



Manganese(III) porphyrin supported on multi-wall carbon nanotubes: A highly efficient and reusable biomimetic catalyst for oxidative decarboxylation of α -arylcarboxylic acids and oxidation of alkanes with sodium periodate

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ABSTRACT

In the present work, the highly efficient oxidative decarboxylation of carboxylic acids and also the oxidation of alkanes with sodium periodate catalyzed by *tetrakis*(*p*-aminophenyl)porphyrinatomanganese(III) chloride, [Mn(TNH₂PP)Cl], supported on functionalized multi-wall carbon nanotubes, MWCNT, is reported. The catalyst, [Mn(TNH₂PP)Cl@MWCNT], was used as an efficient and heterogeneous catalyst for hydroxylation of alkenes with NaIO₄ at room temperature, in the presence of imidazole as an axial ligand. Also, in this system, carboxylic acids were converted to their corresponding carbonyl compounds. This heterogenized catalyst could be reused several times without significant loss of its catalytic activity.

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1. Introduction

Oxidation is one of the most important reactions for the metabolism of many substrates and many enzymes are known to catalyze various types of oxidation in the body. Amongst them, the heme-containing monooxygenase cytochrome P-450 has been most extensively studied [1,2]. Many metalloporphyrin complexes, such as well-designed iron(III) and manganese(III) porphyrins, have been synthesized to reproduce the function of cytochrome P-450. These synthetic models are known to be efficient catalysts for O- and N-dealkylation [3], olefin and arene epoxidation [4–6], alkane hydroxylation [7] and oxidation of nitroso [8] and primary aromatic amines to nitro derivatives [9]. The main disadvantage of homogeneous metalloporphyrins is their instability toward oxidative degradation and the difficulty in recovery of these expensive catalysts, which limit their practical applications in both synthetic chemistry and industrial processes. Therefore, immobilization of metalloporphyrins onto a solid support can counteract this problem, enabling the easier recovery and reuse of the catalysts, which makes them cost-effective. Several heterogenized metalloporphyrin catalysts have been developed for the oxidation of organic substrates [10–18].

Carbon nanotubes (CNTs) are important carbon-based materials. Multi-walled CNTs (MWCNTs) are composed of a series of concentric single-walled CNTs (SWCNTs) with an inter-tube distance

of ~0.34 nm. This unique structure endow CNTs with various superior properties, for example, low density, very high stability, outstanding tensile strength and resilience, good current carrying capacity and heat transmission ability [19,20]. Owing to their excellent properties, CNTs have been intensively studied and have attracted wide attention in the last decade [21–25]. Since CNTs are insoluble in most solvents, these materials can be used as catalyst supports [26–39].

Decarboxylation of organic molecules refers to the removal of a carboxyl group from its chemical structure, being further replaced by a hydrogen atom. Oxidative decarboxylation of carboxylic acids and their derivatives has been extensively studied over various oxidants involving supported manganese(III) porphyrin [40,41], manganese (III) Schiff base complexes [42], active hydroxyl radicals (\cdot OH) [43], peroxy radicals [44] and silver(I)/peroxydisulfate [45].

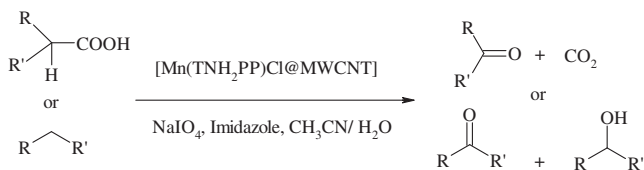
Previously, Mn(TNH₂PP)Cl supported on functionalized multi-wall carbon nanotubes has been used in the epoxidation of alkenes with sodium periodate [35]. Here, we report the use of [Mn(TNH₂PP)Cl@MWCNT] in alkane hydroxylation and decarboxylation of carboxylic acids with NaIO₄ at room temperature (Scheme 1).

2. Experimental

All materials were commercial reagent grade. Alkanes were obtained from Merck or Fluka and were passed through a column containing active alumina to remove peroxidic impurities. *Tetra*(4-aminophenyl)porphyrin was prepared and metallated

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Scheme 1. Decarboxylation of carboxylic acids and hydroxylation of alkanes with NaIO₄ in the presence of [Mn(TNH₂PP)Cl@MWCNT].

according to the literature [46,47]. *Tetrakis(p-aminophenyl)porphyrinatomanganese(III) chloride*, [Mn(TNH₂PP)Cl], supported on functionalized multi-wall carbon nanotubes was prepared according to a recently reported method [35]. FT IR spectra were obtained with potassium bromide pellets in the range 400–4000 cm⁻¹ with a Nicolet Impact 400D spectrometer. A scanning electron micrograph of MWCNT was taken on a Philips XL 30 SEM instrument. A transmission electron micrograph of the catalyst was taken on a Zeiss CEM 902 A instrument. Gas chromatography experiments (GC) were performed with a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20 m. In the GC experiments, *n*-decane was used as an internal standard. ¹H NMR spectra were recorded on a Bruker-Avance AQS 300 MHz spectrometer. MWCNTs containing carboxylic acid groups were purchased from Shenzhen NTP Factory. The specifications of multi-wall carbon nanotubes containing carboxylic acid groups, MWCNT-COOH, are as follows: outside diameter 20–30 nm, inside diameter 5–10 nm, length 30 μm, COOH content 1.5% and specific surface area >110 m²/g.

2.1. General procedure for oxidative decarboxylation of carboxylic acid with NaIO₄ catalyzed by [Mn(TNH₂PP)Cl@MWCNT]

In a 25 mL flask equipped with a magnetic stirring bar, a solution of NaIO₄ (2 mmol in 10 mL H₂O) was added to a mixture of α-aryl carboxylic acid (1 mmol), [Mn(TNH₂PP)Cl@MWCNT] (300 mg, 0.043 mmol) and imidazole (0.2 mmol) in CH₃CN (10 mL). The progress of the reaction was monitored by TLC. After the reaction was completed, the catalyst was filtered and washed with EtOH. At the end of the reaction, the reaction mixture was diluted with Et₂O (20 mL) and filtered. The catalyst was thoroughly washed with Et₂O and combined washings and filtrates were purified on silica-gel plates or with a silica-gel column. The identities of the products were confirmed by IR and ¹H NMR spectral data.

2.2. General procedure for oxidation of alkanes with NaIO₄ catalyzed by [Mn(TNH₂PP)Cl@MWCNT]

To a mixture of alkane (1 mmol), [Mn(TNH₂PP)Cl@MWCNT] (350 mg, 0.05 mmol) and imidazole (0.2 mmol) in CH₃CN (10 mL) was added a solution of NaIO₄ (2 mmol) in H₂O (10 mL). The reaction mixture was stirred magnetically at room temperature. The progress of the reaction was monitored by GC. At the end of the reaction, the reaction mixture was diluted with Et₂O (20 mL) and filtered. The catalyst was thoroughly washed with Et₂O and combined washings and filtrates were purified on silica-gel plates or with a silica-gel column. IR and ¹H NMR spectral data confirmed the identities of the products.

2.3. Catalyst reuse and stability

The reusability of [Mn(TNH₂PP)Cl@MWCNT] was investigated by multiple sequential oxidative decarboxylation reactions. The oxidation of diphenylacetic acid was chosen as a model substrate for studying catalyst reuse and stability. At the end of each

reaction, the catalyst was separated from the reaction mixture by simple filtration, washed with Et₂O and dried carefully before using it in the next run.

3. Results and discussions

3.1. Catalytic experiments

Fig. 1 shows the structure of Mn(TNH₂PP)Cl, supported on functionalized multi-wall carbon nanotubes [35]. The prepared catalyst was used for the oxidative decarboxylation of carboxylic acids and oxidation of alkanes with sodium periodate at room temperature. First, the reaction parameters, such as catalyst amount, kind of solvent, oxidant, were optimized for the decarboxylation of diphenylacetic acid.

3.1.1. Optimization of the conditions in the oxidative decarboxylation of carboxylic acids catalyzed by [Mn(TNH₂PP)Cl@MWCNT]

First, we optimized the catalyst amount in the oxidation of diphenylacetic acid with 2 mmol of NaIO₄. The best results were obtained with 300 mg (0.043 mmol) of the catalyst, whereas trace amounts of products (10%) were detected when the same reaction was carried out in the absence of catalyst at room temperature (Table S1).

The ability of different single oxygen donors, such as NaIO₄, KHSO₅ (Oxone), H₂O₂, NaOCl, *tert*-BuOOH and *n*-Bu₄NIO₄, was investigated in the oxidation of diphenylacetic acid. The results (Table S2) showed that NaIO₄ is the best oxygen source because this oxidant, which is inert in the absence of catalyst, can give good oxidation conversion in CH₃CN/H₂O.

Different solvents were checked for choosing the reaction media. In this manner, mixtures of methanol, ethanol, acetone, acetonitrile (single phase systems) and dichloromethane (two phase system with Bu₄NBr as a phase transfer catalyst) with water were tested, and the 1:1 mixture of acetonitrile/water mixture was chosen as the reaction medium, in which the higher carbonyl compound was obtained (Table S3).

The reactivity of metalloporphyrin catalysts for oxidation reactions can be improved by the addition of donor ligands to mimic the effect of the axially coordinating histidine and thiolate residue in peroxidase and cytochrome P-450 enzymes, respectively. According to previous reports, we used imidazole as an axial base [35].

3.2. Oxidative decarboxylation of carboxylic acids with NaIO₄ catalyzed by [Mn(TNH₂PP)Cl@MWCNT]

The optimum conditions used for the oxidation of diphenylacetic acid with this heterogenized system was catalyst, oxidant, imidazole and substrate in a molar ratio of 0.043:2:0.2:1, respectively.

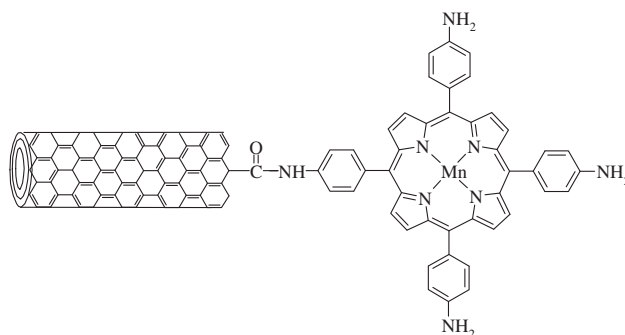


Fig. 1. Structure of the catalyst.

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