



A convenient preparation of polymer-supported manganese porphyrin and its use as hydrocarbon monooxygenation catalyst

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Abstract

A supported tetra(4-pyridyl)porphyrinato manganese(III) was prepared very easily in one step by a quaternization reaction and is found to be an efficient catalyst for alkene epoxidation and alkane hydroxylation by sodium periodate. This catalyst showed high selectivity in epoxidation of stilbenes and *R*-(+)-limonene and exhibits a particular ability to epoxidize linear alkenes. Very inert saturated hydrocarbons as well as alkylbenzene derivatives can be oxidized in the presence of this supported catalyst. The new heterogenized metalloporphyrin catalyst is of high stability and reusability.

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1. Introduction

Biomimetic epoxidation and hydroxylation reactions with synthetic metalloporphyrin complexes have been attracting much attention in the last two decades [1–3]. However, instability of metalloporphyrins toward oxidative degradation and difficulty in recovery of the expensive catalyst limit the practical applications of metalloporphyrin catalysts in both synthetic chemistry and industrial processes. On the other hand, immobilization of metalloporphyrin complexes on solid supports can provide catalysts that are easier to handle, and may exhibit improved selectivities and activities because of the support environment. To date, different approaches have been taken in the design of heterogeneous metalloporphyrin catalysts including: (i) electrostatic binding of charged porphyrins to counter-charged supports; (ii) intercalation or entrapment of porphyrin between the layers of clays or within the pores or matrices of solids; (iii) axial ligation to surface-bound ligands; and (iv) covalent binding to the supports [4–12]. Polymer covalently-bounded

porphyrins are available by polymerization of vinyl group containing porphyrin or by immobilization of suitable porphyrins on reactive polymers [13,14]. These methods suffer from the disadvantages of complicated preparation of suitable porphyrins or polymer supports. In our search for new supported metalloporphyrin catalysts, here we report that simple manganese(III) tetrapyrildorphyrin can be readily immobilized on the well-known chloromethylated styrene–divinylbenzene copolymer by a quaternization reaction. This polystyrene-bound Mn-porphyrin can be used as a robust, reusable, and active heterogeneous catalyst in the alkene epoxidation and alkane hydroxylation by sodium periodate.

2. Results and discussion

2.1. Preparation of polymer-supported manganese porphyrin catalyst (MnTPyP-CMP)

The catalyst-support used in this study was the well-known chloromethylated styrene–divinylbenzene copolymer, which due to its excellent solvation and swelling in *N,N*-dimethylformamide may allow the metalloporphyrin

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










to be attached not only on the surface of the polymer but also within the interior of the cross-linked polymer matrix. The supported manganese porphyrin was prepared by heating a mixture of chloromethylated polystyrene and manganese tetrapyrrolylporphyrin in DMF at 80 °C for 4 h. The polymer-anchored porphyrin is insoluble in common organic solvents. Therefore, it is not possible to measure the conductance and molecular weight or record electronic spectrum of the complex in solution. The reflectance of the polymer-bound porphyrin resembles the solution counterpart spectrum with only a slight red shift and a Soret band at 466 nm and a Q band at 566 nm, which clearly indicates the presence of metalloporphyrin on the surface. As a further indication for quaternization reaction, the supported complex was used as an ion exchange resin in a column through which aqueous NaNO₃ solution was passed. After elution with H₂O, the eluate was analyzed for its chloride content by the potentiometric titration

method. The degree of incorporation of porphyrinato manganese into the polymer was also determined by neutron activation analysis (NAA), which shows a value of about 2.5% (w/w). The covalent bonding of the polymer and the metalloporphyrin is so strong that Mn-porphyrin is not eluted from the polymer with water and common organic solvents.

2.2. Alkene epoxidation with sodium periodate catalyzed by MnTPyP-CMP

The potential of this supported manganese(III) porphyrin catalyst for epoxidation was initially investigated with cyclooctene in the presence of sodium periodate. The reaction was carried out in 2:1, CH₃CN/H₂O mixture, in which high epoxidation yield was observed. The effect of different axial ligands upon the epoxidation rate of cyclooctene was also investigated. The epoxidation rate decreased in the

Table 1
Epoxidation of alkenes with NaIO₄ catalyzed by MnTPyP-CMP^a

Entry	Epoxide	Conversion (%) ^b	Epoxide yield (%) ^b	Time (h)	Turnover/h
1		95	95	3	1538
2		94 ^c	80	5	940
3		97	97	3	1616
4		95 ^d	53	2	2375
5		97 ^e	97	4	1212
6		80	80	3	1333
7		96	96	2	2400
8		92	55 (1,2-Epoxide) ^f 37 (8,9-Epoxide) ^f	3	1533
9		68	68 (trans-Epoxide) ^f	6	566
10		99	88 (cis-Epoxide) ^f 11 (trans-Epoxide) ^f	6	825
11		56	56	4	700

^a Reaction conditions: alkene (1 mmol), NaIO₄ (2 mmol), imidazole (0.2 mmol), catalyst (0.02 mmol), CH₃CN/H₂O (10 mL/5 mL).

^b GLC yield based on starting alkene.

^c The byproducts are 6% allylic alcohol and 8% allylic ketone.

^d The byproduct is acetophenone.

^e Only exo product is obtained.

^f Both ¹H NMR and GLC data approved the reported yields.

order: imidazole > *t*-butylpyridine > 1-methylimidazole > pyridine. The optimum condition used for the epoxidation of cyclooctene with this heterogenized system was catalyst, oxidant, imidazole, and substrate in a molar ratio of 1:100:10:50. During the course of the epoxidation, the reaction solution remained colorless and there was no evidence for leaching of the catalyst from polymeric support into solution. This fact was also investigated by examining the UV-Vis spectrum of the filtered reaction mixture.

Polystyrene-supported tetra(4-pyridyl)porphyrinato manganese(III) can be applied to a wide range of substituted alkenes (Table 1). The conditions used for epoxidation of other alkenes were identical to the procedure described above for cyclooctene. Evidently, this is an efficient catalyst for epoxidation of a wide variety of alkenes. In the case of styrene, *cis*-stilbene, *trans*-stilbene, *R*-(+)-limonene, and camphene, the epoxide yields were higher than sterically hindered homogeneous catalysts and comparable to homogeneous alkene epoxidations using manganese tetraphenylporphyrin [15–17]. In the case of stilbenes, the *cis* isomer is more reactive than the *trans* isomer. The *trans*-stilbene was converted to *trans*-epoxide in 68% yield and *cis*-stilbene gave a 8:1 mixture of *cis*- and *trans*-epoxides. The regioselectivity that observed in the epoxidation of *R*-(+)-limonene is higher than that of the homogeneous system. The ratio among 1,2- and 8,9-epoxides was found to be 1.48:1. The supported catalyst acts very efficiently for epoxidation of

linear alkenes compared to homogeneous tetraarylporphyrin catalysts [15].



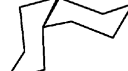
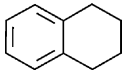
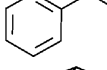
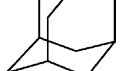
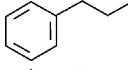
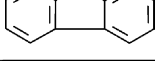
2.3. Alkane hydroxylation with sodium periodate catalyzed by MnTPyP-CMP

The catalytic hydroxylation of alkane with sodium periodate was carried out in the presence of the polystyrene-bound manganese tetrapyrrolylporphyrin (Table 2) under the same condition as described for alkene epoxidation. Cyclooctane, adamantane, and fluorene were converted in good yields to alcohols and ketones within 6 h at room temperature. These yields vary from 37 to 75% depending on the alkane structure. The regioselectivity observed for oxidation of adamantane showed a significant preference for position 1 over position 2. This can be attributed to the unique microenvironment constituted by the porphyrin macrocycle and polymer matrix. These results are consistent with greater reactivity of the supported catalyst than homogeneous ones for oxygenation of arylalkanes and cycloalkanes [18].

About *cis*-decaline and adamantane, the nature of the products has been proved by high resolution NMR (400 MHz), which indicated hydroxylation of the bridgehead carbons.

Other oxygen-donors such as KHSO₅, NaOCl, and H₂O₂ were examined for the alkene epoxidation and alkane hydroxylation under various reaction conditions, but higher

Table 2
Hydroxylation of alkanes with NaIO₄ catalyzed by MnTPyP-CMP^a

Entry	Alkane	Conversion (%) ^b	Ketone (%) ^b	Alcohol (%) ^b	Time (h)	Turnover/h
1		75	43	32	6	625
2		65	62	3	6	541
3		72	27	45	6	600
4		75 ^c	75	0	6	625
5		51 ^d	51	0	6	425
6		37	0	37	6	308
7		55 ^e	55	0	6	458
8		66	66	0	6	550

^a Reaction conditions: alkane (1 mmol), NaIO₄ (2 mmol), imidazole (0.2 mmol), catalyst (0.02 mmol), CH₃CN/H₂O (10 mL/5 mL).

^b GLC yield based on starting alkane.

^c Only α-position was oxidized.

^d The product is acetophenone.

^e The product is ethyl phenyl ketone.

activity and stability of the supported catalyst were observed with sodium periodate than with the other oxygen donors.

2.4. Catalyst reuse and stability

The stability of the supported catalyst was monitored using multiple sequential epoxidation of styrene with sodium periodate. For each of the repeated reactions, the catalyst was recovered, washed exhaustively with water, methanol, acetonitrile, and diethyl ether, and dried before being used for fresh styrene and sodium periodate. The catalyst was consecutively reused four times without a detectable catalyst leaching or a significant loss of its activity.

3. Conclusion

We have shown that polystyrene-bound manganese tetrapyrrolylporphyrin, which is very easily prepared in one step from commercially available compounds, can be an effective catalyst for alkene epoxidation and alkane hydroxylation reactions. The catalyst is robust toward destructive reactions and easily recovered by simple filtration at the end of the reactions.

4. 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. Tetra(4-pyridyl)porphyrin was metallated according to a literature procedure [19].

4.1. Preparation of polymer-supported manganese porphyrin

To a solution of 0.25 g (0.34 mmol) manganese(III) tetrapyrrolylporphyrin in DMF (50 ml) was added chloromethylated polystyrene resin (Merck, 2% cross-linked) (5 g). The mixture was vigorously stirred at 80 °C for 24 h. After cooling, the dark green resin was collected by filtration, washed thoroughly with DMF, water, ethanol, and chloroform, and dried in vacuum at room temperature for several hours. The UV-Vis spectrum (solid film) shows bands (Soret) at 466 and (Q band) at 566 nm. The content of manganese(III) tetrapyrrolylporphyrin on the polymer support was calculated from the manganese content in the heterogenized catalyst determined by neutron activation analysis.

4.2. Typical procedure for oxidation reactions catalyzed by MnTPyP-CMP

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 NaIO₄ (2 mmol) in H₂O (5 ml) was added to a mixture of alkene or alkane (1 mmol), MnTPyP-CMP (20 μmol), and imidazole (0.2 mmol) in CH₃CN (10 ml). The progress of reaction was monitored by GLC. The reaction mixture was diluted with CH₂Cl₂ (20 ml) and filtered. The resin was thoroughly washed with CH₂Cl₂ and combined washings and filterates were purified on silica-gel plates or silica-gel columns. IR and ¹H NMR spectral data confirmed the identities of the products.

4.3. Catalyst reuse and stability

The stability of MnTPyP-CMP 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, washed with water and acetonitrile, and reused. After the use of catalyst for four consecutive times, the epoxide yield was 92%. No manganese was detectable in the filtrates by atomic absorption spectrometry.

Catalyst stability has been followed by IR and solid state UV. The results indicated that the catalyst after being reused several times showed no detectable leaching or change in its IR and solid state UV spectra.

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