

# Immobilization of metalloporphyrins on polystyrene: Efficient catalysts for aerobic oxidation of alcohols

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Received 11 February 2005; received in revised form 8 April 2005; accepted 9 April 2005

Available online 13 June 2005

## Abstract

Metalloporphyrins of iron and cobalt have been successfully encapsulated for the first time using polystyrene matrix, exhibiting high activity for aerobic oxidation of alcohols mimicking cytochrome P-450 dependent mono oxygenases. This communication provides a simple and environmentally friendly protocol for immobilization of metalloporphyrins (MPs) on to polystyrenes in general, which gives stable,<sup>1</sup> reusable (see Footnote 1) and efficient catalysts for aerobic oxidation of alcohols. These catalysts were characterized by UV–vis as well as diffuse reflectance FT-IR spectroscopy. These catalysts not only have high turnover frequencies but also could be recovered quantitatively by simple filtration and reused without loss of activity. Considering their high dispersing capacity in organic solvents, they will definitely find broad spectrum of applications in the electronic as well as optical fields. This methodology will lead to a potential model to mimic the catalytic action of metalloporphyrins in the niche areas such as catalytic oxidations, drug metabolism, DNA cleavage, photodynamic therapy and many others.

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**Keywords:** Metalloporphyrins; Polystyrene; Immobilization; Micro-encapsulation; Aerobic oxidation; Turnover frequency

## 1. Introduction

An economically advantageous and environmentally friendly process is a topic of growing interest. The oxidation of alcohols to ketones is a pivotal reaction in organic chemistry, both for fundamental research and industrial manufacturing [1]. Traditionally, such transformations have been performed with stoichiometric inorganic oxidants which are usually hazardous or toxic and generate large quantities of noxious byproducts involving laborious work up procedures. However, from both economic and environmental point of view, there is an urgent demand for greener, more atom efficient methods that employ clean oxidants such as molecular oxygen and preferably recyclable catalyst [2]. Much attention has recently been focused on the aerobic catalytic oxidation

of alcohols to the corresponding ketones using metal catalysts [3–9]. Metalloporphyrins (MPs) are known to be highly efficient oxidation catalysts which have been used as photo catalysts in the removal of hazardous pollutants like 4-nitrophenol [10], pentachlorophenol [11], 2,4,6-trichlorophenol [12] from the effluent systems. Immobilizing metalloporphyrins on solid polymer support [13–15] enhances their applicability. Such polymer supported MPs possess several advantages over conventional homogeneous catalysts, such as, possibility of better and easy workup, recyclability and controllability of microenvironments. In few recent reports [16,17], MPs have been successfully anchored on polymer matrix, but they are scarcely [18] used for aerobic oxidations of alcohols. During catalytic oxidations using MPs, under homogeneous conditions, we come across problems such as catalyst separation, dimerization and destruction due to self-oxidation. To circumvent these disadvantages, we now report here a polystyrene supported MP catalysts, micro-encapsulated metalloporphyrins (MCMPs), which exhibit high catalytic activity.

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<sup>1</sup> Please refer to [Supplementary data sheet](#).

Micro-encapsulation, [19, see Footnote 1] is a classic method for immobilizing catalysts onto polymers on the basis of physical envelopment by the polymers and the catalysts are firmly anchored through the electronic interactions between the  $\pi$  electrons of the benzene rings of the polystyrene-based polymers and vacant orbital of catalysts. In our previous work [20], by employing the micro-encapsulation technique, we have reported the metallophthalocynines as efficient catalysts for aerobic oxidation of alcohols.

## 2. Experimental

All chemicals were used as received from different commercial sources (Merck, Aldrich, and Fluka) without further purification. Polystyrene was used as supplied by Thermax (India) Ltd. All metallated TPP's and TDCPP's were prepared in our laboratory by the following reported methods.

- TPP was prepared according to reference [21].
- TDCPP was prepared according to reference [22].
- Metallation of the TPP and TDCPP was performed according to the reference [23].

We have tried various organic solvents such as toluene, dichloromethane, 1,2-dichloroethane and acetonitrile, out of which 1,2-dichloroethane (DCE) was found to be most suitable in terms of catalyst solubility, stability and reactivity.

Diffuse reflectance FT-IR spectra were recorded using Shimadzu 8300 instrument with liquid nitrogen cooled MCTD. The UV–vis spectra were recorded on UV-1601PC Shimadzu UV–vis spectrophotometer. The UV–vis data is mentioned in Table A1 and diffuse reflectance FT-IR values for all the catalysts are reported in Table A2. The effect of temperature on aerobic oxidation of 2-phenyl ethanol in E.D.C. by using MCFe(TPP)Cl and MCFe(TDCPP)Cl is shown in Fig. 3.

### 2.1. Method of encapsulation of MP on polystyrene matrix

Polystyrene (5 g) was dissolved in 50 ml of  $\text{CHCl}_3$  at 50 °C. MP (0.5 g) was added and the dark colored solution was stirred for 1 h. Cooling of the solution to 0 °C and further addition of 50 ml of methanol (drop by drop) separates out a thick, highly viscous mass, which on drying gave a hard material (MCMP) that was crushed manually. Percentage loading was determined by increase in weight and confirmed by Atomic Absorption Spectroscopy (AAS) as well as isolating unencapsulated MPs.

### 2.2. Method for oxidation of alcohols

Oxygen gas (25 ml  $\text{min}^{-1}$ ) was continuously bubbled through a solution of alcohol (5 mmol), MCMP (correspond-

ing to 0.056 mol% of MP) in 1,2-dichloroethane (20 ml) and 2-methyl propanal (15 mmol added to reaction mixture at intervals of 2 h till maximum conversion of reactant to product is achieved). The reaction mixture was vigorously stirred at 40 °C and the progress of the reaction was monitored by TLC. After stirring the reaction mixture for stipulated time, it was concentrated to half. Addition of equal volume of methanol precipitated the catalyst that was filtered and the filtrate was evaporated to dryness to give the product. All products were purified by column chromatography and characterized by physical constants and spectroscopic data (IR,  $^1\text{H}$  NMR and mass spectra).

## 3. Results and discussion

### 3.1. Encapsulation of MPs

By following the micro-encapsulation technique, meso-tetraphenyl porphyrins as well as meso-2,6-dichloro-tetraphenyl porphyrin complexes of cobalt [Co (TPP) and Co (TDCPP)] and iron [Fe (TPP)Cl and Fe (TDCPP)Cl] have been successfully anchored on three different varieties of polystyrenes. Out of which, we have selected polystyrene having average molecular weight 2,00,000 for encapsulation, based on the higher loading and batch to batch consistency in our studies. These encapsulated MCMPs thus prepared have been demonstrated to be stable and effective in the aerobic oxidation of alcohols. In all the cases, the catalysts are recovered quantitatively by simple filtration and reused without loss of activity.

### 3.2. Characterization of the catalyst

These encapsulated catalysts were characterized by UV–vis and diffuse reflectance FT-IR spectroscopy (see Footnote 1). The FT-IR spectrum of polystyrene dominates the spectrum of MCFe(TPP)Cl (Fig. 1) and the latter also shows the major peaks of Fe (TPP)Cl spectrum appearing at 804.3, 1004.9, 1174.0 and 1340.4  $\text{cm}^{-1}$ . Similarly, the UV–vis spectra (Fig. 2) of Fe (TPP)Cl and MC (FeTPP)Cl are found to be identical, both having solet band at 417.85 nm. Similar spectral trend is also observed in all other catalysts after encapsulation (see Footnote 1) (Tables A1 and A2). These observations suggest that there is no distortion of Fe (TPP)Cl after encapsulation.

### 3.3. Catalytic runs

Using these catalysts, the aerobic oxidations of different alcohols have been performed at 40 °C, in 1,2-dichloroethane with 2-methylpropanal as sacrificial reductant. These oxidations result in excellent yields with high turnover frequencies as depicted in Table 1. In the oxidation of 2-phenyl ethanol using catalyst MCFe(TPP)Cl, TOF as high as 661 is achieved.

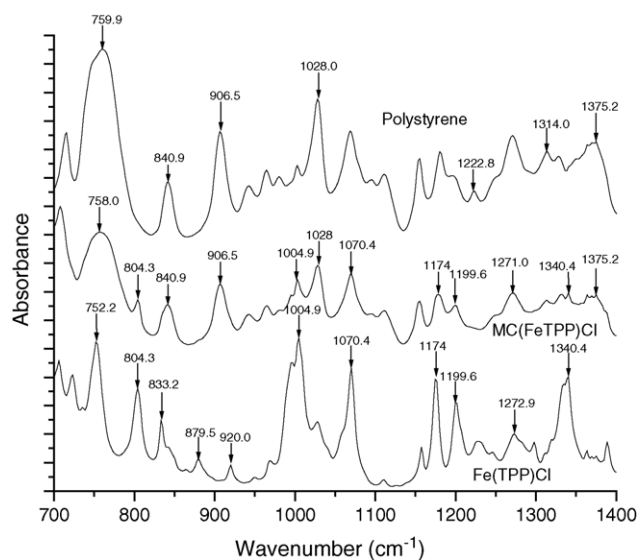


Fig. 1. Diffuse reflectance FT-IR spectra of polystyrene, MC(FeTPP)Cl and Fe(TPP)Cl.

After comparing the TOF values for M(TPP) and MCM(TPP) analogs, it revealed that the TPP catalysts possess marginally higher activity than the MCM(TPP) counterparts. It should also be noted that rates of reactions for MCM(TPP) are faster than those for MCM(TDCPP) as well as the catalysts of iron are marginally more active than those of cobalt. Fig. 3 shows the influence of reaction temperature on conversion of 2-phenyl ethanol to acetophenone, in which the conversion of reactant to product using MCFE(TPP)Cl is 100% at 25 °C, remains constant upto 65 °C

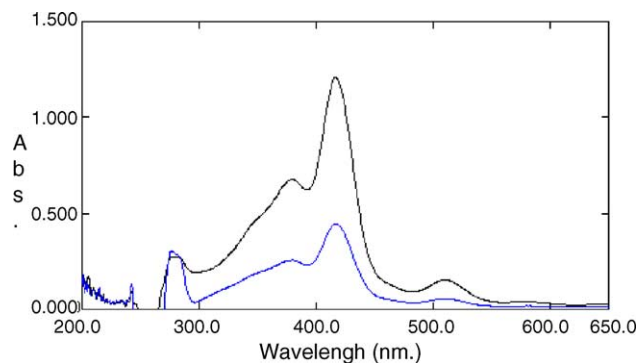


Fig. 2. UV-vis spectra of Fe(TPP)Cl (black) and MCFE(TPP)Cl (blue) in CHCl<sub>3</sub>. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

and slowly decreases as the temperature increases. Similarly conversion using MCFE(TDCPP)Cl catalyst is 100% at 35 °C remains constant upto 70 °C and decreases marginally above 70 °C. Same trend is observed even for cobalt catalysts (see Footnote 1).

It is evident (Table 2) that rate of oxidation increases as catalyst concentration increases. Since, highest TOF achieved is 661 in the entry 2 of Table 2, the catalyst concentration of 0.056 mol% was found to be optimum for all catalytic oxidations.

It can be further noted here that there lies a wide scope for increasing the loading of MPs on to the polymer backbone as per the requisite application where high concentration of MP is desired. Thus, the combination of polymer supported MPs and molecular oxygen as sole oxidant, constitutes an excel-

Table 1

Encapsulated MPs catalyzed oxidation of alcohols by O<sub>2</sub> in DCE, 40 °C<sup>a</sup>

Entry	Substrate	Catalyst <sup>b</sup>	Product	Time (h)	Conversion (%) <sup>c</sup>	TOF <sup>d</sup>	TOF <sup>e</sup>
1	2-Phenyl ethanol	MCFE(TPP)Cl	Acetophenone	2.7	100	661	686
		MCCo(TPP)		3.1	100	576	595
		MCFE(TDCPP)Cl		3.2	100	558	576
		MCCo(TDCPP)		3.3	100	541	558
2	Benzyl alcohol	MCFE(TPP)Cl	Benzaldehyde	2.7	100	661	686
		MCCo(TPP)		3.2	100	558	576
		MCFE(TDCPP)Cl		3.4	100	525	541
		MCCo(TDCPP)		3.6	100	496	510
3	Menthol	MCFE(TPP)Cl	Menthone	6.0	81	241	243
		MCCo(TPP)		6.0	80	238	240
		MCFE(TDCPP)Cl		7.0	79	201	202
		MCCo(TDCPP)		7.0	77	196	198
4	Cyclohexanol	MCFE(TPP)Cl	Cyclohexanone	6.0	82	244	246
		MCCo(TPP)		6.0	81	241	243
		MCFE(TDCPP)Cl		7.0	79	201	202
		MCCo(TDCPP)		7.0	74	203	191

<sup>a</sup> A mixture of alcohol (5 mmol), encapsulated catalyst as metal content (alcohol:metal,  $5 \times 10^3$ :2.8 mol/mol), 1,2-dichloroethane (20 ml) and 2-methyl propanal (15 mmol present in the beginning plus that added as indicated in the experimental section) is treated with O<sub>2</sub> (25 ml min<sup>-1</sup>) at 40 °C.

<sup>b</sup> Encapsulated metal catalysts with polystyrene having average molecular weight of 2,00,000.

<sup>c</sup> Conversions are determined by GC analysis.

<sup>d</sup> Turnover frequencies (TOF) are defined as moles of alcohol reacted per moles of metal per hour.

<sup>e</sup> Turnover frequencies of neat counterparts.

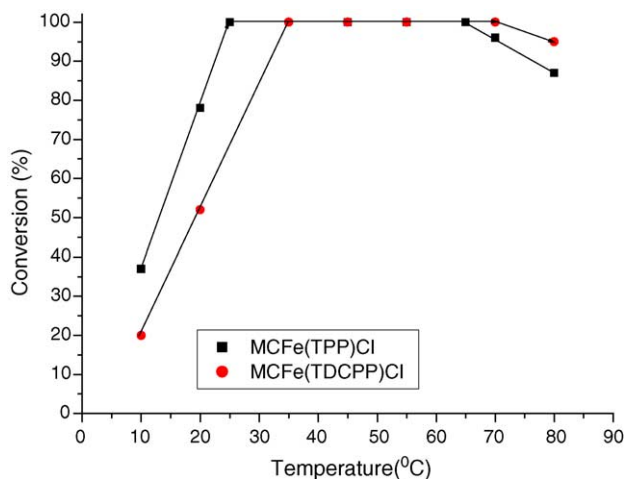


Fig. 3. Effect of temperature on the aerobic oxidation of 2-phenyl ethanol in 1,2-dichloroethane after 4 h using MCFe(TPP)Cl and MCFe(TDCPP)Cl.

Table 2

Effect of catalyst concentration on the aerobic oxidation of 2-phenyl ethanol using MCFe(TPP)Cl catalyst

Entry	Catalyst concentration (mol%)	Reaction time (h)	Conversion (%)	TOF
1	0.112	2.4	100	372
2	0.056	2.7	100	661
3	0.028	6.0	95	565
4	0.014	12.0	80	476

lent example of clean technology process for the oxidation of alcohols.

### 3.4. Stability studies

To test the leaching, after 1 h the reaction mixture was concentrated to half, equal volume of MeOH was added

Table A1

UV–vis spectral data (CHCl<sub>3</sub>)

Sr. No.	Catalyst (refer the figure)	Dilutions	Concentration (N)	$\lambda_{\max}$ (nm)
1	Co(TPP) (Figs. 1 and 3)	0.4 mg diluted to 25 ml	0.02265	543.47(0.219); 430.91(2.336); 419.56(2.081); 315.21(0.316); 276.087(0.426); 246.739(0.231).
2	MCCo(TPP) (Figs. 2 and 3)	5.0 mg diluted to 50 ml	0.1415	545.652(0.159); 431.22(2.190); 413.043(1.215); 318.47(0.249); 271.739(0.358).
3	Fe(TPP)Cl (Figs. 4 and 6)	0.4 mg diluted to 50 ml.	0.0113	577.17(0.040); 510.87(0.153); 417.85(1.21); 380.43(0.67); 346.73(0.45); 279.34(0.27); 242.39(0.09).
4	MCFe(TPP)Cl (Figs. 5 and 6)	2.1 mg diluted to 50 ml	0.0597	580.43(0.017); 509.78(0.056); 417.85(0.45); 378.26(0.258); 277.17(0.302); 242.319(0.119).
5	Co(TDCPP) (Figs. 7 and 9)	0.3 mg diluted to 25 ml	0.0122	554.276(0.26); 430.404(1.306); 416.271(1.091); 319.002(0.298).
6	MCCo(TDCPP) (Figs. 8 and 9)	2.6 g diluted to 50 ml	0.0529	554.276(0.064); 430.404(0.406); 418(0.340); 319.834(0.088); 269.952(0.187); 297.387(0.084); 260.808(0.231); 254.988(0.215).
7	Fe(TDCPP)Cl (Figs. 10 and 12)	0.3 g diluted to 25 ml	0.0122	507.72(0.114); 418.76(0.77); 366.72(0.356); 289.07(0.209); 279.097(0.238); 252.49(0.307).
8	MCFe(TDCPP)Cl (Figs. 11 and 12)	3.2 g diluted to 50 ml	0.0653	507.72(0.029); 418.765(0.218); 366.227(0.093); 294.062(0.035); 269.121(0.136); 260.808(0.177); 254.98(0.156).

to it and filtered (75% conversion by G.C. was achieved at this stage). The filtrate was allowed to react further. No further reaction was detected indicating no leaching of the MP in the solution. Additionally, a UV–vis spectrum of the recovered filtrate did not show any absorption peaks in the corresponding region indicating that possible leaching of MP was below the detection limit (less than 0.02% from MP fixed).

### 3.5. Reusability of encapsulated catalysts

The reusability of the encapsulated catalyst was studied by repetitive oxidation reaction of 2-phenyl ethanol. After completion of the first oxidation, the reaction mixture was concentrated to half and equal volume of methanol was added to it. The precipitated catalyst was washed with methanol by decantation. New portion of substrate stock solution was added to the recovered catalyst to perform a second oxidation following the same procedure once more. The catalytic activity of the recovered solid material remained almost unchanged: 99, 98 and 96% conversions were observed by GC in the 1st, 2nd and 3rd run, respectively.

## 4. Conclusion

In summary, this communication provides an efficient and easy method for immobilization of MPs on to polystyrenes in general which gives stable, reusable, and very effective catalysts for aerobic oxidation of alcohols. The simplicity and extended scope of the system and the versatility of the method towards a wide range of activated and non-activated alcohols makes these polymer supported metalloporphyrins catalyzed oxidation an attractive synthetic tool for the oxidation of alcohols to ketones by molecular oxygen.

Table A2

Diffuse reflectance FT-IR spectral data

Sr. No.	Catalyst [refer the figure]	$\lambda_{\max}$ (cm <sup>-1</sup> )
1	Co(TPP) (Fig. 13)	709.7(1.547); 744.5(1.551); 794.6(1.444); 835.2(1.342); 898.8(0.888); 964.4(0.979); 1006.8(1.557); 1074.3(1.276); 159.2(0.736); 1178.4(0.983); 1207.4(0.896); 1311.5(0.914); 1350.1(1.384)
2	MCCo (TPP) (Fig. 13)	794.6(1.047); 838.9(0.984); 906.5(0.955); 964.4(0.894); 1006.8(1.076); 1072.3(1.029); 1155.3(0.932); 1178.4(0.969); 205.4(0.915); 1272.9(0.963); 1350.1(1.034)
3	Fe (TPP)Cl (Fig. 14)	705.9(1.199); 723.3(1.098); 752.2(1.331); 804.3(1.003); 833.2(0.782); 879.5(0.512); 920.0(0.465); 1004.9(1.359); 1028.0(0.769); 1070.4(1.146); 1157.2(0.592); 1174.6(1.068); 1199.6(0.906); 1272.9(0.685); 1340.4(1.085); 1388.6(0.627)
4	MCFe(TPP)Cl (Fig. 14)	707.8(1.581); 758.0(1.399); 804.3(0.927); 840.9(0.892); 906.5(1.036); 964.4(0.884); 1002.9(1.069); 1028.0(1.168); 1070.4(1.109); 1110.9(0.849); 1155.3(0.917); 1178.4(0.963); 1199.6(0.890); 1271.0(0.974); 1340.4(0.974); 1375.2(0.962);
5	Co (TDCPP) (Fig. 15)	725.2(1.162); 779.2(1.353); 802.3(1.412); 839.0(0.894); 883.3(0.596); 970.0(0.432); 1002.9(1.306); 1076.2(1.035); 1151.4(0.614); 1191.9(0.974); 1238.2(0.616); 1315.4(0.557); 1346.2(1.145); 1377.1(0.608)
6	MCCo (TDCPP) (Fig. 15)	709.7(0.747); 763.7(0.842); 802.3(0.581); 839.0(0.467); 906.5(0.533); 964.4(0.416); 1003.0(0.593); 1028.0(0.654); 1070.4(0.564); 1111.0(0.456); 1155.3(0.527); 1180.4(0.539); 1271.0(0.508); 1346.2(0.537)
7	Fe (TDCPP)Cl (Fig. 16)	732.9(1.065); 779.2(1.380); 806.2(1.416); 837.0(1.037); 885.26(0.729); 991.1(0.685); 1072.3(0.763); 1172.3(0.166); 1153.4(0.322); 1190.0(0.651); 1322.0(0.595)
8	MCFe(TDCPP)Cl (Fig. 16)	761.8(1.138); 806.2(0.573); 839.0(0.385); 906.5(0.673); 964.34(0.434); 1001.0(0.656); 1070.4(0.711); 1153.4(0.551); 1180.4(0.582); 1271.0(0.597); 1328.0(0.579)
9	Polystyrene (Figs. 13–16)	715.5 (0.690); 759.9(1.276); 840.9(0.342); 906.5(0.697); 964.4(0.427); 1002.9(0.461); 1028.0(0.926); 1068.5(0.703); 1110.9 (0.399); 1155.3 (0.508); 1180.4(0.557); 1122.8(0.282); 271.0 (0.670); 1314.0 (0.561); 1375.2(0.627)

The combination of polymer supported MPs and molecular oxygen as sole oxidant constitutes an excellent example of clean technology process for the oxidation of alcohols.

### Acknowledgements

We thank Thermax (India) Ltd. for supplying polystyrenes. We thank Dr. K.N. Ganesh for his encouragement. We are also thankful to D.S.T, New Delhi, for financial support.

### Appendix A

UV–vis spectral data (CHCl<sub>3</sub>) and diffuse reflectance FT-IR spectral data are shown in Tables A1 and A2, respectively.

### Appendix B. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [10.1016/j.molcata.2005.04.041](https://doi.org/10.1016/j.molcata.2005.04.041).

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