

# Manganese *meso*-tetra-4-carboxyphenylporphyrin immobilized on MCM-41 as catalyst for oxidation of olefins with different oxygen donors in stoichiometric conditions

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**ABSTRACT:** Oxidation of olefins with *tert*-butyl hydroperoxide (TBHP), tetra-*n*-butylammonium periodate (TBAP) and potassium peroxomonosulfate (Oxone) in the presence of MCM-41 immobilized *meso*-tetra-4-carboxyphenylporphyrinatomanganese(III) acetate has been studied. The results of this study show better catalytic performance of the heterogonous catalyst using TBHP as oxidant in comparison with Oxone and TBAP in oxidation of the used olefins with the exception of cyclooctene. However, different order of reactivity of various olefins has been observed in the presence of Oxone and TBHP. In spite of the absence of good electron-withdrawing groups at the periphery of porphyrin ligand, the catalyst was recovered and reused (at least four times) without detectable catalyst leaching or a significant loss of the catalytic efficiency. All results have been obtained in the absence of using excess molar ratios of olefin to the oxidant, commonly employed as a strategy to overcome the instability of metalloporphyrins in oxidative conditions.

KEYWORDS: manganese, porphyrin, mesoporous, olefin, heterogeneous catalyst, oxidation.

## INTRODUCTION

Metalloporphyrins have been investigated intensely as biomimetic models of cytochrome P450s, catalases, peroxidases or as transmembrane electron transport agents [1–3]. The use of chemical model systems will help scientists for overcoming the difficulties in working with enzymes *in vivo* and *in vitro*. The main problem in developing these model systems is the high cost of synthetic porphyrins that makes their recovery imperative. Therefore, immobilization of the methalloporphyrins on solid supports not only helps to improve the recyclability of these expensive catalysts but also enhances the catalyst stability toward oxidative degradation. Alumina [4], silica resins have been widely used to anchor metalloporphyrins to solid surfaces. Compared with the zeolite-Y with a small pore size, a large and tunable pore size and also very large specific surface area (approximately 1000 m<sup>2</sup>.g<sup>-1</sup>) of MCM-41 family make them very attractive candidates to host large molecules such as metalloporphyrins [18-20] for heterogeneous catalytic systems. In order to prevent catalyst leaching, the strength of the attachment to the support surface is a very important factor that should be considered during immobilization process. In most metalloporphyrin-based biomimetic oxidation of organic compounds, using purely siliceous MCM-41 or aluminated MCM-41 to encapsulate metalloporphyrins, Ru complexes of electron-rich porphyrins or Mn complexes of electron-deficient porphyrins have been used to overcome the problems associated with the stability of electron-rich metalloporphyrins [21]. In the case of electron-rich Mn-porphyrins, due to the low

[5-8], zeolites [9-14], clays [15], polymers [16, 17] and

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stability of these complexes towards strong oxidants, large excess molar ratios of substrate to the catalyst are usually used to decrease the oxidative degradation of catalyst in reaction conditions [22–26]. However, this strategy decreases the contribution from the stability of metalloporphyrin in the efficiency of the catalyst. In the present work, we have studied the oxidation of olefins with *tert*-butyl hydroperoxide (TBHP), tetra-*n*-butylammonium periodate (TBAP) and potassium peroxomonosulfate (Oxone, 2KHSO<sub>5</sub>'KHSO<sub>4</sub>'K<sub>2</sub>SO<sub>4</sub>) in the presence of a Mn complex of *meso*-tetra-4-carboxyphenylporphyrin (H<sub>2</sub>TCPP) immobilized in mesoporous MCM-41 using the stoichiometric ratios of olefin to oxidant.

## EXPERIMENTAL

#### Instruments and reagents

<sup>1</sup>H NMR spectrum was obtained in dimethyl sulfoxide (DMSO) solutions with a Bruker FT-NMR 500 (500 MHz) spectrometer. The electronic absorption spectra were recorded on a single beam spectrophotometer (Cam Spec-M330) in DMF. The standard linear calibration curve was recorded by using GVC 932 Plus, equipped with air-acetylene flame. An X-Pert MDP diffractrometer with cobalt anode, typically run at a voltage of 40 kV and a current of 30 mA, was used to record the X-ray diffraction patterns. IR spectra were recorded on an ABB Bomem: FTLA 2000–100 in the range of 4000–400 cm<sup>-1</sup> using spectral-grade KBr. The oxidation products were analyzed with a gas chromatograph (Shimadzu, GC-14B) equipped with a SAB-5 capillary column (phenyl methyl siloxane 30 m  $\times$  320 mm  $\times$  0.25 mm) and a flame ionization detector.

Chemicals were purchased from Merck or Fluka chemical companies.

**Preparation of porphyrin and metalloporphyrin precursors.** H<sub>2</sub>TCPP was prepared by successive addition of 4-carboxybenzaldehyde (300 mg, 2 mmol) and pyrrole (0.12 mL, 1.8 mmol) to refluxing propionic acid as described by Adler *et al.* [27]. UV-vis (DMF):  $\lambda_{max}$ , nm 421, 515, 549, 592, 646. <sup>1</sup>H NMR (500 MHz; DMSO):  $\delta_{\rm H}$ , ppm 8.69 (8H, br, β-pyrrole), 8.31–8.33 (8H, d, *o*-phenyl), 8.08–8.11 (8H, d, *m*-phenyl). Mn(TCPP) OAc was prepared according to the literature method [28]. UV-vis (DMF):  $\lambda_{max}$ , nm 477, 577, 609.

**Preparation of MCM-41.** MCM-41 mesoporous silica was synthesized according to the literature [29] using the following procedure: 7.48 g tetradecyl(trimethyl) ammonium bromide was dissolved in 80.0 g water. Then, an aqueous solution of sodium silicate (9.9 g in 30.0 g water) was added dropwise under vigorous magnetic stirring. After 30 min, the pH was adjusted to 10 using 2 M sulphuric acid solution. This mixture was transferred into a Teflon lined autoclave and heated statically at 100 °C for 2 days. The obtained solid material was filtered, washed with water and dried at 60 °C. The sample was then calcined in flowing nitrogen at 550 °C (2 °C/min), then in air at the same temperature for 5 h. The formation of MCM-41 was confirmed by low angle X-ray diffraction pattern.

**Preparation of MCM-41-Mn(TCPP)OAc.** Synthesis of MCM-41-Mn(TCPP)OAc was carried out as follows: to a mixture of MCM-41 (250.0 mg) and Mn(TCPP)OAc (4.0 mg, 0.005 mmol) in 25 mL DMF, 2-(1*H*-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium tetrafluoroborate (TBTU) (2.0 mg, 0.006 mmol) and *N*,*N*'-diisopropylamine (DIPEA) (2.0 mg, 0.01 mmol) were added and the mixture was stirred for 2 days at room temperature [30]. The weakly adsorbed metalloporphyrins on the mesoporous surface were removed through washing the solid products with DMF until the filtrate became colorless. The solid residue was finally dried at room temperature (Scheme 1).

#### General oxidation procedure

Typically, the reaction was initiated by adding the oxidant (0.1 mmol) to the solution of substrate (1 mmol) and the catalyst (4  $\mu$ mol), in a 10 mL glass flask containing 1 mL acetonitrile, under magnetic stirring at room temperature. The solid catalyst was then filtered, and the organic phase was analyzed by GC.

## **RESULTS AND DISCUSSION**

#### Characterization of MCM-41-Mn(TCPP)OAc

The covalent bonding of Mn-porphyrin to MCM-41 mesoporous silica is due to the acid-base reaction between the porphyrin carboxylic acid and hydroxyl group of MCM-41 mesoporous silica in the presence of



Scheme 1. Preparation of Mn(TCPP)OAC-MCM-41



Fig. 1. XRD patterns of: (a) MCM-41 (b) Mn(TCPP)-OAC-MCM-41

2-(1H-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium tetrafluoroborate (TBTU) as a highly effective uronium salt in the presence of N.N'-diisopropylamine (DIPEA) in DMF at room temperature. The prepared catalyst, MCM-41-Mn(TCPP)OAc, was characterized by IR spectroscopy and X-ray powder diffraction (XRD) studies. XRD pattern confirms the incorporation of Mn-porphyrin in the MCM-41 pores. The manganese content of the catalyst was determined by atomic absorption spectroscopy. Based on this value, the Mn content of the catalyst was determined to be about 230 µmol per gram of the catalyst. The XRD pattern of the calcined MCM-41 (Fig. 1) shows a reflection in the 2 $\theta$  range of 1.88°, indexed for a hexagonal cell as d<sub>100</sub>. Upon the inclusion of the Mn-porphyrin complex (MCM-41-Mn(TCPP)OAc, a characteristic diffraction peaks in XRD were still observed at about 2.01° but with slight shift of the  $d_{100}$  reflection to a higher angle (Fig. 1), demonstrating that the long range hexagonal symmetry of the mesoporous host was maintained after inclusion of Mn-porphyrin.

The IR spectrum of MCM-41 showed three bands at 1093, 810 and 461 cm<sup>-1</sup> and they are assigned to stretching vibrations of Si–O–Si (mesoporous framework). Also IR spectrum of MCM-41-Mn(TCPP)OAc, showed a strong band in 1663 cm<sup>-1</sup> which was assigned to the formed esteric bond after immobilization of the manganese porphyrin into MCM-41. Comparatively, weak bands observed at 1499 cm<sup>-1</sup> and around 1391 cm<sup>-1</sup> can be related to the C-H stretching vibrations of the CH<sub>2</sub> groups immobilized on the pore surface of MCM-41.

## **Oxidation of olefins**

Oxidation of cyclooctene with different oxygen donors catalyzed by MCM-41-Mn(TCPP)OAc has been

achieved to find out the effect of different parameters such as solvent, oxidant and co-catalyst on the efficiency of the catalyst. In this regard, TBHP, TBAP and Oxone, have been used as oxidant. The results are summarized in Table 1. With the exception of Oxone, little or no oxidation of cyclooctene has been observed in the absence of the catalyst, for a reaction time of 24 h. Oxidation of cyclooctene in this condition led to formation of cyclooctene oxide with conversions of 19, 5 and 1% for Oxone, TBHP and TBAP, respectively.

According to Table 1 and in spite of the 19% contribution of noncatalytic path in the total conversion, using Oxone gives the highest yield of cyclooctene oxide as the sole product.

Table 2 shows that the 1:1 molar ratio of cyclooctene to oxidant gives higher yield of epoxide compared to the 1:2 one. This observation may be due to the decreased self degradation of the catalyst in the presence of higher amount of cyclooctene [22].

The catalytic activity of Mn-porphyrins has been shown to be strongly enhanced in the presence of different nitrogen donors especially imidazole [31-33]. Different molar ratios of catalyst:imidazole were examined and the 1:10 ratio has been found to be the optimized one (Table 3). The results demonstrate that in the absence of ImH, no product is formed and 1:10 molar ratio of catalyst to ImH gives maximum yield of the product. Beyond this ratio, a decrease in catalytic efficiency is observed which may be attributed to the formation of a MnTCPP(ImH)<sub>2</sub> species [28]. Also, the formation of hydrogen bonds with HSO<sub>5</sub> which prevents the coordination of oxidant to the metal center may be considered as a possible cause of this observation. The stability of active intermediates has been also shown to be significantly increased due to the formation of such hydrogen bonds [34].

Oxidation of various olefins with Oxone was carried out in the presence of MCM-41-Mn(TCPP)OAc under the optimized reaction conditions (Table 4). While reactivity of cyclohexene, styrene and α-methyl styrene was lower than cyclooctene in this catalytic system, the use of TBHP as oxidant led to lower reactivity of cyclooctene with respect to the other olefins (Table 5). This finding may be explained by considering different pathways and active oxidants previously proposed for metalloporphyrin-catalyzed oxidation of alkenes with various oxidants (Schemes 1 and 2) [33-38]; a concerted mechanism with the involvement of a six coordinate Mn(III) one (Scheme 2, I) or a high-valent Mn-oxo species (Scheme 2, II) may be considered for oxidation of cyclooctene with Oxone. On the other hand, in oxidation of styrene,  $\alpha$ -methyl styrene and cyclohexene with TBHP, allylic products have been obtained in addition to epoxide. This observation suggests a radical pathway for the reaction [35, 36]. In the first step, TBHP coordinates to the manganese center of Mn(TCPP)OAc/MCM-41 to give an oxomanganese(V)porphyrin (Scheme 3, I) (or oxomanganese(IV) porphyrin  $\pi$ -cation radical

 Table 1. Oxidation of cyclooctene with various oxidants in the presence of Mn(TCPP)OAC/MCM-41 in acetonitrile<sup>a</sup>

Entry	Oxidant	Epoxide yield, % <sup>b,c</sup>	Time, h
1	TBHP	4	2
2		5	4
3		16	24
4	Oxone	6	2
5		8	4
6		56	24
7	TBAP	1	2
8		2	4
9		11	24

<sup>a</sup> Conditions: the molar ratios for catalyst:ImH:cyclooctene:oxidant are 1:10:25:50. <sup>b</sup> GC yields based on the starting olefin. <sup>c</sup> Cylooctene oxide is the sole product.

 Table 2. Effect of cyclooctene/oxone molar ratio in oxidation of cyclooctene in acetonitrile<sup>a</sup>

Entry	Cyclooctene:oxidant (molar ratio)	Epoxide yield, %
1	1:2	56
2	1:1	68

<sup>a</sup> Conditions: the molar ratios for catalyst:ImH is: 1:10.

**Table 3.** Oxidation of cyclooctene with Oxone in the presence of different amounts of ImH<sup>a</sup>

Entry	Mn(TCPP)OAC/ MCM-41:ImH	Epoxide yield, %
1	1:0	trace
2	1:10	68
3	1:15	51

<sup>a</sup> Conditions: the molar ratios for catalyst:ImH:cyclooctene:oxidant are 1:X:50:50.

(Scheme 3, **II**)) which acts as an active species. This active species can transfer oxygen atom to the double bond to form epoxide product or cause allylic oxidation via H-atom abstraction. According to Tables 4 and 5, with the exception of cyclooctene, TBHP is a stronger oxidant relative to Oxone in oxidation of the other olefins. One of the parameters influencing the rate of oxidation reaction is the solubility of oxidant in the used solvent. TBAP and TBHP are soluble in acetonitrile but Oxone is completely insoluble. However, the stability of metalloporphyrin towards oxidative degradation with different oxidants should be also considered in this comparison. Our previous studies demonstrated significant degradation of the metalloporphyrins in the presence of Oxone as oxidant [37, 38].

Table 4. Oxidation of various olefins with Oxone in thepresence of  $Mn(TCPP)OAC/MCM-41^{a}$ 

Entry	Alkene	Conversion, %	Epoxide yield, %
1		4	0
2	Me	11	9
3		68	68
4	$\bigcirc$	2	2

<sup>a</sup> Conditions: the molar ratios for catalyst:ImH:cyclooctene:oxidant are 1:10:50:50 and reaction time: 4 h.

**Table 5.** Oxidation of various olefins with TBHP in the presence of Mn(TCPP)OAC/MCM-41 in acetonitrile<sup>a</sup>

Entry	Alkene	Conversion, %	Selectivity, % (epoxide)
1		23	35
2	Me	56	27
3		17	100
4		51	14

<sup>a</sup> Conditions: the molar ratios for catalyst:ImH:cyclooctene:oxidant are 1:10:50:50 and reaction time: 4 h.

#### Catalyst reusability

Oxidation of olefins with Oxone catalyzed by metalloporphyrins is accompanied by extensive degradation of the catalyst within the first few minutes of reaction [37, 38]. Mn(TCPP)OAc has been shown to be remarkably degraded within the first 5 min after the addition of the oxidant to the reaction mixture. Interestingly, under the conditions given in Table 1, the catalyst was consecutively reused at least four times without detectable catalyst leaching or a significant loss of epoxide yield (Table 6). In other words, the degradation of Mn(TCPP)OAc has been significantly decreased by immobilization of the metalloporphyrin on MCM-41. The enhanced efficiency of the immobilized catalyst with



Scheme 2. Proposed catalytic cycle for oxidation with Oxone in the presence of Mn(TCPP)OAC/MCM-41



Scheme 3. Proposed catalytic cycle for oxidation with TBHP in the presence of Mn(TCPP)OAC/MCM-41

Table 6. Efficiency of the recovered catalyst for
oxidation of cyclooctene with Oxone for a reaction
time of 24 h

Entry	Rinsing solvent	Epoxide yield, %
1		67
2	CH <sub>3</sub> CN	74
3	CH <sub>3</sub> CN	63
4	CH <sub>3</sub> CN	60
5	CH <sub>3</sub> CN	50

<sup>a</sup> The molar ratios for catalyst:ImH:alkene:oxidant are 1:10:50:50.

respect to Mn(TCPP)OAc seems to be due to decreased oxidative degradation of the former relative to the latter.

# CONCLUSION

In summary, MCM-41 immobilized meso-tetra-4carboxyphenylporphyrinatomanganese(III) acetate, a bearing poor electron-withdrawing Mn-porphyrins groups at the meso-positions, has been used as a reusable catalyst for efficient oxidation of olefins with TBHP, TBAP and Oxone using the stoichiometric ratios of olefin to the oxidant. The results show significant increase in the stability of the heterogenized Mn-porphyrin towards oxidative degradation under reaction conditions compared to the non-immobilized one. Different order of reactivity of olefins in the case of the Oxone and TBAH suggests different reaction pathways in the presence of the two oxidants. With the exception of cyclooctene, the catalysts have been more efficient in the presence of TBHP as oxidant compared to Oxone and TBAP.

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