Catalytic activity of multi-wall carbon nanotube supported manganese (III) porphyrin: an efficient, selective and reusable catalyst for oxidation of alkenes and alkanes with urea—hydrogen peroxide

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ABSTRACT
Manganese complex of meso-tetrakis(4-hydroxyphenyl)porphyrin immobilised onto functionalised multi-wall carbon nanotubes (MWCNT) has been synthesised and characterised by elemental analysis, Fourier transform infrared (FT-IR), ultraviolet-visible (UV-Vis) spectroscopy, powder X-ray diffraction and scanning electron microscopy. This catalyst, [Mn(THPP)OAc@MWCNT], was successfully applied for efficient epoxidation of alkenes and alkanes with urea—hydrogen peroxide. The role of the stoichiometric amounts of the acetic anhydride as an oxidant activator which introduce in situ peracetic acid has been discussed. This heterogeneous catalyst was highly reusable in the oxidation reactions and reused several times without significant loss of its catalytic activity.

1. Introduction
Catalytic olefin epoxidation in the liquid phase is an important topic for the synthesis of fine chemicals,[1] because epoxides are highly useful intermediates to manufacture a wide range of important commercial products such as glue, resin, polyethers, diols and amino alcohols.[2] A well-known type of monooxygenation enzyme is cytochrome P-450(CP-450), which features an iron porphyrin core, and can catalyse a variety of oxidation reactions including epoxidation, hydroxylation and dealkylation. [3] Metalloporphyrins, with a core structure similar to that of the iron porphyrin core of cytochrome P-450, have been extensively studied as catalysts to oxidise a series kind of reactions mimic the natural style.[4—7] Despite the high catalytic activity of homogeneous metalloporphyrins, these expensive catalysts are deactivated or degraded in the reaction media. One way to overcome these problems is to immobilise them on solid supports. Heterogeneous metalloporphyrins present many advantages such as higher stability of the catalyst and recovery of the catalyst from the reaction media, easy separation and protection of the catalyst against destruction.[8,9] Many oxidants have been used to
synthesise epoxides. However, there is a current intense interest in using urea—hydrogen peroxide (UHP) as eco-friendly oxidant that produces urea and water as by-product. In the absence of an activator, the lower oxidation power of UHP seems to be due to the poor leaving tendency of the hydroxide ions, though the need for an activation method capable to modify the orbital energy, so as to tune the electrophilic/nucleophilic behaviour of the oxidant itself may be a possible cause for the observed low oxidising ability of UHP. In the present research, we report highly efficient epoxidation of alkenes with UHP catalysed by meso-tetrais(4-hydroxyphenyl)porphyrinomanganese(III) acetate, Mn (THPP)OAc, supported on functionalised multi-wall carbon nanotubes.

2. Experimental

Chemicals were purchased from Merck or Fluka chemical companies. Meso-tetakis(4-hydroxyphenyl)porphyrin (H₂THPP) was prepared according to the literature.[10] The [Mn(THPP)OAc] and [Mn(THPP)OAc@MWCNT] were prepared and characterised according to the reported procedure.[11,12] Infrared spectra were recorded as KBr pellets using Unicam Matson 1000 Fourier transform infrared (FT-IR) in the range of 400–4000 cm⁻¹. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-1460 field emission scanning electron microscope using Acc voltage of 15 kV. Transmission electron microscopy (TEM) image was obtained on Philips EM 208. Gas chromatography (GC) analyses were conducted on a Shimadzu chromatograph (model GC-14B) equipped with flame ionisation detector and capillary column SAB-5 (phenyl methyl siloxane 30 m × 320 mm × 0.25 mm). Thermogravimetry analysis (TGA) of the samples was carried out on a STA 409 PC/PG instrument from NETZSCH. All samples (typically 4–5 mg) were heated under nitrogen flow (200 cm³ min⁻¹) to 900 °C at a rate 10 °C min⁻¹.

2.1. General heterogeneous oxidation procedure

Catalytic performance of [Mn(THPP)OAc@MWCNT] was carried out in a 5 mL test tube that consists of 1 mL solvent, 0.3 mmol substrate, 0.003 mmol of catalyst, 0.15 mmol of imidazole, 0.75 mmol UHP and 1.8 mmol of acetic anhydride as a specific reaction. The reaction mixture was stirred for 4 h at room temperature. Finally, the reaction products were monitored by means of GC. The sulphide oxidation products were measured by comparison with valid samples (retention times in GC).

2.2. Catalyst reuse and stability

Reusability of the heterogeneous catalyst was investigated in the numerous consecutive oxidation reactions. At the end of each reaction, the catalyst was detached from the catalytic solution by simple filtration. After isolation, the solid catalyst was washed with reaction solvent, separated from the solvent and dried in the air before using in the next run.
3. Results and discussions

3.1. Catalyst characterisation

The specification of multi-wall carbon nanotubes containing carboxylic acid groups, MWCNT-COOH, which was used as the support, is listed in Table 1. Figure 1 shows the preparation route for the [Mn(THPP)OAc@MWCNT]. The covalent bonding between the metalloporphyrin and MWCNT-COOH was carried out by acid–base reaction between the porphyrin hydroxyl groups and carboxylic acid of MWCNT-COOH using 2-(1H-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium tetrafluoroborate as a highly effective uronium salt in the presence of N,N'-diisopropylamine.[13]

The prepared catalyst was characterised by FT-IR spectroscopy, SEM and TEM. The nitrogen content of the catalyst was determined by elemental analysis, which showed a value of 0.8% for the Mn-catalyst. Based on this value, the manganese–porphyrin content of the catalyst obtained was about 357 μmol/g of the catalyst. The Mn content of the catalyst was also measured by atomic absorption spectroscopy, and this was comparable to data obtained by CHN analysis.

In the FT-IR spectra (Figure 2), a sharp band observed at 1709 cm⁻¹ is related to the esteric bond formed between carboxylic acid groups of the carbon nanotubes and OH groups of the Mn–porphyrin. The band at 3430 cm⁻¹ is attributed to O–H stretching.

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

| Outside diameter | Inside diameter | Length | COOH content | Specific surface area |
|------------------|----------------|--------|--------------|-----------------------|
| 10–20 nm         | 5–10 nm        | ~30 μm | 2%           | >200 m²/g             |

![Figure 1. Preparation path of [Mn(THPP)OAc@MWCNT].](image)
vibrations due to the presence of carboxyl groups and eventually from residual adsorbed water.

Also, SEM image of the catalyst shows the morphology and shape of the supported nanotubes (Figure 3). Comparison of SEM images of [Mn(THPP)OAc@MWCNT] (Figure 3(b)) and of the carbon nanotube (Figure 3(a)) clearly indicates that the manganese–porphyrin has been supported on multi-wall carbon nanotubes (MWCNT).

TEM images of MWCNT and [Mn(THPP)OAc@MWCNT] are shown in Figure 4. TEM of MWCNT coated with Mn(THPP)OAc (Figure 4(b)) showed Mn(THPP)OAc nanoparticles on MWCNT without any detectable large-scale aggregation of the porphyrin molecules indicating a good dispersion onto the surface.

Figure 2. (Colour online). FT-IR spectra of the Mn(THPP)OAc (down) and [Mn(THPP)OAc@MWCNT] (top).

Figure 3. SEM image of the MWCNT (a) and [Mn(THPP)OAc@MWCNT] (b).
X-ray diffraction (XRD) patterns of MWCNT and \([\text{Mn(THPP)OAc@MWCNT}]\) in the 2\(\theta\) range between 10° and 90° are shown in Figure 5. The XRD pattern of original MWCNT shows two main peaks at 2\(\theta\), 25.6° and 43.0°, corresponding to the lattice parameters (002) and [(100), (101)] planes, respectively. These are characteristic diffraction peaks of carbon nanotubes.[14] After the metalloporphyrin immobilisation (Figure 4 (b)), the peaks around 43° are due to the (100) and (101) graphitic planes plus a small amount of the catalyst particle encapsulated inside the walls of the MWCNTs.[15,16] The characteristic peaks of the attached catalyst were not observed clearly, which indicates that the Mn–porphyrin complex well dispersed on the MWCNTs.

The ultraviolet-visible (UV-Vis) spectrum of the \([\text{Mn(THPP)OAc@MWCNT}]\) in ethanol suspension shows the Q bands centered at 568 nm, 606 nm and also the Soret band centered at 471 nm, similar to the spectrum of Mn(THPP)OAc in solution (Figure 6). This demonstrated that the structure of metalloporphyrin ring remains the same after being absorbed by the MWCNT.
TGA have been used to characterise metal complexes linked to the MWCNTs surface. The thermal behaviour of [Mn(THPP)OAc@MWCNT] is illustrated in Figure 7(b) in comparison with the Mn(THPP)OAc complex (a). The neat complex of Mn showed weight loss at 300 °C. However, for the corresponding encapsulated complex [Mn(THPP)OAc@MWCNT], the first step occurs at temperature 200 °C with 9 wt% loss due to the presence of adsorbed water. The second decomposition step at 200–300 °C is mainly attributed to the deprotonation of COOH.[17] The rest of the porphyrin ligand decomposes in the next step from 300 to 700 °C.[18]

### 3.2. Catalytic oxidation

The catalytic activity of the heterogeneous catalyst was investigated on the oxidation of cyclooctene with UHP and acetic anhydride as an activator. A series of blank experiments revealed that the presence of catalyst, oxidant and activator is essential for an effective catalytic reaction (Table 2). Also, heterogeneous catalyst shows higher catalytic activity.

Figure 6. UV-Vis spectra of (a) Mn(THPP)OAc in ethanol; (b) [Mn(THPP)OAc@MWCNT] was obtained as a suspension in ethanol.

Figure 7. TGA curves of (a) Mn(THPP)OAc and (b) [Mn(THPP)OAc@MWCNT].
relative to the bare MnTHPPOAc (Table 2, entry 5). In order to increase the conversion, the effect of different parameters was studied.

In order to find an appropriate solvent for the oxidation of cyclooctene with UHP, different solvents such as methanol, ethanol, dichloromethane, chloroform, acetonitrile and the mixture of MeOH:CH$_2$Cl$_2$ were applied (Table 3) and the highest conversion was obtained in the mixture of chloroform/methanol (9/1).

In the absence of an oxidant activator, the reaction does not proceed, while in the presence of acetic anhydride 11% cyclooctene was obtained. In order to find the optimum amount of acetic anhydride on the oxidation of cyclooctene, different amounts of acetic anhydride were used and 1:2.4 molar ratio was chosen to be used (Table 4).

The catalytic activity of metalloporphyrins increases in the presence of imidazoles co-catalyst,[19–22] and imidazole as a strong π-donor has been found to show the highest co-catalyst activity.[23] Therefore, the effect of different molar ratios of imidazole/catalyst on the oxidation of cyclooctene has been investigated (Table 5). The highest conversion was achieved in the 1:50 molar ratio of the catalyst to imidazole. In the absence of imidazole, no oxidation product was obtained. Surplus of imidazole led to a decrease in the conversion that might be due to the formation of the inactive six coordinated species.

The [Mn(THPP)OAc@MWCNT] catalyst was used for oxidation of various olefins with UHP under optimised conditions (Table 6). Cyclohexene was oxidised in 100% yield and cyclohexene oxide was the sole product.

Table 2. Blank experiments on catalytic activity of cyclooctene at room temperature$^a$.

| No. | Catalyst | Oxidant | Activator | Conversion% |
|-----|----------|---------|-----------|-------------|
| 1   | None     | UHP     | None      | 0           |
| 2   | [Mn(THPP)OAc@MWCNT] | None | None | 0 |
| 3   | None     | UHP     | Acetic anhydride | 11 |
| 4   | [Mn(THPP)OAc@MWCNT] | UHP | Acetic anhydride | 82 |
| 5   | MnTHPPOAc | UHP | Acetic anhydride | 35 |

Note: Reaction time: 4 h.
$^a$The molar ratio for catalyst:Imidazole:cyclooctene:UHP:acetic anhydride is 1:50:100:250:600.

Table 3. Solvent effect on the oxidation of cyclooctene catalysed by [Mn(THPP)OAc@MWCNT] with UHP at room temperature$^{a,b}$.

| Entry | Solvent         | Epoxide yield% |
|-------|-----------------|----------------|
| 1     | MeOH            | 18             |
| 2     | CHCl$_3$       | 54             |
| 3     | CH$_3$CN       | 0              |
| 4     | CH$_2$Cl$_2$   | 15             |
| 5     | EtOH           | 0              |
| 6     | CHCl$_3$:MeOH(9:1) | 82 |

$^a$The molar ratio for catalyst:ImH:cyclooctene:UHP:acetic anhydride is 1:50:100:250:600.
$^b$Reaction time: 4 h.

Table 4. The effect of acetic anhydride amounts on the epoxidation of cyclooctene catalysed by [Mn(THPP)OAc@MWCNT] with UHP$^{a,b}$.

| Entry | Anhydride/UHP | Conversion% |
|-------|---------------|-------------|
| 1     | 0             | 0           |
| 2     | 1.2           | 57          |
| 3     | 2.4           | 82          |
| 4     | 4.8           | 65          |

$^a$The molar ratio for catalyst:ImH:cyclooctene:UHP:acetic anhydride are 1:50:100:240:X.
$^b$Reaction time: 4 h. Solvent:MeOH:CHCl$_3$ (1:9).
The [Mn(THPP)OAc@MWCNT] catalyst was used for oxidation of several alkanes with UHP under optimised conditions (Table 7).

In the absence of the catalyst, 11% cyclooctene oxide will be achieved. It may be due to the *in situ* formation of the peracetic acid that is able to convert cyclooctene to epoxide.

| Table 5. Effect of the molar ratio of the catalyst/ImH on oxidation of cyclooctene with UHP at room temperature. |
|---------------------------------------------------------------|
| **ImH/MnTHPP-MWCNT** | **Epoxide yield%** |
| 0 | 0 |
| 37 | 63 |
| 50 | 82 |
| 100 | 61 |

Note: Reaction time: 4 h.

The catalyst:ImH:cyclooctene:UHP:acetic anhydride is 1:50:100:250:600.

Table 6. Epoxidation of various olefins using UHP and HOAc, catalysed by [Mn(THPP)OAc]@MWCNT under optimised conditions.

| Entry | Alkene Conversion% | Selectivity to epoxide% | TON |
|-------|--------------------|-------------------------|-----|
| 1     | 82(100)c           | 100                     | 82f |
| 2     | 69(78)c            | 100                     | 69f |
| 3     | 28(63)c            | 100                     | 28f |
| 4     | 24(43)c            | 100                     | 24f |
| 5     | 81(93)c            | 100                     | 81f |
| 6     | 56(74)c            | 100                     | 56f |
| 7     | 18(25)c            | 100                     | 18f |
| 8     | 11(22)c            | 100                     | 11f |

Note: Reaction time: 4 h.

*Reaction conditions: the molar ratio for catalyst:ImH:cyclooctene:UHP:acetic anhydride is 1:50:100:250:600.
*GC yield based on the starting alkene.
*The values in the parentheses are due to a 2 h reflux.
*The conversion and selectivity has been double checked by 1H NMR spectroscopy.
*TON: (total turnover number) the ratio of the number of moles of product to the number of moles of catalyst.
*TOF (Turnover frequency) (h⁻¹) for oxidation of cyclooctene is 42.
Addition of catalyst into the reaction mixture resulted in an increase in catalytic activity. This observation proposed that peracetic acid will be activated by coordination to the Mn-centre [24–28] and then oxygen transfer will be occurred to the olefin (Scheme 1, II).

**Table 7. Oxidation of alkanes with UHP by [Mn(THPP)OAc]@MWCNT under optimised conditions**

| No. | Alkane           | Conversion(%) | TON |
|-----|------------------|---------------|-----|
| 1   | Indane<sup>b</sup> | 8(12)<sup>c</sup> | 8   |
| 2   | Adamantane<sup>b</sup> | 0(5)   | 0   |
| 3   | Tetra-hydronaftalen<sup>b</sup> | 4(18) | 4   |
| 4   | Ethylbenzol<sup>e</sup> | 9(15) | 9   |
| 5   | Cyclooctane<sup>d</sup> | 5(17) | 5   |

Note: Reaction time: 4 h.

<sup>a</sup>Reaction conditions: the molar ratio for catalyst:ImH:cyclooctene:UHP:acetic anhydride is 1:50:100:250:600.

<sup>b</sup>Mixture of alcohol and ketone was obtained.

<sup>c</sup>The values in the parentheses are due to a 2 h reflux.

<sup>d</sup>Cyclooctanone is the sole product.

<sup>e</sup>1-phenylethanol is the sole product.

(Scheme 1, I). Addition of catalyst into the reaction mixture resulted in an increase in catalytic activity. This observation proposed that peracetic acid will be activated by coordination to the Mn-centre [24–28] and then oxygen transfer will be occurred to the olefin (Scheme 1, II).
The reusability of supported catalysts is one of the most important benefits which make them useful for commercial applications. The homogeneous [Mn(THPP)OAc] is readily degraded and cannot be recovered even once, in contrast, the nanotube supported manganese–porphyrin catalyst can be filtered and reused several times without significant loss of its activity. The reusability of the catalyst was investigated in the multiple sequential epoxidation of cyclohexene with UHP. The catalyst was separated by simple filtration, washed with MeOH:CHCl₃ (1:9) and completely dried before using in the subsequent run. After using of each catalyst for three consecutive times, the epoxide yields were 100% (Figure 8). The filtrates were used for determining the catalyst leaching and the results showed that after first three runs, no manganese was detected in the filtrates by atomic absorption spectrometry. Furthermore, The IR spectrum of the recovered catalyst indicated that the catalyst, after reusing it several times, showed no change in its IR spectra.

4. Conclusions

In conclusion, this catalytic system is highly efficient for biomimetic epoxidation of alkenes and alkanes with UHP. Addition of acetic anhydride to the manganese–porphyrin/UHP system led to a remarkable increase in the conversions. Finally, this catalyst is a robust and recoverable catalyst toward hydrocarbon oxidation with UHP.

Disclosure statement

No potential conflict of interest was reported by the authors.

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