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Manganese porphyrin supported on activated carbon as a new catalyst for epoxidation of alkenes with hydrogen peroxide

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ABSTRACT

The Manganese complex of *meso*-tetrakis (4-carboxyphenyl) porphyrin was immobilized onto the surface of functionalized activated carbon and used as a heterogeneous catalyst for the oxidation of different alkenes. The heterogenized catalyst has been fully characterized using Ultraviolet–visible (UV-Vis), Fourier-transform infrared (FTIR), and atomic absorption spectroscopies as well as thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and nitrogen adsorption-desorption (BET method) analyses. The Catalytic activity of the catalyst was investigated in the epoxidation of alkenes with H_2O_2 as a green oxidant. The influence of different parameters including time of reaction, molar ratio of catalyst, imidazole, and amount of oxidant on the efficiency of the catalyst was investigated. Complete conversion of the indene, α-methyl styrene, and 4-methyl styrene was achieved after 4 h at room temperature.

Keywords: Catalyst; Manganese porphyrin; Amine functionalized activated carbon; Epoxidation

1. Introduction

Epoxidation of alkenes has received more attention due to its importance in synthesizing organic materials [1-4]. It means that epoxides are kinds of intermediate compounds, which are important for producing a wide range of commercial products [5-6]. Surfactants, lubricants, and detergents are such products which has been manufactured from epoxides. Epoxides such as cyclooctene oxides have significant chemical properties which are widely used in pharmaceutical and polyester industries [7]. Generally, selective oxidation of hydrocarbons is a major challenge in chemistry and transition metal complexes have been used as catalysts for selective oxidation of alkenes [8]. Metalloporphyrin as a biomimetic model of cytochrome P-450 are used in the epoxidation of olefins with various oxidants such as iodosyl benzene, TBHP, $NaIO_4$, H_2O_2, and molecular oxygen [9-19]. Manganese and iron porphyrins are highly effective and selective catalysts for the hydroxylation of alkanes and oxidation of alkenes [20-24]. Carbon materials are widely used as adsorbents and catalysts in various chemical processes [25]. Activated carbon is a porous and inexpensive material [26] which was widely utilized as a catalyst and adsorbent [27]. It should be noted that activated carbon can also be used as support for a wide variety of heterogeneous catalysts [28]. Surface modification of activated carbon is also an interesting task which has been done in recent years by chemical physical and biological methods [29].

Metalloporphyrins were immobilized onto the surface of various solid supports such as carbon nanotubes and used for the oxidation of organic compounds [15, 30-36]. Schiff base complexes, polyoxometalates, and Au-Pd catalysts have been investigated as some examples which have been supported on activated carbon [37-40]. In the present research, we are going to immobilize a manganese porphyrin complex onto functionalized activated carbon and use it for the oxidation of alkenes with hydrogen peroxide.

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## 2. Experimental

2.1. Materials and instruments

All chemicals are purchased from Merck, Aldrich, Scharlau, or Fluka chemical companies and used without further purification. Lambda 25 Perkin Elmer from 400-700 nm was used as a UV-Vis spectrophotometer. FT-IR spectra were recorded (KBr pallets) in the range of 400-4000 cm^{-1} on an ABB Bomem: FTLA 2000-100. Varian AA240 atomic absorption spectrometer was employed for the determination of manganese content in a solid catalyst. The morphology features of the catalyst were investigated by Scanning electron microscopy (SEM; ESEM Philips XL30). The Thermal stability of catalyst was analyzed using TGA (Thermogravimetric analysis) by (Mettler-Toledo TGA 851e). Elemental analysis was carried out with employing EDX (Energy-dispersive X-ray spectroscopy; ESEM Philips XL30). Nitrogen adsorption-desorption analysis (Brunauer–Emmett–Teller (BET) method; PHSCHINA-PHS 1020) was employed for the determination of specific surface area and characterization of pores inside the surface of catalyst. Determination of the products yields after catalytic reactions were accomplished by Gas chromatography method with a flammable ionization detector (GC-FID) on an Agilent 7890B instrument using a SAB-5 capillary column (phenylmethyl siloxane 30m × 0.32 mm × 0.25 μm).

2.2. Preparation of catalyst

At first *meso*-tetrakis(4-carboxyphenyl) porphyrin (H$_2$TCPP) and related manganese porphyrin (MnTCPP(OAC)) were synthesized according to Adler's method [41, 42]. Functionalization of activated carbon with amine groups was done by KMnO$_4$ to obtain hydroxylated activated carbon and then react with 3-aminopropyltriethoxysilane (APTS) to get amine functionalized activated carbon (AC-NH$_2$) according to the reported method [43]. Immobilization of metalloporphyrin onto the surface of functionalized activated carbon was done by formation of amide bonds between –COOH groups of manganese porphyrin and –NH$_2$ groups of functionalized activated carbon using 2-(1H-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium tetrafluoroborate (TBTU) and N,N'-diisopropylamine (DIPEA) as coupling reagents [44]. In brief, amine functionalized activated carbon (AC-NH$_2$) (0.3 g) was dispersed in 30 ml DMF. Then TBTU (0.2 g) and DIPEA (0.15 g) were added to the solution and then MnTCPP (0.3 g) was added. After 48 h stirring at room temperature, the prepared MnTCPP@AC-NH$_2$ was filtered and washed with DMF (**Scheme 1**).

2.3. General procedure for the oxidation of alkenes

0.0025 mmol of catalyst (0.0037 g), 0.12 mmol of imidazole, 0.15 mmol of a substrate, and 0.7 ml of H$_2$O$_2$ as oxidant were added into a tube containing 1 mL of acetonitrile. Catalytic reactions were conducted at room temperature with constant stirring for a suitable time. At the end of the reactions, the catalyst was separated and final solutions were analyzed by GC to verify the products.
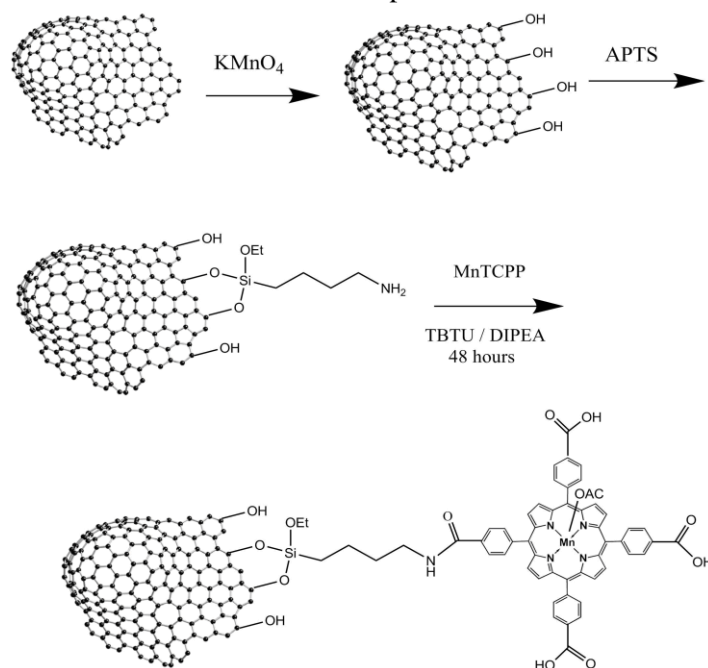
Scheme 1. Immobilization of MnTCPP onto the surface of activated carbon.

3. Results and Discussion

3.1. Characterization of the catalyst MnTCPP@AC-NH₂

The supported catalyst has been fully characterized. Atomic absorption spectroscopy (AAS) was employed for the determination of manganese content in solid catalysts. Based on the results each gram of catalyst contains 677 µmol of MnTCPP.

In the FT-IR spectra of AC-NH$_2$, absorption band at 2919 cm^{-1} is related to C-H stretching vibration, and two the absorption bands at 1029 and 1135 cm^{-1} are corresponding to Si-O-C groups [43]. Absorption bands at 3431, 3390 cm^{-1} [1], and 1645 cm^{-1} can be attributed to the N-H stretching and bending, respectively (**Fig. 1b**). Investigation of a band at 1389 cm^{-1} is related to the C-O vibration of MnTCPP. A peak at 1665 cm^{-1} indicates attachment of MnTCPP to AC-NH$_2$ through the amide bond (**Fig. 1c**). Absorption band at 3420 cm^{-1} can be related to O-H vibration in hydroxylated activated carbon (**Fig. 1a**).

Energy-dispersive X-ray (EDX) spectroscopy analysis of the catalyst also shows the peaks of Si and Mn, which indicates the presence of 3-aminopropyltriethoxysilane (APTS) and metalloporphyrin on the surface of activated carbon (**Fig. 2**).
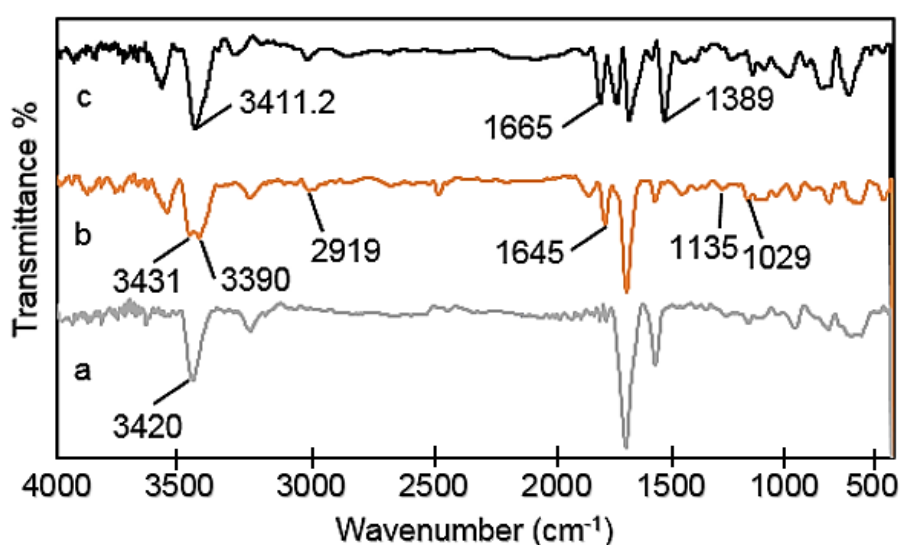

Fig. 1. FT-IR spectra of (a) Hydroxylated activated carbon (b) Amine functionalized activated carbon (AC-NH$_2$) and (c) Catalyst (MnTCPP@AC-NH$_2$)
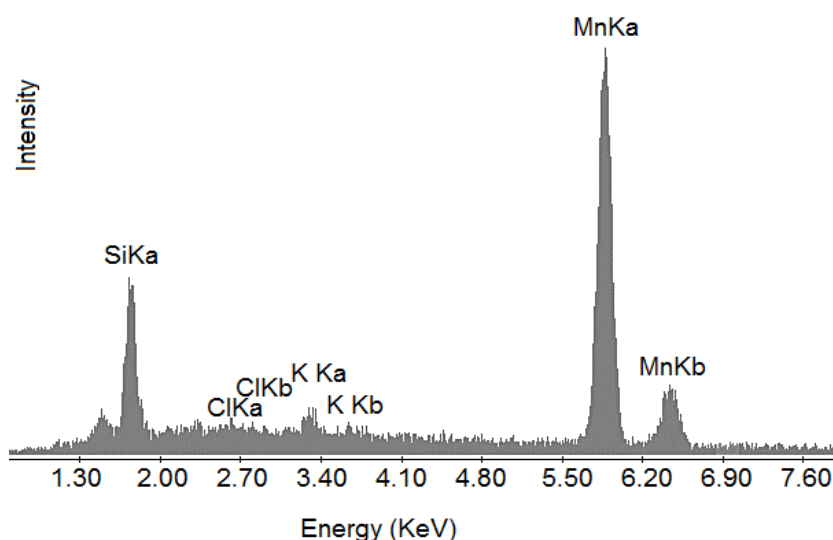

Fig. 2. EDX spectrum of MnTCPP@AC-NH$_2$ (Bands of carbon, nitrogen, and oxygen cannot be detected in an instrument which was used in this work.).

Thermogravimetric analysis was employed to study the thermal behaviour of the prepared catalyst and functionalized activated carbon in the temperature range of 25-800 °C in the air at a heating rate of 10 °C /min (**Fig. 3**). In the case of the catalyst, weight loss between 80-300 °C can be ascribed to the evaporation of physically-adsorbed water molecules. The other weight loss in the range of 350-450 °C is related to degradation of manganese porphyrin. Probably, destruction of functional groups on the surface of activated carbon occurs in the range of 400-550 °C. In the final step between 550-800 °C, the destruction of activated carbon and conversion to a graphitic structure may be occurred in both catalyst and AC-NH₂ [27].

UV-visible spectra of the catalyst and amine - functionalized activated carbon is shown in **Fig. 4**. Absorption band at 473 nm for catalyst is attributed to the Soret band of metalloporphyrin. This band does not exist in the corresponding spectrum of activated carbon confirming the immobilization of manganese porphyrin onto amine- functionalized activated carbon.

More non-uniformity is visible in the scanning electron microscopy (SEM) of the catalyst in comparison with AC-NH₂ which shows that metalloporphyrin is dispersed on the surface of activated carbon (**Fig. 5**).
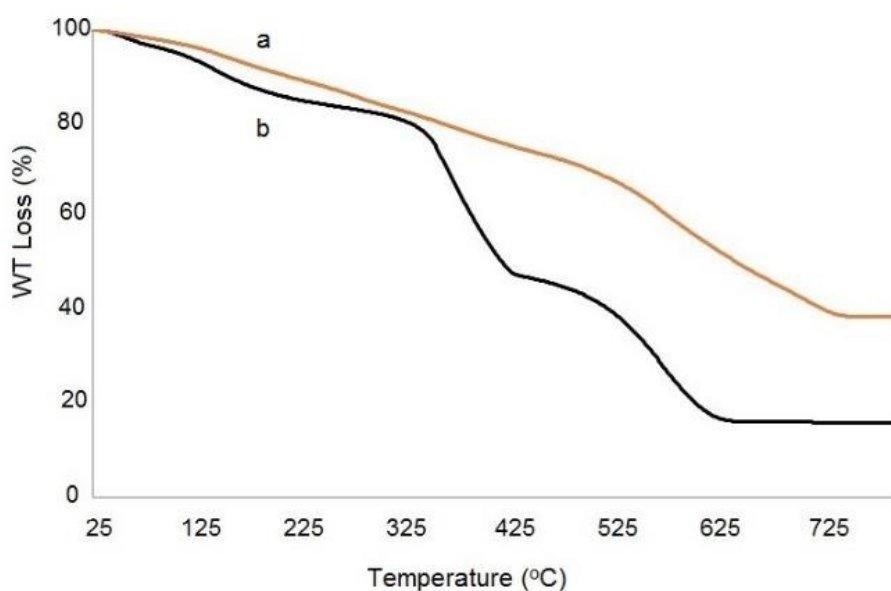

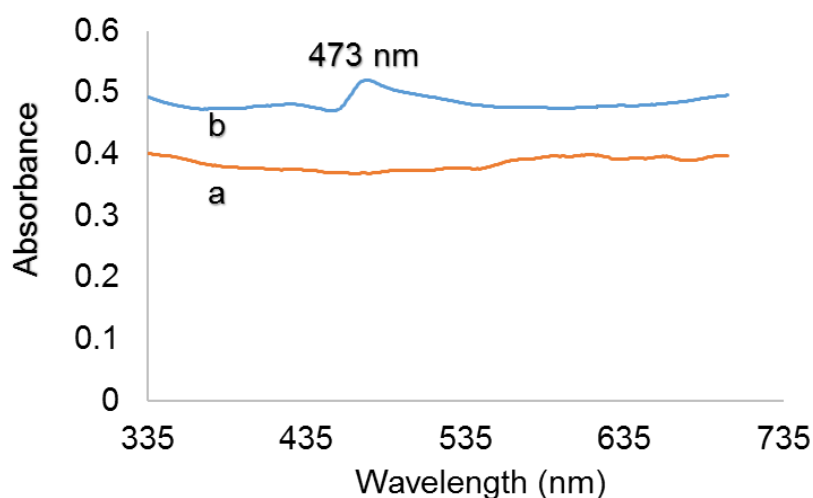**Fig. 3.** TGA curves of (a) AC-NH₂ and (b) MnTCPP@AC-NH₂.
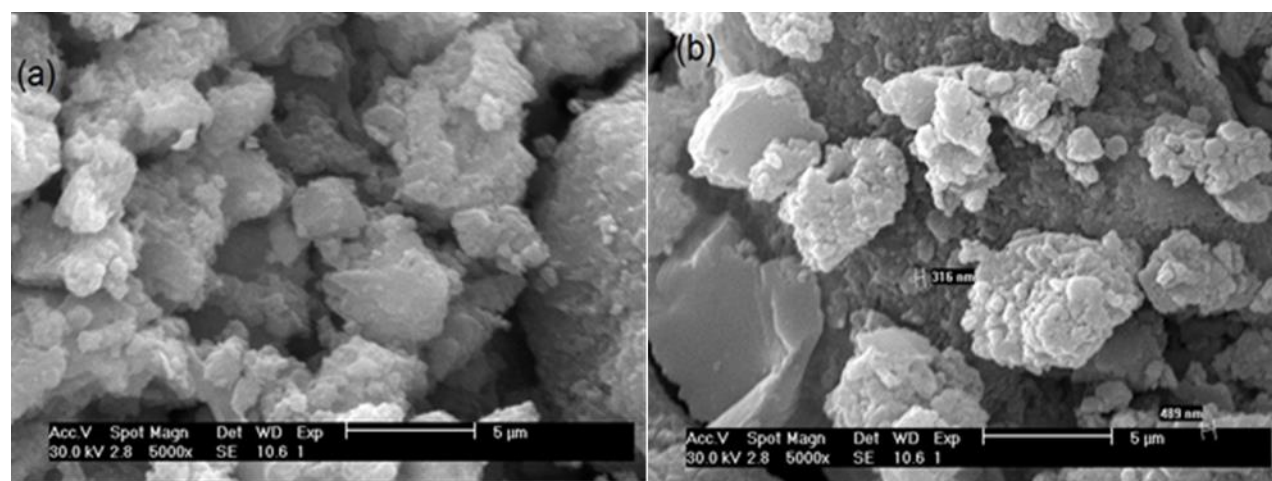

Fig. 4. UV spectra of (a) AC-NH₂ and (b) MnTCPP@AC-NH₂.

Fig. 5. SEM images of (a) AC-NH$_2$ and (b) MnTCPP@AC-NH$_2$.

The Specific surface area (S$_{BET}$) of MnTCPP@AC-NH$_2$ was found to be about 104.93 m^2/g which is lower than activated carbon (1195 m^2/g) [27]. Hence, decreasing in the value of S$_{BET}$ confirmed the presence of manganese porphyrin on the surface of activated carbon. Barrett, Joyner, and Halenda (BJH) method was employed to calculate the mean pore diameter of the catalyst which is in the value of 4.29 nm. Surface properties of prepared catalyst is given in **Table 1**.

3.2. Catalytic activity of MnTCPP@AC-NH$_2$

The behaviour of MnTCPP@AC-NH$_2$ was evaluated in the oxidation of alkenes. Imidazole was used as a co-catalyst and H$_2$O$_2$ (35%) was used as a green oxidant and cyclooctene was employed as initial substrate.

Reaction parameters including time of reaction, molar ratio of catalyst, imidazole, and amount of oxidant have been optimized. 0.0025 mmol of catalyst (0.0037 g) and 1 mL of acetonitrile were used for all reactions. In order to study the effect of oxidant concentration in the oxidation of cyclooctene, different amount of H$_2$O$_2$ (35%) (0.1, 0.35, 0.7, and 1 mL) were used and 0.7 mL of H$_2$O$_2$ was deduced as the optimum amount of oxidant (**Table 2**).

To achieve more catalytic performance, catalytic reactions were also carried out at 2, 3, and 5 h. After 2 h, no product was detected while 58% conversion was obtained after 3 h. The reaction did not proceed after 5 h and 4 h was selected for further studies (**Fig. 6**).

Table 1. Surface Properties of prepared catalyst.

Sample	Mn[a] content (μmol/g)	S$_{BET}$ (m^2/g)	Pore[b] diameter(nm)	V$_T$ (ml/g)[c]
MnTCPP @AC-NH$_2$	677	104.93	4.29	0.113

[a]Analysed by atomic absorption spectroscopy.
[b]Calculated using BJH technique.
[c]Total pore volume at p/p$_0$ = 0.98

Table 2. Optimization of the amount of H$_2$O$_2$ in the oxidation of cyclooctene in the presence of prepared catalyst.[a]

Entry	Volume of H$_2$O$_2$ (ml)	Conversion, %
1	0	0
2	0.1	0
3	0.35	4
4	0.7	65
5	1	56

[a]Reaction condition: The molar ratio of catalyst: imidazole: cyclooctene is (1:50:80),
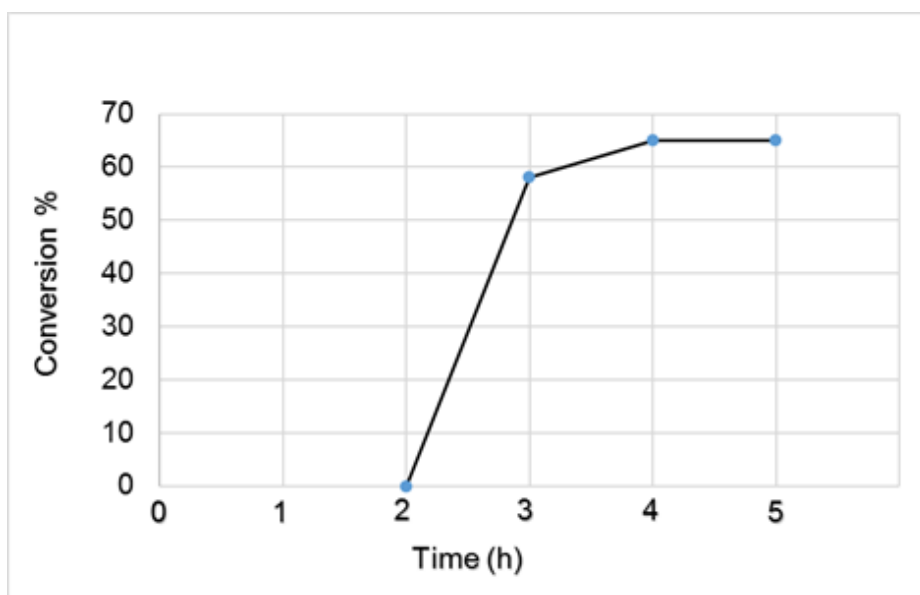Acetonitrile: 1mL, Time: 4h, Temperature: 25^{0}C, Catalyst: 0.0025 mmol.

Fig. 6. Effect of time on the oxidation reaction of cyclooctene with H_2O_2 in the presence of prepared catalyst. Reaction condition: The molar ratio of catalyst: imidazole: cyclooctene is (1:50:80), CH_3CN: 1mL, H_2O_2: 0.7 mL, Temperature: 25^0C, Catalyst: 0.0025 mmol.

Finally, the effect of imidazole concentration in the catalytic reaction was investigated. The highest conversion was obtained when the mole ratio catalyst: imidazole was 1:50 (**Table 3**).

To study the catalytic performance of the heterogenized catalyst, blank tests were performed. In the absence of catalyst, only 3% of the product was obtained. A low conversion (7%) obtained in the presence of functionalized activated carbon shows that the presence of manganese porphyrin is essential for catalytic reaction (**Table 4**).

Oxidation of various alkenes with hydrogen peroxide in the presence of MnTCPP@AC- NH_2 was studied (**Table 5**). The highest conversion was obtained for oxidation of 4-methyl styrene. The low oxidation product for 1-octene as a terminal alkene may be due to the poor electron density in the C=C bond compared to cyclic alkenes. Excellent selectivity for epoxide formation was obtained for cyclooctene, styrene, 1-octene, and 4-chloro styrene.

Table 3. Effect of molar ratio of catalyst: imidazole on the oxidation reaction of cyclooctene with H_2O_2 in the presence of prepared catalyst.[a]

Entry	Cat:Imidazole	Conversion, %
1	Non-imidazole	0
2	1:25	8
3	1:50	86
4	1:75	71

[a]Reaction condition: The molar ratio of catalyst: cyclooctene is (1:60), CH_3CN: 1mL, H_2O_2: 0.7 ml, Time: 4h, Temperature: 25^0C, Catalyst: 0.0025 mmol.

Table 4. Oxidation reaction of cyclooctene with H_2O_2 in the presence of prepared catalyst, free manganese porphyrin and modified activated carbon.

Entry	Catalyst	Conversion[a], %	TON[b]
1	Blank	3	-
2	MnTCPP(Free)	74	44.4
3	MnTCPP@AC-NH₂	86	51.6
4	AC-NH₂	7	-

[a]Reaction condition: The molar ratio of catalyst: Imidazole: cyclooctene is (1:50:60), CH_3CN: 1ml, H_2O_2: 0.7 ml, Time: 4h, Temperature: r.t, Catalyst: 0.0025 mmol. [b]TON: mmol product/ mmol catalyst.

Table 5. Oxidation reaction of alkenes with H_2O_2 in the presence of MnTCPP@AC-NH$_2$.

No	Alkene	Conversion[a], %	Selectivity[b], %
1	Cyclooctene	86	100
2	Indene	97	50
3	1-Octene	19	100
4	Cis- stilbene	23	88
5	Styrene	80	100
6	4-chloro styrene	47	100
7	α-methyl styrene	98	70
8	4-methyl styrene	100	84
9	Cyclohexene	90	92
10	1-methyl-1- cyclohexene	60	94

[a]Reaction condition: The molar ratio of catalyst: Imidazole: cyclooctene is (1:50:60), CH$_3$CN: 1ml, H$_2$O$_2$: 0.7 ml, Time: 4h, Temperature: 25^{0}C, Catalyst: 0.0025 mmol. [b]Selectivity to the corresponding epoxide.

A Comparison of the catalytic activity of MnTCPP@AC-NH$_2$ was done with those reported in the literature. As shown in **Table 6**, the satisfied reaction time is a significant advantage of the prepared catalyst compared to the previous reports.

The proposed mechanism for this catalytic reaction may be comprised of two pathways. Imidazole and H$_2$O$_2$ coordinate to metal center of the catalyst. In one of the pathways, alkene can attack to the oxygen atom of coordinated hydrogen peroxide and in the other pathway, a high-valent manganese-oxo will be produced which can transfer oxygen to the substrate (**Scheme 2**).

3.3. Reusability of MnTCPP@AC-NH$_2$

The Reusability of catalyst was evaluated on the oxidation of cyclooctene. After each run, catalyst was separated from a solution by centrifuge and washed with acetone three times, and finally dried at 50^0 C. This catalyst shows at least three times reusability (**Fig. 7**).

Table 6. Oxidation reaction of cyclooctene in the presence of catalysts at room temperature.

No	Catalyst	Oxidant	Time (h)	Conv.[a], %	Ref
1[b]	[Fe(THPP) Cl@ MWCNT]	H$_2$O$_2$	80 min	100	[35]
2	[Mn(THPP)OAc@ MWCNT]	UHP	4	82	[36]
3[c]	PW$_4$-NH$_2$-AC	H$_2$O$_2$	8	81	[43]
4	Fe$_3$O$_4$/SiO$_2$/NH$_2$-Mn(TCPP) OAc	H$_2$O$_2$	5	87	[45]
5[c]	Fe$_3$O$_4$/SiO$_2$/NH$_2$-Fe(TCPP)Cl	H$_2$O$_2$	5	97	[45]
6	MnTCPP@AC-NH$_2$	H$_2$O$_2$	4	86	This work

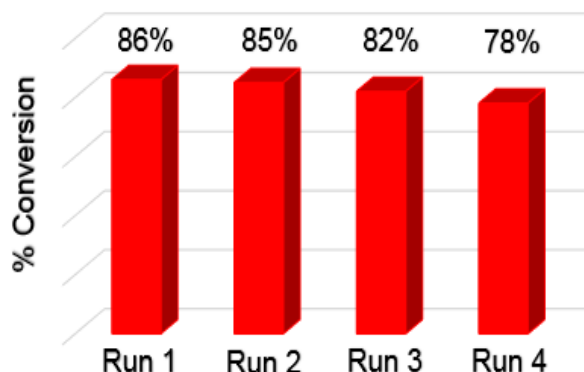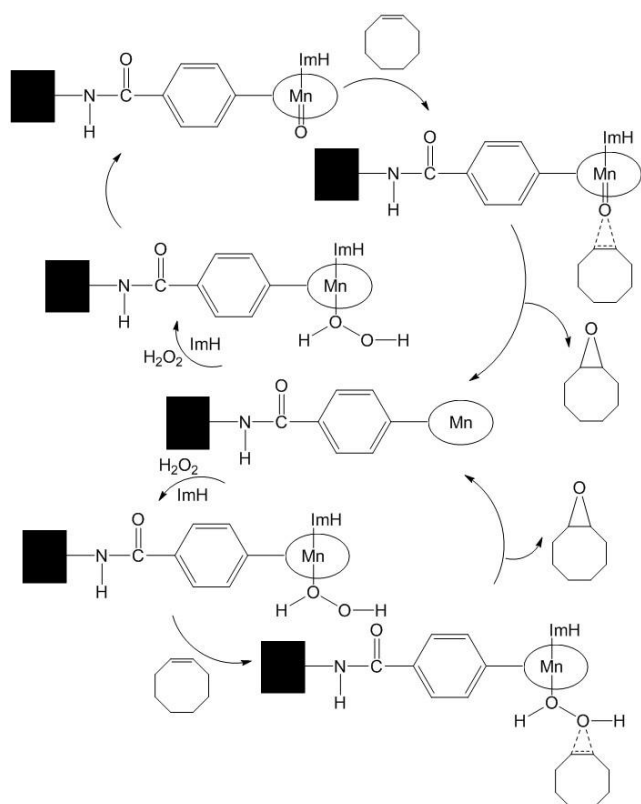[a] % Conversion. [b] Under ultrasonic irradiation. [c] Under reflux.

Fig. 7. Reusability of catalyst on the oxidation reaction of cyclooctene with H$_2$O$_2$. Reaction condition: The molar ratio of catalyst: imidazole: cyclooctene is (1:50:60), CH$_3$CN: 1mL, H$_2$O$_2$: 0.7 mL, Time: 6h, Temperature: 25^{0}C

Scheme 2. Proposed mechanism of oxidation of cyclooctene with H_2O_2 in the presence of MnTCPP@AC-NH$_2$.

4. Conclusions

Manganese porphyrin was synthesized and supported on amine-functionalized activated carbon *via* covalent amide bonds. This new catalyst (MnTCPP@AC-NH$_2$) was employed for the oxidation of alkenes with H_2O_2 (35%) as green oxidant and imidazole as a co-catalyst. Results indicated that 86% conversion of cyclooctene to its epoxide was obtained after 4 h with H_2O_2 at room temperature.

Acknowledgements

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