



Manganese porphyrin immobilized on magnetite nanoparticles as a recoverable nanocatalyst for epoxidation of olefins



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HIGHLIGHTS

- The [Mn(TPP)Cl] was supported on silica coated magnetic nanoparticles.
- The [Mn(TPP)Cl@Im-SiO₂-Fe₃O₄] heterogeneous catalyst was characterized.
- The [Mn(TPP)Cl@Im-SiO₂-Fe₃O₄]/NaIO₄ catalytic system was used for alkene epoxidation.
- The catalyst was efficient and reusable.

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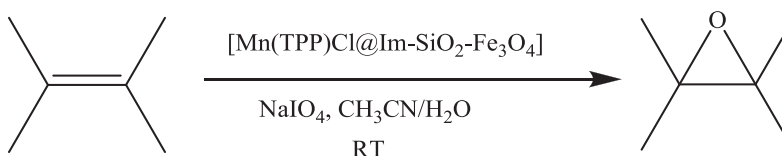
Nanostructures

Oxidation

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GRAPHICAL ABSTRACT



ABSTRACT

Efficient epoxidation of alkenes catalysed by tetraphenylporphyrinatomanganese(III) chloride, [Mn(TPP)Cl], supported on silica coated magnetite nanoparticles, SiO₂-Fe₃O₄, is reported. First, the SiO₂-Fe₃O₄ nanoparticles were modified with triethoxysilylpropyl chloride and then with imidazole. In the final step, [Mn(TPP)Cl] was attached to the support *via* axial ligation. The prepared catalyst was characterized by elemental analysis, FT-IR and diffuse reflectance UV-vis spectroscopic methods, and scanning electron microscopy. This new heterogenized catalyst was used for efficient epoxidation of alkenes with NaIO₄ at room temperature. The catalyst is of high reusability in the epoxidation reactions, in which it was reused several times without significant loss of its catalytic activity.

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1. Introduction

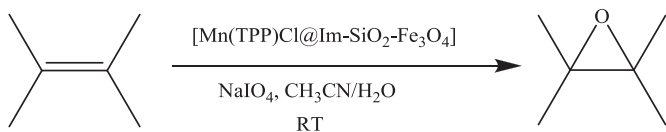
Cytochrome P-450 monooxygenation enzyme is very important in the detoxification of foreign bodies and is catalytically active in the oxidation of a variety of xenobiotics and biological substrates. This enzyme can selectively oxidize a very extensive range of endogenous and exogenous organic compounds, such as chain alkanes, steroidal and polyaromatic compounds and very large molecules like cyclosporine. The active site of this enzyme is an iron

porphyrin which is surrounded by proteins [1,2]. In order to simulate the function of cytochrome P-450, catalytic oxidation of hydrocarbons by metalloporphyrins has been extensively investigated. Simple oxidizing reagents such as H₂O₂, NaIO₄, PhIO and NaClO have been used in the oxidation reactions catalysed by metalloporphyrins [3–5].

Unfortunately, these homogeneous catalysts degraded in the reaction media due to the formation of inactive dimeric μ -oxo species and cannot be recovered, and therefore contaminate the products [6,7]. In order to solve this problem and achieve better performance in many heterogeneous catalytic applications, they have to be immobilized on solid supports. In comparison with the homogeneous catalysts, heterogeneous systems present many advantages such as higher stability of the catalytic species, simple

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Scheme 1. Oxidation of alkenes with NaIO_4 catalysed by $[\text{Mn}(\text{TPP})\text{Cl}@\text{Im-SiO}_2\text{-Fe}_3\text{O}_4]$.

recovery and reutilization of the catalyst and catalyst protection against destruction. Hence, the immobilization of homogeneous catalysts, especially biomimetic catalysts such as metalloporphyrins, is much desired [8]. Over the last two decades, several homogeneous and heterogenized metalloporphyrin catalysts have been developed for the oxidation of organic compounds [9–18]. Although the heterogenized catalysts have some advantages, they are significantly less selective and reactive than their homogeneous counterparts. So, there is a need to find new methods and strategies in order to overcome these limitations [19].

Fe_3O_4 magnetic nanoparticles have been studied extensively due to their superparamagnetism property, large surface area to volume ratio and easy functionalization [20]. Because of these advantageous, these compounds have found various biological applications such as drug delivery [21], magnetic resonance imaging (MRI) [22], bioseparation [23], biomolecular sensors [24] and magneto-thermal therapy [25]. Recent reports show that magnetic nanoparticles are efficient supports and can facilitate the isolation and recycling of expensive catalysts from the reaction media [26,27].

The aim of this work is combining of the features of tetraphenylporphyrinatomanganese(III) chloride, $[\text{Mn}(\text{TPP})\text{Cl}]$, and magnetic nanoparticles. In this manner, the Fe_3O_4 magnetic nanoparticles were synthesized, silica-coated and functionalized with 3-chloropropyltriethoxysilane and then with imidazole. The imidazole-bound magnetic nanoparticles were used as support for

immobilization of $[\text{Mn}(\text{TPP})\text{Cl}]$ via axial ligation and its catalytic activity as a magnetically recyclable catalyst was investigated in the epoxidation of alkenes with NaIO_4 (Scheme 1).

2. Experimental

2.1. Materials

Alkenes were obtained from Merck chemical company and passed through a column containing active alumina to remove the peroxidic impurities. Tetraphenylporphyrin was prepared and metallated according to the literature [28,29].

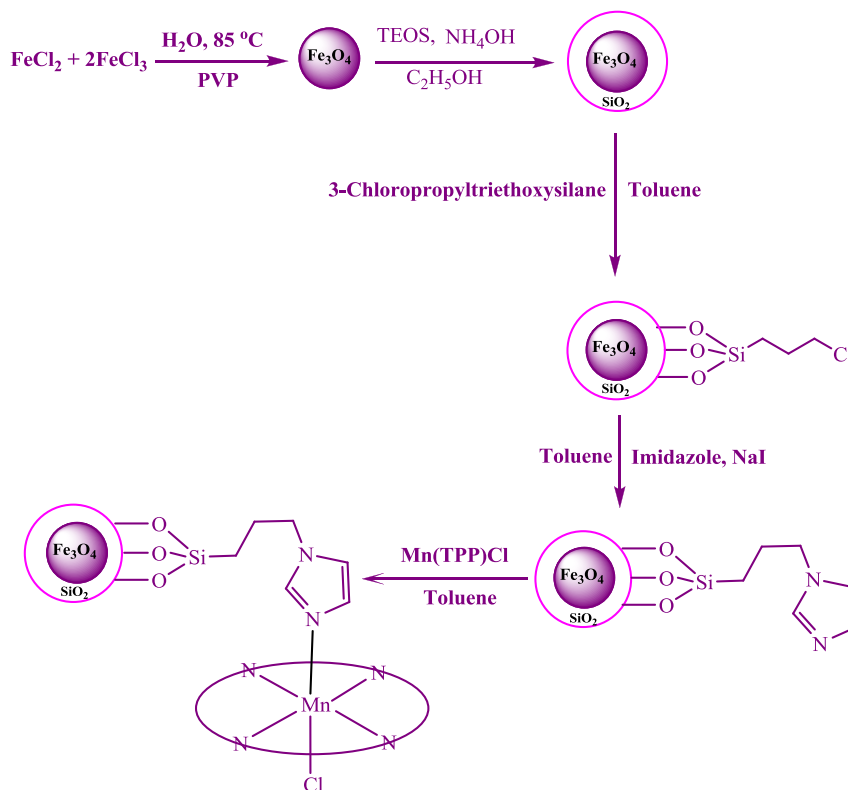
2.2. Apparatus

FT-IR spectra were obtained with potassium bromide pellets in the range $400\text{--}4000\text{ cm}^{-1}$ with a JASCO 6300 spectrometer. The diffuse reflectance UV–vis spectra were recorded on a JASCO V-670 UV–vis spectrophotometer. Scanning electron micrograph of MNPs was taken on a Philips XL 30 SEM instrument. X-ray powder diffraction (XRD) patterns were recorded using a Bruker D8ADVANCE X-ray diffractometer equipped with Nickel monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$). Gas chromatography experiments (GC) were performed with a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20m. In the GC experiments, *n*-decane was used as an internal standard.

2.3. Materials preparation

2.3.1. Synthesis of PVP-stabilized magnetite nanoparticles, Fe_3O_4

Magnetite (Fe_3O_4) nanoparticles were prepared in a co-precipitation step based on the procedure of Massart et al. [30]



Scheme 2. The preparation route for catalyst.

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