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ORIGINAL PAPER

Iron and manganese (III) porphyrin covalently bound to poly(acryloyl chloride) as biomimetic heterogeneous catalysts for alkene epoxidation by $NaIO_4$: advantage of iron (III) porphyrin and significance of nitrogen donor axial ligands

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Abstract Poly(acrylic acid) (PAA) was converted to poly(acryloyl chloride) (PAC) by thionyl chloride and the prepared PAC was used as support for iron tetrakis(4-benzylamine)porphyrin (Fe(T_{Bamin}P)OAc). The Fe-porphyrin was covalently bound to the PAC to produce Fe(T_{Bamin}P)OAc@PAC as reusable heterogeneous catalysts for alkene epoxidation with sodium periodate ($NaIO_4$). The newly synthesized Fe catalyst was characterized by FT-IR, EDX, SEM and TEM techniques. A similar procedure was followed for synthesis and characterization of Mn(T_{Bamin}P)OAc@PAC using Mn(T_{Bamin}P)OAc and PAC. The Fe and Mn content of the catalysts were measured by atomic absorption spectroscopy (AAS). We have found that among Mn(T_{Bamin}P)OAc, Fe(T_{Bamin}P)OAc (heterogeneous catalysts), Mn(T_{Bamin}P)OAc@PAC and Fe(T_{Bamin}P)OAc@PAC (homogenous catalysts) the later is the best catalyst for alkene epoxidation by $NaIO_4$ in CH_3CN/H_2O. The epoxidation reactions are sensitive to the nature and concentration of nitrogen donor axial ligands (i.e., imidazole) and the activity of the catalysts and the epoxidation yields increased with using such ligands in the reaction mixture. The Fe(T_{Bamin}P)OAc@PAC was found to be a stable catalyst and can be recycled for at least four times without considerable loss of catalytic activity.

Keywords Poly(acrylic acid) · Porphyrin · Heterogeneous catalyst · Epoxidation · Alkene

Introduction

Metalloporphyrins may structurally and functionally resemble the cytochrome P-450 monooxygenase enzymes [1, 2]. In order to understand the mechanism of cytochrome P-450 enzymes, synthetic metalloporphyrins in association with single oxygen atom donors such as PhIO, $NaIO_4$, NaClO, H_2O_2 and ROOH have been used as model compounds for oxidation reactions [3–9]. In metalloporphyrin-mediated reactions, the homogenous metalloporphyrin catalysts are generally destroyed by the oxidants or by their metal-oxo intermediates, leading to obtain low yields, low selectivities and turnover frequencies. In cytochrome P-450 enzymes, the heme groups are immobilized on the protein chain by axial ligands of the protein residues [10, 11]. The strategy prevents the degradation and inactivation of heme groups as active site of the enzymes. Similarly, the use of synthetic metalloporphyrins substituted with active groups and their immobilization on an appropriate support has resulted in efficient, reusable and selective catalysts for catalytic oxidation reactions. In addition to this, the immobilization prevents molecular aggregation by π–π interactions or irreversible bimolecular oxidative self-destruction reactions via an intermolecular process, which cause a reduction in the activity of homogeneous catalysts [12–22]. Furthermore, the use of supported metalloporphyrins as the active heterogeneous catalyst provides an easy way to handle and eliminate the difficulty in recovery and recycle of these expensive catalysts from the reaction media. In recent years, many papers have attested to the value and importance of supporting metalloporphyrins on the polymer supports [23, 24]. Poly(acrylic acid) (PAA) is a hydrophilic; water soluble polymer used in many applications including surface modification, biotech and pharmaceuticals [25–29].

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The repeated units of PAA contain both carboxyl groups and a long chain hydrocarbon. It could be converted into modified polymers with the targeted functional groups (-COOH) through the reaction with different organic and/or inorganic compounds.

In this work, the carboxyl end group of PAA was converted to acyl group by using thionyl chloride to obtain poly (acryloyl chloride) (PAC). The prepared PAC was used for supporting of iron and manganese tetrakis(4-benzylamine)porphyrins to attain Fe(T_{Bamin}P)OAc@PAC and Mn(T_{Bamin}P)OAc@PAC as heterogeneous catalysts for epoxidation of alkenes by sodium periodate ($NaIO_4$).

Experimental

All chemicals were obtained from Merck or Fluka chemical companies. Tetrakis(4-benzylamine)porphyrin ligand, (T_{Bamin})P, was successfully synthesized previously by our group through the reduction of tetrakis(4-cyanophenyl)porphyrin (T_{CN})P with lithium aluminum hydride in anhydrous diethyl ether [30]. Fe(T_{Bamin}P)OAc and Mn(T_{Bamin}P)OAc are obtained by metallation of the (T_{Bamin})P with iron(II) acetate or manganese(II) acetate in DMF according to the method described by Buchler et al. [31]. Poly(acryloyl chloride) (PAC) was prepared following literature procedure by the reaction of commercial PAA (average Mv ca. 450,000) with thionyl chloride [32].

The FT-IR spectra were recorded using a Jasco FT-IR-460 plus spectrophotometer, in KBr pellets. The micrographs from scanning electron microscopy (SEM) were obtained using a Philips XL-30 microscope equipped with an EDS system. The microstructure of samples was studied using a Zeiss, EM10C transmission electron microscope (TEM) model with 100 kV. GC analyses were performed on a 6890 N Agilent gas chromatograph (USA) equipped with a flame ionization detector (FID) and a capillary column 19095J-623 (5 % phenyl, 95 % dimethylpolysiloxane 30 m × 0.53 mm × 5 µm).

Preparation of Fe(T_{Bamin}P)OAc@PAC catalyst

Fe(T_{Bamin}P)OAc@PAC was prepared by the interaction of Fe(T_{Bamin}P)OAc and PAC in the presence of triethylamine. In a 500 mL round bottom flask, 3.0 g of PAC was suspended in 150 mL of tetrahydrofuran/toluene (1:1; v/v) and the suspension was stirred vigorously for 30 min. Another 150 mL tetrahydrofuran/toluene (1:1 v/v) containing 0.6 g, (0.72 mmol) Fe(T_{Bamin}P)OAc and 2.91 g (28.81 mmol) triethylamine was prepared and added dropwise to the polymer suspension. The mixture was then refluxed for 12 h and cooled down to room temperature. The resulting brown solid was filtered off, washed thoroughly with MeOH and CH_2Cl_2 and dried under vacuum at 90 °C. A similar procedure was followed for preparing Mn(T_{Bamin}P)OAc@PAC as a slime green solid using Mn(T_{Bamin}P)OAc and PAC in the presence of triethylamine. IR (KBr,υ,cm^{-1}): 1625 (C=O), 3440-3500 (N–H amide and NH_2 amine), 1410 (C–N amide).

Epoxidation reactions

To an acetonitrile solution (2 mL) containing alkene (0.3 mmol), axial ligand (i.e., imidazole; 0.025 mmol; 0.0017 g) and Fe(T_{Bamin}P)OAc@PAC (0.1 g), an aqueous solution (1.0 mL) of $NaIO_4$ (0.325 mmol; 0.069 g) was added. The reaction was stirred at room temperature for required time and monitored by gas chromatography (6890N, Agilent USA). All reactions were run at least in triplicate, and the data represent an average of these reactions with standard deviation of the means less than 2–4 %.

Catalyst reusability

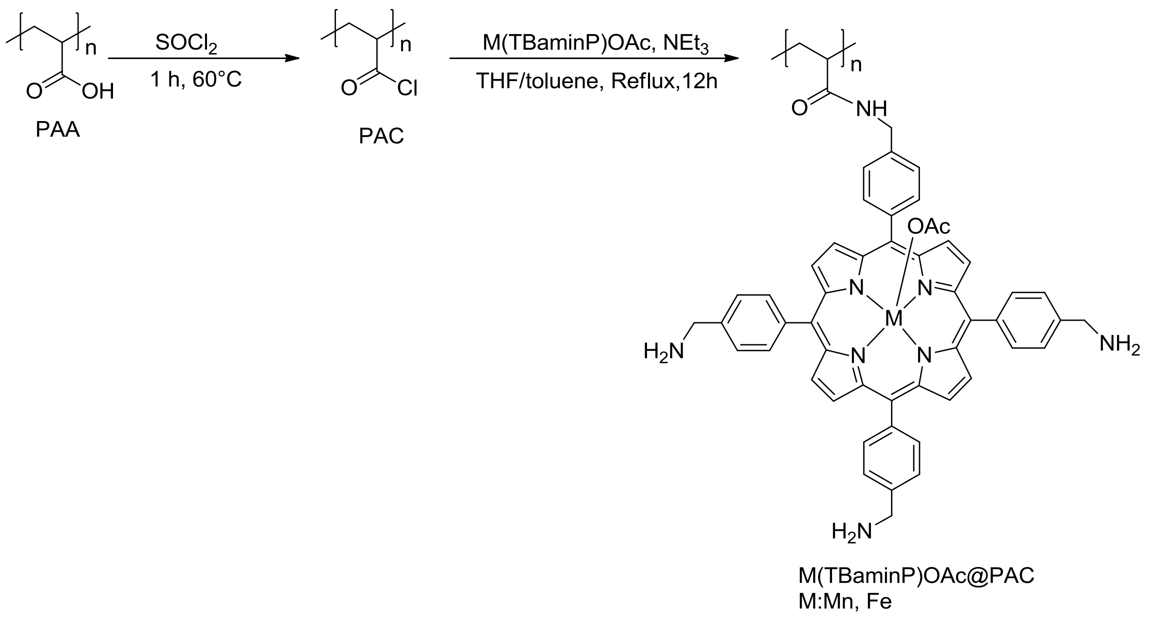
The recycle and reuse experiments for Fe(T_{Bamin}P)OAc@PAC were performed to examine its stability. In the epoxidation of styrene, the catalyst was separated from the reaction mixture by filtration, washed with CH_3CN and dried before being used in the next run. It can be observed that during the consecutive reuse of 4 times, the combination catalyst was stable to some extent.

Results and discussion

Synthesis and characterization of supported metalloporphyrin catalysts

The overall reaction pathway for preparing supported metalloporphyrin catalysts is shown in Scheme 1. The carboxylic acid groups in PAA were converted to acyl chloride to obtain PAC and then the Fe and Mn porphyrin catalysts were reacted with PAC to obtain the heterogeneous catalysts. It seems probable that the metalloporphyrins anchor the polymer film by one or more -NH_2 groups. This may enhance the stability and reusability of the catalyst [33, 34].

The Fe(T_{Bamin}P)OAc@PAC catalyst was characterized by FT-IR, EDX, SEM and TEM, techniques. The Fe content of the catalyst was measured by atomic absorption spectroscopy (AAS) which was found to be ca. 489 µmol per gram of the catalyst, indicating the appropriate supporting of the catalyst on the polymer.



Scheme 1 Overall reaction pathway for preparation of Mn and Fe(T_{Bamin}P)OAc@PAC

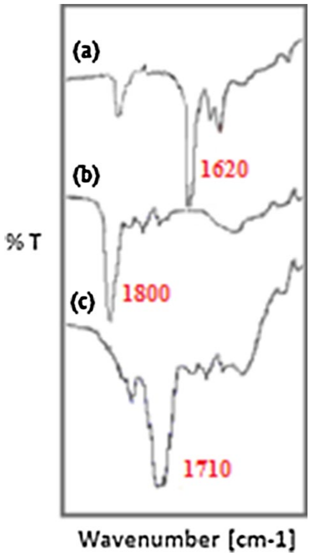


Fig. 1 The FT-IR spectra(C=O stretching region) of (*a*) Fe(T_{Bamin}P)OAc@PAC, (*b*) PAC and (*c*) PAA

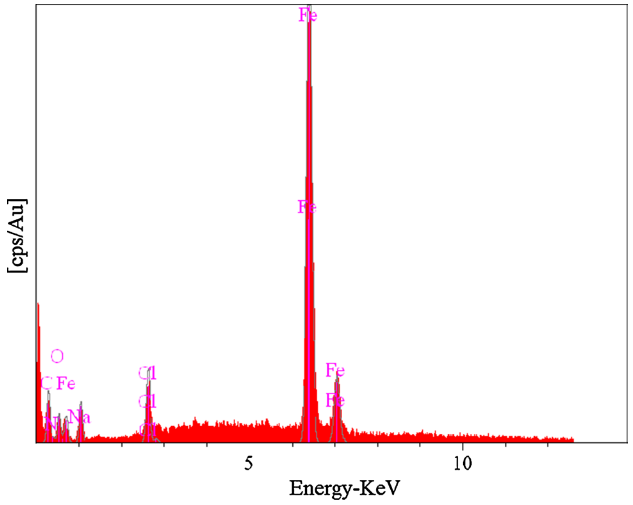


Fig. 2 The EDX pattern of Fe(T_{Bamin}P)OAc@PAC

The FT-IR spectroscopy gives valuable information about covalent anchoring of Fe(T_{Bamin}P)OAc@PAC on the functionalized polyacrylic acid that is obtained by comparison of the IR spectra of PAA, PAC and Fe (TBaminP) OAc@PAC (Fig. 1). The C=O stretching band of the acidic groups in PAA appeared at 1710 cm^{-1}. This vibration shifted to 1800 cm^{-1} upon conversion to the acid chloride in PAC. When the porphyrin was attached to PAC, the C=O band shifted to 1620 and the N–H and C–N amide vibration (not shown) were observed at 3438 and 1400 cm^{-1}, respectively.

Moreover, the band at 1798 cm^{-1} might be contributed by the unreacted acyl groups in Fe(T_{Bamin}P)OAc@PAC catalyst. These observations clearly confirmed the attachment of the iron porphyrin to the PAC.

The EDX analysis of the catalyst showed presence of Fe as shown in Fig. 2 that confirmed the loading of Fe(T_{Bamin}P)OAc on the polymer support. From the EDX data (not shown) we have found that the amount of the Fe-porphyrin loaded on PAC was ca. 504 mmol per gram of the catalyst. This result is coincident with that obtained by

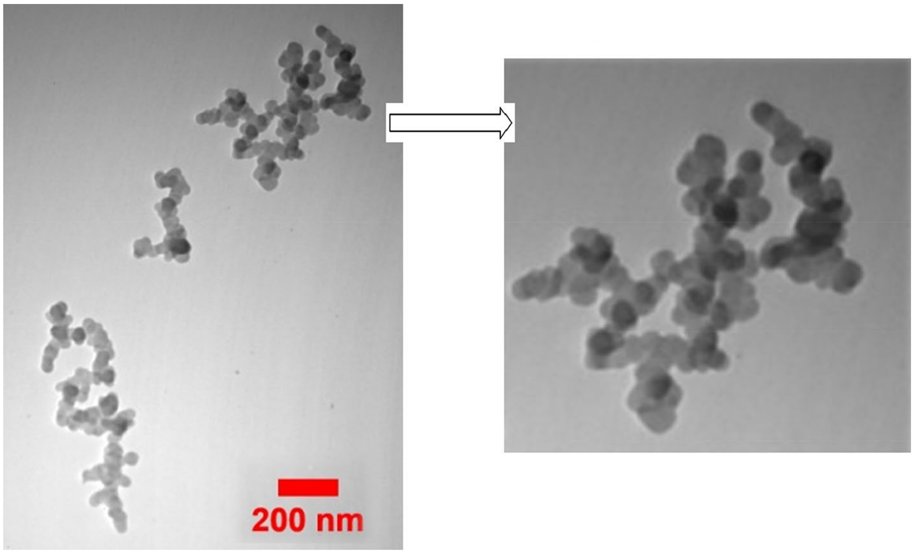


Fig. 3 TEM image of Fe(T_{Bamin}P)OAc@PAC

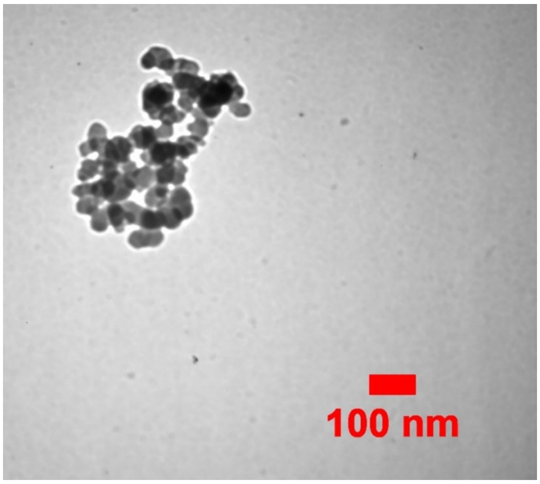


Fig. 4 TEM image of Mn(T_{Bamin}P)OAc@PAC

AAS, and consequently all the oxidations under study (vide infra) were achieved by ca. 0.1 g of Fe(T_{Bamin}P)OAc@PAC which contains 0.005 mmol of the catalyst.

The particle size and structural morphology of the Fe(T_{Bamin}P)OAc@PAC were also investigated by TEM technique. The TEM image of the catalyst presented in Fig. 3, showed that the catalyst particles were approximately spherical in shape on the polymer chain and their size in diameters was found to be in the range of 60–80 nm.

A similar feature was also obtained for Mn(T_{Bamin}P)OAc@PAC, demonstrating the morphology and pattern of the catalyst particles (Fig. 4).

Scanning electron micrograph (SEM), was recorded for PAC, Fe(T_{Bamin}P)OAc@PAC and Mn(T_{Bamin}P)OAc@PAC to examine the morphological changes occurring on the surface of the polymer. A clear change in the morphology of the polymer, after supporting of the porphyrin complexes, was observed by SEM (Fig. 5). The morphology of the heterogeneous catalysts was tailored to maximize the contact between Fe(T_{Bamin}P)OAc and Mn(T_{Bamin}P)OAc particles and the PAC itself, at increasing degrees of support-catalysts contact.

After interaction of the catalysts with the PAC, the color of the PAC changed from white to brown in the case of Fe(T_{Bamin}P)OAc@PAC and to slime green in the case of Mn(T_{Bamin}P)OAc@PAC (Fig. 6). This change also indicates the supporting of the catalysts on the PAC.

The Mn content of Mn(T_{Bamin}P)OAc@PAC was determined by AAS, which showed a value of 846 µmol per gram of the catalyst. Therefore, the oxidation reactions catalyzed by Mn(T_{Bamin}P)OAc@PAC were performed with 0.006 g of the catalyst which is equivalent to ca. 0.005 mmol of Mn(T_{Bamin}P)OAc.

Epoxidation reactions

It should be noted that the epoxidation does not proceed in the absence of catalyst or in the presence of PAA and/or PAC. So, the catalytic experiment was carried out with styrene and $NaIO_4$ in the presence of both the heterogeneous and homogeneous Fe and Mn porphyrin catalysts. In a typical experiment, the catalytic oxidation of styrene (0.3 mmol) in different solvent mixtures was experienced by $NaIO_4$ (0.325 mmol) and the Fe or Mn catalysts (0.005 mmol) at room temperature. The results are shown in Table 1. We have found that among different solvent mixtures, CH_3CN/H_2O (2:1, v/v, 3 mL) is expedient solvent because higher epoxidation yield was obtained with this solvent. H_2O is necessary because of the solubility consideration of $NaIO_4$.

Moreover, the higher epoxide yield obtained with Fe(T_{Bamin}P)OAc@PAC reflects the higher activity of this

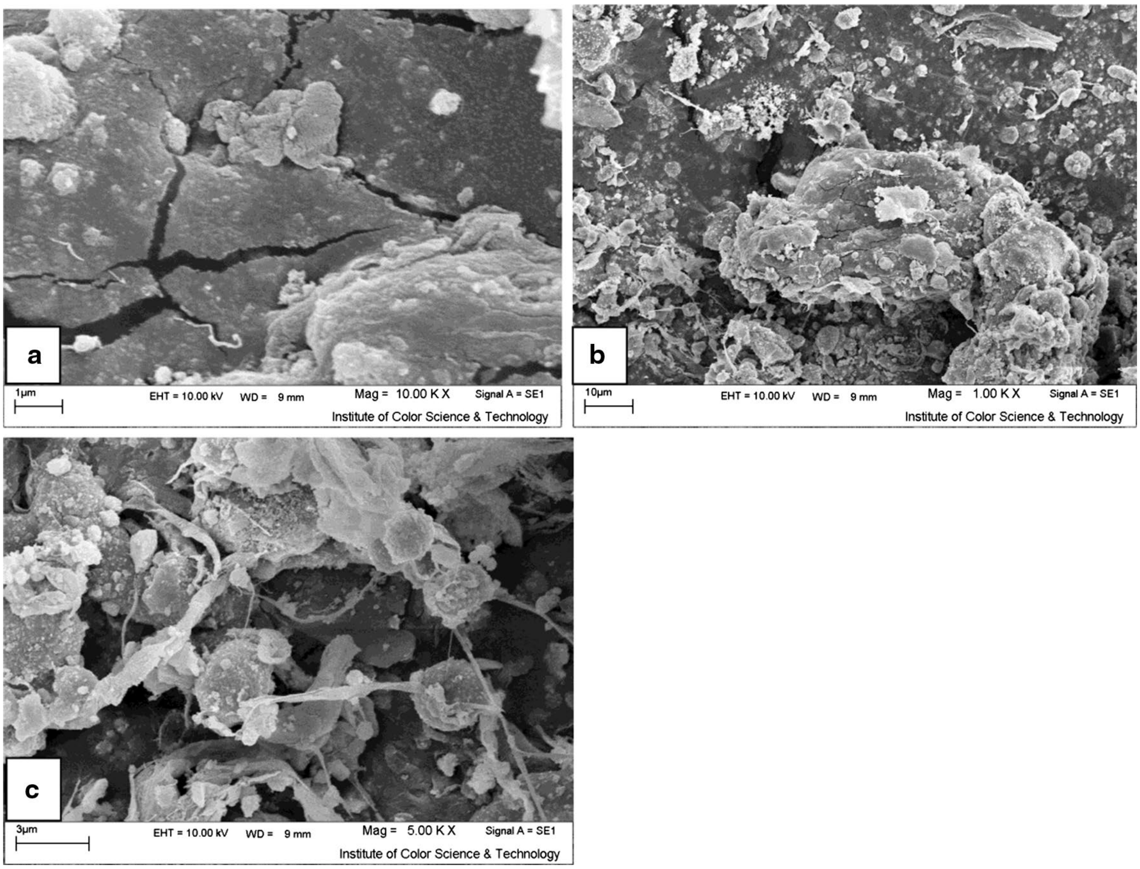


Fig. 5 Scanning electron micrograph (SEM) of **a** poly(acryloyl chloride), **b** Fe(T_{Bamin}P)OAc @PAC and **c** Mn(T_{Bamin}P)OAc@PAC

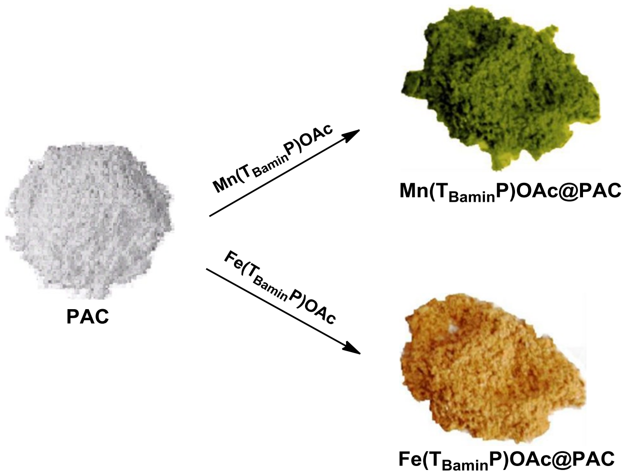


Fig. 6 An identifiable color change during the preparation of Fe(T_{Bamin}P)OAc@PAC and Mn(T_{Bamin}P)OAc@PAC from PAC

catalyst. Hence, among the catalyst mentioned in Table 1, Fe(T_{Bamin}P)OAc@PAC displayed higher catalytic activity for styrene epoxidation with $NaIO_4$. The heterogeneous Fe and Mn catalysts are more effective than that of the homogeneous catalysts. This may be related to high specific surface area of the catalyst which resulted from supporting of the catalyst to the PAC chain.

In the next approach, we investigate the influence of the nature and concentration of nitrogen donor axial ligands on the epoxidation of styrene with $NaIO_4$. It was found that metalloporphyrin-mediated systems are much improved by the use of such ligands [35–37]. Nitrogen donor axial ligands are reported to weaken the M–O bond in the oxidized form of the catalyst by donating electron density into the M–O antibonding orbitals [38, 39].

Previously, we have studied the effect of various nitrogen donor axial ligands on epoxidation of alkenes with $NaIO_4$ and found that nitrogen donor axial ligands with π-donor capability are much more effective co-catalysts than pure σ-donors, suggesting the importance of π-bonding interactions of the nitrogenous bases [39]. Table 2 represents the epoxidation of styrene with the Fe and Mn porphyrin catalysts and $NaIO_4$ in CH_3CN/H_2O at room temperature in the presence of different nitrogen donor axial ligands.

In the absence of nitrogen donor axial ligands (Table 2, run 1, Im/cat = 0:1) the epoxidation does not proceed effectively and only 12.5 % styrene epoxide was formed with

Table 1 Epoxidation of styrene by $NaIO_4$ in the presence of Fe and Mn catalysts in different solvent mixtures

Solvent	Epoxide (%) with:			
	$Fe(T_{Bamin}P)OAc$	$Fe(T_{Bamin}P)OAc@PAC$	$Mn(T_{Bamin}P)OAc$	$Mn(T_{Bamin}P)OAc@PAC$
CH_2Cl_2/H_2O	4.7	3.8	5.2	7.1
$CHCl_3/H_2O$	2.7	4.2	nd	5.9
CH_3CN/H_2O	5.0	12.5	6.8	9.3
DMF/H_2O	nd	3.4	nd	nd
$MeOH/H_2O$	–	2.5	–	nd

The reactions were carried out in room temperature at 1 h with 3 mL solvent mixture containing 2 mL organic solvent and 1.0 mL H_2O and it was analyzed by GLC (Agilent 6890N, Capillary Column 19095J-623,SE-30, 30 m; USA)

nd not detected

Table 2 Effect of the nature and concentration of various nitrogen donor axial ligands on the epoxidation of styrene with $NaIO_4$ catalyzed by Fe and Mn porphyrins

Run	Nitrogen donor axial ligands (B)	pK_a $(BH^+)^a$	Epoxide % with:			
			$Fe(T_{Bamin}P)OAc$	$Fe(T_{Bamin}P)OAc@PAC$	$Mn(T_{Bamin}P)OAc$	$Fe(T_{Bamin}P)OAc@PAC$
1	Im (0:1)	6.95	5	12.5	6.8	9.3
2	Im (1:1)	6.95	10.2	14.8	–	13.4
3	Im (5:1)	6.95	11.0	44.7	21.3	25.0
4	Im (10:1)	6.95	8.8	23.5	–	30.6
5	4(5)-MeIm (5:1)	7.27	–	10.0	–	6.1
6	2-EtIm (5:1)	7.86	–	8.9	–	5.0
7	Py (5:1)	5.25	5.5	7.3	–	9.8
8	3,4-NH_2Py (5:1)	9.05	–	7.7	–	7.5
9	Ph_2NH (5:1)	–	–	10.0	–	6.4
	His (5:1)	6.00	11.3	17.4	–	14.5

The reactions were achieved in CH_3CN/H_2O under atmospheric conditions at 1 h and the yields are GC yields based on the starting alkene. The data in the parentheses are the molar ratio of nitrogen donor axial ligands (B) to catalyst (cat)

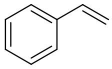
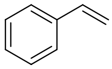
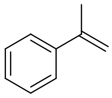
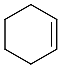
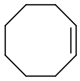
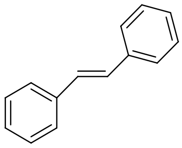
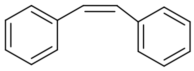
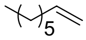
Im imidazole, *4(5)-MeIm* 4- or 5-methylimidazole (tautomeric), *2-EtImH* 2-ethylimidazole, *His* histidine amino acid

[a] pK_a values obtained from Ref. [40]

$Fe(T_{Bamin}P)OAc@PAC$ catalyst. However, with increasing the Im/cat ratio in the reaction mixture (Table 2, run 2, Im/cat = 1:1) the epoxidation become facile. With the ratio of cat/Im = 5:1, the epoxide yields reached maximum amounts of 11, 44.7, 21.3 and 25 % with $Fe(T_{Bamin}P)OAc$, $Fe(T_{Bamin}P)OAc@PAC$, $Mn(T_{Bamin}P)OAc$ and $Mn(T_{Bamin}P)OAc@PAC$, respectively (Table 2, run 3). Comparison of the epoxide yields obtained with cat/Im = 5:1 (Table 2, run 3) and 10:1 (Table 2, run 4) showed that when the ratio increased to 10:1, the epoxide yields decreased in the case of $Fe(T_{Bamin}P)OAc@PAC$ and increased in the case of $Mn(T_{Bamin}P)OAc@PAC$. The low yield in $Fe(T_{Bamin}P)OAc@PAC$ catalyzed epoxidation in the presence of imidazole (Im) was often attributed to the formation of the 6-coordinate bis-ligated catalyst complex [36, 41].

The $Mn(T_{Bamin}P)OAc@PAC$ catalyst is not virtually sensitive to the imidazole concentration. Comparison of the epoxide yields obtained by different nitrogen donor axial ligands (Table 2, run 3–10) show that (1) the cat/Im ratio of 5:1 is the best choice for epoxidation and so other reactions were achieved with this molar ratio, (2) imidazole with strong π-donor ability to metal center of the metalloporphyrins, is far better co-catalysts than all the nitrogen donors presented in Table 2, (3) there is no direct correlation between co-catalytic activities and the pK_a values of the nitrogen donors. It is inserting that histidine ($pKa = 6$; side chain group) [42] could also act as co-catalyst for the styrene epoxidation (run 10), leading to 11, 17, and 14.5 % epoxide yields with $Fe(T_{Bamin}P)OAc$, $Fe(T_{Bamin}P)OAc@PAC$ and $Mn(T_{Bamin}P)OAc@PAC$, respectively. The results again show higher catalytic activity of the $Fe(T_{Bamin}P)OAc@PAC$ compared to the other catalysts. Therefore based on the available data in this study, the optimal conditions for epoxidation include $Fe(T_{Bamin}P)OAc@PAC$, imidazole, alkene and $NaIO_4$ (in CH_3CN/H_2O 2:1 v/v, 3 mL)

Table 3 Epoxidation of alkenes with $NaIO_4$ catalyzed by $Fe(T_{Bamin}P)OAc@PAC$ and imidazole

Run	Alkene	Conv. (%)	Epox. (%)	Epoxide selectivity (%)	Time (h)	TOF (h^{-1})^a
1		28.4	17.1	60.2	2.5	4.1
2		57.8	56.0	96.9	1.5	22.4
3		49.4	49.4	100	1.5	19.7
4		72.5	72.5	100	2	21.7
5		79.2	79.2	100	2.5	19.0
6		47.7	46.0	96.4	1	27.6
7		56.0	54.7	97.0	1	32.4
8		23.8	21.0	88.2	2.5	5.0

Turnover number is the ratio of the number of moles of produced epoxide to the number of moles of catalyst and turnover frequency (abbreviated TOF) is used to refer to the turnover per unit time

with the molar ratio of 1:5: 60:65, respectively at room temperature.

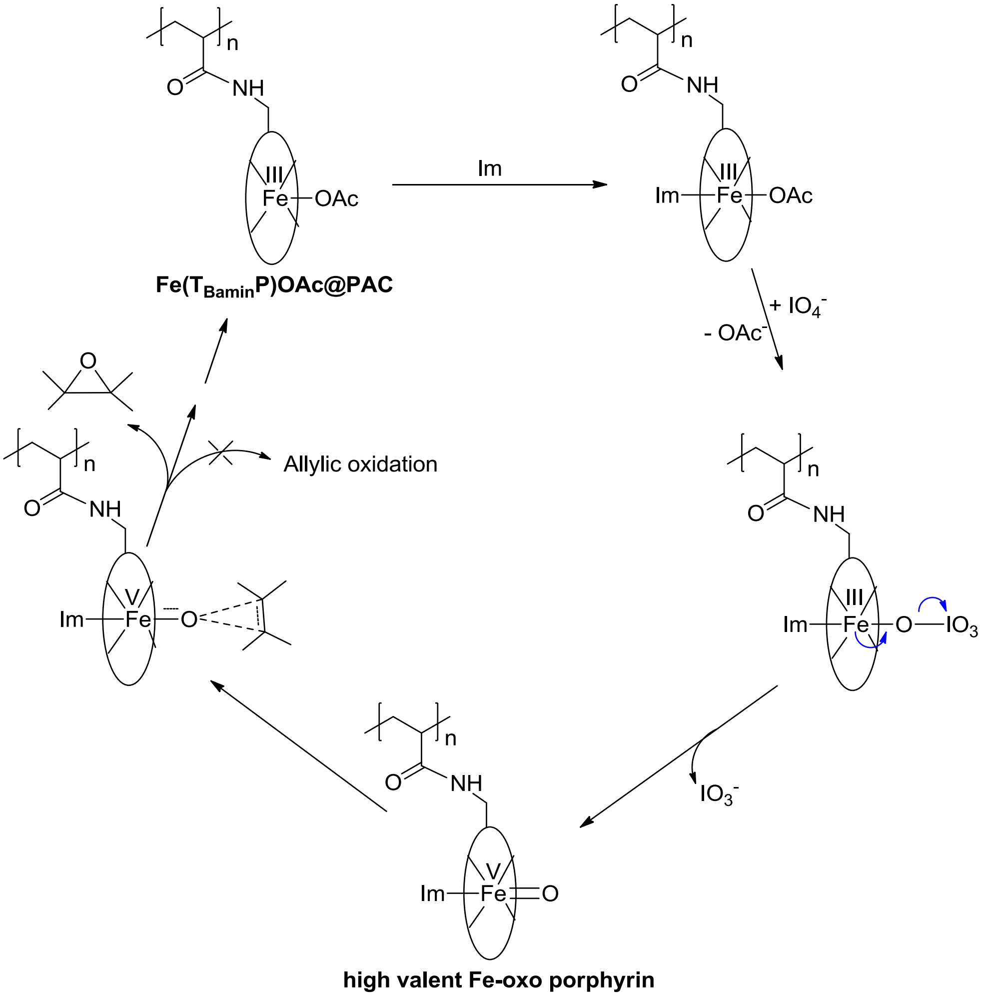
The optimal conditions were applied for epoxidation of some other alkenes. The results are summarized in Table 3. As it can be seen, epoxidation of styrene with $Fe(T_{Bamin}P)OAc$ as heterogeneous catalyst leaded to 28.4 % conversion with 60.2 % selectivity for styrene epoxide (Table 3, run 1). Moreover, the turnover frequency is very low (4.1 h^{-1}) in this case. However, $Fe(T_{Bamin}P)OAc@PAC\text{-}Im/NaIO_4$ system shows better catalytic activity toward alkenes, so that styrene was epoxidized in 56 % with ca. 96.9 % selectivity and 22.4 h^{-1} TOF (Table 3, run 2). No benzaldehyde or other products were found, probably due to the formation of a high valent Fe-oxo porphyrin intermediate which could epoxidize styrene directly through the interaction of the intermediate and the alkene substrate [43].

The possible interactions between the catalyst and the other species involved in the epoxidation reaction were shown in Scheme 2. It is reasonable to assume that the epoxidation was achieved directly with the high valent Fe-oxo porphyrin without any allylic oxidation which results benzaldehyde and other by products. Although, the C=C bond in α-methylstyrene (Table 3, run 3) is more electron-rich than styrene, the epoxide yield of α-methylstyrene is lower than that of styrene. This may be related to the steric hindrance existing in the former. Cyclohexene (Table 3, run 4) and cyclooctene (Table 3, run 5) were epoxidized moderately with 100 % selectivity and high TOFs. Although, the epoxide yield obtained for *trans*-stilbene (Table 3, run 6) is lower than that of *cis*-stilbene (Table 3, run 7) which may attribute to steric effect of the former, the TOF value of *cis*-stilbene was higher than that of *trans*-isomer. In 1-octene (Table 3, run 8), the C=C bound is an electron poor double bond and thus gives low yield and low TOF.

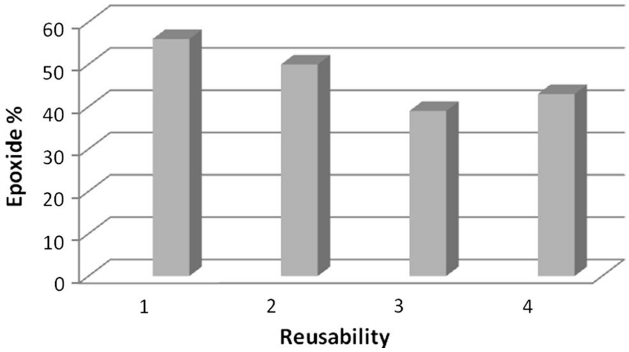
Reusability of the catalyst

Metalloporphyrins are expensive catalysts to produce for several reasons. They are made in very small quantities, and small-scale production tends to be expensive. These catalysts virtually require multistep syntheses and purifications, which add costs. Moreover, the main disadvantage of heterogeneous metalloporphyrin catalyst is that the catalysts are destroyed in the reaction mixtures and cannot be recovered or reused. One way to overcome this drawback is to immobilize the metalloporphyrin to solid support which leads the formation of heterogeneous reusable catalyst.

We have found that the homogeneous $Fe(T_{Bamin}P)OAc$ catalyst is degraded in styrene epoxidation and cannot be recovered and reused for several times. However,



Scheme 2 A simple epoxidation mechanism proposed for epoxidation of alkenes with $NaIO_4$ catalyzed by Fe(T$_{Bamin}$P)OAc@PAC



Scheme 3 Reusability of Fe(T$_{Bamin}$P)OAc@PAC catalyst in epoxidation of styrene with NaIO4 in the presence of imidazole

the Fe(T$_{Bamin}$P)OAc@PAC catalyst could be easily recovered from the reaction mixture and reused under the same condition employed for alkene epoxidation. For instance, in the epoxidation of styrene, the Fe(T$_{Bamin}$P)OAc@PAC catalyst was separated from the reaction mixture by filtration, washed with CH_3CN and dried before use. As shown in Scheme 3, the yield of styrene epoxide was still 43 % after four reaction cycles, indicating the reusability and validity of the catalyst for alkene epoxidation by $NaIO_4$.

An overall improvement in some characteristics of the present polymer- supported catalyst was observed which can be counted as short reaction time with high yield and selectivity accompanied by high stability and reusability of the catalyst [43, 44].

Conclusions

In conclusion, poly(acryloyl chloride) (PAC) is a convenient support for Fe(T$_{Bamin}$P)OAc and Mn(T$_{Bamin}$P)OAc, because the active -NH_2 functional groups in the porphyrin could easily react with the acyl groups in PAC and produce polymer-anchored metalloporphyrin complexes as stable heterogeneous catalysts. We have found that (1) Fe(T_{Bamin}P)OAc@PAC is the best among other homogenous and heterogeneous Fe and Mn porphyrin catalysts for alkene epoxidation with $NaIO_4$;(2) acetonitrile/water (2:1, v/v) has been found to be the best solvent for reaction performed in the presence of the Fe(T_{Bamin}P)OAc@PAC, (3) nitrogen donor axial ligands (i.e., imidazole) can greatly enhance the catalytic activity of the metalloporphyrin, (4) only a 0.005 mmol of the Fe(T_{Bamin}P)OAc@PAC catalyst was taken to achieve the epoxidation reactions and the optimal molar ratio of the catalyst, imidazole, alkene and $NaIO_4$ was 1:5: 60:65, respectively, which applied for alkene epoxidation at room temperature, (5) the epoxidations were achieved in moderate yields with high selectivity for epoxide, and (6) the catalyst is reusable and can be applied at least for four times without any significant loss of its activity.

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