Peroxynitric Acid: A Convenient Oxygen Source for Oxidation of Organic Compounds Catalyzed by Polyimide-Supported Manganese (III) Tetrakis(4-methoxylphenyl)porphyrin Acetate

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ABSTRACT: *In this work, a polyimide (PI) containing triazole units was synthesized using 3,5-diamino-1,2,4-triazole and pyromellitic dianhydride in N-methyl-2-pyrrolidinone. This polymer was used as support of manganese (III) tetrakis(4-methoxylphenyl)porphyrin acetate to attain a heterogeneous catalyst; namely Mn(T4-OMePP)OAc@PI. The synthesized PI and Mn(T4-OMePP)OAc@PI were characterized by different spectroscopic and analytical techniques. The resulted catalyst was applied for epoxidation of alkenes and dehydrogenation of Hantzsch 1,4-dihydropyridines (1,4-DHP) by peroxynitric acid (PNA; $HOONO_2$) as a convenient new oxygen source. In association with $HOONO_2$, Mn(T4-OMePP)OAc@PI was stable and proved to be an efficient, reusable and selective catalyst for epoxidation of alkenes (36-96% yield) and dehydrogenation of Hantzsch 1,4-DHP's (94-100% yield).*

KEYWORDS: *Peroxynitric acid; Epoxidation, Hantzsch 1,4-dihydropyridines; Catalyst; Supported manganese porphyrin.*

INTRODUCTION

The oxidation of hydrocarbons (*i.e* alkenes) with molecular oxygen is efficiently proceeds by monooxygenase such as P-450 enzymes and this oxidation rout is still a fascinating goal among chemists. So far, the most efficient catalytic methods for oxidation of hydrocarbons with synthetic metalloporphyrins have been obtained with single oxygen donors such as ROOH, PhIO, $NaIO_4$, NaOCl, $KHSO_5$, H_2O_2, etc [1- 9]. In these catalytic reactions the natures of porphyrin, central metal atom and the kind of used oxidant have dramatic influence on the yield and selectivity of the reactions. Moreover, they may also influence the nature of the active oxidizing intermediate being generated by metalloporphyrins and consequently affect the mechanism of the oxidations [10-14].

We wish here to report our results on the catalytic oxidation of alkenes and Hantzsch 1,4-DHP's by peroxynitric acid (PNA; $HOONO_2$) in the presence of polyimide-supported manganese (III) tetrakis(4-methoxylphenyl)porphyrin acetate, [Mn(T4-OMePP)OAc@PI] as a new heterogeneous catalytic system. To the best of our knowledge, there is no report

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of using $HOONO_2$ as oxygen donor on organic oxidation catalyzed by metalloporphyrins. $HOONO_2$ is an oxo acid of nitrogen which may also be classified as an inorganic peracid. It is a biological relevant oxidizing agent containing reactive oxygen which possesses two-electron oxidative behavior [15, 16]. On the other hand, Mn(T4-OMePP)OAc@PI was used as catalyst because immobilizing of metalloporphyrins on a suitable support materials not only improves the catalysts stability and the selectivity of the product but also promotes the easy recover and reuse of the catalysts.

EXPERIMENTAL SECTION

Materials and instruments

All materials were of commercial reagent grade. Alkenes were purchased from Merck or Fluka and used as received. Hantzsch 1,4-DHP's were synthesized by the reported procedure [17]. The free base porphyrin H_2(4-OMePP) and its manganese complex Mn(4-OMePP)OAc were prepared by the proposed methods [18, 19]. The UV–Vis spectra of the porphyrins were obtained using a JASCO, V-570 spectrophotometer. Scanning Electron Microscopy (SEM) images were obtained from LEO instrument model 1455VP. Microstructure of samples was studied using a Zeiss, EM10C transmission Electron Microscope (TEM) model with 100 kV. The TGA was done using a Rheo Metric Scientific Instrument STA-1500 model. IR spectra were recorded as KBr pellets on a FT-IR JASCO 460 spectrophotometer. Atomic Absorption Spectra (AAS) were recorded on a Varian-240 spectrophotometer using a flame approach, after acid (HNO_3/HCl) dissolution of known amounts of Mn(T4-OMePP)OAc@PI.

Preparation of $HOONO_2$ solution

Fresh $HOONO_2$ solution was prepared by the modification of method suggested by *Appelman* [20]. 1.067 g (15 mmol) 98% $NaNO_2$ was dissolved in 3 mL of 30% H_2O_2 and the solution was cooled to 0 °C in an ice bath. Another 2 mL of the H_2O_2 was mixed with 0.3 mL 70% $HClO_4$ and the mixture is cooled to -5 °C. The nitrite-peroxide solution was then added to the stirred peroxide-acid solution in 1.0 mL increments. Finally, a further 1.0 mL of 70% $HClO_4$ was added to this solution and stirred in -5 °C for 2 minutes. This fresh peroxynitric acid was demonstrated approximately 1.7 M in peroxynitric acid, corresponding to a 75% yield based on sodium nitrite [20] and should immediately be used.

Preparation of polyimide (PI)

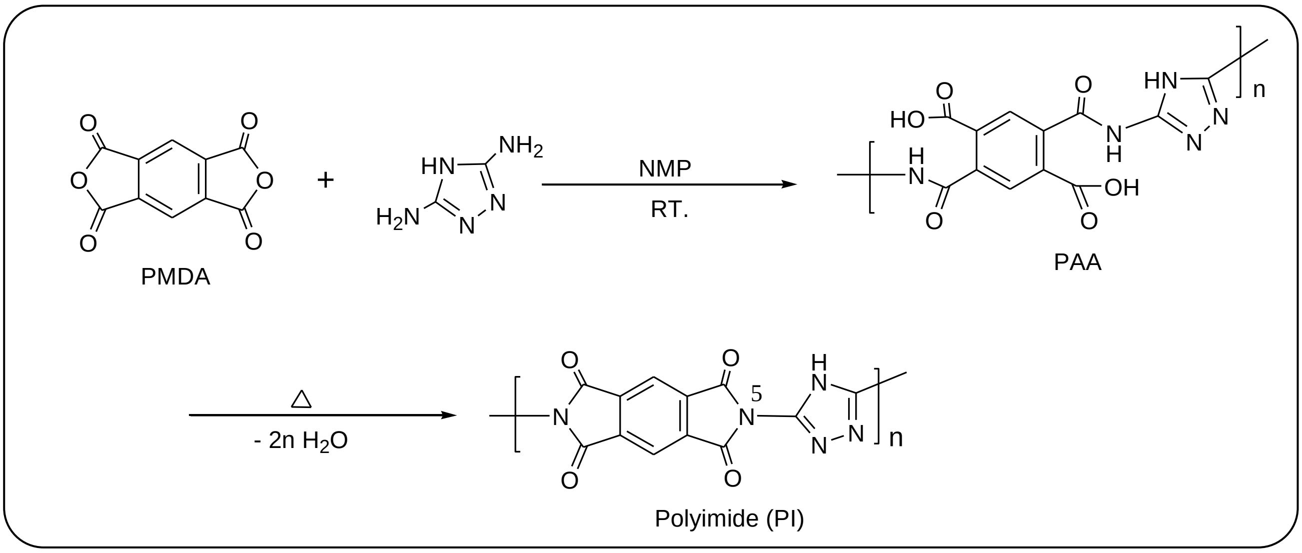
In the first step, poly(amic acid) (PAA) was synthesized as precursor polymer precursor [21]. To a 50 mL three-necked round-bottom flask equipped with a high power electromagnetic stirrer and nitrogen inlet was added 3,5-diamino-1,2,4-triazole (0.50 g, 5.05 mmol) and freshly distilled *N*-methyl-2-pyrrolidinone (NMP) (4 mL). A clear diamine solution formed after stirring for 5 min. Then, pyromellitic dianhydride (PMDA) (1.100 g, 5.05 mmol) was added immediately, followed by additional NMP (2 mL) to adjust the solid content of the mixture to be 20% (wt %). The mixture was stirred at room temperature for 24 h to afford an almost colorless, highly viscous solution. The inherent viscosity of the resulting PAA was 0.81 dL/g, measured in DMF at a concentration of 0.5 g/dL at 30 °C. In the second step, it was dried and transformed into heterocyclic PI by sequentially heated at 110, 150, 180, 210, 230 and 280 °C for 30 minutes each. Then, the fully imidized polymer film was stripped from the glass substrate by being soaked in water.

Preparation of polyimide-supported manganese(III) tetrakis(4-methoxylphenyl)porphyrin acetate; Mn(T4-OMePP)OAc@PI

0.32 g (0.38 mmol) of Mn(T4-OMePP)OAc was added to 3.2 g of PI in DMF (30 mL). The reaction mixture was vigorously stirred at 80 °C for 24 h. After cooling, the dark green solid was collected by filtration, washed thoroughly with DMF/CH_2Cl_2 (1:1) and dried under vacuum at 105 °C for 24 h. Atomic absorption spectroscopy shows Mn loading of ~ 0.1mmol/g of PI .

Oxidation reactions

All epoxidation reactions were carried out at 5-10 °C under air in a 10 mL round bottom flask equipped with a stirrer bar. 0.025 mmol of alkene, 0.005 mmol of tetrabutylammonium bromide (TBAB, phase transfer catalyst) and 0.75 mL of CH_2Cl_2 are successively added to 4.5 mg of Mn(T4-OMePP)OAc@PI (containing ~ 4.5×10^{-4} mmol of the Mn-porphyrin). Then, 20 μL of $HOONO_2$ solution was added by syringe to the organic phase and the reaction was analyzed by GC. Oxidation of



Scheme 1: Synthesis of polyimide.

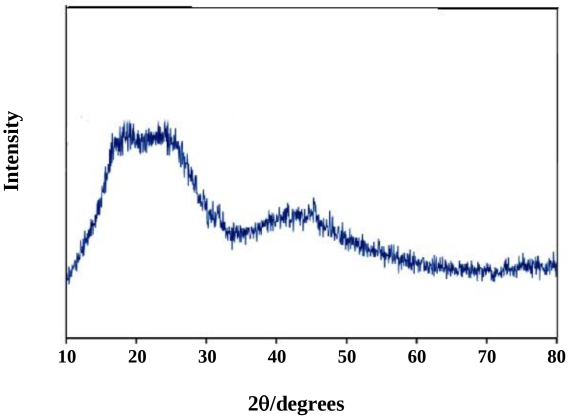


Fig. 1. XRD pattern of PI.

Hantzsch 1,4-DHP's were achieved using a similar molar ratios of the substrates and catalyst and the products were separated by TLC plates and analyzed as previously reported by spectroscopic methods [22].

RESULTS AND DISCUSSION

Synthesis and characterization of polyimide (PI)

As shown in Scheme 1, the free PI was prepared from treatment of pyromellitic dianhydride (PMDA) with 3,5-diamino-1,2,4-triazole in the presence of *N*-methyl-2-pyrrolidinone (NMP), followed by the heating at required temperatures [21].

Molecular weight of the polymer was measured by GPC in THF and polystyrene was used as standard. The PI exhibited number-average molecular weight (M_n) and weight-average molecular weight (M_w) in 1.09×10^5 and 2.19×10^5 respectively. The molecular weight of the polymer was high enough to obtain flexible and tough polymer film by casting from their NMP solutions.

The crystallinity of the PI was studied using wide-angle XRD (Fig. 1). The broad peak in XRD spectrum of PI shows that it is completely amorphous. Presence of the non-coplanar and twisted units in the backbone of the polymer decreased the intermolecular forces between the polymer chains leading to reduce the crystallinity of this polymer.

The SEM images of PI film (Fig. 2) shows the information of surface topography, indicating the amorphous nature of the polymer.

The thermal property of PI was studied using TGA at a heating rate of 10 °C/min, under a nitrogen atmosphere (Fig. 3). This study shows that PI is thermally stable up to 350 °C. The 10% weight loss temperature of this polymer was recorded in 400 °C in a nitrogen atmosphere.

The amount of residue (char yield) of that in a nitrogen atmosphere was more than 48% at 800 °C. Char yield can be applied as decisive factor for estimating Limiting Oxygen Index (LOI) of the polymers based on Van Krevelen and Hoftyzer equation:

$$LOI = 17.5 + 0.4CR$$

where CR is char yield. The LOI value calculated for the untreated PI sample was higher than 36. On the basis of LOI value, such macromolecule can be classified as a self-extinguishing polymer [23, 24].

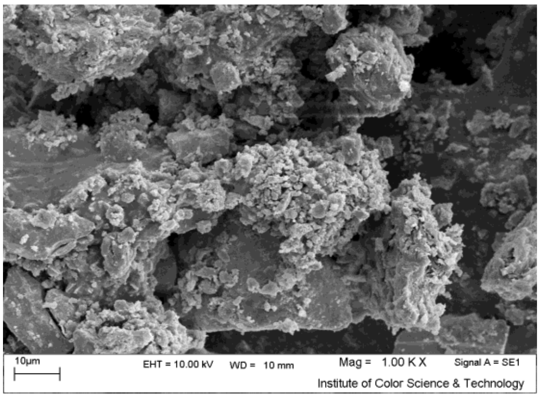


Fig. 2: The SEM image of the PI.

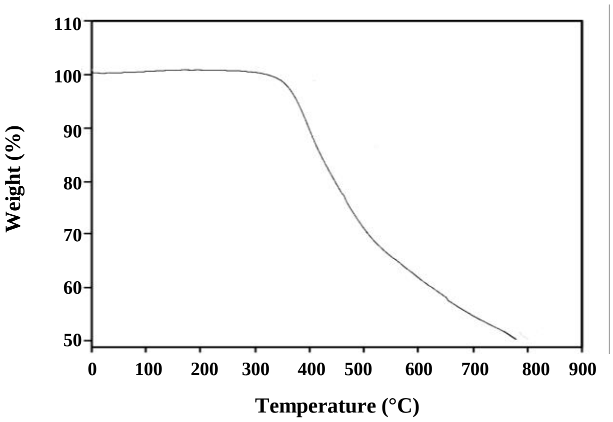


Fig. 3: TGA of PI.

The FT-IR spectrum of the PI (Fig. 4 b, *vide infra*) exhibited distinct features that clearly indicate imide rings. The characteristic absorption bands of carboxyl groups of amic acid in 2400-3700 cm^{-1} disappear and those of the imide ring appear near 1725 cm^{-1} (asymmetric stretching vibrations of the carbonyl group), 1687 cm^{-1} (vibration of C=N) 1402 cm^{-1} (vibration of C-N), 1029 cm^{-1}, and at 765 cm^{-1} (imide ring deformation).

Synthesis and characterization of Mn(T4-OMePP) OAc@PI

The synthesized PI contains triazole units which is capable of coordination to Mn center of the porphyrin. The bonding is probably achieved through the interaction of the triazole nitrogen atoms with Mn(T4-OMePP)OAc, as observed in cytochrome P-450 and related enzymes which a histidine acts as a catalytic residue in the distal heme pocket [25-32]. Another possibility for bonding PI to the Mn porphyrin consists of PI-N5 with sp^3 hybridization (see scheme 1), which leads a "face-on" orientation of PI and Mn(T4-OMePP)OAc, means that the porphyrin plane is parallel with the polymer surfaces. So, it is reasonable to assume that the triazole groups hold not only the Mn-porphyrin firmly in the polyimide but also act as nitrogenous axial ligand for Mn(T4-OMePP)OAc. Nitrogenous ligands such as imidazole, pyridine and their derivatives are reported to enhance catalytic activity and stability of metalloporphyrins *via* the cleavage of M-O bond in the oxidation form of the catalysts (i.e. high valent metal-oxo porphyrins) and to prevent auto-degradation of the catalyst [33-36].

The Mn content of Mn(T4-OMePP)OAc@PI was measured by dissolving a known mount of the solid in conc. HNO$_3$/HCl (1:4 v/v), from this solution the Mn contents was estimated using Atomic Absorption Spectrometer (AAS). The Mn content was found to be ~ 0.1 mmol/g, indicating the appropriate supporting of Mn(T4-OMePP)OAc on PI.

The FT-IR spectra of PI, Mn(T4-OMePP)OAc and Mn(T4-OMePP)OAc@PI are shown in Fig. 4. As explained above, the FT-IR spectrum of PI shows major bands at 3365 cm^{-1} (NH), 1725 cm^{-1} (C=O imide) and 1687 cm^{-1} (C=N). Also the characteristic bands of Mn(T4-OMePP)OAc appear at 3436,1606, 1498, 1176, 1114 and 1004 cm^{-1}. The characteristic bands of Mn(T4-OMePP)OAc at 1606, 1498 and 1176 cm^{-1} appear again in the Mn(T4-OMePP)OAc@PI spectrum, suggesting the precise supporting of the porphyrin on the polymer. Moreover, the band of 1687 cm^{-1} of C=N in PI shifted towards lower frequency at 1658 cm^{-1}, which is probably due to the coordination of the triazole to Mn center.

Fig. 5, represents the SEM image of Mn(T4-OMePP)OAc@PI, indicating the morphology of the heterogeneous catalyst and a bulk microstructure composed of distributed network of Mn(T4-OMePP)OAc presented on the polyimide.

The TEM images of PI (Fig. 6, a), and Mn(T4-OMePP)OAc@PI (Fig. 6, b), clearly indicate the polymer chains and manganese porphyrin as approximately spherical dark points supported on PI with nearly nanoscale dimensions.

The result of thermal analysis of Mn(T4-OMePP)OAc@PI catalyst, is shown in Fig. 7.

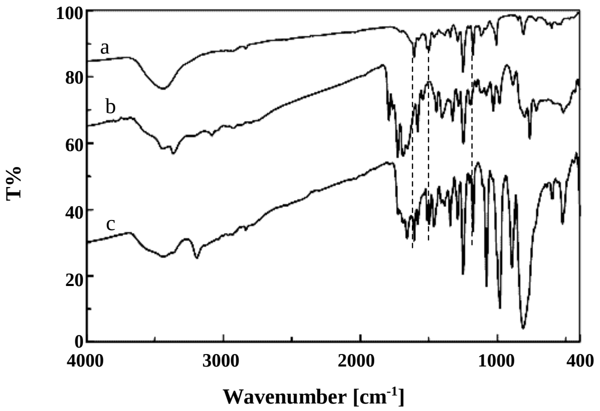


Fig. 4: FT-IR spectra of Mn(T4-OMePP)OAc (a), PI (b) and Mn(T4-OMePP)OAc@PI(c).

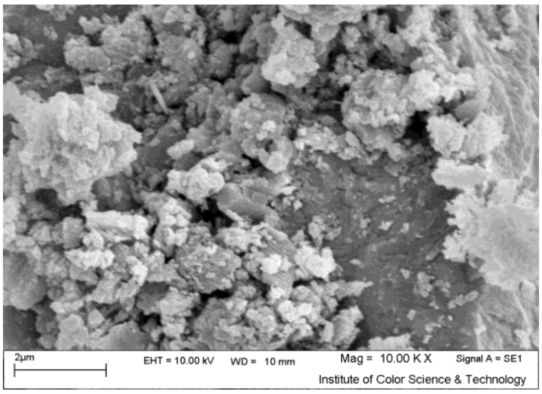


Fig. 5: SEM image of Mn(T4-OMePP)OAc@PI.

It is observed that the catalyst is more stable in comparison to PI itself. The weight loss of the catalyst is about 20% at 800 °C, indicating that Mn(T4-OMePP)OAc@PI does not undergo major weight loss at high temperature.

Epoxidation of alkenes

The earliest reports of $HOONO_2$ date back to the work of *D'Ans* & *Friederich* [37] and the subsequent study by *Schwarz*, [38] convincing characterization of the compound was only obtained in relatively recent times after its photochemical synthesis in the vapor phase by the combination of NO_2 with HO_2 [39]. A more practical synthetic method was next developed by *Appelman et al.* consisting of reaction of $NaNO_2$ with 30% hydrogen peroxide and 70% $HClO_4$ at -20 °C, which permitted to investigate chemical and spectroscopic properties of the acid [20]. It is claimed that production of $HOONO_2$ in aqueous solutions governed by the simple stoichiometric reaction as:

$$NaNO_2 + 2H_2O_2 + HClO_4 \longrightarrow$$
$$HOONO_2 + 2H_2O + NaClO_4$$

It was shown that peroxynitric acid is stable for 30-45 min in pH<3 especially at low temperature [16, 40]. This allows us for using it as oxidant in controlled experimental condition of temperature and pH for oxidation of organic compounds.

Initially, styrene was oxidized by H_2O_2 and $HOONO_2$ in the absence of any catalyst under N_2 atmosphere in CH_2Cl_2 at 10 °C. The results of GC analysis showed that the oxidation does not occur under these conditions (Table 1, run 1 and 2; vide infra). Then, the epoxidation was tested with H_2O_2 in the presence of homogeneous Mn(T4-OMePP)OAc catalyst and imidazole (Im; co-catalyst). The epoxide was obtained in 15% with 57% selectivity (Table 1 run 3; vide infra). Similarly, with Mn(T4-OMePP)OAc and $HOONO_2$, the epoxidation yield was 68% with 88% selectivity (Table 1 run 4), indicating the preference of $HOONO_2$ over H_2O_2 as oxidant. The nitrogenous ligand imidazole has positive effect and facilitates the epoxidation, since in the absence of imidazole the epoxidation yield and selectivity are very low. However, under these conditions both the catalyst and styrene epoxid were quietly demolished with increasing the reaction time and/or temperature.

As shown in Fig. 8, the amount of Mn(T4-OMePP)OAc decreased over the time, so that a ~74% of the catalyst is destructed in the reaction mixture after 60 minutes (that is, only a ~26 % remained unchanged). Also, the amount of styrene epoxide increased steadily in the reaction mixture and reached a maximum amount (68 %) after ~20 minutes and then actually begins to drop off. One reason to fading the catalyst may be due to acidic media of the $HOONO_2$ solution which already contains various radical species [41, 42], capable of poisoning and/or destructing the catalyst. Another may relate to degradation of the catalyst in the reaction mixture that occurs generally for homogenous catalysts. A similar explanation can be applied to why the epoxides are not stable in the reaction mixtures.

However, the epoxidation was more efficient with *heterogeneous* Mn(T4-OMePP)OAc@PI catalyst, so that

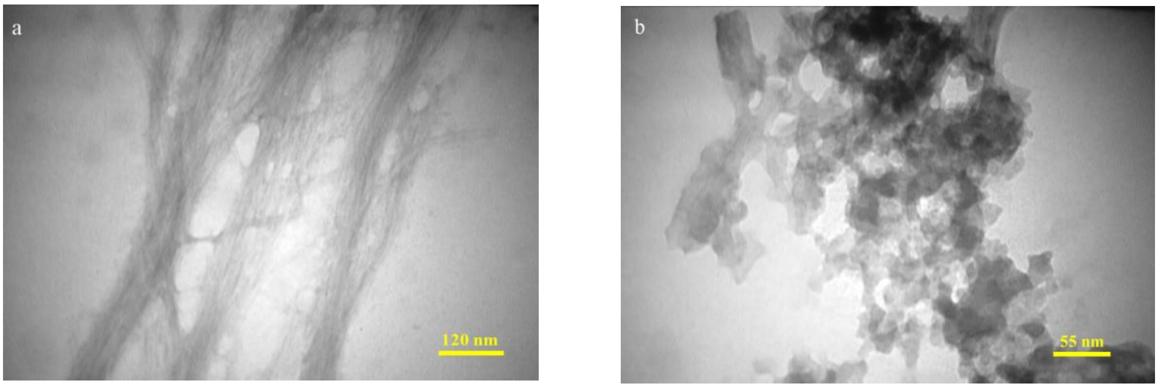


Fig. 6: TEM images of PI (a) and Mn(T4-OMePP)OAc@PI(b).

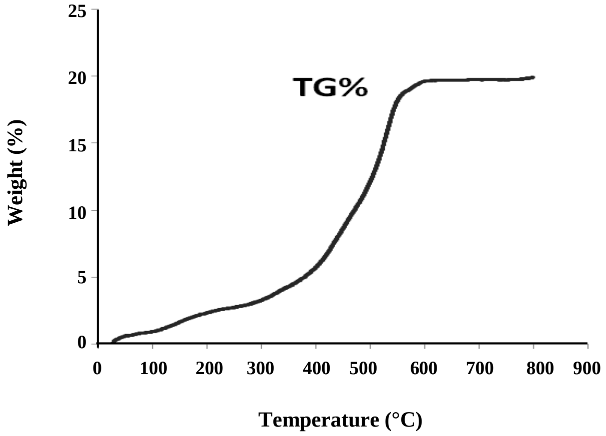


Fig. 7: TG analysis of Mn(T4-OMePP)OAc@PI.

epoxidation of styrene with Mn(T4-OMePP)OAc@PI/ $HOONO_2$ in 5-10 °C leads to the formation of the epoxide in 96% yield accompanied by high selectivity and turnover number within 15 minutes; surprisingly without significant degradation of the catalyst and the epoxide (Table 1, run 5). As shown in Fig. 9, the amount of styrene epoxide and the catalyst are 95% and 87% respectively even up to 60 minutes. Here, there is no need to use nitrogenous axial ligand as co-catalyst, since the PI in Mn(T4-OMePP)OAc@PI structurally has triazole units which could act as both support and axial ligand for Mn(T4-OMePP)OAc (see scheme1). This was examined with imidazole and found a little change in epoxide yield with and without imidazole.

We also found that turnover number (TON; the ratio of the number of moles of produced epoxide to the number of moles of catalyst) for Mn(T4-OMePP)OAc and Mn(T4-OMePP)OAc@PI was ~68 and ~ 312, respectively [43], indicating that Mn(T4-OMePP)OAc@PI as heterogeneous catalyst is about 4.6 fold more efficient than Mn(T4-OMePP)OAc for the epoxidation. Furthermore, Mn(T4-OMePP)OAc@PI could easily be recovered by phase separation and reused for styrene epoxidation for several times. As shown in Fig. 10, the yield of styrene epoxide after 5 recycling was 0% and 42% with Mn(T4-OMePP)OAc and Mn(T4-OMePP)OAc@PI respectively in 60 minutes, demonstrating again the reusability and validity of the former for alkene epoxidation with $HOONO_2$.

Moreover, UV-Vis spectra taken from reaction mixture of styrene epoxidation by (T4-OMePP)OAcI@PI/ $HOONO_2$ showed that no significant leaching of Mn(T4-OMePP)OAc occur under experimental conditions studied. This indicates that the synthesized PI are ideal supports to stabilize Mn-porphyrin.

The optimal conditions of epoxidation employed for styrene were also applied for some other alkenes and the results were summarized in Table 1.

It is plausible that the steric and electronic properties of alkene substrates affect the epoxide yields and reaction times. The reactions were found to take place in 36-96 % epoxide yields. It seems that electron rich C=C bonds with less steric hindrance show higher activity for epoxidation. For instance, *cis*-stilbene (run 7; 70 % yield) is more reactive than that of *trans*-stilbene (run 8; 47% yield). Moreover, the selectivity obtained for *tras*-stilbene

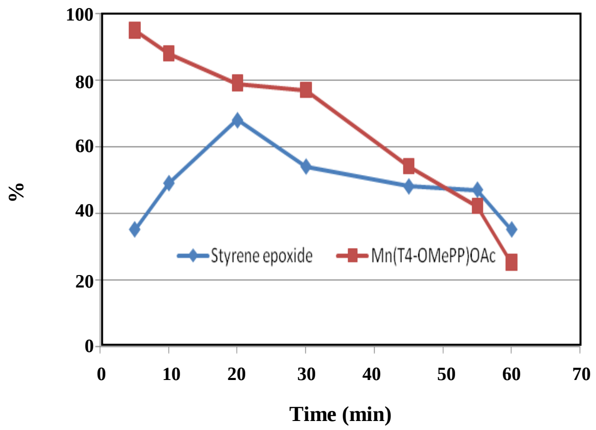


***Fig. 8:** Epoxidation of styrene by Mn(T4-OMePP)OAcI-Im/ $HOONO_2$ in CH_2Cl_2 showing the amount of styrene epoxide (♦) and Mn(T4-OMePP)OAc (■).*

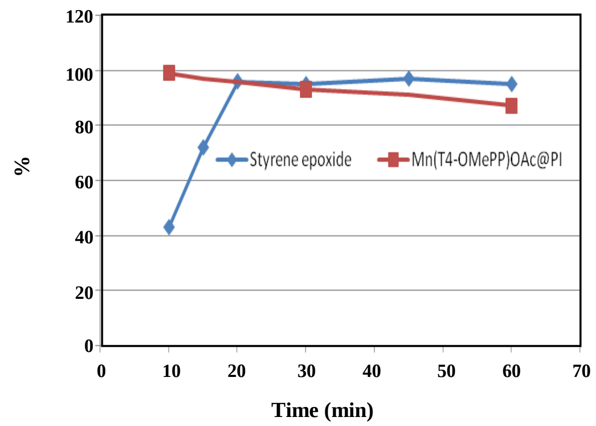


***Fig. 9:** Epoxidation of styrene by Mn(T4-OMePP)OAcI@PI/ $HOONO_2$ in CH_2Cl_2 showing the amount of styrene epoxide (♦) and Mn(T4-OMePP)OAc (■).*

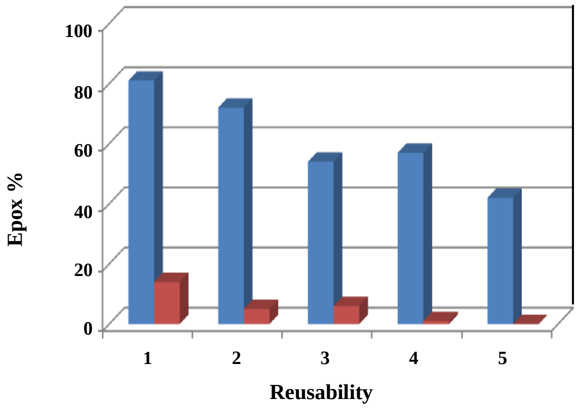


***Fig. 10:** Reusability of Mn(T4-OMePP)OAc and Mn(T4-OMePP)OAc@PI in styrene epoxidation.*

was shown to be lower (47/54; 87 %) than that of the *cis* isomer (70/71; 98%). Similar comparisons may also be made with styrene (run 5) and α-methylstyrene (run 6), and with cyclooctene (run 10) and 1-octene (run 11) considering the reaction times, selectivities, turnover numbers and electronic/steric properties of alkenes.

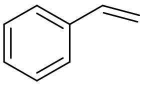
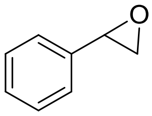
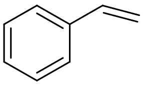
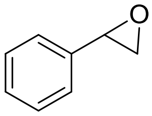
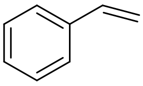
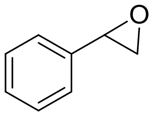
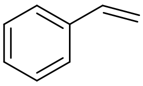
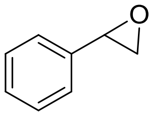
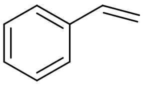
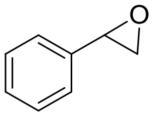
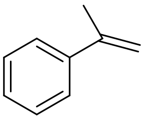
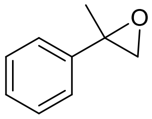
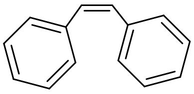
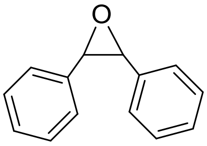
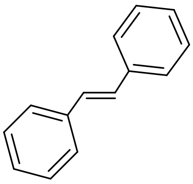
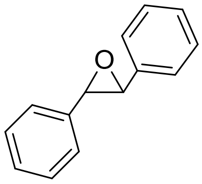
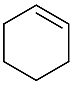
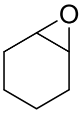
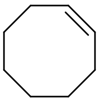
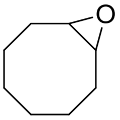
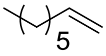
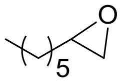
Oxidative dehydrogenation of Hantzsch 1,4-dihydropyridines (1,4-DHPs)

Hantzsch 1,4-DHP's are important class of drugs for the treatment of cardiovascular diseases such as hypertension and angina pectoris [44, 45]. In human body the main metabolic route of dihydropyridine drugs involve their oxidation by cytochrome P-450 in the liver [46, 47]. Here, the oxidation of various Hantzsch 1,4-DHP's was followed by the same method described above for the epoxidation. As shown in Table 2, the oxidations lead to the formation of the corresponding pyridine derivatives in high yields in few minutes. These oxidation reactions were fast in all cases requiring less than 5-15 minutes, including the substrates having either electron donating (*i.e* entry 4 and 6) or electron withdrawing groups (*i.e.* entry 5, 7 and 8) at the phenyl substituent. In addition to dehydrogenated products, in some cases (*i.e.* run 4, 5 and 7) dealkylated pyridine derivatives were also obtained, though the amounts of dealkylated pyridines are very low compared with the amount of the dehydrogenated pyridines.

CONCLUSIONS

We report on a novel catalytic system based on a polyimide-supported manganese (III) tetrakis(4-methoxylphenyl)porphyrin acetate [Mn(T4-OMePP)OAc@PI] as a heterogeneous catalyst, which catalyzed epoxidation of alkenes and dehydrogenation of Hantzsch 1,4-dihydropyridines (1,4-DHP) with moderate to high yields and selectivities by $HOONO_2$. We found that the polyimide is an appropriate support for Mn(T4-OMePP)OAc. The supporting route may achieve coordination of the nitrogen triazole units in the polymer to the Mn-porphyrin. In the epoxidation reactions the homogeneous Mn(T4-OMePP)OAc was not an appropriate catalyst, since the epoxide and catalyst were demolished in the reaction mixture specially in temperature more than 15 °C. However, Mn(T4-OMePP)OAc@PI/$HOONO_2$ was found to be a

Table 1: Epoxidation of alkenes with $HOONO_2$ catalyzed by Mn(T4-OMePP)OAc@PI at 5-10°C.

Entry	Alkene	Product	Conversion (%)	Epoxide (%)[f]	Time, min.	TON[g]
1			*nd*[a]	*nd*	60	-
2			4[b]	*nd*	60	-
3			26[c]	15(57)	30	8.3
4			77[d]	68(88)	30	37.7
5			98	96(98)	15	53.3
6			91	83(91)	50	46
7			71[e]	70(98)	40	38.9
8			54e	47(87)	60	26
9			74	72.5(98)	15	40
10			90	86(95)	40	47.7
11			36	36(100)	60	20

As described in experimental, GLC yield was determined based on the starting alkane and the molar ratio of Mn(T4-OMePP)OAc@PI; TBABr; alkene and $HOONO_2$ was 1:11:55:75 respectively. nd; Not determined.

a) With H_2O_2; b) with $HOONO_2$ in the absence of the catalyst. C) With H_2O_2 ;

d) With $HOONO_2$ in the presence of homogeneous Mn(T4-OMePP)OAc catalyst.

e) Cis and trans- stilbeneoxides were examined by ^{1}HNMR (Bruker Avance DPX 250 MHz) spectroscopy.

f) The data in the parentheses represent selectivity for epoxide formation.

g) TON; Turnover number with the molar ratios described in experimental (1:11:55:75).

Table 2: Dehydrogenation of Hantzsch 1,4-DHP's with $HOONO_2$ catalyzed by Mn(T4-OMePP)OAc@PI at 5-10°C[a].

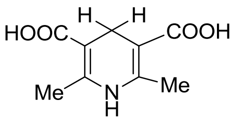
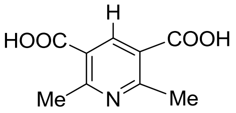
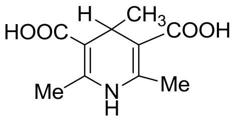
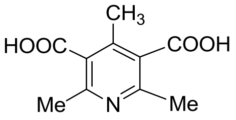
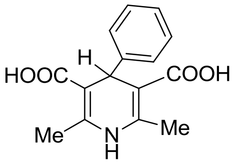
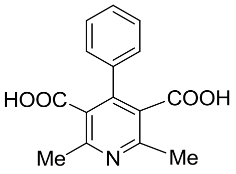
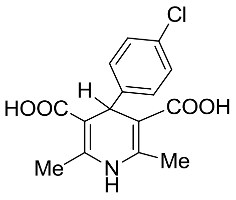
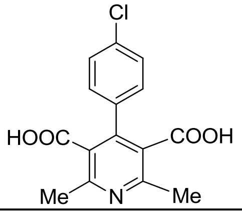
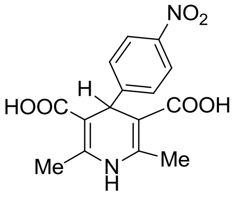
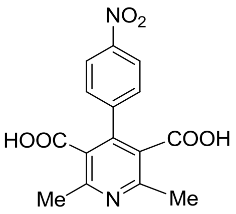
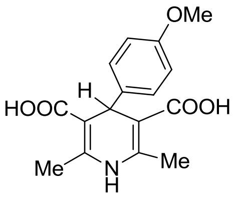
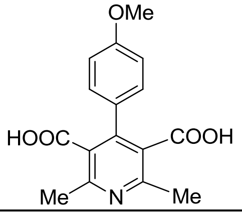
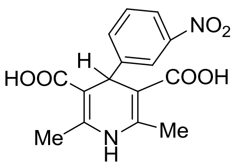
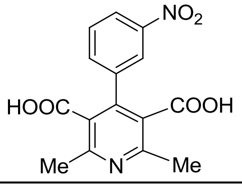
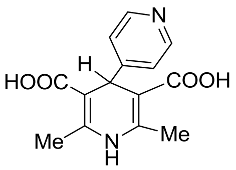
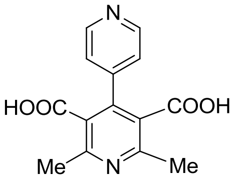
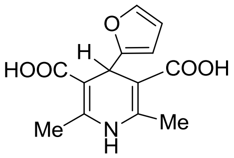
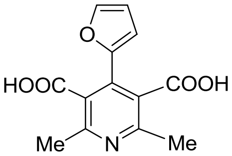
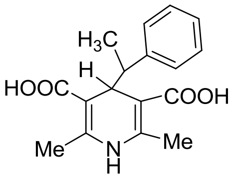
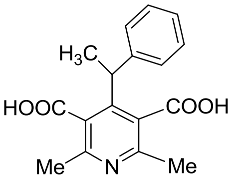
Entry	1,4-DHP	Product	(Yield %)	Time, min.
1			97	5
2			98	5
3			100	11
4			96b	10
5			96b	5
6			97	7
7			93b	10
8			94	8

Table 2: Continue.

Entry	1,4-DHP	Product	(Yield %)	Time, min.
9			87b	10
10			89[b]	15

a) As our previous work, all products were isolated and identified by comparison with authentic samples (IR, 1H NMR, m.p.)[22].
b) 4-7% of dealkylated pyridines was formed.

convenient catalytic system for the oxidations, since the reactions were achieved with high yields, selectivity and good turnover number. Moreover, the Mn(T4-OMePP)OAc@PI is reusable at least up to 4-5 times without an appreciable loss of the activity and selectivity for the oxidation. To the best of our knowledge, there is no report on oxidation of organic compounds by $HOONO_2$ in the presence of metalloporphyrins or supported metalloporphyrins and our next goal is to develop a selective artificial oxidation of other organic compounds (i.e. alkanes, alcohols, thiols,…) by this catalytic system.

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