



Silica supported Mn(Br₈TPP)Cl and Mn(TPP)Cl as efficient and reusable catalysts for selective hydrocarbon oxidation under various reaction conditions: The effect of substituted bromines on the catalytic activity and reusability

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ABSTRACT

The imidazole-modified silica (SiIm) was used for immobilization of octabromotetraphenylporphyrinatomanganese(III) chloride, Mn(Br₈TPP)Cl and tetraphenylporphyrinatomanganese(III) chloride, Mn(TPP)Cl. SiIm is not only a heterogeneous axial base but also a support for immobilization of manganese porphyrins. [Mn(Br₈TPP)Cl-SiIm] and [Mn(TPP)Cl-SiIm] as biomimetic oxidation catalysts catalyze alkene epoxidation and alkane hydroxylation with NaIO₄ under agitation with magnetic stirring. Ultrasonic irradiation enhanced the catalytic activity of these catalysts in alkene epoxidation and alkane hydroxylation and this led to shorter reaction times and higher product yields. These new heterogenized catalysts could be reused several times without significant loss of their catalytic activity.

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1. Introduction

An iron porphyrin surrounded by proteins is known to be the active site of the enzyme P-450 monooxygenase, which can selectively catalyze the oxidation in particular the epoxidation of a wide range of substrates [1]. Synthetic metalloporphyrins have been used as cytochrome P-450 models and have been found to be highly efficient homogeneous catalysts for alkene epoxidation and alkane hydroxylation [2–8]. Several simple oxidants such as PhIO, ClO⁻, H₂O₂, ROOH and IO₄⁻ have been extensively studied in oxygenation reactions catalyzed by metalloporphyrins in order to understand the mechanism of cytochrome P-450 monooxygenation enzyme [9–14]. However, the synthesis of metalloporphyrins is challenging and low-yielding. Immobilization onto a solid support can counteract this problem, enabling the easier recovery and reuse of the catalysts, which makes them cost-effective. Moreover, the support can also reduce the instability of the metalloporphyrins during the epoxidation reaction, *i.e.* self-oxidation leading to the formation of a catalytically inactive μ-oxo porphyrin dimer in solution [15–19].

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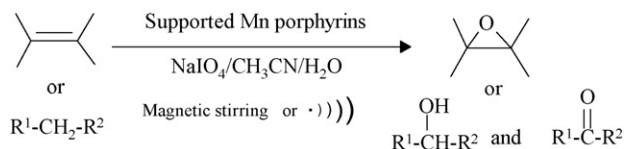
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Over the last two decades, several homogeneous and heterogenized metalloporphyrins have been developed for alkene epoxidation and alkane hydroxylation [20–44]. Previously, we have reported the use of supported manganese(III) porphyrins in the oxidation of organic compounds with NaIO₄ [45–54]. Here, we report the use of silica-supported octabromotetraphenylporphyrinatomanganese(III) chloride, [Mn(Br₈TPP)Cl]-SiIm, and tetraphenylporphyrinatomanganese(III) chloride, Mn(TPP)Cl in alkene epoxidation and alkane hydroxylation with NaIO₄ under mechanical stirring and ultrasonic (US) irradiation conditions (Scheme 1).

2. Experimental

All materials were of the commercial reagent grade. Alkene, alkane and alkylaromatic compounds were obtained from Merck or Fluka. All of these compounds were passed through a column containing active alumina to remove peroxidic impurities. Tetraphenylporphyrin was prepared, brominated and metallated according to the literature [55–57]. FT-IR spectra were obtained with potassium bromide pellets in the range 400–4000 cm⁻¹ with a Nicolet Impact 400D spectrometer. Scanning electron micrographs of the catalyst and silica were taken on a Philips XL 30 SEM. Gas chromatography (GC) experiments were performed with a Shi-



Scheme 1. Alkene epoxidation and alkane hydroxylation catalyzed by silica-supported manganese porphyrins.

madzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20 m. ^1H NMR spectra were recorded on a Bruker-Arance AQS 300 MHz spectrometer.

2.1. Preparation of silica-supported manganese porphyrins, $\text{Mn}(\text{Br}_8\text{TPP})\text{Cl-Silm}$ and $\text{Mn}(\text{TPP})\text{Cl-Silm}$

3-Chloropropylsilica gel functionalized imidazole, as support, was prepared according to the reported procedure [27]. IR and elemental analysis were in accordance with those previously described. To a solution of 0.5 g manganese porphyrins in toluene (100 ml), was added 3-chloropropylsilica gel functionalized imidazole (5 g). The mixture was vigorously stirred at 80°C for 24 h. After cooling, the green silica was collected by filtration, washed thoroughly with dichloromethane, methanol, and ether, successively, and dried in vacuum at room temperature for several hours. The manganese(III) porphyrin loading of silica support, which was calculated from the manganese content in heterogenized catalyst, was determined by neutron activation analysis (NAA).

2.2. General procedure for oxidation reactions catalyzed by $\text{Mn}(\text{Br}_8\text{TPP})\text{Cl-Silm}$ or $\text{Mn}(\text{TPP})\text{Cl-Silm}$ under agitation with magnetic stirring

All of the reactions were carried out at room temperature under air in a 25 ml flask equipped with a magnetic stirrer bar. To a mixture of alkene or alkane (1 mmol), manganese porphyrins (30 μmol) and CH_3CN (10 ml) was added a solution of NaIO_4 (2 mmol) in H_2O (10 ml). The progress of reaction was monitored by GC. The reaction mixture was diluted with Et_2O (20 ml) and filtered. The catalyst was thoroughly washed with Et_2O and combined washings and filtrates were purified on a silica gel plates or a silica gel column. IR and ^1H NMR spectral data confirmed the identities of the products.

2.3. General procedure for oxidation reactions catalyzed by $\text{Mn}(\text{Br}_8\text{TPP})\text{Cl-Silm}$ or $\text{Mn}(\text{TPP})\text{Cl-Silm}$ under ultrasonic irradiation

All reactions were carried out at room temperature in a 40 ml glass reactor. A UP 400S ultrasonic processor equipped with a 3 mm wide and 140 mm long probe, which was immersed directly into the reaction mixture, was used for sonication. The operating frequency was 24 kHz and the output power was set at 0–400 W through manual adjustment. The total volume of the solution was 20 ml. The temperature reached to 40°C during sonication.

A solution of NaIO_4 (2 mmol in 10 ml H_2O) was added to a mixture of alkene or alkane (1 mmol) in CH_3CN (10 ml). After addition of manganese porphyrins (30 μmol), the mixture was sonicated. Progress of the reaction was followed by GC. At the end of reaction, the polymer beads were filtered off and the filtrates were extracted with Et_2O and were purified on a silica gel plate or a silica gel column (eluent: $\text{CCl}_4\text{-Et}_2\text{O}$). The identities of products were confirmed by IR and ^1H NMR spectral data.

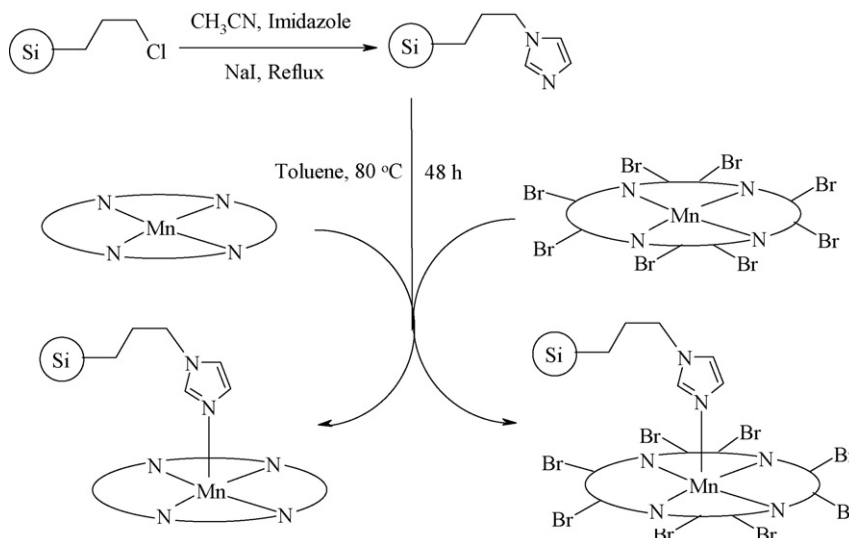
2.4. Catalyst reuse and stability

The reusability of $[\text{Mn}(\text{Br}_8\text{TPP})\text{Cl-Silm}]$ and $[\text{Mn}(\text{TPP})\text{Cl-Silm}]$ was studied in repeated epoxidation reactions. The epoxidation of cyclooctene was chosen as a model substrate for the study of catalyst reuse and stability. The catalyst was separated from the reaction mixture after each experiment by simple filtration, washed with methanol and dried carefully before using it in the subsequent run.

3. Results and discussion

3.1. Preparation of the catalysts, $[\text{Mn}(\text{Br}_8\text{TPP})\text{Cl-Silm}]$ and $[\text{Mn}(\text{TPP})\text{Cl-Silm}]$

Silica surface modification with imidazole to give the Si-Im was carried out through the method described by Cooke and Lindsay Smith [26]. The supported catalysts were prepared by the reaction of chloropropylated silica gel with imidazole in dichloromethane. The supported manganese catalysts, $[\text{Mn}(\text{Br}_8\text{TPP})\text{Cl-Silm}]$ and $[\text{Mn}(\text{TPP})\text{Cl-Silm}]$, were obtained by stirring a suspension of silica-modified imidazole in a solution of the manganese porphyrins in toluene (Scheme 2). The bonding of the silica and the manganese



Scheme 2. Preparation of silica-supported manganese porphyrins.

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