaternary ammonium and phosphotungstate anion ($PW_{12}O_{40}{}^{3-}$) can be used as a temperature-responsive catalyst for the oxidation of alcohols, causing thermoregulated formation of stable emulsion species at 90 °C in water [23]. Water-soluble HPA-conjugated chitosan matrix was revealed to be an effective catalyst for the triphase epoxidation of allylic alcohols [24]. Also noticeably, the amino groups tethered to IL cations have been demonstrated to be the catalytic promoters for HPA active sites in epoxidations due to the electron transfer from aminos to HPA frameworks [18]. Accordingly, it is rational to design and prepare a HPA-based amino-containing ionic copolymer catalyst for epoxidation of alkenes with hydrogen peroxide by combining amino-functionalized IL copolymers with HPAs with a more structural stability, because of the involvement of a polymeric framework in the catalyst.

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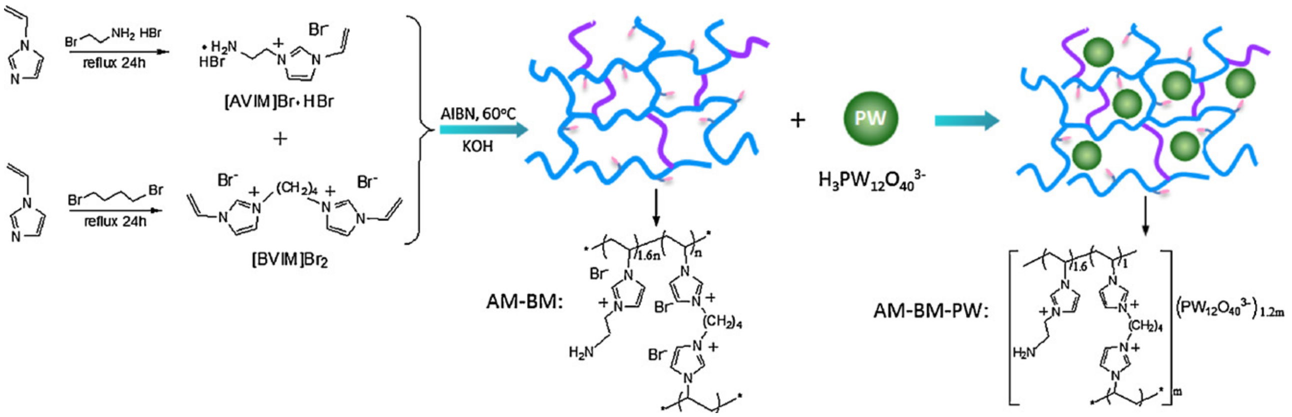


Scheme 1. Synthesis of the ionic hybrid AM–BM–PW.

In this study, we synthesize a task-specific cross-linked ionic copolymer *via* the radical copolymerization of a dicationic IL with an amine-functionalized IL. Then the ionic copolymer is anion-exchanged with phosphotungstic acid $H_3PW_{12}O_{40}$ (PW) to provide the new HPA-based amino-containing ionic copolymer catalyst that is designated as AM–BM–PW (Scheme 1). The obtained hybrid catalyst leads to a liquid–solid heterogeneous epoxidation of alkenes with aqueous H_2O_2, showing high conversion and selectivity, easy recovery, and very steady reuse.

2. Experimental

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. ^1H NMR spectra were measured with a Bruker DPX 300 spectrometer at ambient temperature in D_2O using TMS as internal reference. Elemental analyses were performed on a CHN elemental analyzer (FlashEA 1112). ESR spectra were recorded on a Bruker EMX-10/12 spectrometer at X-band. The measurements were done at 155 K in a frozen solution provided by a liquid/gas nitrogen temperature regulation system controlled by a thermocouple located at the bottom of the microwave cavity within a Dewar insert. Solid UV–vis spectra were measured with a PE Lambda 950 spectrometer, and $BaSO_4$ was used as an internal standard. XRD patterns were collected on the Bruker D8 Advance powder diffractometer using Ni-filtered Cu Kα radiation source at 40 kV and 20 mA, from 5 to 80° with a scan rate of 4°/min. 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 °C/min.

2.2. Catalyst preparation

2.2.1. Preparation of [AVIM]Br·HBr and [BVIM]Br$_2$

[3-Aminoethyl-1-vinylimidazolium]Br·HBr ([AVIM]Br·HBr): The amino-containing ionic liquid (IL) monomer [AMIM]Br·HBr was prepared according to the literature [25]. N-vinylimidazole (9.42 g, 0.10 mol) and 2-bromoethylamine hydrobromide (20.49 g, 0.10 mol) were dissolved in acetonitrile (50 mL) at 80 °C for 12 h under nitrogen atmosphere with stirring. On completion, the liquid was poured out and the solid was washed with anhydrous ethanol three times to remove the unreacted starting materials. After drying under vacuum, [3-aminoethyl-1-vinylimidazolium]Br·HBr was obtained (yield: 85%). ^1H NMR (300 MHz, D_2O, TMS) δ (ppm) = 3.47 (m, 2H, —CH_2), 4.58 (m, 2H, —CH_2), 5.40 (dd, 1H, —CH), 5.81 (dd, 1H, —CH), 7.13 (m, 1H, —CH), 7.66 (s, 1H, —CH), 7.81 (s, 1H, —CH), 9.18 (s, 1H, —CH).

[1,1′-(Butane-1,4-diyl)-bis(3-vinylimidazolium)]Br$_2$ ([BVIM]Br$_2$): [BVIM]Br$_2$ was prepared according to the previous report [26]. N-vinylimidazole (18.84 g, 0.20 mol) and 1,4 dibromobutane (0.10 mol) were dissolved in isopropanol (50 mL) at 80 °C for 24 h under nitrogen atmosphere. On completion, the white solid of [BVIM]Br$_2$ was obtained after the removing of solvent and washing with THF (yield: 90%). ^1H NMR (300 MHz, D_2O, TMS) δ (ppm) = 2.00 (s, 2H, —CH_2), 4.34 (s, 2H, —CH_2), 5.44 (d, 1H, —CH), 5.86 (d, 1H, —CH), 7.18 (m, 1H, —CH), 7.63 (s, 1H, —CH), 7.81 (s, 1H, —CH), 9.11 (s, 1H, —CH).

2.2.2. Preparation of ionic liquid copolymer AM–BM

The procedure for the synthesis of amino containing cross-linked IL polymer (AM–BM) was similar to that for the copolymerization of ILs and divinylbenzene (DVB) [27]. The obtained IL [AVIM]Br·HBr (1.0 g), [BVIM]Br$_2$ (1.0 g), and azobisisobutyronitrile (AIBN) (0.03 g) were dissolved in methanol (10 mL) under nitrogen. The mixture was refluxed at 60 °C with stirring. After 24 h, the white solid formed was filtrated and was washed with ethanol and water (1.65 g solid was obtained). AM–BM was obtained by the addition of KOH (0.168 g, 3.0 mmol) into the aqueous solution of the above solid for neutralization of HBr, followed by filtration and dried in vacuum at 60 °C for 12 h. According to the amount of KOH consumed in the neutralization of HBr, the composition of the ionic copolymer AM–BM was calculated to be AM$_{1.6}$–BM. The cross-linked IL polymers (BM) of [BVIM]Br$_2$ was prepared accordingly, without using the amino-functionalized IL [AVIM]Br·HBr. The ^1H NMR data for the copolymer AM–BM is not provided because it is insoluble in various solvents, such as H_2O, $CHCl_3$, DMF, DMSO, and CH_3OH.

2.2.3. Preparation of the HPA-based polymeric hybrid AM–BM–PW

AM–BM (0.3 g) was dissolved in 30 mL deionized water with stirring to form a transparent gel. The aqueous solution containing 2 g of $H_3PW_{12}O_{40}$ (PW) was added to the above solution of AM–BM, and the resulting slurry was stirred at room temperature for 24 h. The thus obtained solid catalyst (AM–BM–PW) was filtered and washed with water for three times, followed by drying in a vacuum. Elemental analysis, found: C: 8.24%, N: 3.71% and H: 1.30%. BM–PW was synthesized by reacting BM and $H_3PW_{12}O_{40}$ with the monomer molar ratio of 1.5:1.

2.3. Catalytic test

Cyclooctene (10 mmol), CH_3CN (10 mL), and AM–BM–PW (0.1 g) were added to a 25 mL flask. The reaction started after the addition of aqueous H_2O_2 (30 wt.%, 4 mmol) at 70 °C within 10 min under vigorous stirring. After reaction, the product

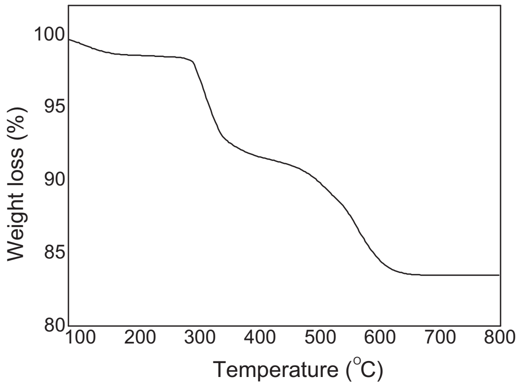


Fig. 1. TG pattern of AM–BM–PW.

mixture was analyzed by gas chromatography (GC). Conversion = 100% × (mol epoxide product + mol byproducts)/mol initial H_2O_2. Selectivity = 100% × mol epoxide product/(mol epoxide product + mol byproducts). The concentration of H_2O_2 in the reacted mixture was determined by the titration with sodium thiosulfate (starch as the indicator) in the presence of potassium iodide, sulfuric acid and ammonium molybdate. No remaining H_2O_2 was detected due to the self-decomposition of H_2O_2 accompanying with the oxidation of the alkene. In this case, the conversion of the substrate based on H_2O_2 calculated by the formula above also reflects the H_2O_2 utilization efficiency. Other alkene substrates were tested accordingly. For a three-run operation of the epoxidation of cyclooctene to test the catalytic stability of AM–BM–PW, the catalyst was recovered by a filtration immediately after reaction, followed with washing with ethanol and vacuum drying.

3. Results and discussion

3.1. Characterization of AM–BM–PW

The TG profile in Fig. 1 shows that AM–BM–PW was quite stable up to 280 °C. The weight loss of nearly 7% in the range 280–400 °C was due to the elimination of the amino-functionalized ILs AM [27]. The further weight loss of 8% in 400–600 °C was attributed to the decomposition of dicationic IL BM. Thus, estimatively, the molar ratio of AM to BM was 1.6/1, which is consistent with that calculated from the amount of KOH consumed for the neutralization of HBr in the synthesis of AM–BM. Moreover, the elemental analysis for the catalyst AM–BM–PW showed 8.24 wt.% for the weight percentage of C, 3.71 wt.% for N, and 1.30 wt.% for H, which is very near to the theoretical values of C: 7.93%, N: 3.25%, and H: 1.01%, demonstrating that AM–BM–PW has the structure illustrated in Scheme 1.

The XRD pattern in Fig. 2 displayed the featured diffraction peaks for the secondary crystal structure of the neat $H_3PW_{12}O_{40}$. However, all these peaks disappeared in the case of AM–BM–PW, indicating definitely a noncrystal structure of the hybrid. It is thus suggested that the hybrid catalyst largely inherits the amorphous structure of the ionic copolymer after the introduction of Keggin anions into the copolymer matrix by the anion-exchange, rather than retains the HPA crystal structure. The unsharp profiles for the micrometer sized particles of the IL copolymer AM–BM and the hybrid AM–BM–PW in the SEM image (Fig. 3) also confirms an amorphous structure for them.

3.2. Epoxidation of alkenes with H_2O_2 over AM–BM–PW and various control catalysts

With the epoxidation of cyclooctene by aqueous H_2O_2 as a model reaction, catalytic performances of the HPA-based amino-containing cross-linked hybrid AM–BM–PW and various control catalysts are listed in Table 1. AM–BM–PW caused a liquid–solid heterogeneous epoxidation system, and exhibited a 98.5% conversion with 100% selectivity (entry 1). On the other hand, the amino-free cross-linked counterpart BM–PW (entry 2), another desirable heterogeneous catalyst, showed a low conversion of 17.3%, implying that the amino groups in the IL copolymer are indispensable for the high epoxidation activity of AM–BM–PW. Also without amino groups, pure $H_3PW_{12}O_{40}$ (entry 3), though as a homogeneous catalyst, only gave a 12.9% conversion with 82.3% selectivity. This implies that the featured cross-linked polymeric framework of AM–BM–PW endows the catalyst with an insoluble nature in the reaction media.

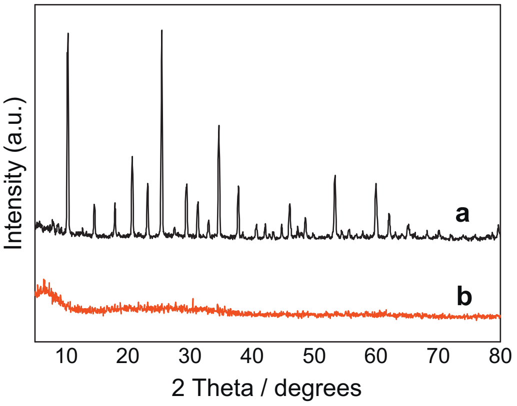


Fig. 2. XRD patterns of (a) $H_3PW_{12}O_{40}$ and (b) AM–BM–PW.

In order to investigate the scope of the AM–BM–PW catalyst for epoxidation reactions, the substrates such as cyclohexene, 1-octene, and 1-hexene were also investigated on the catalysts AM–BM–PW, BM–PW, and $H_3PW_{12}O_{40}$, with the results shown in entries 4–12 of Table 1. It can be seen that the present cross-linked polymeric hybrid AM–BM–PW could be applied to the epoxidation of various alkenes using H_2O_2, and good to excellent activities and selectivity were obtained in all cases. However, amino-free hybrid BM–PW and $H_3PW_{12}O_{40}$ were inactive or exhibit very low catalytic activities for all those substrates, which further confirms the promotional role of amino groups for the high epoxidation activity of AM–BM–PW.

3.3. Understanding of the catalytic behavior of AM–BM–PW

To investigate the promotional effects of the amino groups in the polymeric AM–BM–PW catalyst on epoxidations, the UV–vis profiles of AM–BM–PW and amino-free hybrid BM–PW are compared in Fig. 4. AM–BM–PW showed a absorption band in the range of 600–800 nm that is assignable to the intramolecular charge transfer from the amino-tethered cations to PW anions [28], but the band was undetectable for the amino-free counterpart BM–PW, suggesting the reduction of W^{6+} in AM–BM–PW by amino groups. The ESR signals at *ca.* 3500 G in Fig. 5 also confirms the existence of low valent W^{5+} species for AM–BM–PW. Therefore, these observations suggest that the redox property of W species might be significantly tuned through the intramolecular charge transfer from the amino groups to HPA frameworks.

The neat HPA and the polymeric hybrid AM–BM–PW were characterized by the IR spectra in Fig. 6. The four characteristic bands for the Keggin structure of neat $H_3PW_{12}O_{40}$ appeared at the wavenumbers of 1080 ($P{-}O_a$), 982 ($W{=}O_d$), 889 ($W{-}O_b{-}W$), and 804 cm^{-1} ($W{-}O_c{-}W$) (curve a). However, for the polymeric hybrid AM–BM–PW (curve b), the $P{-}O_a$ band at 1080 cm^{-1} splitted into two bands at 1080 and 1049 cm^{-1}, due to the formation of

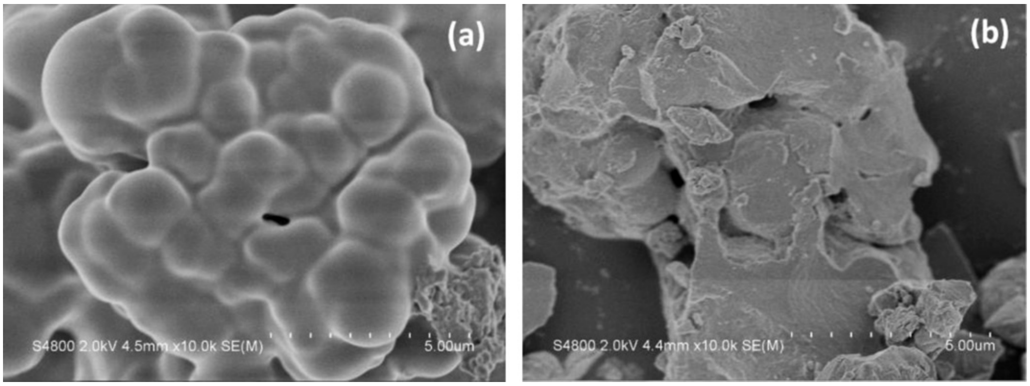
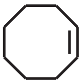


Fig. 3. SEM images of (a) AM–BM and (b) AM–BM–PW.

Table 1
Catalytic performance of various catalysts for the epoxidation of alkenes with H_2O_2.[a]

Entry	Substrate	Catalyst	Solubility in reaction	Con[b] (%)	Sel[c] (%)
1		AM–BM–PW	Insoluble	98.5	100
2		BM–PW	Insoluble	17.3	100
3		$H_3PW_{12}O_{40}$	Soluble	12.9	82.3
4		AM–BM–PW	Insoluble	94.7	92.5
5		BM–PW	Insoluble	40.5	67.4
6		$H_3PW_{12}O_{40}$	Soluble	28.7	32.4
7		AM–BM–PW	Insoluble	89.0	100
8		BM–PW	Insoluble	7.6	89.6
9		$H_3PW_{12}O_{40}$	Soluble	1.7	48.6
10		AM–BM–PW	Insoluble	78.1	100
11		BM–PW	Insoluble	3.3	100
12		$H_3PW_{12}O_{40}$	Soluble	0	–

[a] Reaction conditions: catalyst (0.1 g), substrate (10 mmol), 30% H_2O_2 (4 mmol), acetonitrile (10 mL), 70 °C for 4 h, 6 h for cyclohexene, 8 h for 1-octene and 1-hexene.
[b] Conversion of the substrate based on H_2O_2.
[c] Selectivity for the epoxide product; byproducts for entry 3: 2-cycloocten-1-ol and 2-cycloocten-1-one; entries 4–6: 2-cyclohexen-1-ol and 2-cyclohexen-1-one; 8 and 9: 2-octanone and octylaldehyde.

hydrogen bondings between the terminal oxygens of PW and the amino groups of copolymer [29,30]. Moreover, a new peak at 951 cm^{-1} branched from 982 cm^{-1} for W^{VI}=O is assignable to the reduced W^{5+} species due to the intramolecular charge transfer from aminos to terminal oxygens [31,32]. This result consolidates the evidence for the effective modification of the oxidation property of W species in the polymeric hybrid by the tethered amino groups in the cross-linked copolymer matrix, which relates to the good performances in the epoxidation of alkenes.

More insight into the HPA-based polymeric hybrid-catalyzed epoxidation was gained by the IR measurement of the AM–BM–PW after reacting with 30% H_2O_2 in CH_3CN at 70 °C for 10 min, which mimics the practical reaction but in the absence of any olefin substrates (curve c, Fig. 6). The intensities of the bands at 1049 and 951 cm^{-1} decreased significantly, which might be indicative of the fadeaway of the intramolecular electron delocalization and the hydrogen bonding interaction. The more noteworthy point is that a new distinct peak at 840 cm^{-1} for the peroxo–oxygen band ν(O—O) in peroxo–W species occurred, which has been known as the active species for $\{PO_4[WO(O_2)_2]_4\}^{3-}$-based epoxidations [6,8,33]. However, it seems that the HPA polymeric hybrid with amino-functional groups was easier to generate the peroxo–W species, because the band at 840 cm^{-1} could not be observed for the H_2O_2-treated amino-free hybrid BM–PW. This result clearly

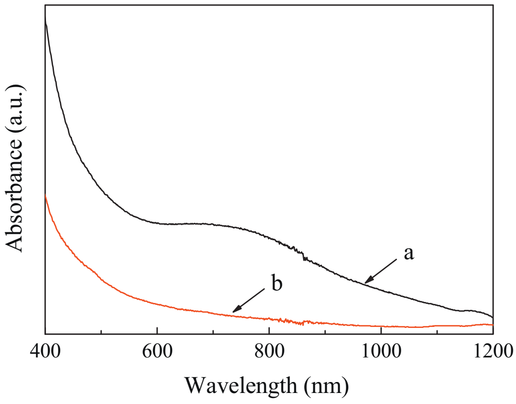


Fig. 4. UV–vis spectra of (a) AM–BM–PW and (b) BM–PW.

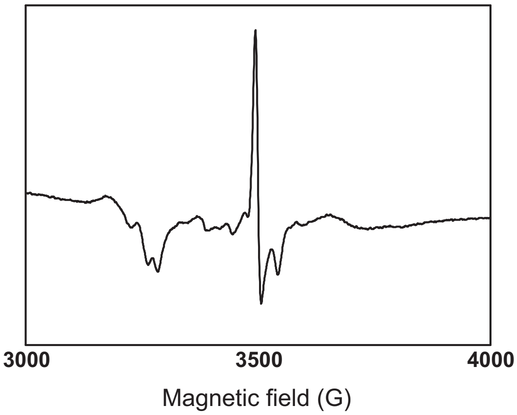


Fig. 5. ESR spectrum of AM–BM–PW.

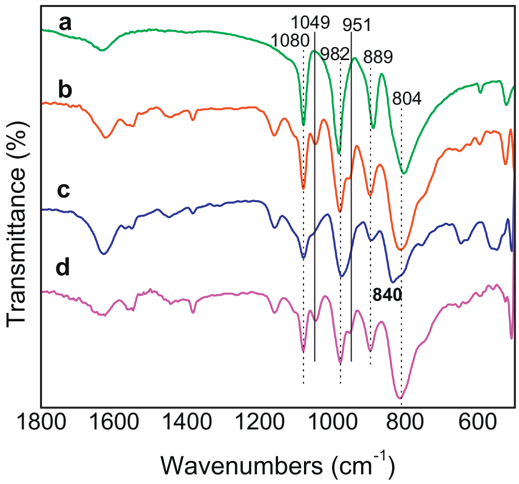


Fig. 6. FT-IR spectra of (a) $H_3PW_{12}O_{40}$, (b) fresh AM–BM–PW, (c) H_2O_2 treated AM–BM–PW, and (d) recycled AM–BM–PW.

indicate that peroxo–W species improved by the amino groups were the possible intermediate active species, which may directly associate with the high activity and selectivity of AM–BM–PW for the epoxidation of alkenes.

3.4. Catalyst reusability

As it is very convenient to recover the polymeric hybrid catalyst by filtration or centrifugation after a reaction, the solid catalyst could be readily reused for the next run. Table 2 displays the catalytic recycling property for AM–BM–PW in the epoxidation of cyclooctene with H_2O_2, the three-run test gave 100% selectivity without significant loss of conversion, revealing a quite steady reusability. ICP-AES elemental analysis for the reacted filtrates indicates that less than 3 wt.% W of AM–BM–PW leached into the reaction media during the first run, and in the followed runs, the leaching is negligible. Furthermore, the IR spectrum for the recovered AM–BM–PW in Fig. 6, curve (d) was well consistent with that of the fresh one, which demonstrates a durable catalyst structure and accounts for the steadily catalytic reuse.

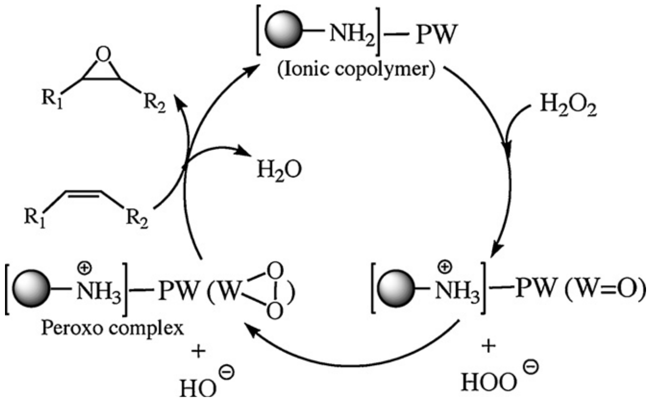
In order to test the possible catalysis of the slightly leached species in the reaction solution from the catalyst, an experiment was carried out under the reaction conditions shown in Table 2. The conversion 65.3% and selectivity 100% were obtained at the reaction time 2 h. Then, the solid catalyst was hot-filtered and the reaction proceeded for another 4 h with the homogeneous filtrate, which resulted in almost unchanged conversion 65.7% and selectivity 100%. This result strongly indicates the heterogeneous nature of the present catalyst AM–BM–PW for the epoxidation reaction.

Our previous report [18] revealed that a HPA-based non-polymeric ionic hybrid catalyst prepared by protonating and anion-exchanging the 3-aminoethyl-1-methylimidazolium IL with $H_3PW_{12}O_{40}$ offered a high conversion of 95.7% with 100% selectivity. However, 10.5% of the W in the monocationic hybrid had leached out during the first run of the reaction, which is much higher than that of the present cross-linked polymeric hybrid AM–BM–PW. This allows to draw that the hybrid HPA catalyst with cross-linked polymeric cations is more structural stable, with a great improvement of the leaching-resistance property.

Table 2
Catalytic reusability of the polymeric hybrid catalyst AM–BM–PW for the epoxidation of cyclooctene with H_2O_2.[a]

Run	1	2	3
Con[b] (%)	98.5	98.0	97.2
Sel[c] (%)	100	100	100

[a] Reaction conditions: catalyst (0.1 g), cyclooctene (10 mmol), 30% H_2O_2 (4 mmol), acetonitrile (10 mL), 70 °C for 4 h.
[b] Conversion of the substrate based on H_2O_2.
[c] Selectivity for the epoxide product.



Scheme 2. Proposed mechanism for the heterogeneous epoxidation of alkenes with H_2O_2 over the HPA-based ionic copolymer catalyst AM–BM–PW.

3.5. Catalysis mechanism

The mechanism for the traditional $H_3PW_{12}O_{40}$-catalyzed epoxidations was demonstrated previously, involving derived $\{PO_4[WO(O_2)_2]_4\}^{3-}$ from Keggin precursors in the presence H_2O_2, with peroxo–W as the active centres [6,34]. In the present work, the polymeric hybrid catalyst AM–BM–PW revealed a undegradable solid nature in H_2O_2 attributed to the amino-containing cross-linked polymeric cations, which allows to easily recover the used solid catalyst and to provide the evidence for the peroxo–W active species. Based on the above results, the reaction mechanism for the epoxidation of alkenes with H_2O_2 over AM–BM–PW can be described as in Scheme 2. The catalytic cycle starts from the reaction of H_2O_2 with amino groups to form a quaternary ammonium and a perhydroxyl. Simultaneously, the perhydroxyl reacts with the amino-modified W sites in the HPA framework, leading to the generation of the peroxo–W complex that is supposed to be the active site for epoxidation. Finally, the peroxo–W complex is resumed to the original state of W=O by inserting its oxygen into the alkene reactant to produce an epoxide product.

4. Conclusion

In summary, we have developed and synthesized an heteropolyanion-based amino-containing cross-linked ionic copolymer catalyst for the liquid–solid heterogeneous epoxidation of alkenes with H_2O_2. The new polymeric catalyst exhibits very high conversions and selectivity, coupled wih convenient recovery and steady reusability. The cross-linked structure of the copolymer cations is responsible for the catalyst's stable structure, and the evidenced peroxo–W active sites in HPA frameworks promoted by the amino groups in polymer matrix is revealed to account for the catalyst's excellent performances in epoxidation of alkenes with H_2O_2.

Acknowledgments

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