

# The preparation of some polystyrene-supported porphyrinatoiron(III) and their catalysis in hydroxylation of cyclohexane with molecular oxygen

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## Abstract

Some polystyrene-supported porphyrinatoiron(III) with different stereostructure were prepared using a new method and characterized by EA, UV–Vis, IR and EPR. Their catalytic activities in hydroxylation of cyclohexane with molecular oxygen have been found to be high compared with corresponding non-supported porphyrinatoiron(III). The difference of the catalytic activities of these polystyrene-supported porphyrinatoiron(III) are discussed through stereostructure of porphyrinatoiron(III) molecule relative to surface of polystyrene.

*Keywords:* Cyclohexane; Hydroxylation; Iron; Porphyrins; Polystyrene; Supported catalysts

## 1. Introduction

It is well known that synthetic metalloporphyrins are good models for cytochrome P450 as an oxygen transfer enzyme catalyzing various hydrocarbon oxidation reaction. Pretreated organic polymer-supported metalloporphyrins as more useful catalysts for a variety of redox reactions have long been an interesting subject for many research groups and have been extensively studied [1–5]. We have reported the hydroxylation of cyclohexane with molecular oxygen catalyzed by metalloporphyrins as homogeneous catalysts [6]. In this paper, we report the preparation of some polystyrene-supported porphyrinatoiron(III) using a new method and their catalysis in hydroxylation

of cyclohexane with molecular oxygen. The effects of the steric environment of porphyrinatoiron(III) on the catalytic activity have also been examined.

## 2. Preparation and characterization of polystyrene-supported porphyrinatoiron(III)

5-(4-Hydroxyphenyl)-10,15,20-triphenylporphyrin (HPTPP), 5,10,15,20-tetra(4-hydroxyphenyl)porphyrin (THPP), 5,10,15,20-tetra(4-hydroxyl-3-methoxyphenyl)porphyrin (THMPP) and their iron(III) coordination compounds (Fe(III)(HPTPP)Cl, Fe(III)(THPP)Cl and Fe(III)(THMPP)Cl) were synthesized as described in the literature [7–9]. All these compounds were identified by EA, UV–Vis, IR. 10.0

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g chloromethylated polystyrene (17% Cl, 7% divinyl benzene cross-linked) and 3.0 g anhydrous  $K_2CO_3$  were added to 20 ml 1,2-dichloroethane solution of chloroporphyrinatoiron(III) (0.02 mmol). The mixture was refluxed at 80°C for 48 h with magnetic stirring. After cooling, resins were filtered and washed successively with 1,2-dichloroethane, ethanol, acetone, 3.0 mol/l HCl and water. The Soxhlet extraction of the resins was performed with 1,2-dichloroethane until colourless filtrates were obtained. The residues were dried in vacuo at 60°C for 24 h, then the brown products PS-Fe(III)(HPTPP)Cl, PS-Fe(III)(THPP)Cl and PS-Fe(III)(THMPP)Cl were obtained.

In some literature methods [4,5], polystyrene-supported metalloporphyrins were prepared as follows: metal-free porphyrins were reacted with modified polystyrene first, then metal ions were incorporated into polystyrene-supported porphyrins by the reaction of supported porphyrin with excess acetates of corresponding metal ions in acetic acid. This method easily embeds the metal ions in the polystyrene pore and makes it difficult to determine the content of metalloporphyrins. In the method we report here, polystyrene-supported porphyrinatoiron(III) was obtained by the reaction of porphyrinatoiron(III) with chloromethylated polystyrene. This method provided pure products without any free ferric ion in polystyrene pore. Because the reaction of porphyrinatoiron(III) with chloromethylated polystyrene was carried out at 80°C, demetallization of the porphyrinatoiron(III) did not result [10]. So we can determine the porphyrinatoiron(III) content by analyzing the iron content in polystyrene-supported porphyrinatoiron(III). The results are as follows: PS-Fe(III)(HPTPP)Cl, 0.144%; PS-Fe(III)(THPP)Cl, 0.252%; PS-Fe(III)(THMPP)Cl, 0.104%.

UV-Vis, EPR and IR spectra of these synthetic supported porphyrinatoiron(III) were obtained. Solid state UV-Vis spectra showed the Soret band at about 430 nm, EPR data at 77 K ( $g_{\perp} = 5.892$ ,  $g_{\parallel} = 2.003$ ) indicated the presence of high-spin ferric porphyrin complexes. All these are attrib-

uted to the presence of supported porphyrinatoiron(III). Solid state IR spectra showed three new vibration bands of  $\nu(C-O-C)$  at 1245, 1045 and 558  $cm^{-1}$  compared to chloromethylated polystyrene and non-supported porphyrinatoiron(III). These new bands were resulted from the reaction between the  $-CH_2Cl$  group in polystyrene and the  $-OH$  group in the phenyl ring of porphyrinatoiron(III). It is obvious that the porphyrinatoiron(III) is covalently bonded to polystyrene.

### 3. Hydroxylation of cyclohexane with oxygen catalyzed by polystyrene-supported porphyrinatoiron(III)

The catalytic system, consisting of the polystyrene-supported porphyrinatoiron(III) or non-supported porphyrinatoiron(III) ( $4.0 \times 10^{-3}$  mmol), coreductant (1.0 mmol ascorbic acid,  $4.0 \times 10^{-2}$  mmol thiosalicylic acid), acetone-water (9:1, 10 ml) as solvent, was mixed with substrate (cyclohexane, 5.55 mmol) in a specially constructed reaction vessel at  $30.0 \pm 0.5^\circ C$ . Pure oxygen (101.325 kPa) was passed into the solution through the inlet valve of vessel with magnetic stirring. The products were detected and analyzed by GC (Shimadzu GC-9A) equipped with a microprocessor (C-R2A, Japan). n-Pentanol was used as internal standard. The results both in supported porphyrinatoiron(III) systems and non-supported porphyrinatoiron(III) systems are all listed in Table 1. Blank experiments were conducted to check if the hydroxylation is in fact catalyzed by supported porphyrinatoiron(III) in related systems. No reaction was observed in absence of the supported porphyrinatoiron(III) and in the presence of chloromethylated polystyrene. Therefore, the hydroxylation is catalyzed by the supported porphyrinatoiron(III).

As is shown in Table 1, although the reaction did not reach completion (only 4 h), yet cyclohexanol and cyclohexanone were produced in various ratios, with the total turnover numbers ranging from 7.2–26.7, catalyzed by polystyrene-supported porphyrinatoiron(III).

Table 1

The catalytic activity of some polystyrene-supported porphyrinatoiron(III) and their correspondent non-supported porphyrinatoiron(III)

Catalyst	Reaction time (h)	Cyclohexanol ( $\times 10^3$ mmol) (Turnover number <sup>a</sup> )	Cyclohexanone ( $\times 10^3$ mmol) (Turnover number)	Total ( $\times 10^3$ mmol) (Turnover number)
PS-Fe(III)(HPTPP)Cl	4	78.8 (19.7)	27.8 (7.0)	106.6 (26.7)
Fe(III)(HPTPP)Cl	4	20.7 (5.2)	6.8 (1.7)	27.5 (6.9)
PS-Fe(III)(THPP)Cl	4	17.9 (4.5)	11.0 (2.7)	28.8 (7.2)
Fe(III)(THPP)Cl	4	11.9 (3.0)	1.6 (0.4)	13.5 (3.4)
PS-Fe(III)(THMPP)Cl	4	42.6 (10.7)	22.3 (5.5)	64.9 (16.2)
Fe(III)(THMPP)Cl	4	22.6 (5.6)	5.1 (1.3)	27.7 (6.9)

<sup>a</sup> Turnover number = [product] mmol/[catalyst] mmol

The results demonstrate unambiguously that the C–H bond of cyclohexane is activated under mild conditions and the supported porphyrinatoiron(III) has high catalytic activity compared to corresponding non-supported porphyrinatoiron(III). As we know, the catalytic cycle that cytochrome P450 catalyze hydroxylation of substrates by using dioxygen and a reducing agent involves the reduction of its resting ferric state to the ferrous state, the binding of O<sub>2</sub> to the Fe(II) state, the one-electron reduction of the Fe(II)–O<sub>2</sub> intermediate and the formation of active oxygen complex(Fe(V)=O) [11]. We believe that the dispersion and the hydrophobic environment of porphyrinatoiron(III) molecule bonded to the surface of the polystyrene may be advantageous to the formation of Fe(V)=O and is one of the reasons for their high catalytic activity. In addition, that the dispersion of porphyrinatoiron(III) molecule in supported catalyst can effectively prevent the formation of the inactive  $\mu$ -oxo dimer may be another reason for their high catalytic activity.

For the different polystyrene-supported porphyrinatoiron(III), the catalytic activity was found to decrease in the following order: PS-Fe(III)(HPTPP)Cl > PS-Fe(III)(THMPP)Cl > PS-Fe(III)(THPP)Cl. This order is not accord with the order found in non-supported porphyrinatoiron(III) systems. It seems that the catalytic activity of the supported porphyrinatoiron(III) is related to the steric environment of the porphyrinatoiron(III) molecule. Stereostructures of the porphyrinatoiron(III) molecule relative to the

surface of polystyrene are not the same for these three supported porphyrinatoiron(III) systems. The difference of the stereostructure may be arise from the number of 4-hydroxyphenyl in the porphyrin ring. As is shown in Fig. 1, Fe(III)(HPTPP)Cl, with one 4-hydroxyphenyl, is bonded to polystyrene by one ether linkage, while Fe(III)(THPP)Cl, with four 4-hydroxy-

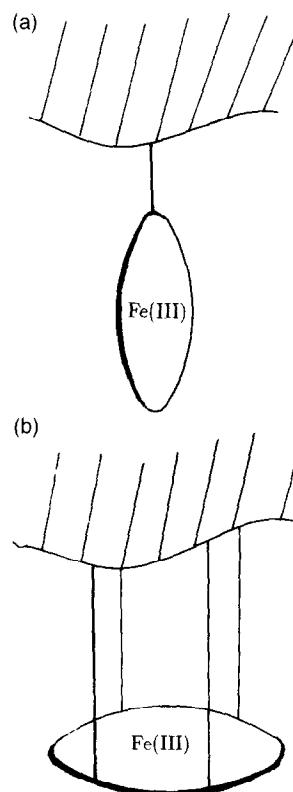


Fig. 1. The stereostructure of porphyrinatoiron(III) relative to polystyrene in polystyrene-supported porphyrinatoiron(III): (a) in PS-Fe(III)(HPTPP)Cl; (b) in PS-Fe(III)(THPP)Cl.

phenyl, can be bonded to polystyrene by four. It is quite evident that PS–Fe(III) (HPTPP)Cl has less steric hindrance. According to the catalytic cycle of cytochrome P450 as indicated above, the stereostructures of porphyrinatoiron(III) relative to polystyrene are believed to play a predominant role here in view of the catalytic process. The lower steric hindrance of PS–Fe(III) (HPTPP)Cl enhances its ability to activate molecular oxygen. For Fe(III) (THMPP)Cl, the presence of 3-methoxy in the phenyl ring gives PS–Fe(III) (THMPP)Cl lower steric hindrance than PS–Fe(III) (THPP)Cl and the catalytic activity of PS–Fe(III) (THMPP)Cl is higher than that of PS–Fe(III) (THPP)Cl.

The studies of the effects of coreductant, solvent, recovery and temperature on the catalytic activity are now in progress.

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