Manganese(III) porphyrin anchored onto multiwall carbon nanotubes: An efficient and reusable catalyst for the heterogeneous reduction of aldehydes and ketones

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\textbf{ABSTRACT}

Reduction of a variety of carbonyl compounds with NaBH\textsubscript{4} using Mn-porphyrin, \textit{meso}-tetrakis(4-hydroxyphenyl)porphyrinatomanganese(III), supported onto functionalized multiwall carbon nanotubes has been investigated. The heterogeneous catalyst was characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and UV–vis spectroscopy. The amount of catalyst loading on the nanotubes was determined by atomic absorption spectroscopy. Thermogravimetric analysis (TGA) demonstrated that the nanocatalyst was thermally stable to almost 300 °C, exhibiting high thermostability of the catalyst over a broad range of temperatures. This heterogeneous catalyst proved to be an efficient catalyst in the aerobic reduction of various aldehydes and ketones with NaBH\textsubscript{4}. In the presence of the nanocatalyst, NaBH\textsubscript{4} can readily reduce a variety of aldehydes in good to excellent yields (50–100%) and ketones in excellent yields (100%) to their corresponding alcohols. The separation of the catalyst is very simple and economic. Also, FTIR spectra after four successive cycles showed that the catalyst was strongly anchored to the nanotubes.

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1. Introduction

Chemoselective reduction of aldehydes and ketones is an efficient method to obtain the corresponding alcohols. The latter are found in various natural or medicinal compounds and are readily converted to other useful functionalized compounds [1, 2]. Various methods involving chemical and biological procedures have been developed for reduction of aldehydes and ketones. Sodium borohydride is one of the most conventional reducing agents in organic synthesis due to its stability, high selectivity, and ease of handling. Therefore, the reductions of aldehydes and ketones were performed with sodium borohydride [3]. However, its reactivity can be increased by adding transition-metal catalysts for the reduction of various functional groups [4].

We have developed many catalytic systems using metalloporphyrins for various oxidative chemical transformations [5]. In comparison to the application of metalloporphyrins as oxidative catalysts, their ability to reduce has received less attention [6]. As an ongoing effort to emphasize the role of metalloporphyrins as reduction-promoting catalysts, herein, we report an efficient method for the reduction of aldehydes and ketones with NaBH₄ in the presence of a manganese complex of meso-tetrakis(4-hydroxyphenyl)porphyrin immobilized onto functionalized multi-wall carbon nanotubes [Mn(THPP)OAc@MWCNT].

2. Experimental

2.1. Materials

All materials were of commercial reagent grade and purchased from Merck or Fluka and treated when necessary. MWCNTs (multiwall carbon nanotubes containing −COOH groups, purity 96%) were purchased from Shenzen NTP Factory (China). Specifications of MWCNT–COOH used in this study were as follows: outside diameter (10–20 nm), inside diameter (5–10 nm), length (30 μm), −COOH content (2%) and specific surface area (200 m² g⁻¹). The free base porphyrin, H₂THPP and its manganese complex were synthesized as reported in the literature [7, 8].

5,10,15,20-Tetrakis(4-hydroxyphenyl)porphyrin: Dark violet solid; m.p. >320 °C; '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); FT-IR (KBr), cm⁻¹: 1271 (ν C–O–H), 1349 (ν C–N), 1445 (ν C=N), 1484 (ν C=C_Pyrrol), 1591 (ν C=C_Pyrrol), 3425 (ν N–H); UV–vis, DMF (∆λ max): 422, 517, 555, 594, 647; Anal. Calcd for C₄₄H₃₀N₄O₄: C, 77.85; H, 4.46; N, 8.25. Found: C, 77.93; H, 4.51; N, 8.32%.

5,10,15,20-Tetrakis(4-hydroxyphenyl)porphinatomanganese(III) acetate: dark green solid, m.p. >300 °C; FT-IR (KBr, cm⁻¹): 1005 (ν C–N_Pyrrol), 1078 and 1167 (δ C–H Ph), 1340 (ν C=N), 1439 (ν C=N), 1587 (ν C=C_Pyrrol), 3061 (ν C–H_Ph). UV–vis, MeOH (∆λ max): 474 (Soret), 537, 585, 628; Anal. Calcd for C₄₆O₆MnH₃₁N₄: C, 69.87; H, 3.95; N, 7.08. Found: C, 69.81; H, 3.91; N, 7.19%.

Also, the manganese porphyrin, Mn(THPP)OAc, was supported onto MWCNT according to our reported procedure [9].

2.2. Physicochemical characterization techniques

Transmission electron microscopy (TEM) image was obtained on Philips EM 208. For powder X-ray diffraction (XRD) analysis, self-oriented films were placed on neutral glass sample holders. The patterns were obtained in the reflection mode on a Bruker AXS D8 Avance diffractometer using monochromated Cu Kα radiation as the incident beam.

Thermogravimetric analysis (TGA) 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 10 °C min⁻¹.

Ultraviolet-visible (UV–vis) spectra were recorded from 400–700 nm with a Lambda 25 Perkin Elmer spectrophotometer. Analyses for liquid samples were accomplished using a quartz cell with 1 cm path length. Spectra for solid samples were recorded with thin solid films produced by drying a drop of the solid suspension on a glass substrate.
Conversions and yields of the products were measured by GC-FID on a Shimadzu GC-14B instrument equipped with a flame ionization detector and a SAB-5 capillary column (phenyl methyl siloxane 30 m × 320 μm × 0.25 μm). In the GC experiments, n-octane was used as an internal standard. The manganese content of the catalyst was determined by atomic absorption spectrophotometry (AAS) with flame atomization (Varian AA240). Quantification was made by the standard addition method.

### 2.3. General procedure for catalytic reduction of aldehydes with NaBH₄

To a mixture of aldehyde (0.1 mmol), [Mn(THPP)OAc@MWCNT] (0.002 mmol) and imidazole (0.07 mmol) in methanol (1 mL), 1.8 mg NaBH₄ (0.05 mmol) was added. The reaction mixture was stirred magnetically at room temperature for 2 min and progress of the reaction was monitored by GC.

### 2.4. General procedure for reduction of ketones using pre-modified borohydride

Exclusive formation of premodified [10] sodium borohydride: in a precooled vessel at 0 °C, fine grained NaBH₄ (10.8 mg, 0.3 mmol) was placed in a mixture of solvents CHCl₃ (0.5 mL) and EtOH (0.5 mL) for 30 min.

Catalytic borohydride reduction: The initially employed catalyst/imidazole/substrate/reductant molar ratio was of 1 : 35 : 50 : 150, achieved through addition of 0.10 mmol substrate, 2 μmol catalyst, and 0.07 mmol imidazole. They were added to the solution of premodified sodium borohydride and the mixture was stirred for 5 min at 0 °C. The progress of the reaction was monitored by GC.

### 2.5. Recycling procedure of [Mn(THPP)OAc@MWCNT]

The reusability of [Mn(THPP)OAc@MWCNT] was investigated in multiple sequential reductions of acetophenone. At the end of each reaction, the catalyst was separated from the reaction mixture by simple filtration. After isolation, the solid catalyst was washed with methanol (2 mL) and dried in an oven overnight before using it in the next run.

### 3. Results and discussion

#### 3.1. The characterization of [Mn(THPP)OAc@MWCNT]

Mn(THPP)OAc is anchored onto MWCNT through covalent bonding between the hydroxyl group of the Mn–porphyrin and carboxylic acid group of MWCNT using 2-(1H-benzotriazole-1-yl)-1,1,3,3-tetramethyuronium tetrafluoroborate (TBTU) and N,N'-diisopropylamine (DIPEA) in DMF at room temperature (Scheme 1) [11].

![Scheme 1. Synthesis of Mn–porphyrin immobilized onto functionalized multiwall carbon nanotubes [Mn(THPP)OAc@MWCNT].](image-url)
TEM images of MWCNT and [Mn(THPP)OAc@MWCNT] are shown in Figure 1. TEM of MWCNT coated with Mn(THPP)OAc (Figure 1(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. X-ray diffraction patterns of MWCNT and [Mn(THPP)OAc@MWCNT] in the $2\theta$ range between 10° and 90° are shown in Figure 2. The XRD pattern of original MWCNT shows two main peaks at 20°, 25.6°, and 43.0°, corresponding to the lattice parameters (002) and [(100), (101)] planes, respectively. These are characteristic diffraction peaks of carbon nanotubes [12]. After the metalloporphyrin immobilization (Figure 2(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 MWCNTs [13]. The characteristic peaks of the attached catalyst were not observed clearly, which indicates that the Mn–porphyrin complex is well dispersed on MWCNTs.

FTIR spectroscopy was used to ensure the esterification step, with disappearance of the C=O stretch of the carboxylic acid group of MWCNT–COOH (1650 cm$^{-1}$) and the appearance of a peak at 1709 cm$^{-1}$ associated with C=O stretch of the ester group. The signal at 1647 cm$^{-1}$ was related to the stretch of the phenyl rings at the meso positions [9, 14].

The thermal behavior of [Mn(THPP)OAc@MWCNT] is illustrated in Figure 3(c) in comparison with that of MWCNT (a) and Mn(THPP)OAc (b), which shows the thermal stability of the nanohybrid material. For both Mn(THPP)OAc and [Mn(THPP)OAc@MWCNT], the weight loss below 300 °C is mainly attributed to deprotonation of COOH groups and loss of adsorbed water [15]. The subsequent weight loss from 300–700 °C is due to decomposition of Mn(THPP)OAc [16].

Figure 1. The TEM image of (a) MWCNT and (b) [Mn(THPP)OAc@MWCNT].

Figure 2. XRD pattern of (a) MWCNT and (b) nanocatalyst.
The UV–vis spectrum of [Mn(THPP)OAc@MWCNT] in the solid (Figure 5(b)) resembles its solution counterpart (Figure 4), but with a slight red shift. The appearance of the Soret and Q bands of Mn-porphyrin in the supported catalyst clearly indicates the presence of metalloporphyrin on the surface of MWCNTs. This demonstrates that the structure of metalloporphyrin ring remains the same after being absorbed by MWCNTs.

The Mn content of the supported catalyst determined by atomic absorption spectroscopy revealed that the Mn–porphyrin content of the catalyst is 470 μmol per gram of the catalyst.

### 3.2. Catalytic experiments in the reduction of aldehyde

The high catalytic activity of [Mn(THPP)OAc@MWCNT] in the oxidation of alkenes [5] prompted us to explore its catalytic activity in the reduction of aldehydes and ketones with sodium borohydride at
room temperature. The prepared catalyst was used for the reduction of 4-methylbenzaldehyde with sodium borohydride at room temperature. To find suitable reaction conditions, the effect of various reaction parameters was studied. Catalyst concentration and catalyst/imidazole (ImH) molar ratio have been evaluated.

Different catalyst concentrations have been used in reduction of 4-methylbenzaldehyde (Figure 6). Reduction of 4-methylbenzaldehyde required 4 mg of catalyst for completion.

Reactivity of metalloporphyrin catalysts in the oxidation reactions can be improved by addition of different nitrogenous bases as cocatalyst [17–19]. For a better understanding of the role of the imidazole in this catalytic system, the effect of different molar ratios of the ImH/catalyst on the reduction of 4-methylbenzaldehyde was investigated. In the absence of imidazole, the reaction proceeds only in 21% yield, whereas the addition of imidazole increased the reaction conversion (Figure 7). An increase in the ImH/catalyst molar ratio up to 35 remarkably improved the reaction rate. Beyond this ratio, a significant decrease in catalytic efficiency is observed, which may be attributed to the formation of a six-coordinate (MnTHPP(ImH)$_2$) inactive species [20].

To establish the general applicability of this catalytic system, under optimized conditions, the reduction of different aldehydes was performed in the presence of a catalytic amount of [Mn(THPP)OAc@MWCNT] (Table 1).

Aldehydes were reduced rapidly with 0.5 M equivalents of NaBH$_4$ by using catalytic amounts of [Mn(THPP)OAc@MWCNT] in MeOH at room temperature. The yields were high to excellent (50–100%). Running the reaction in the absence of [Mn(THPP)OAc@MWCNT] gave the products with yields of ca. 50% for the aldehydes. In the presence of the catalyst, conversions of ca. 100% were obtained for most...
Figure 7. The screening of the different ImH/catalyst molar ratios on the reduction of 4-methylbenzaldehyde. See the caption of Figure 6.

Table 1. Reduction of aldehydes with NaBH₄ in the presence of [Mn(THPP)OAc@MWCNT] in methanol at room temperature.ₐ,ᵇ

| Entry | Substrate | Productᵇ | Time (min) | Conversion% |
|-------|-----------|----------|------------|-------------|
| 1     | [Image]   | [Image]  | 2          | 74          |
| 2     | [Image]   | [Image]  | 2          | 77          |
| 3     | [Image]   | [Image]  | 2          | 85          |
| 4     | [Image]   | [Image]  | 2          | 100         |
| 5     | [Image]   | [Image]  | 2          | 70          |
| 6     | [Image]   | [Image]  | 5          | 100ᵇ        |
| 7     | [Image]   | [Image]  | 5          | 100ᵇ        |
| 8     | [Image]   | [Image]  | 2          | 100ᵇ        |
| 9     | [Image]   | [Image]  | 2          | 50          |
| 10    | [Image]   | [Image]  | 2          | 100ᵇ        |

ₐReaction conditions: the molar ratios for catalyst/ImH/substrate/NaBH₄ are 1:35:50:25, in 1 mL methanol.

ᵇThe formation of alcohol as the product was also confirmed with GC-Mass analysis (for a typical spectrum, see Supporting Information).

ᶜThe reactions were carried out in 2 mL methanol.
of the aldehydes. According to Table 1, the introduction of different substituents on the phenyl ring of the aromatic aldehydes had little effect on the reactivity of the aldehydes.

The regioselective reduction of \(\alpha,\beta\)-unsaturated aldehydes is an appropriate way to prepare allylic alcohols which are important in organic synthesis. \(\text{NaBH}_4\) in combination with catalytic amount of [\(\text{Mn(THPP)OAc@MWCNT}\)] is efficient for the preparation of the corresponding allylic alcohols at room temperature in high to excellent yields (50–100%) (Table 1, entries 9 and 10).

### 3.3. Catalytic experiments in the reduction of ketone

The catalytic performance of [\(\text{Mn(THPP)OAc@MWCNT}\)] in the reduction of acetophenone, as a model substrate, and sodium borohydride as the source of hydrogen was investigated. In order to find the optimum reaction conditions, the effect of various reaction parameters that may affect the conversion of the reaction was investigated. Solvent, catalyst concentration and the concentration of \(\text{NaBH}_4\) have been evaluated. Various methods have been developed for the reduction of ketones. Nagata et al. reported the modification of \(\text{NaBH}_4\) with tetrahydrofurfuryl alcohol (THFA)–ethanol or THFA–methanol for the reduction of ketones [21]. The influence of ethanol on the efficiency of the reduction reaction was investigated (Figure 8). Without ethanol, the phenylethanol was obtained in a yield of less than 10% but in the presence of ethanol, the yield improved to 57%. Further improvement in the conversion may be obtained by using ethanol–chloroform mixed solvent in 1 : 1 ratio. It should be noted that running the noncatalytic reaction in the mixed solvent gave product in a yield of less than 3%.

In order to optimize the catalyst amount, different amounts of catalyst were used in the reduction of acetophenone with \(\text{NaBH}_4\). The best results were obtained with 4 mg (0.002 mmol) of the catalyst (Figure 9).

In order to investigate the effect of reducing agent in the reduction reaction, different \(\text{NaBH}_4\) concentrations have been studied in the reduction of acetophenone (Table 2). Two concentrations show that the reduction of ketones requires larger amount of \(\text{NaBH}_4\) (3 M equivalent) than aldehyde (0.5 M equivalent, Table 1) for completion. This concentration of \(\text{NaBH}_4\) (Table 2, entry 1) gives the maximum yield of acetophenone in the presence of blank, whereas decrease in the concentration of \(\text{NaBH}_4\) (Table 2, entry 2) has effect on the percentage yield of acetophenone in the presence of blank reaction and decrease it.

In order to establish the general applicability of this catalytic system, under optimized conditions, the reduction of a variety of structurally different ketones to their corresponding alcohols was performed efficiently with this reducing system (Table 3).
Reduction of acetophenone, propiophenone, benzophenone, and 2-butanone led to formation of the corresponding alcohol as the sole product (Table 3).

A comparison of the results obtained for our present catalytic system with those reported in the literature using sodium borohydride as a reducing agent [22–29] reveals that the reaction time is shorter than with other systems and that higher conversion rates are achieved for reduction.

The reusability of catalyst is one of the most attractive features of the heterogeneous catalysts [30]. The homogeneous catalyst, [Mn(THPP)OAc], was completely degraded under the reaction condition. In contrast, the nanotube-supported manganese porphyrin catalyst can be filtered and reused several times without significant loss of selectivity (Figure 10). The reusability of the catalyst was investigated.

### Table 2. The influence of the NaBH₄ concentration on the reduction of acetophenone.

| Acetophenone: NaBH₄ | Conversion (%)<sup>b,c</sup> |
|---------------------|-------------------------------|
| Blank               | 3                             |
| 1 : 3               | 30                           |
| 1 : 2               | 57                           |

<sup>a</sup>See the caption of Figure 8.

<sup>b</sup>GLC yield based on starting ketone.

<sup>c</sup>Alcohol was formed as the sole product.

### Table 3. Reduction of ketones with NaBH₄ in the presence of [Mn(THPP)OAc@MWCNT] under optimized conditions.

| Entry | Substrate | Product | Time (min) | Conversion (%)<sup>b</sup> |
|-------|-----------|---------|------------|-----------------------------|
| 1     | ![Substrate 1](image1) | ![Product 1](image2) | 5           | 100                         |
| 2     | ![Substrate 2](image3) | ![Product 2](image4) | 15          | 100                         |
| 3     | ![Substrate 3](image5) | ![Product 3](image6) | 40          | 100                         |
| 4     | ![Substrate 4](image7) | ![Product 4](image8) | 20          | 100                         |

<sup>a,b</sup>See the footnotes of Table 2.

Reduction of acetophenone, propiophenone, benzophenone, and 2-butanone led to formation of the corresponding alcohol as the sole product (Table 3).

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in sequential reduction of acetophenone with sodium borohydride under optimized conditions. The catalyst was separated from the reaction mixture after each experiment by filtration, washed with methanol (two times) and dried carefully before being used in the subsequent run.

In order to understand the progressive loss of catalytic activity upon recycling experiments, the materials after the 4th catalytic run were characterized by FTIR (Figure 11). The FTIR spectra of the recovered catalysts (Figure 11(b)) show less intense Mn–porphyrin vibration, suggesting partial leaching of the metalloporphyrin.

The reduction of acetophenone with sodium borohydride in the presence of Mn(THPP)OAc and [Mn(THPP)OAc@MWCNT] (Table 4) showed significantly enhanced catalytic activity of the latter.

A comparison of our catalyst with some previous catalysts reported for the reduction of acetophenone with NaBH₄ is shown in Table 5. The present method offers advantages in terms of short reaction times, high yields, and high degree of selectivity in addition to inherent advantages of heterogeneous catalysts.
The catalytic effect of Mn(THPP)OAc in the reduction reactions with sodium borohydride may be due to Lewis acidity of Mn(THPP)OAc, and coordination of carbonyl group to the Mn center and an increase in the positive charge on the carbon of the carbonyl group [34]. This facilitates nucleophilic attack of hydride to carbon of the C=O bond [35] and the protonation of anionic intermediate gives the product [29]. Another catalytic effect of Mn(THPP)OAc should be formation of new reductant species such as [Mn-BH4] that actively catalyzes the decomposition of borohydride [6].

4. Conclusion

[Mn(THPP)OAc@MWCNT]/NaBH4 presents an effective catalytic system to achieve selective reduction of various aldehydes and ketones to the corresponding alcohols. The present method offers various advantages such as high yield of products, shorter reaction time, milder conditions, simple work-up procedure, and reusability of the catalyst. The catalyst was reused for four consecutive runs without significant loss of selectivity. The comparison of the catalytic efficiency of the nonimmobilized manganese porphyrin and the immobilized one under the optimized conditions showed significantly enhanced activity of the latter.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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