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FULL PAPER

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A practical innovative method for highly selective oxidation of alkenes and alkanes using Fe (III) and Mn (III) porphyrins supported onto multi-wall carbon nanotubes as reusable heterogeneous catalysts

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Functionalized multi-walled carbon nanotubes were used for covalent immobilization of *meso*-tetrakis(4-carboxyphenyl) porphyrinatoiron (III) chloride [Fe (TCPP)Cl] and *meso*-tetrakis(4-carboxyphenyl) porphyrinatomanganese (III) acetate [Mn (TCPP)OAc]. The full characterization of the hybrid porphyrinic nanomaterials, by Fourier transform-infrared and UV–Vis spectroscopy, transmission electron microscopy, thermogravimetry and flame atomic absorption spectrometry is described. The oxidation of alkenes and alkanes with molecular oxygen as green oxidant in the presence of Mn- and Fe-catalysts has been studied in a comparative manner. The Fe-catalyst was shown to have higher catalytic activity compared with the Mn-catalyst. In addition, both separable solid catalysts can be recovered and reused at least 10 times along with good yields.

KEYWORDS
catalyst, molecular oxygen, multi-walled carbon nanotubes, oxidation of alkenes and alkanes, porphyrin

1 | INTRODUCTION

The hydrocarbons C–H bond activation with oxygen donors are practically one of the paramount reactions in organic synthesis, as the oxidation of these compounds gives a variety of products, such as carbonyl compounds, epoxides, alcohols, diols and aldehydes. Most of them are included in the most useful synthetic intermediates considering their industrial value.[1,2] The past decades have witnessed significant progress in the catalytic methods for oxidation of olefines with organocatalysts or metal-based catalysts, such as V,[3–5] Mn,[6,7] Fe,[8–10] Co,[8,11] Cu,[12,13] etc.

Oxidation of hydrocarbons can be carried out using a variety of oxidants, such as iodosylbenzene,[14,15] alkyl hydroperoxides,[16,17] hydrogen peroxide[18,19] and molecular oxygen.[20–22] The use of molecular oxygen as a green oxidant because of its low cost, ease of controlling and less toxic byproducts during reaction compared with other oxygen donors has absorbed much attention in the oxidation of olefins.[23,24] Molecular oxygen has very little tendency to enter the oxidation reaction process at low temperatures due to its triplet state (two unpaired electrons in ground-state).[25] In order to overcome these difficulties of exploiting O_2, nature has provided families of enzymes to transport O_2, and to catalyze, operate and control its reduction. A great number of these enzymes contain first-row transition metals, such as iron, copper and rarely manganese with unpaired d-electrons.[26] These systems can simplify the activation of triplet ground-state oxygen, which starts with the binding of O_2 to the central metal.[27] Cytochrome P-450 is one such enzyme, which can carry out many chemical transformations.[28–30] In recent years, the development of efficient catalytic systems for oxidation reactions that mimic the action of cytochrome P-450 has attracted much attention.[31,32] In this regard, metalloporphyrins, owing to their direct relationship with cytochrome P-450 enzymatic oxidations as catalysts for the epoxidation of olefins, are now a meeting point for chemistry, chemicals, catalysis and biology. Metalloporphyrin-catalyzed aerobic epoxidation of olefins has become an important and highly gratifying protocol for important feedstock for petrochemical and fine chemical industries.[33,34]

In several reports on the catalytic epoxidation with molecular oxygen, high temperatures or extremely long reaction times have been evaluated to activate the triplet dioxygen.[21,35,36] Because the stoichiometry of oxygenation requires two electrons and two protons to reduce the second oxygen atom of dioxygen to water, the majority of reports mentioned an electron source such as borohydride, hydrogen and colloidal platinum, zinc powder, electrons from an electrode or aldehyde as reductant. These materials will gently moderate the reaction condition.[37–41] One of the effective reducing agents for the epoxidation of olefins with O_2 is aldehydes. Many metalloporphyrins demonstrated highly catalytic performance for aerobic oxidation in the presence of aldehyde, which is involved in the reaction mechanism.[42–45]

Another desirable option is to use heterogenized catalysts because the synthesis of metalloporphyrins is challenging and low yielding. Immobilization of porphyrins onto a solid support can overcome this problem, and cause easier recovery and reuse of the catalysts. Subsequently, the support can also reduce the decomposition of the metalloporphyrins during the epoxidation reaction and increase the stability of the catalyst.[46–49] There is a broad range of solids, including framework-substituted molecular sieves, inorganic oxide and supported catalysts, and porous materials.

Encapsulated metal complexes, layered-type materials, peroxometalates and supported porphyrin catalysts have been used for these reactions. All these catalytic systems have shown potential in olefin epoxidation, sometimes depending on the reaction conditions.[50] Multi-walled carbon nanotubes (MWCNTs) with functional groups are one of the recommended solid supports for immobilization of metal complexes due to their unique structural, mechanical, thermal and electronical properties along with high surface area and insolubility in most solvents.[10,51–53] In the recent works in our group, the [Fe (THPP)Cl] immobilized onto functionalized MWCNTs has proven to be an excellent catalyst for the epoxidation of olefins in the presence of molecular oxygen and isobutylaldehyde.[54]

In this study, *meso*-tetrakis(4-carboxyphenyl) porphyrinatoiron (III) chloride [Fe (TCPP)Cl] and *meso*-tetrakis(4-carboxyphenyl) porphyrinatomanganese (III) acetate [Mn (TCPP)OAc] were immobilized onto the functionalized MWCNTs with hydroxyl groups. The catalytic activities of two heterogenized catalysts were compared in the aerobic oxidation of olefins and saturated alkanes.

2 | EXPERIMENTAL

2.1 | Materials and characterization techniques

Functionalized MWCNTs with an outside diameter of 10–20 nm, inside diameter of 5–10 nm, length of ~30 μm and specific surface area of > 200 $m^2\ g^{-1}$ containing 3.06 wt% hydroxyl groups were used as the solid support. Other materials and solvents were purchased from Aldrich, Merck or Fluka chemical companies and used as received. The electronic absorption spectra were recorded on PerkinElmer Lambda 25 UV–Vis spectrophotometer. Analyses for liquid samples were accomplished using a quartz cell with 1 cm path length. The morphology of the solid catalysts was investigated by transmission electron microscopy (TEM; Philips EM 208). The thermal properties of the prepared heterogenized catalysts were investigated using a thermal analyzer (Mettler-Toledo TGA 851e) along with thermogravimetric (TGA) and differential thermogravimetric analysis (DTGA) at a heating rate of 10°C per minute in a dry air atmosphere. The modified MWCNTs and heterogeneous catalysts were identified by X-ray powder diffraction (XRD) using a Panalytical Xpert PRO X Ray Diffractometer (Xpert Pro MPD) with Cu-Kα radiation ($\lambda = 0.15405$ Å) at 40 kV and 30 mA. Infrared spectra were recorded (KBr pellets) on an ABB Bomem: FTLA 2000–100 in the range of 400 to 4000 cm^{-1}. The manganese and iron contents of the catalyst were determined by atomic absorption spectrophotometry (AAS) with flame atomization (Varian AA240). Quantification was made by the standard addition method. An Agilent 7890B instrument using a SAB-5 capillary column (phenyl methyl siloxane 30 m × 0.32 mm × 0.25 μm) and a flame ionization detector performed gas chromatography experiments (GC).

2.2 | Preparation of the Fe (TCPP) Cl@MWCNTs and Mn (TCPP) OAc@MWCNTs

Meso-tetrakis(4-carboxyphenyl) porphyrin (H_2TCPP) was synthesized according to the procedure described by

Adler et al.[55] Fe (III) and Mn (III) complexes of the prepared porphyrin {[Fe (TCPP)Cl] and [Mn (TCPP)OAc]} were synthesized according to the literature.[56]

To promote covalent linkage of metalloporphyrins on the surface of functionalized MWCNTs, basic coupling reagents [2-(1*H*-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium tetrafluoroborate (TBTU)/*N*,*N*′-diisopropylethylamine (DIPEA)] were used to afford the more convenient esterification at room temperature under mild conditions.[10,49,57] A mixture of functionalized MWCNTs, Fe (TCPP)Cl [or Mn (TCPP)OAc], TBTU and DIPEA in 50 mL DMF were stirred for 48 hr at room temperature. The solid products were filtered and washed with DMF to remove the weakly adsorbed metalloporphyrins, and the dark solid was separated by vacuum pump and eventually dried at 60°C for 24 hr.

2.3 | Assay for the oxidation of styrene

Catalytic reactions at atmospheric pressure were carried out in a 5-mL test tube in a water bath (temperature between 40 and 45°C). The solid catalyst [Fe (TCPP)Cl@MWCNTs; 1.8 mg, 0.0042 mmol based on Fe content of the compound), 0.189 mmol of styrene and 0.567 mmol of isobutyraldehyde were added to 1 mL of acetonitrile. A pure oxygen gas balloon was directly attached to the reaction system. The mixture was stirred for 2 hr. For Mn (TCPP)OAc@MWCNTs 1.2 mg (0.0042 mmol based on Fe content of the compound) the same condition was performed and the mixture was stirred for 4 hr. Eventually, the catalysts were removed from the reaction by centrifugation and the products were characterized by GC.

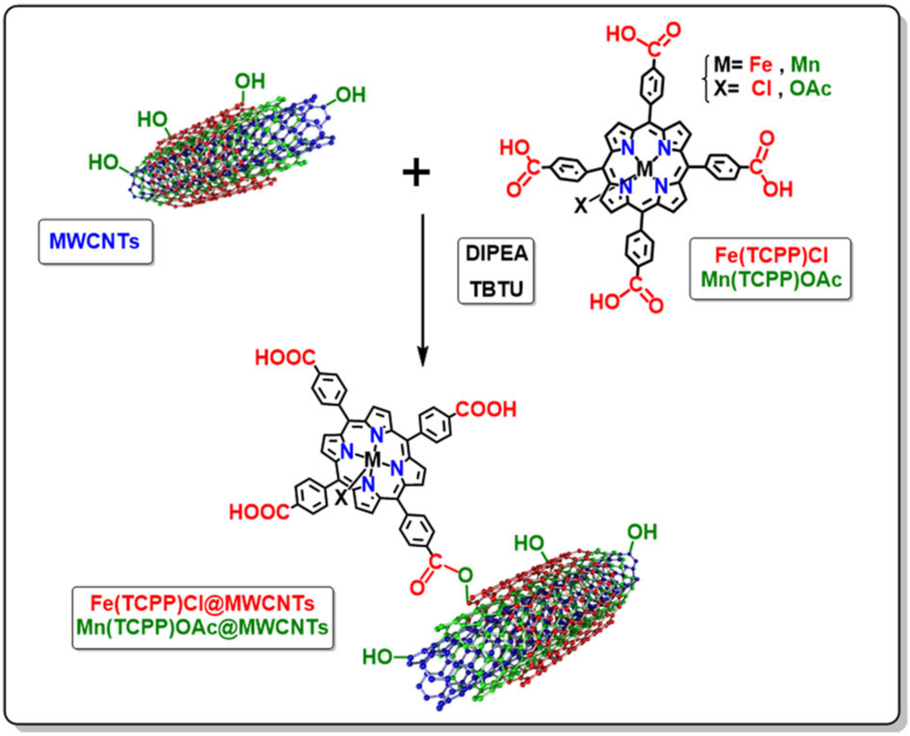
3 | RESULTS AND DISCUSSION

The separable solid catalysts {[Fe (TCPP)Cl@MWCNTs] and [Mn (TCPP)OAc@MWCNTs]} were synthesized as demonstrated in Scheme 1. Fe (TCPP)Cl and Mn (TCPP)OAc are covalently bonded onto modified MWCNTs through an ester bond between the hydroxyl group of the MWCNTs and the carboxylic acid group of the metalloporphyins, which was confirmed by the following characterizations.

3.1 | Characterization of [Fe (TCPP)Cl@MWCNTs] and [Mn (TCPP)OAc@MWCNTs]

Fourier transform-infrared (FT-IR) spectroscopy was carried out for MWCNTs, Fe (TCPP)Cl@MWCNTs and Mn (TCPP)OAc@MWCNTs, in which the spectra were recorded from 400 to 4000 $\mathrm{cm^{-1}}$ (Figure 1a–c). A band at about 1709 $\mathrm{cm^{-1}}$ is due to a formed ester bond between Fe- or Mn-porphyrin and the surface of MWCNTs.

X-ray powder diffraction patterns of [Fe (TCPP)Cl@MWCNTs] and [Mn (TCPP)OAc@MWCNTs] in



SCHEME 1 Schematic preparation of M (TCPP)X@MWCNTs

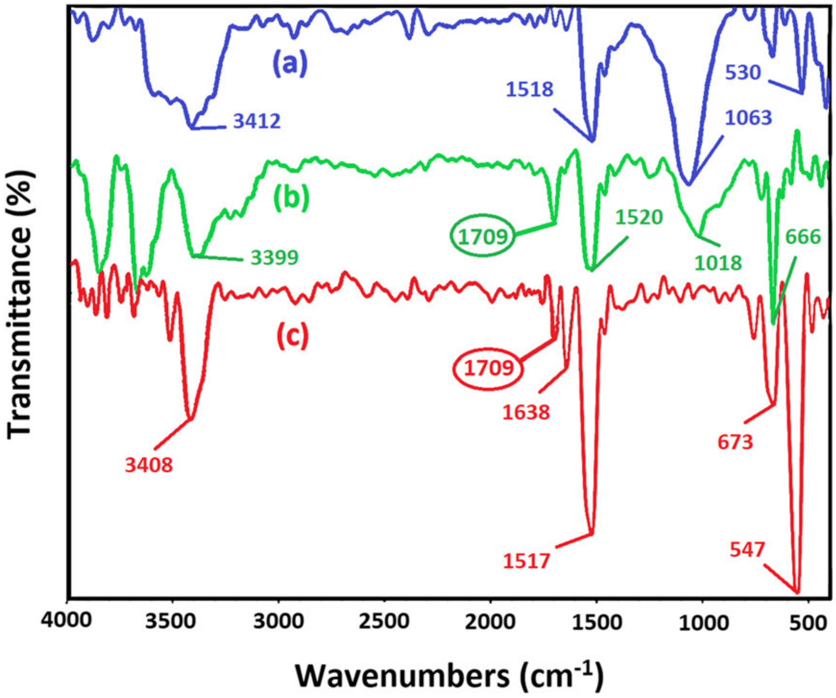


FIGURE 1 Fourier transform-infrared (FT-IR) patterns of (a) multi-walled carbon nanotubes (MWCNTs), (b) Mn (TCPP)OAc@MWCNTs and (c) Fe (TCPP) Cl@MWCNTs

the 2θ between 10° and 80° are shown in Figure 2. As can be seen, in both catalysts the characteristic diffraction peaks of carbon nanotubes include a sharp peak at about 26° and a less intense peak at 43°, which show the presence of graphitic planes, and are still noticeable after immobilization of metalloporphyrins (Figure 2a and b).[58]

The thermal behaviors of Fe (TCPP)Cl@MWCNT and Mn (TCPP)OAc@MWCNT were studied by TGA, which proved the thermal stability up to 300°C for both iron and manganese catalysts. Figure 3 shows the TGA curves, representing the variations in residual mass of the samples with increasing temperature. The first stage of weight loss at below 250°C is due to removal of adsorbed physical and chemical water.[59] The weight loss at about 300–350°C may be related to the decomposition of the metalloporphyrin, and the step at about 650°C may be due to the oxidation of MWCNTs.[10,47]

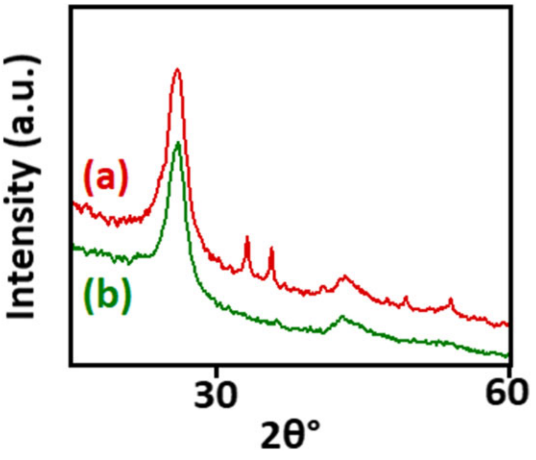


FIGURE 2 X-ray powder diffraction (XRD) patterns of (a) Fe (TCPP)Cl@MWCNTs and (b) Mn (TCPP)OAc@MWCNTs

The TEM images of Fe (TCPP)Cl@MWCNTs and Mn (TCPP)OAc@MWCNTs (Figure 4) show that the cylindrical nanostructure of the MWCNTs remains unchanged after the immobilization process. Besides, the Fe- and Mn-porphyrins on the surface of nanotubes may be located in the darker parts of the images, which can reveal the linkage of the catalyst and MWCNTs.

The qualitative UV–Vis spectra of the complexes [Fe (TCPP)Cl, Mn (TCPP)OAc], immobilized catalysts [Fe (TCPP)Cl@MWCNTs and Mn (TCPP)OAc@MWCNTs] and the solid modified support (MWCNTs; Figure 5 a–e) was also recorded. The presence of the Soret bands at 420 and 470 nm in the spectra of Fe (TCPP) Cl@MWCNTs and Mn (TCPP)OAc@MWCNTs (Figure 5c and d) resembles the position of the Soret band of the typical metalloporphyrins in the spectra of Fe (TCPP)Cl and Mn (TCPP)OAc (Figure 5a and b). This observation confirms the presence of metalloporphyrins on the modified MWCNTs. The solid MWCNTs (Figure 5e) do not display expressive bands in the region of the interest, as expected.

The metal-porphyrin content of catalyst loading on the modified MWCNTs was estimated by AAS and, based on this value, the Fe and Mn contents of the catalyst were determined to be about 2.63 mmol and 3.46 mmol per gram of the catalysts.

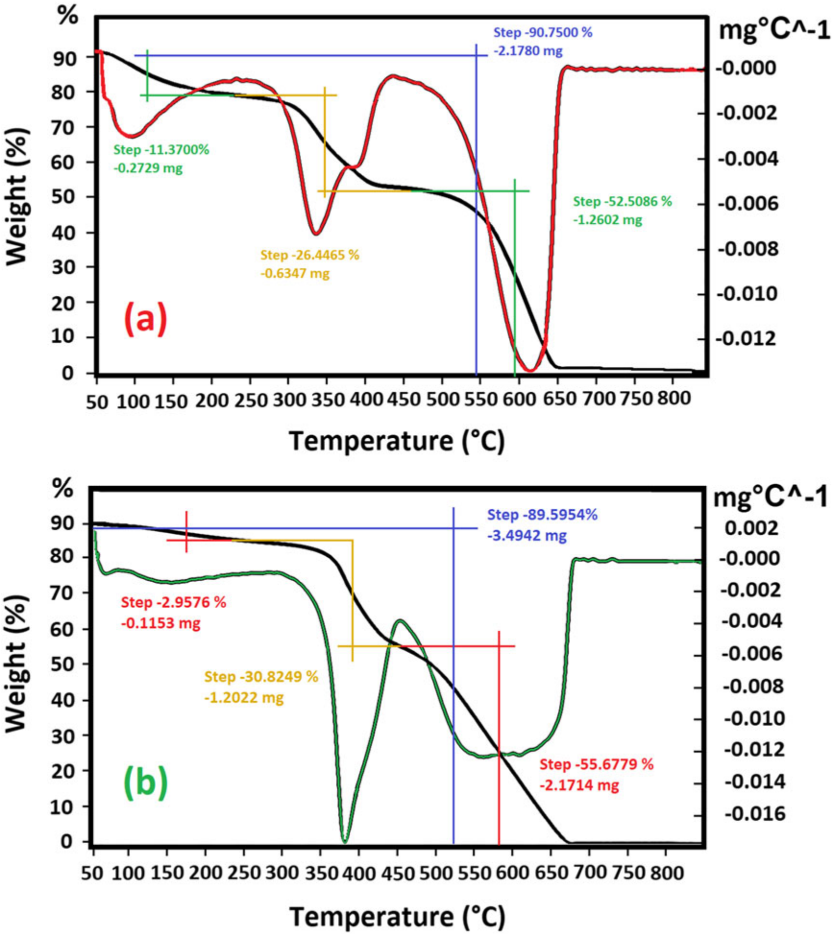


FIGURE 3 Thermogravimetric analysis (TGA)/differential thermogravimetric analysis (DTGA) curves of (a) Fe (TCPP) Cl@MWCNTs and (b) Mn (TCPP) OAc@MWCNTs

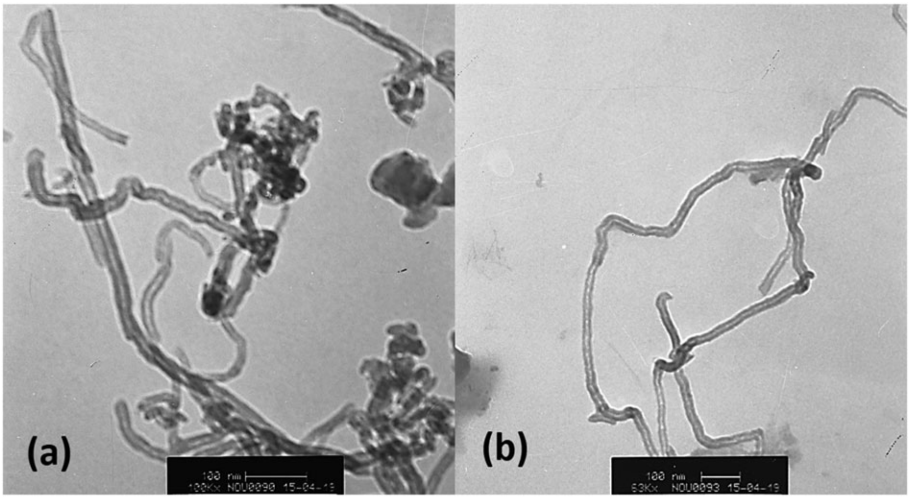


FIGURE 4 Transmission electron microscopy (TEM) images of (a) Fe (TCPP)Cl@MWCNTs and (b) Mn (TCPP)OAc@MWCNTs

3.2 | Catalytic activity of the prepared immobilized metalloporphyrins

In order to appraise the role of the central metal of the porphyrin rings in the catalytic activity of the immobilized metalloporphyrins onto carbon nanotubes, oxidation of olefins with molecular oxygen in the presence of isobutyraldehyde was studied. Styrene was used as a model substrate to identify the optimal reaction conditions. The reaction parameters, such as the nature of the solvent, reaction time, the amount of catalyst, temperature and the amount of isobutyraldehyde, were required

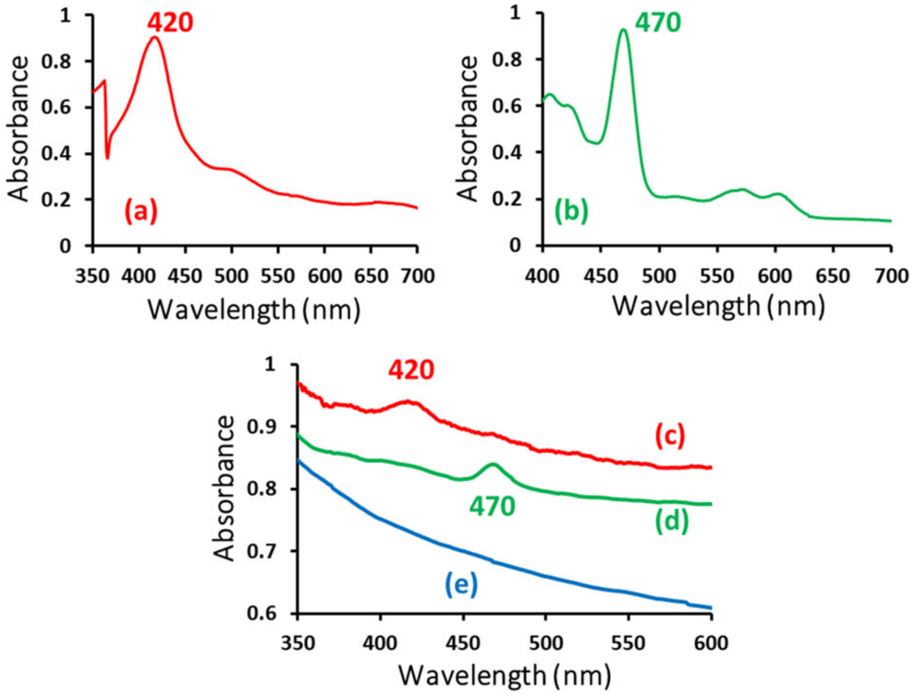


FIGURE 5 Qualitative UV–Vis absorption spectra of: (a) Fe (TCPP)Cl and (b) Mn (TCPP)OAc in DMF, and (c) Fe (TCPP)Cl@MWCNTs, (d) Mn (TCPP)OAc@MWCNTs and (e) MWCNTs in EtOH

to be precisely optimized. Initially, the oxidation reaction gave no significant reaction product in the absence of catalysts after 2 hr under magnetic stirring at 40–45°C (Table 1, entry 1). Therefore, the existing catalyst proved to be necessary in obtaining the considered products. In addition, the unsupported Fe-porphyrin or Mn-porphyrin yielded 100% oxidation products (Table 1, entries 2 and 3), which was obviously predicted as the homogeneous phase allows the styrene to access the completely catalytic sites to do the oxidation process, while heterogenized Fe-catalyst and Mn-catalyst gave 81% and 33% oxidation product, respectively (Table 1, entries 4 and 5). The activity of the heterogenized Fe-catalyst is higher than the Mn-catalyst.

The nature of the solvent usually can have a critical effect on the conversion values of oxidation reactions.[60] The solvent dependence of catalytic oxidation of styrene with O_2/isobutyraldehyde has been studied, and the results are shown in Table 2. Although the highest conversion (100%) was achieved in dichloromethane, acetonitrile was selected as the optimized solvent because of the toxicity of the halogenated solvents.

To obtain the best concentration of catalyst, various amounts of catalyst were used in the aerobic oxidation of styrene in acetonitrile, and the reaction conversions were monitored over different reaction times. As can be seen in Figure 6, the highest conversion was obtained with 0.0084 mmol (3.2 mg) of catalyst in 150 min.

The effect of reaction temperature on the oxidation of styrene with molecular oxygen catalyzed by Fe (TCPP) Cl@MWCNTs has been investigated. The results showed that no oxidation products were detected at 0–5°C. An

TABLE 1 Comparing the catalytic activity of the heterogenized Fe-catalyst with the homogenized one and the solid support

Entry	Catalyst	Conversion (%)[a]
1	none	0
2	Fe (TCPP)Cl	100
3	Mn (TCPP)OAc	100
4	Fe (TCPP)Cl@MWCNTs	81
5	Mn (TCPP)OAc@MWCNTs	33

[a] Reaction conditions: the molar ratio of catalyst:styrene:isobutyraldehyde was 1:45:135 and O_2 (balloon), solvent: 1 mL CH_3CN, temperature: 40–45°C in water bath, under magnetic stirrer, reaction time:120 min.

TABLE 2 The effect of the nature of solvents on the aerobic oxidation of styrene catalyzed by Fe (TCPP)Cl@MWCNTs

Entry	Solvent	Conversion (%)[a]
1	Ethanol	0
2	Acetone	60
3	Chloroform	32
4	Dichloromethane	100
5	Acetonitrile	81

[a] Reaction condition: Fe (TCPP)Cl@MWCNTs:styrene:isobutyraldehyde (1:22.5:112.5) and O_2 (balloon), solvent amount: 1 mL, room temperature, under magnetic stirrer, reaction time:120 min.

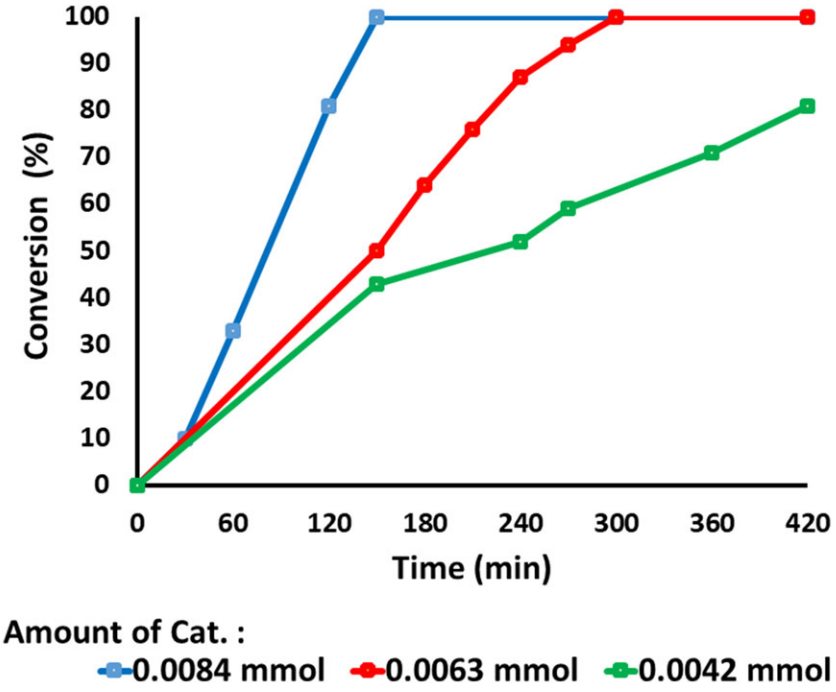


FIGURE 6 Optimization of the amount of catalyst on the catalytic activity of Fe (TCPP)Cl@MWCNTs for the epoxidation of styrene. Reaction conditions: 0.189 mmol styrene, 0.945 mmol isobutyraldehyde and O_2 (balloon), solvent: 1 mL CH_3CN, room temperature, under magnetic stirrer

increase in the reaction temperature up to 25–30°C would lead to high yields of oxidation products (Figure 7). The highest conversion (˃ 99%) was achieved at 40–45°C.

The urgency to use isobutyraldehyde as a reducing agent in these reactions has been checked, and the results can be seen in Table 3. The oxidation did not proceed in

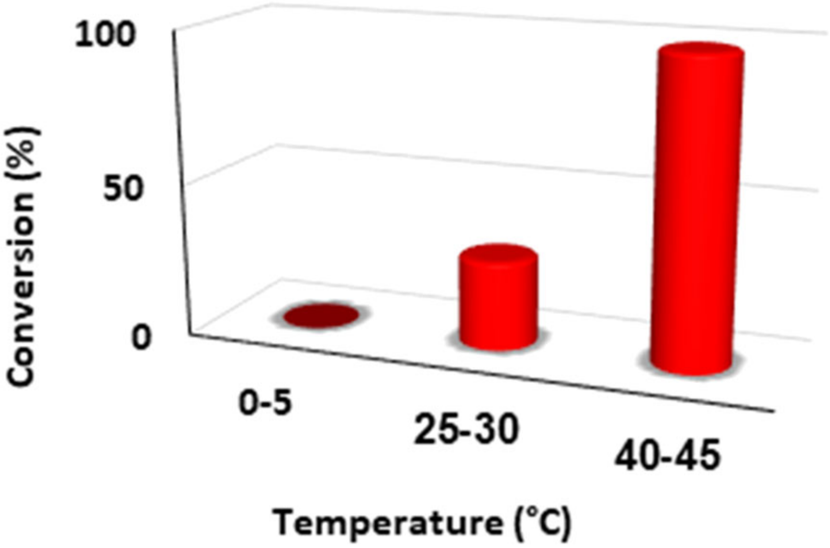


FIGURE 7 The effect of temperature on the aerobic oxidation of styrene catalyzed by Fe (TCPP)Cl@MWCNTs. Reaction conditions: Fe (TCPP)Cl@MWCNTs: styrene:isobutyraldehyde (1:45:225) and O_2 (balloon), solvent: 1 mL CH_3CN, under magnetic stirrer, reaction time: 30 min

TABLE 3 Optimization of the amount of isobutyraldehyde in the catalytic activity of Fe (TCPP)Cl@MWCNTs for the oxidation of styrene

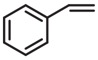
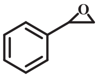
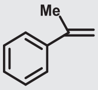
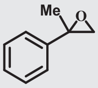
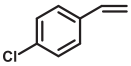
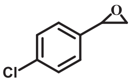
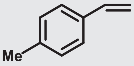
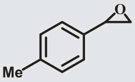
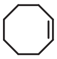
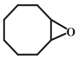
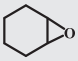
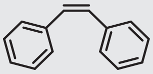
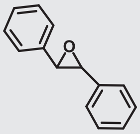
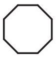
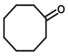
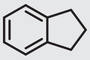
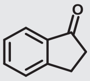
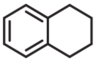
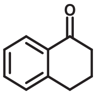
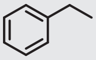
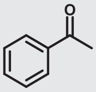
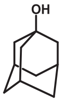
Entry	Amount of isobutyraldehyde (mmol)	Time (hr)	Conversion (%)[a]
1	0	2	0
2	0.567	2	81
3	0.945	0.5	˃ 99

[a] Reaction condition: 0.0042 mmol catalyst, 0.189 mmol styrene and O_2 (balloon), solvent: 1 mL CH_3CN, temperature: 40–45°C in water bath, under magnetic stirrer.

the absence of isobutyraldehyde. Obviously, the use of isobutyraldehyde is necessary for the oxidation of styrene (Table 3, entry 1). Indeed, the aldehyde acted as a sacrificial co-reductant, which could improve the reaction rate by the activation of triplet molecular oxygen under mild conditions. The decision between 0.567 mmol and 0.945 mmol of isobutyraldehyde for the optimum amount is down to the time, because 2 hr is not a long time, the smaller amount of isobutyraldehyde would be preferred.

With the optimal reaction conditions in hand, a collection of alkenes was tested to demonstrate the universal aerobic oxidation applicability using Fe (TCPP) Cl@MWCNTs and Mn (TCPP)OAc@MWCNTs (Table 4, Entries 1–8). A variety of cyclic olefins, such as styrene and its derivatives, cyclooctene and cyclohexene and even a linear alkene like 1-octene, participated well in this epoxidation reaction with the formation of the epoxide as the major product (70–100%). In addition, the existence of electron-withdrawing substituent decreased the catalytic activity of the heterogeneous catalyst in these olefins (Table 4, entry 3). Encouraged by the significant results achieved in the aerobic oxidation of alkenes, the activity

TABLE 4 The oxidation of various alkenes and alkanes catalyzed by Fe (TCPP)Cl@MWCNTs and Mn (TCPP)OAc@MWCNTs[a]

			Fe (TCPP)Cl@MWCNTs		Mn (TCPP)OAc@MWCNTs	
Entry	**Sub.**	**Major product**	**Time (hr)**	**Conversion (selectivity[b]) (%)**	**Time (hr)**	**Conversion (selectivity[b]) (%)**
1			2	81 (67)	4	87 (64)
2			1	100 (100)	2	100 (83)
3			3	70 (50)	4	92 (50)
4			1	98 (75)	3	98 (72)
5			1	98 (100)	2	87 (100)
6			1	98 (90)	2	98 (88)
7			4	70 (100)	4	20 (100)
8			3	81 (90)	3	71 (78)
9			3	16 (50)	3	9 (77)
10			2	21 (86)	2	14 (64)
11			2	50 (100)	4	50 (100)
12			2	13 (100)	4	3 (100)
13			2	50 (87)	4	40 (80)

[a] The molar ratio of catalyst:substrate:isobutyraldehyde was 1:45:135 and O_2 (balloon), solvent: 1 mL CH_3CN, temperature: 40–45°C in water bath, under magnetic stirrer.

[b] Selectivity for the major product.

of this catalytic system towards various organic alkanes was also studied (Table 4, entries 9–13). Substrates like cyclooctane, indane, tetrahydronaphthalene and ethylbenzene were oxidized to the corresponding ketones. Adamantane underwent oxidation to alcohol as the major product. All the organic alkanes have been led to an acceptable conversion, as their oxidation was much harder than alkenes.

Recycling of the catalyst was investigated. For this purpose, cyclohexene as a model compound was oxidized with molecular oxygen in the presence of heterogenized catalysts. After being used in a first cycle in the oxidation

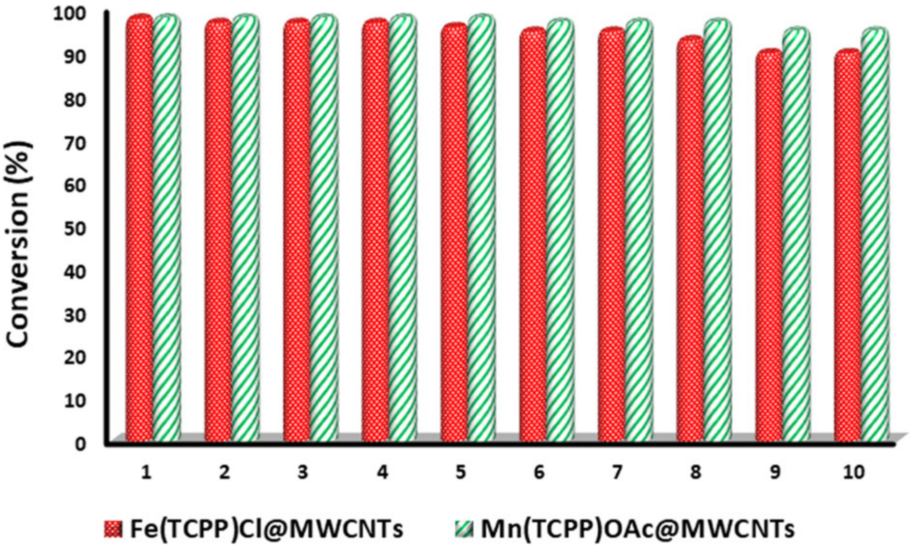
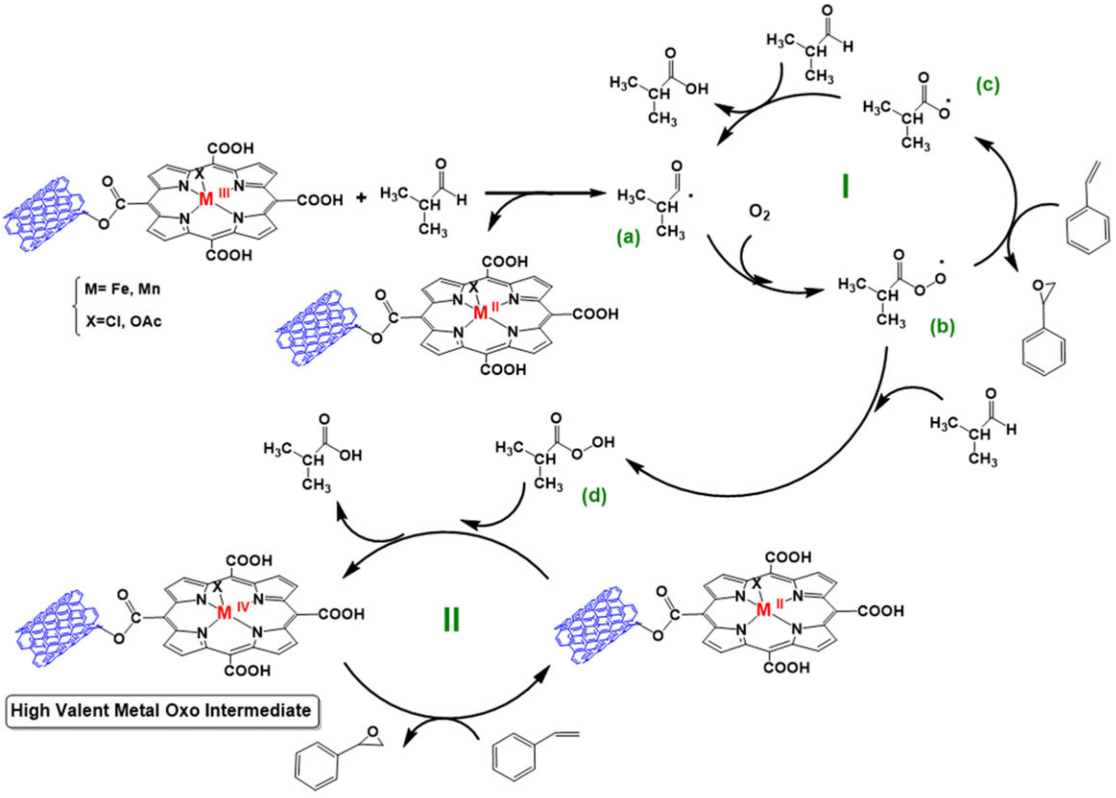


FIGURE 8 The recycling of the catalytic system for the oxidation of cyclohexene catalyzed by Fe (TCPP)Cl@MWCNTs after 1 hr and Mn (TCPP)OAc@MWCNTs after 2 hr. Reaction conditions: the molar ratio of catalyst:cyclohexene:isobutyraldehyde was 1:45:135 and O_2 (balloon), solvent: 1 mL CH_3CN, temperature: 40–45°C in water bath, under magnetic stirrer



SCHEME 2 Plausible mechanism for the oxidation of styrene catalyzed by Fe (TCPP)Cl@MWCNTs and Mn (TCPP)OAc@MWCNTs in the presence of molecular oxygen and isobutyraldehyde

of cyclohexene, the Fe (TCPP)Cl@MWCNTs (after 60 min) and Mn (TCPP)OAc@MWCNTs (after 120 min) were separated, washed with acetonitrile (2 mL) and acetone (1 mL), dried and used in similar catalytic reactions. Both catalysts still displayed considerable catalytic activity after 10 recycles, as can be observed in Figure 8.

3.3 | The proposed mechanism

A mechanism for the epoxidation of styrene by dioxygen in the presence of Fe (TCPP)Cl@MWCNTs or Mn (TCPP)OAc@MWCNTs and isobutyraldehyde has been proposed (Scheme 2). It can be assumed that the M^{III} (TCPP)X@MWCNTs (M = Fe, Mn, X = Cl, OAc) reacts with the isobutyraldehyde to make an acyl radical (Scheme 2a), and the acyl radical then reacts with molecular oxygen to give an acylperoxy radical (Scheme 2b). The acylperoxy radical could continue the mechanism in two pathways. Firstly, it can generate carboxylic acid (pathway I). Secondly, the acylperoxy radical reacts with another isobutyraldehyde molecule as a carrier to give peroxyacid (Scheme 2d), then generating another acyl radical (pathway II). Formation of epoxide is granted by active high valent metal oxo intermediates, which are formed by the reaction of the peroxyacid with the metalloporphyrin.[61]

4 | CONCLUSIONS

In conclusion, reusable solid biomimetic catalysts were prepared through covalently immobilizing of Fe (TCPP) Cl and Mn (TCPP)OAc to the modified MWCNTs within the ester bond. The catalytic activities of these catalysts were compared in the aerobic oxidation of various alkanes and alkenes. The use of molecular oxygen as a source of oxygen atom clearly made aerobic epoxidation a highly desirable, economically viable and environmentally acceptable reaction, although it has to activated by a sacrificial material, such as isobutyraldehyde. After optimization of different reaction parameters, it was discovered that Fe (TCPP)Cl@MWCNTs has a higher reaction rate than Mn (TCPP)OAc@MWCNTs for all the substrates. Both catalysts are efficient and highly reusable after 10 times of use.

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