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Catalytic activity of carbon nanotube supported iron(III) and manganese(III) porphyrins in oxidation of olefins with *tert*-butyl hydroperoxide: Higher activity of the iron(III) porphyrin

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ABSTRACT

Oxidation of olefins with *tert*-butyl hydroperoxide (TBHP) catalyzed by carbon nanotube supported iron(III) and manganese(III) complexes of *meso*-tetrakis(4-hydroxyphenyl)porphyrin is reported. The results show higher catalytic activity of the Fe(III) complex compared to the Mn(III) one. With the exception of cyclooctene which gives cyclooctene oxide as the sole product, oxidation of styrene, α-methyl styrene and cyclohexene leads to the formation of benzaldehyde, acetophenone and cyclohexene-1-one as the major product, respectively. In this study, acetonitrile has been found to be the best solvent for reaction performed in the presence of the manganese and iron porphyrin. In comparison of the two metalloporphyrins, catalytic activity of the manganese porphyrin is more sensitive to the type of solvent than the iron one. In spite of the crucial role of imidazole (ImH) on catalytic performance of the manganese porphyrin, the presence of ImH has a negative effect on the activity of the iron porphyrin. The nano-tube supported iron porphyrin may be recovered and reused at least four times without significant loss of the catalytic activity.

Considerable insights into the nature of the enzymatic processes have been obtained from experimental and theoretical studies on the synthetic metalloporphyrins as models for cytochrome P450 [1]. The synthesis of metalloporphyrins resistant enough to oxidation is the first step in mimicking the oxidation reactions mediated by heme-enzymes of the cytochrome P450 family [1]. The introduction of bulky and/or electron-withdrawing substituents at the *meso* positions of the synthetic metalloporphyrins has been among the main strategies commonly employed with the aim of increasing the stability of the aromatic heterocycle towards oxidative degradation in reaction condition. Heterogenizing homogeneous catalysts may also be used to increase the oxidative stability of metalloporphyrins [2]. The heme center of cytochrome p450 enzymes may be considered as an immobilized iron porphyrin attached through the iron to the cysteine residue of the protein part of the enzyme as the support [3,4]. In addition to the effects of protein structure and dynamic on the spin state of the metal center, the oxidative stability of heme is significantly determined by the steric effects of the protein part of the enzyme [3]. Iron and manganese porphyrins have been extensively studied as model complexes of cytochrome p450 enzymes [5–7]. The difference between catalytic activity of porphyrin complexes of metals such as iron, manganese, chromium, cobalt, osmium and ruthenium in homogeneous condition have been investigated in some studies [5]. Recently, the catalytic activity of iron and cobalt porphyrins and phthalocyanines supported on carbon nanotubes towards oxygen reduction has been studied in a comparative manner [8]. In the present work, the catalytic activity of a nano-tube supported iron porphyrin in oxidation of olefins with *tert*-butyl hydroperoxide (TBHP) has been studied and compared with the corresponding manganese counterpart. Also, the influence of different parameters on the catalytic activity of the iron and manganese porphyrins has been investigated.

MWNTs containing ~2 mol% carboxylic acid groups were used for the study (Table 1).

Meso-tetrakis(4-hydroxyphenyl)porphyrin (H_2THPP) was prepared as described by Adler et al. [9,10]. Iron(III) porphyrin (FeTHPPCl) and manganese(III) porphyrin (MnTHPPOAc) were obtained by metallation of the H_2THPP with ferrous chloride tetrahydrate and manganese acetate tetrahydrate respectively in DMF with the method described by Buchler et al. [11,12]. In order to support metalloporphyrins on the multi-wall carbon nanotubes, to a mixture of 250 mg of MWCNT-COOH in 25 ml DMF, FeTHPPCl or MnTHPPOAc (0.3 mmol), 2-(1*H*-benzotriazole-1-yl)-1,1,3,3-

Table 1
The structural characteristics of MWCNT-COOH used in this study.

Outside diameter (nm)	Inside diameter (nm)	Length (μm)	COOH content (wt.%)	Specific surface area (m^2/g)
10–20	5–10	~30	2	>200

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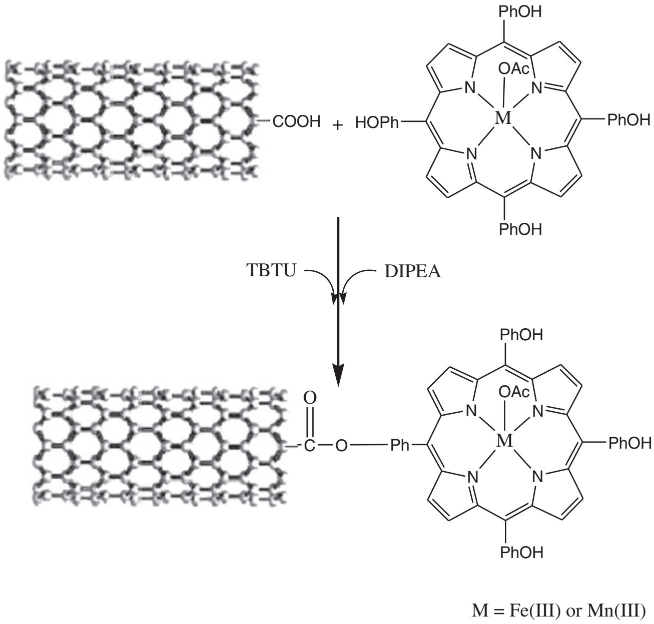


Fig. 1. Preparation of multi-wall carbon nanotubes supported metalloporphyrins.

tetramethyluronium tetrafluoroborate (TBTU) (90 mg, 0.2 mmol) and *N*, *N′*-diisopropylamine (DIPEA) (70 mg, 0.5 mmol) were added and the reaction mixture was stirred for 2 days at room temperature [13]. The dark solid product was then filtered, and washed with DMF to remove the weakly adsorbed metalloporphyrins. The solid residue was dried at room temperature (Fig. 1).

The covalent bonding between the metalloporphyrins and MWCNT-COOH was carried out by acid–base reaction between the porphyrin hydroxyl groups and carboxylic acid of MWCNT-COOH using TBTU as a highly effective uranium salt in the presence of DIPEA [13]. The prepared catalyst was characterized by IR spectroscopy and scanning electron microscopy (SEM). The metal content of the catalyst was determined by atomic absorption spectroscopy. Accordingly, the metal content of the catalysts was found to be ca. 821 and 355 μmol per gram of the catalysts, in the case of the iron and manganese porphyrins respectively. The nitrogen content of the catalysts was determined by CHN analysis, which showed a value of 2% and 0.8% for the Fe and Mn-catalyst respectively. Based on these values, the manganese porphyrin content of the catalyst was about 357 μmol per gram of the Mn-catalyst and the iron porphyrin one was ca. 815 μmol per gram of the Fe-catalyst. These results are in good agreement with those obtained by atomic absorption spectroscopy. The scanning electron micrograph of MWCNT-COOH (Fig. 2) shows the morphology of MWCNT-COOH used in this study. The comparison of SEM images of FeTHPPCl-MWCNT and MnTHPPOAc-MWCNT and the carbon nanotube, indicates that the metalloporphyrins have been supported on the nanotubes.

The most informative spectroscopic data, confirming the covalent anchoring of FeTHPPCl and MnTHPPOAc on MWCNT-COOH, were obtained by comparison of the IR spectra of MWCNT-COOH and FeTHPPCl-MWCNT (Fig. 3). The C═O stretching band of the carboxylic acid group of MWCNT-COOH appears at 1642 cm^{-1}. When the metalloporphyrin was attached to MWCNT-COOH, a strong band was observed at 1714 cm^{-1} in the case of FeTHPPCl-MWCNT and at 1709 cm^{-1} in the case of MnTHPPOAc-MWCNT, respectively which were assigned to the formed esteric bond between the metalloporphyrins and the nanotubes.

The prepared heterogeneous catalyst was used for the oxidation of olefins with TBHP at room temperature. The effect of various

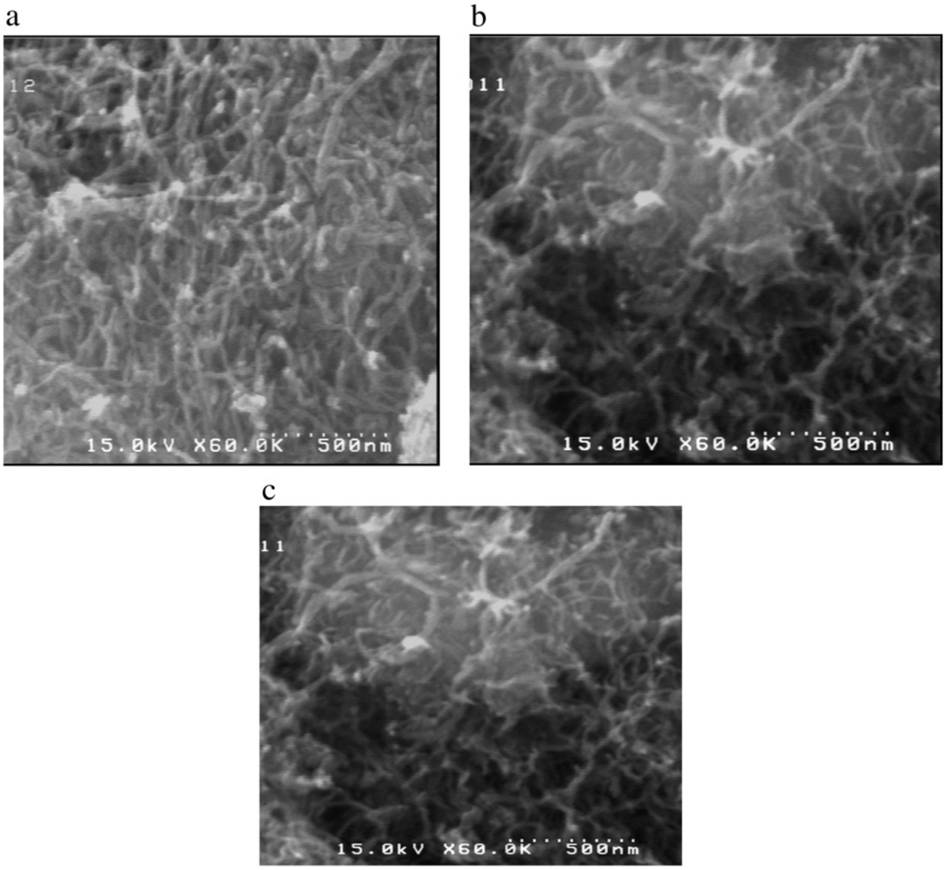


Fig. 2. SEM images of MWCNT-COOH (a), FeTHPPCl-MWCNT (b) and MnTCPPOAc-MWCNT (c).

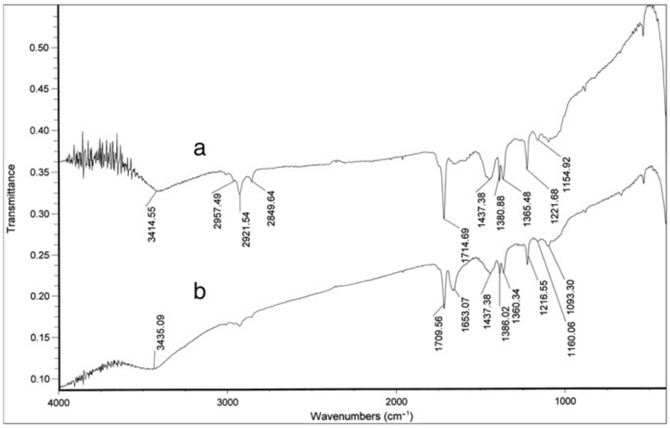


Fig. 3. The IR spectra of: (a) FeTHPPCl-MWCNT and (b) MnTHPPOAc-MWCNT.

parameters such as catalyst loading, nature of solvent, type of oxidant and axial base was investigated to optimize the oxidation conditions. In reactions catalyzed by metalloporphyrins, the conversion values, product yields and product distribution are usually influenced by the type of solvent, especially due to its effects on the nature and stability of the intermediate species [14]. Methanol, dichloromethane, chloroform and acetonitrile were chosen as reaction media for oxidation of cyclooctene with TBHP in the presence of FeTHPPCl-MWCNT and MnTHPPOAc-MWCNT (Table 2) and acetonitrile was found to be the best one, apparently due to its high dielectric constant.

Since the catalytic activity of Mn-porphyrins usually increases in the presence of different nitrogenous bases as co-catalyst [15–17], the effect of imidazole as co-catalyst on the oxidation of cyclooctene has been studied (Table 3). The presence of imidazole led to a decrease in the catalytic activity of the iron catalyst. This observation may be due to the formation of the inactive six coordinate species i.e. FeTHPP(ImH)$_2$ [7]. Otherwise, the existence of imidazole as co-catalyst is essential for oxidation of cyclooctene in the presence of manganese catalyst.

The reaction was also carried out using two other peroxides. 30% aqueous hydrogen peroxide and urea hydrogen peroxide (UHP) were used as oxidant; almost no product was observed in the case of UHP and hydrogen peroxide.

Table 2
Solvent effect on the oxidation of cyclooctene with TBHP at room temperature, for a reaction time of 4 h.

Entry	Solvent	Dielectric constant	Epoxide yield (%) FeTHPPCl-MWCNT[a]	Epoxide yield (%) MnTHPPOAc-MWCNT[b]
1	CH_3CN	37.5	17	5
2	$CHCl_3$	4.8	7	–
3	CH_2Cl_2	9.1	8	–
4	MeOH	33	6	–

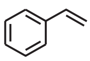
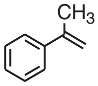
[a] The molar ratios for catalyst:cyclooctene:TBHP are 1:25:50.
[b] The molar ratios for catalyst:ImH:cyclooctene:TBHP are 1:10:50:50.

Table 3
Effect the molar ratio of the catalyst/ImH on oxidation of cyclooctene with TBHP in acetonitrile at room temperature.[a,b]

FeTHPPCl-MWCNT/ImH	Epoxide yield (%)	MnTHPPOAc-MWCNT/ImH	Epoxide yield (%)
1:0	17	1:0	–
1:10	4	1:10	5

[a] The molar ratios for catalyst:ImH:cyclooctene:oxidant are 1:X:25:50, respectively.
[b] For a reaction time of 4 h.

Table 4
Oxidation of olefins with TBHP catalyzed by FeTHPPCl-MWCNT in acetonitrile at room temperature.[a,b]

Entry	Olefine	Conversion (%)	Selectivity (%)	
			Epoxide	Others
1		56 (22)[c]	16 (10)	84 (90)[d]
2	 CH_3	96 (78)	2 (4)	98 (96)[e]
3		20 (17)	100 (100)	–
4		54 (23)	6 (4)	81 (74)[f]

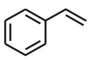
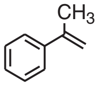
[a] The molar ratios for catalyst:olefin:oxidant are 1:25:50, respectively.
[b] For a reaction time of 24 h.
[c] The values in the parentheses are due to a 4 h reaction time.
[d] Benzaldehyde is the main product.
[e] Acetophenone is the main product.
[f] 2-Cyclohexene-1-one is the major product.

FeTHPPCl-MWCNT/TBHP and MnTHPPOAc-MWCNT are efficient heterogeneous catalytic systems for the oxidation of various alkenes under the optimized reaction conditions (Tables 4 and 5). The significant yields of allylic oxidation products obtained in the catalytic oxidation of cyclohexene, styrene and α-methyl styrene with may be due to the H-abstraction from the substrate by a high valent iron or manganese oxo species (see the proposed mechanism).

Higher reactivity of the conjugated double bonds (Table 4, entries 1, 2) in comparison with the unconjugated ones may be interpreted on the basis of the π-electron donor ability of phenyl-group to the double bond. Also α-methyl styrene was found to be more reactive than styrene towards the allylic oxidation reaction. It leads to the formation of acetophenone as the product. On the other hand, apparently due to the steric hindrance of the methyl group, α-methyl styrene is less reactive than styrene towards epoxidation reaction.

In this catalytic system, the reactivity of cyclohexene, styrene and α-methyl styrene is higher than that of cyclooctene (Tables 4 and 5). This finding seems to be due to the involvement of different reaction mechanisms and active oxidants in the catalytic cycles of the used olefins.

Table 5
Oxidation of olefins with TBHP catalyzed by MnTHPPOAc-MWCNT in acetonitrile at room temperature.[a,b]

Entry	Olefin	Conversion (%)	Selectivity (%)	
			Epoxide	Others
1		19 (15)[c]	21 (4)	79 (96)[d]
2	 CH_3	38 (24)	13 (16)	87 (84)[e]
3		10 (5)	100 (100)	–
4		33 (11)	12 (9)	70 (64)[f]

[a] The molar ratios for catalyst:olefin:oxidant are 1:25:50, respectively.
[b] For a reaction time of 24 h.
[c] The values in the parentheses are due to a 4 h reaction time.
[d] Benzaldehyde is the main product.
[e] Acetophenone is the main product.
[f] 2-Cyclohexene-1-one is the major product.

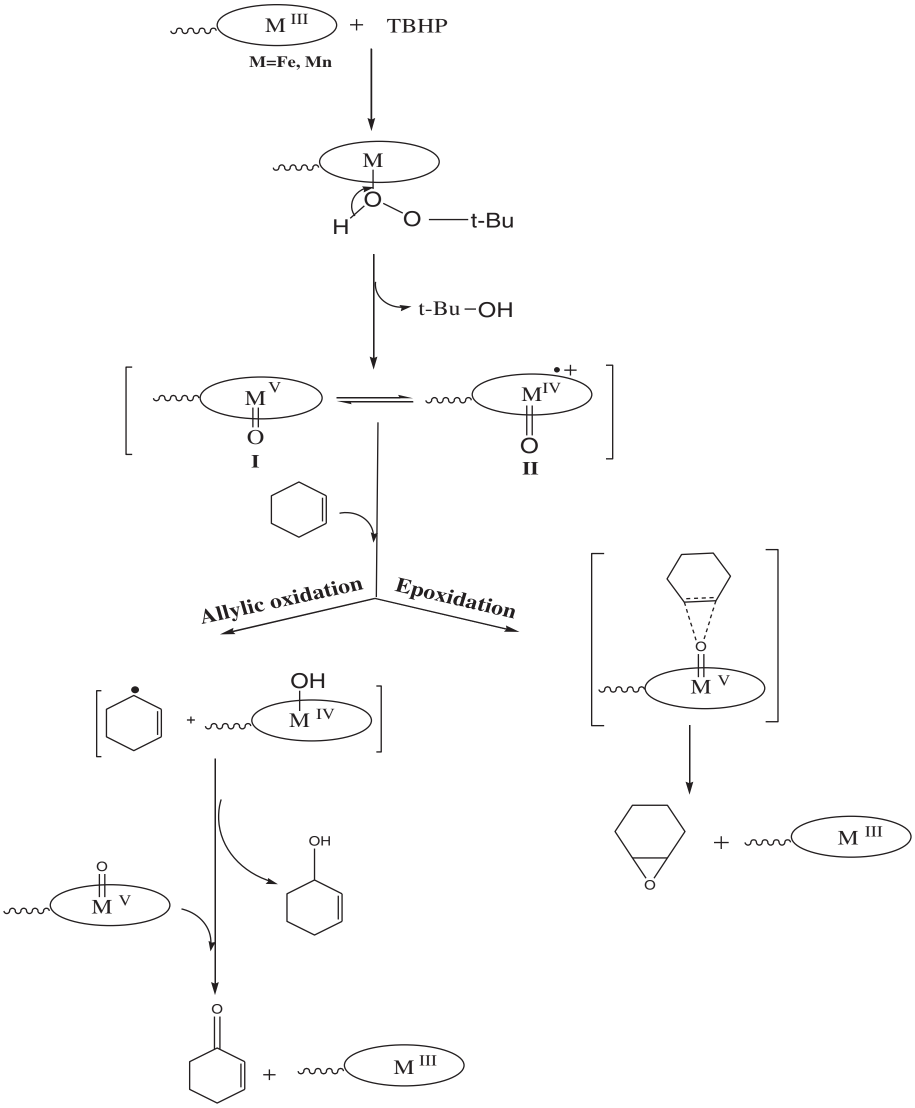


Fig. 4. Proposed mechanism for oxidation of olefins with TBHP.

The involvement of a high-valent metal–oxo species (Fig. 4, I) may be considered for oxidation of cyclooctene with TBHP. In the case of styrene, α-methyl styrene and cyclohexene the formation of allylic products suggests that a radical pathway is involved. In the first step, TBHP coordinates to the metal center of FeTHPPCl-MWCNT or MnTHPP-MWCNT to form a high valent metal–oxo species (Fig. 4, I) or an oxo–iron/manganese(IV) porphyrin π-cation radical (Fig. 4, II) as the active oxidant species. The active oxidant species may transfer an oxygen atom to the double bond to form epoxide product or cause the allylic oxidation via the H-abstraction form the allylic positions of the substrates.

The reusability of a heterogeneous catalyst is of prime importance in catalyst design. Under homogeneous conditions, FeTHPPCl is readily degraded but the carbon-nanotube supported iron-porphyrin catalyst can be filtered and reused several times without detectable catalyst leaching or a significant loss of the catalytic efficiency (Table 6). The reusability of FeTHPPCl-MWCNT was investigated in epoxidation of cyclooctene with TBHP. The catalyst was separated from the reaction mixture after each experiment by filtration, washed with acetonitrile or methanol dried before use. After using the catalyst five consecutive times, the epoxide yield was 11% (Table 6). Furthermore, the IR spectrum of the recovered catalyst was prepared and no detectable change was observed.

The observed increase in the epoxide yield in the 5th run may be caused by the ability of alcoholic solvent to break the weaker covalent bonds between the Fe-porphyrin and multi-wall the nanotubes i.e. slight leaching of the catalyst.

Carbon nano-tube supported iron *meso*-tetrakis(4-hydroxyphenyl) porphyrin has been found to show higher catalytic activity in oxidation of olefins with *tert*-butyl hydroperoxide compared to the manganese counterpart. While the oxidation of cyclooctene gives cyclooctene oxide as the sole product, oxidation of styrene, 2-methylstyrene and cyclohexene leads to the formation of benzaldehyde, acetophenone and cyclohexene-1-one as the major product, respectively. Catalytic activity

Table 6
The recovery and reuse of FeTHPPCl-MWCNT in the oxidation of cyclooctene with TBHP for a reaction time of 4 h.

Run	Rinsing solvent	Epoxide yield (%)
1	–	17
2	CH_3CN	13
3	CH_3CN	10
4	CH_3CN	7
5	MeOH	11

The molar ratios for catalyst:alkene:oxidant are 1:25:50, respectively.

of the manganese porphyrin is more sensitive to the type of solvent than the iron one. Although the presence of ImH is necessary for efficient catalytic performance of the manganese porphyrin, the presence of ImH has a negative effect on the activity of the iron porphyrin. The nanotube supported iron porphyrin may be recovered and reused at least four times without significant loss of the catalytic activity. In this study, acetonitrile has been found to be the best solvent for reaction performed in the presence of the manganese and iron porphyrin.

Acknowledgments

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[10] H_2THPP: UV–vis (DMF): λ_{max} (nm): 422, 517, 555, 594, 647. ^{1}H NMR (MeOD, 500 MHz, δ (ppm)): 8.88 (s, 8H, β-pyrrole), 7.99–8.02 (d, 8, *o*-phenyl), 7.19–7.22 (d, 8H, *m*-phenyl).

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