

# Preparation of an insoluble polymer-supported Mn (III) porphyrin and its use as a new alkene epoxidation and alkane hydroxylation catalyst<sup>†</sup>

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An easy and effective method to prepare a new supported Mn(III)-porphyrin by immobilisation of Mn(III)-5,10,15,20-Tetrakis(p-sulfonatophenyl)porphyrin, [Mn(TPPS)], on poly(4-styrylmethyl)pyridinium chloride (PSMP) is reported. This catalyst was found to be efficient for catalysing alkene epoxidation and alkane hydroxylation with sodium periodate. This new heterogenised metalloporphyrin catalyst is of high stability and reusability.

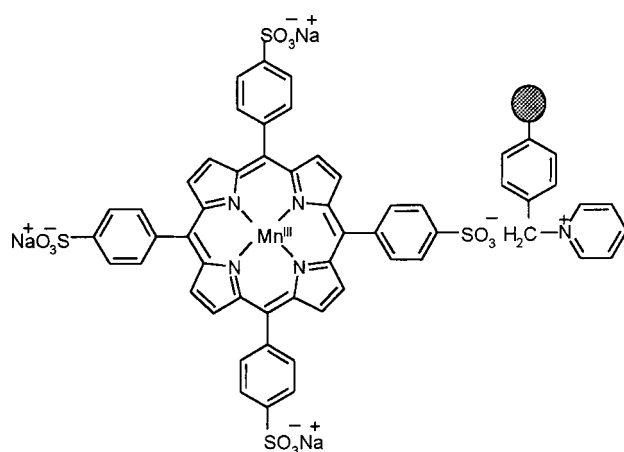
**Keywords:** Mn(III) porphyrin, alkene epoxidation, alkane hydroxylation catalyst

Alkene epoxidation and alkane hydroxylation catalysed by metalloporphyrins is a subject of much research.<sup>1</sup> Various single oxygen-atom donors such as PhIO,<sup>2,3</sup> ClO<sup>-</sup>,<sup>4,5</sup> KHSO<sub>5</sub><sup>6</sup> and IO<sub>4</sub><sup>-</sup><sup>7-9</sup> have been used for these oxygenation reactions. The high efficiency of some of these systems make them potentially useful for preparative oxidations in organic chemistry. The utility of these catalysts, however, would be increased significantly if they could be readily attached to solid supports. Such immobilisation can (1) make the catalyst readily separable from the products and reusable, (2) enhance the catalyst stability toward oxidative degradation and (3) allow preparation of environmentally friendly catalysts.

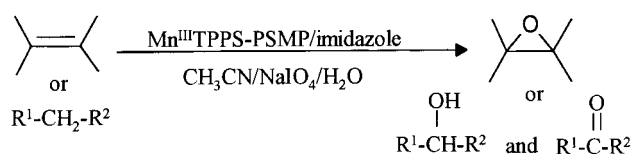
Many heterogenised metalloporphyrin catalysts have been reported for alkene epoxidation and alkane hydroxylation in the literature.<sup>10-21</sup> However, complicated multistep preparation of catalyst and its leaching and loss of catalytic activity toward some substrates are drawbacks of these catalysts.

In our search for new supported catalysts for oxidation reactions, we have employed chloromethylated styrene-divinylbenzene copolymer quaternerised with pyridine, [poly(4-styrylmethyl)pyridinium chloride], as a simple support for manganese porphyrin complex (Scheme 1).

The catalyst exhibits a high activity and stability in alkene epoxidation and alkane hydroxylation by NaIO<sub>4</sub> (Scheme 2)



Scheme 1



Scheme 2

## Results and discussions

The metalloporphyrin was supported on the polymer from 50% v/v aqueous acetone as described in the experimental section. Alkane hydroxylation and alkene epoxidation were performed at room temperature under air in CH<sub>3</sub>CN/H<sub>2</sub>O medium containing alkene or alkane, oxidant, imidazole and MnTPPS-PSMP in 1:2:0.2:0.0145 ratio, respectively. The effect of different axial ligands upon the epoxidation rate of cyclooctene was also investigated. The epoxidation rates decrease in the following order:

imidazole = 1-methylimidazole > *t*-butylpyridine > pyridine

In the absence of imidazole, the catalytic system is less efficient in oxidation of hydrocarbons.

The catalytic system led to epoxidation of alkenes (Table 1) in good yields (48–91%). In the case of stilbenes, *trans*-stilbene was converted into the *trans*-epoxide in 70% yield and *cis*-stilbene gave a 77:8 mixture of *cis* and *trans* epoxides. The MnTPPS-PSMP/NaIO<sub>4</sub> catalytic system exhibited a good regioselectivity for epoxidation of (*R*)-(+)-limonene. In this case, the ratio of 1,2-epoxide to 8,9-epoxide was found to be 3:1.

Selective partial alkane oxidation is a particularly challenging problem in organic synthesis. MnTPPS-PSMP/NaIO<sub>4</sub> could oxidise alkanes to the corresponding alcohols and ketones (Table 2). In the absence of metalloporphyrin catalyst, the alkenes and alkanes remained unchanged by NaIO<sub>4</sub> in CH<sub>3</sub>CN/H<sub>2</sub>O after several hours.

## Experimental

All materials were 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. H<sub>2</sub>TPPS was prepared and metallated according to literature procedures.<sup>23</sup>

**Preparation of poly(4-styrylmethyl)pyridinium chloride as support:** The chloromethylated polystyrene was quaternerised (PSMP) by pyridine as follows: Chloromethylated polystyrene (Merck, 2% crosslinked) (5 g) was treated in pyridine (50 ml) and heated at 80°C for 2 hours. The polymer was filtered and washed with acetone to remove remaining pyridine and dried at 100°C.

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<sup>†</sup> This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

**Table 1** Epoxidation of alkenes with NaIO<sub>4</sub> catalysed by MnTPPS-PSMP in the presence of imidazole at room temperature

Alkene	Conversion /% <sup>a</sup>	Epoxide yield/% <sup>a</sup>	Reaction time/h
Cyclooctene	90	90	5
Cyclohexene	98	82	4
Styrene	98	84	4
α-Methylstyrene	91	65	2
(+)-Comphene	80	80	6
1-Heptene	49	49	6
Indene	80	80	6
(+)-R-Limonene	91	69(1,2-Epoxide) <sup>b</sup> 22(8,9-Epoxide) <sup>b</sup>	6
<i>cis</i> -Stilbene	78	78( <i>trans</i> -Epoxide) <sup>b</sup>	6
<i>trans</i> -Stilbene	85	75( <i>cis</i> -Epoxide) <sup>b</sup> 10( <i>trans</i> -Epoxide) <sup>b</sup>	6

<sup>a</sup>GLC yield based on starting alkene.<sup>b</sup>Both <sup>1</sup>H NMR and GLC data approved the reported yields.

*Immobilisation of manganese porphyrin on support:* MnTPPS (0.5 g) was dissolved in a mixture of acetone:water (1:1) and PSMP (5 g) was added to the solution. The mixture was stirred at 80°C for 8 h. The mixture was cooled to room temperature, filtered, washed with water, acetone and dried.

*Typical procedure for oxidation reactions catalysed by MnTPPS-PSMP:* All of the reactions were carried out at room temperature under air in a 25 ml flask equipped with a magnetic stirring bar. A solution of NaIO<sub>4</sub> (2 mmol) in H<sub>2</sub>O (10 ml) was added to a mixture of alkene or alkane (1 mmol), MnTPPS-PSMP (14 μmol) and imidazole (0.2 mmol) in CH<sub>3</sub>CN (10 ml). The progress of reaction was monitored by GLC. The reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (20 ml) and filtered. The resin was thoroughly washed with CH<sub>2</sub>Cl<sub>2</sub> and combined washings and filtrates were purified on silica-gel plates or a silica-gel column. IR and <sup>1</sup>H NMR spectral data confirmed the identities of the products.

*Catalyst reuse and stability:* The stability of MnTPPS-PSMP was studied in repeated epoxidation reactions. The epoxidation of styrene was chosen as a model substrate for studying of catalyst reuse and stability. The reaction was carried out as described above. At the end of the reaction, the catalyst was removed by filtration and washed with water and acetonitrile and reused. The dried catalyst was consecutively reused four times. After the use of catalyst for four consecutive times, the epoxide yield was 90%. The amount of leached Mn (1.2%) was determined by atomic absorption.

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**Table 2** Hydroxylation of alkanes with NaIO<sub>4</sub> catalysed by MnTPPS-PMP in presence of imidazole at room temperature

Alkane	Ketone /% <sup>a</sup>	Alcohol /% <sup>a</sup>	Reaction time/h
Cyclooctane	19	23	8
Cyclohexane	25	–	8
<i>cis</i> -Decaline	15	38	8
1,2,3,4-Tetrahydronaphthalene	65	–	8
Ethylbenzene	35	–	8
Diphenylmethane	45	–	8
Propylbenzene	31	–	8
Fluorene	75	–	8

<sup>a</sup>GLC yield based on starting alkene.

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