Reactivity of polyhalogenated and zeolite-encapsulated metalloporphyrins in oxidation with dioxygen

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Abstract

Catalytic activity of some halogenated and perhalogenated metalloporphyrins in the reaction of cyclohexane oxidation with dioxygen in the presence of aldehyde have been investigated. Also, the effects derived from encapsulation of some metalloporphyrins in zeolite micropores and their influence on the reaction course have been examined. Both, the changes in the structure and the encapsulation have been found to exert significant effect on the catalyst stability, activity and selectivity. From the changes in the distribution of the main reaction products some important conclusions concerning the reaction mechanism are drawn.

1. Introduction

The development of efficient catalytic systems for oxidation, mimicking the action of cytochrome P-450 based enzymes has received a lot of attention [1,2]. Synthetic metalloporphyrins have been used to catalyze the transfer of an oxygen atom from great variety of oxidizing agents into hydrocarbon molecules. The main drawback for practical use of protein-free metalloporphyrins is their potential self-destruction by oxidative degradation. Therefore efforts have been done to circumvent this problem by creating more resistant porphyrin ligands. It has

been found that extensive halogenation of the porphyrin macrocycle enhances both the stability and the catalytic activity of the porphyrin complexes [3–10]. The stability of the metalloporphyrin catalysts may be also improved by binding to supports or by encapsulation in microporous materials such as zeolites [11,12].

From the point of view of potential practical use of the metalloporphyrin-based systems for oxidation the research emphasis should be directed to the use of cheap, easily accessible and environmentally friendly oxidants such as molecular oxygen and hydrogen peroxide. Molecular oxygen is not an efficient oxidant under mild conditions and can only be activated in the specific biological environment. In reac-

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tions carried out with simple synthetic metallo-porphyrins it requires the presence of a reductive agent [13].

To find an efficient catalytic system for oxidation of hydrocarbons with molecular oxygen, we have investigated the reaction of cyclohexane with dioxygen in the presence of propionaldehyde, and halogenated as well as perhalogenated metalloporphyrins have been used as catalysts. For the sake of comparison of the effects derived from the enhanced stability of the metalloporphyrin complexes some reaction have been carried out with metalloporphyrins encapsulated in zeolites.

2. Experimental

Reactions were carried out in a thermostated glass reactor of 10 ml volume equipped with magnetic stirrer. The reactor was connected to a system of magnetic valves, which when the gas pressure dropped, supplied oxygen to maintain a constant, normal pressure over the reacting solution. In a standard experiment the reactor was filled with oxygen under normal pressure and catalyst was introduced. Then the solution of benzene, cyclohexane and propionaldehyde was added. The reagent mixture of total volume 2 ml was vigorously stirred and the reaction was carried out for 40 min. The progress of the reaction was followed by measuring the oxygen uptake. After 30–40 min the oxygen uptake curves were already at plateau, indicating that the reaction was completed. The molar ratio of the reagents was: [catalyst]:[propionaldehyde]:[cyclohexane] = 1:475:450 or 1:225:450 in the reactions carried out with the zeolite samples.

The yields of cyclohexanol and cyclohexanone were determined using a GC Chrom 5 with columns filled with Carbowax 20 M. The yield of carbon dioxide was determined using a TCD with columns filled with Porapak QS. The amount of peroxy acid was determined by iodometric titration. The yields given in the tables

correspond to the amounts of products found in the reacting solutions at the end of the reaction.

In a blank experiment carried out in the absence of any catalyst the yields obtained were of an order of magnitude lower than those found in the catalytic reactions with the lowest turnovers.

The reproducibility of the experimental results was within 10%. Hence significant interpretations of the differences in the ketone: alcohol ratios found for various reactions are justified for the values exceeding 0.2.

Benzene used as solvent as well as cyclohexane, purchased from POCH Gliwice, were of pure grade. Propionaldehyde produced by Fluka was redistilled under argon before each series of measurements.

Metalloporphyrins were synthesized according to the procedure described in [3,14–16] and their purity checked by taking UV–Vis and NMR spectra.

Encapsulation of some metalloporphyrins in zeolite micropores was achieved by using the procedure described in [11]. Ultrastable NH_4-Y zeolite (SK–Union Carbide) (1 g), prepared according to the procedure described in [17], was suspended in distilled water (25 ml) and the mixture was degassed by bubbling nitrogen for two hours at room temperature. $MnSO_4 \cdot H_2O$ (0.5 g) was dissolved in degassed distilled water (3 ml) under nitrogen and the solution was added to the zeolite suspension. The resultant mixture was stirred at 80–90°C for 2 h and then filtered. The residue was washed with water until SO_4^{2-} ions were completely removed. Then the residue was rinsed with methanol and dried. A similar procedure was employed for preparation of cobalt and iron encapsulated samples using $CoCl_2$ and $FeSO_4 \cdot 7H_2O$ complexes. The loadings of these metals in the zeolite as shown by atomic absorption analysis were as follows: Fe 1.25%, Mn 1.51% and Co 1.1% by weight.

The following procedure was employed to synthesize the porphyrin complexes. The metal-containing zeolite sample (0.25 g) was suspended in degassed methanol (25 ml), then
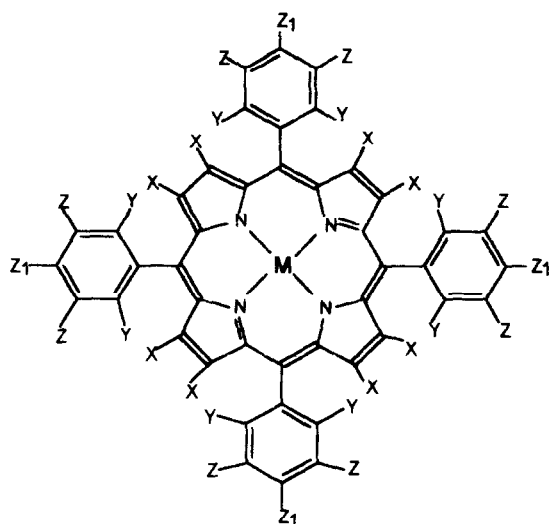
LIGAND	X	Y	Z	Z_1
TTP	H	H	H	CH_3
TMP	H	CH_3	H	CH_3
TDCPP	H	Cl	H	H
TPFPP	H	F	F	F
TDCP-β-Cl₈P	Cl	Cl	H	H

Fig. 1. Structures of the substituted metalloporphyrins. TTP: 5,10,15,20-tetrakis(tolyl)porphyrin; TDCPP: 5,10,15,20-tetrakis(ortho-dichlorophenyl)porphyrin; TPFPP: 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin; TDCP-β-Cl$_8$-P: 2,3,7,8,12,13,17,18-octachlorotetrakis(ortho-dichlorophenyl)porphyrin; TMeP: 5,10,15,20-tetrakis(methyl)porphyrin.

acetaldehyde (1 ml) and pyrrole (0.75 ml) were added. The resulting solution was refluxed under nitrogen for 2 h and then allowed to stand for 24 h at room temperature. Filtration, intensive washing with methanol and dichloromethane, and drying were carried out in air. Diffuse reflectance visible spectra of the catalyst powders were recorded on a Kontron UV IKON 820 spectrophotometer. The Soret band around 500 nm is easily seen, indicating the presence of the porphyrin structure. The results from the elemental analysis of the encapsulated samples of the cobalt, iron and manganese tetramethylporphyrins showed that the ratios of metal:ligand were equal to 1. X-ray analysis of the zeolite sample containing Fe(TMeP) showed enlargement of the zeolite cell due to the incorporation of the complex.

The structures of the complexes are shown in Fig. 1.

3. Results and discussion

The main products of cyclohexane oxidation were cyclohexanol and cyclohexanone. Simultaneously, the products of the aldehyde oxidation, such as peroxy acid and carbon dioxide, were found. As can be seen from the data presented in Tables 1 and 2 the efficiency of the system as well as the distribution of the main reaction products depend on both the character of the metal centre and the structure of the porphyrin ligand. Table 1 shows the effects derived from such metal centres as manganese(III), iron(III), cobalt(II) and cobalt(III) bound to tetra-ortho-dichlorophenylporphyrin ligand. The order of their activities expressed by turnovers i.e. the

Table 1
Distribution of the main reaction products in the reactions catalyzed by tetra-ortho-dichlorophenylporphyrin complexes

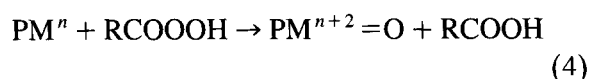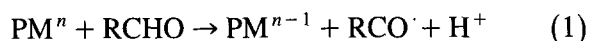| M(TDCPP) (X) M =	Alcohol yield mole × 10^5	Ketone yield mole × 10^5	Ketone:alcohol ratio	Peroxy acid yield mole × 10^5	CO_2 yield mole × 10^5	Turnover [a]	[A + K]/[Cy]	Oxygen consumption mole × 10^4
Mn(III)	2.5	4.1	1.6	4.0	46	16.5	3.0	9.4
Fe(III)	2.5	2.1	0.8	10	168	11.5	2.6	6.75
Co(II)	1.9	2.2	1.1	34	63	10.2	2.2	11.0
Co(III)	2.6	3.6	1.4	104	35	15.5	3.3	11.8

Conditions: [catalyst] = 2 × 10^{-3} M, [propionaldehyde] = 0.95 M, [cyclohexane] = 0.9 M. Temperature 30°C.
[a] Turnover = [A + K]/[cat.], Cy = cyclohexane, reaction time 40 min.

ratio of the produced alcohol and ketone to the catalyst concentration is following:

$$Mn(III) \approx Co(III) > Fe(III) > Co(II)$$
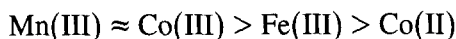
Although the differences in turnovers are not large, there are important differences in the product distributions, and also in the ratio of the ketone and alcohol generated, which depend on the metal used. These data supply information concerning the mechanism of the reactions. As was shown in our earlier papers, [18–20] the investigated system employs two oxidants: molecular oxygen and peroxy acid. Dioxygen participates mainly in reoxidation of the metal centre previously reduced by the aldehyde (Eqs. 1 and 2), and the acyl radicals generated in Eq. 1 react with dioxygen to yield peroxy acid (Eq. 3), which in turn oxidizes metalloporphyrins to their active, oxygen-containing forms capable of introducing an oxygen atom to the hydrocarbon molecule. Schematically this process may be described by the following sequence of the reactions:

$$PM^n + RCHO \rightarrow PM^{n-1} + RCO^{\cdot} + H^+ \qquad (1)$$

$$PM^{n-1} + O_2 \rightarrow PM^n \cdots O - O^{\cdot} \qquad (2)$$

$$RCO^{\cdot} + O_2 \overset{RCHO}{\rightarrow} RCOOOH \qquad (3)$$

$$PM^n + RCOOOH \rightarrow PM^{n+2} = O + RCOOH \qquad (4)$$

Initiation of the reaction proceeds also by abstraction of a hydrogen atom from the hydrocarbon molecule by a high-valent metal centre to yield alkyl radicals (Eq. 5) which can react directly with dioxygen to yield carbonyl compounds such as ketones [21,22]. The C–H bond energy in hydrocarbons is higher than that in the aldehyde and therefore a high oxidation potential at the metal centre is necessary to carry out reaction 5.

$$PM^n + RH \rightarrow [M^{n-1} + RH^{+\cdot}]$$
$$\rightarrow M^{n-1} + R^{\cdot} + H^+ \qquad (5)$$
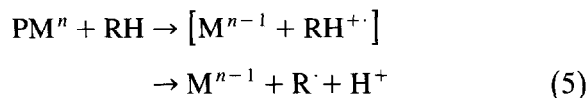
In the case of Co(III) porphyrin complex, such a reaction mechanism is likely to operate from the very beginning, resulting in a higher efficiency of the Co(III) system when compared with Co(II). The latter must be first oxidized by dioxygen or the generated peroxy acid according to Eq. 6. The generated RCOO · radicals undergo decomposition to yield CO$_2$ (Eq. 7).

$$PCo(II) + RCOOOH \rightarrow PCo(III)^+ + RCOO^{\cdot} + OH^- \qquad (6)$$

$$RCOO^{\cdot} \rightarrow R^{\cdot} + CO_2 \qquad (7)$$
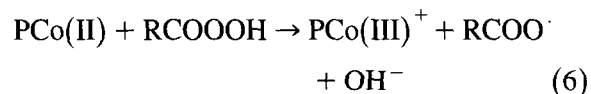
In contrast, the Co(III) complex is not effective in the decomposition of peroxy acid as shown by the large amount of the acid found at the end of reaction. The activity of iron(III) tetra-ortho-dichlorophenylporphyrin is similar to that of the Co(II) porphyrin, however, the former appeared more reactive in the decomposition of peroxy acid to carbon dioxide.

Manganese porphyrin which is the most efficient catalyst in the reaction investigated forms

Table 2
Distribution of the main reaction products in the reaction catalyzed by manganese porphyrins with various ligands

(X)MnP P =	Alcohol yield mole × 10^5	Ketone yield mole × 10^5	Ketone:alcohol ratio	Peroxy acid yield mole × 10^5	CO$_2$ yield mole × 10^5	Turnover [a]	[A + K]/[Cy]	Oxygen consumption mole10^4
TDCPP	2.5	4.1	1.6	4	46	16.5	3.0	9.4
TDCPβCl$_8$P	1.8	7.8	4.3	16	75	24	5.0	12.0
TPFPP	1.9	3.4	1.8	0	35	13.2	2.8	5.5
TTP	0.9	1.2	1.4	0	48	5.4	–	–

Conditions as in Table 1.
[a] Turnover = [A + K]/[cat.].

two active forms in the presence of peroxy acid: PMn(IV)=O and PMn(V)=O$^+$ [23,24]. The latter is effective in hydroxylation reaction [25].

The effects derived from the porphyrin ligand bound to the manganese centre are shown in Table 2. All three types of porphyrin ligands are present: simple porphyrin (TTP), halogenated on phenyl rings (TDCPP and TPFPP) and perhalogenated i.e. having chlorine substituents in both the phenyl and pyrrole rings. The character of the ligand present in the metalloporphyrin molecule influences strongly the activity of the catalyst as well as its selectivity. In agreement with our expectations manganese porphyrin bearing the perhalogenated ligand was the most active and the yield of ketone significantly exceeded the yields obtained with other porphyrins.

The results of the experiments in which cyclohexanol rather than cyclohexane was oxidized under the same conditions, in the presence of the cobalt and manganese halogenated (TDCPP) and perhalogenated (TDCP-β-Cl$_8$P) porphyrins showed that about 50–60% of alcohol is transferred to ketone. A large excess of ketone over alcohol found for the manganese perhalogenated porphyrin indicates that the reaction pathway of direct oxidation of the alkyl radicals with dioxygen to yield ketone is also operating. Manganese porphyrins with halogen substituents present only on phenyl rings were less active and the lowest activity was observed for tetratolylporphyrin which is a simple unprotected porphyrin. The influence of the ligand on the catalytic activity of metalloporphyrins should

be discussed in terms of its stability and resistance to the oxidative degradation as well as the electron-withdrawing effect. It has been shown that a large number of halogen atoms present at the porphyrin periphery results in a higher oxidation potential at both the metal centre and the porphyrin ligand, leading to increased stability of the complex under oxidizing conditions and rendering the metal centre more electrophilic and hence more catalytically active [26]. Extensive perhalogenation leads to a distortion of the porphyrin ring from planarity which creates favourable conditions for the coordination of substrates [16,27]. However, it is difficult to discriminate between the effects derived from the steric and electronic factors.

Stability of the metalloporphyrins used was checked spectrophotometrically by taking UV–Vis spectra at the beginning and at the end of the reactions. However, at lower concentrations, only polyhalogenated metalloporphyrins were recovered at the end of the reaction as proved by the presence of the Soret band.

Metalloporphyrins may also be stabilized by encapsulation in zeolites. Table 3 contains the results obtained in the reaction of cyclohexane oxidation with molecular oxygen in the presence of propionaldehyde, catalyzed by manganese(III), iron(III) and cobalt(II)/(III) tetramethylporphyrins (TMeP) encapsulated in the zeolite micropores. Such an unprotected porphyrin would immediately lose its monomeric character, due to the interactions of π systems of the macrocycles, in solution. Encapsulation preserves its identity as proved by taking the re-

Table 3

Distribution of the main products of the reactions catalyzed by the encapsulated metalloporphyrins

M(TMeP) M =	Alcohol yield mole × 10^5	Ketone yield mole × 10^5	Ketone:alcohol ratio	Peroxy acid yield mole × 10^5	CO$_2$ yield mole × 10^5	Turnover [a]	[A + K]/[Cy]	Oxygen consumption mole × 10^4
Mn(III)	1.3	1.6	1.2	1.2	70	7.2	1.5	2.5
Fe(III)	1.8	2.1	1.1	71.0	57	9.7	2.1	4.6
Co(II)/(III)	2.0	3.9	1.9	1.0	97	14.7	3.1	4.6

Conditions: [catalyst] = 2 × 10^{-3} M, [propionaldehyde] = 5 × 10^{-1} M, [cyclohexane] = 0.9 M, temperature 40°C, reaction time 40 min.
[a] Turnover = [A + K]/[cat.], Cy = cyclohexane.

Table 4
Distribution of the main products of the reactions catalyzed by the encapsulated metal ions

Metal ion	Alcohol yield mole $\times$ 10^5	Ketone yield mole $\times$ 10^5	Ketone/alcohol ratio	Peroxy acid yield mole $\times$ 10^5	CO_2 yield mole $\times$ 10^5	Turnover [a]	[A + K]/[Cy]	Oxygen consumption mole $\times$ 10^4
Mn(III)	1.38	1.96	1.4	1.4	104	8.3	1.8	3.0
Fe(III)	1.9	2.2	1.1	69.0	48	10.2	2.2	2.5
Co(II)/(III)	1.0	1.0	1	0	75	5.2	1.1	2.3

Conditions as in Table 3.
[a] Turnover = [A + K]/[cat.].

flectance spectrum which was identical with that published in [11]. For the sake of comparison the data obtained for the systems in which only metal ions, without the porphyrin ligand, were introduced into the zeolite micropores, are displayed in Table 4. It may be seen that only cobalt porphyrin encapsulation brings about an important effect: both the turnover and the yield of the main reaction products (i.e. alcohol and ketone) are increased and the amount of ketone is two times higher than that of alcohol. The high ratio of ketone:alcohol obtained with the

encapsulated cobalt porphyrin suggests that the reaction proceeds to a large extent by formation of alkyl radicals (according to Eq. 5) and their further reaction with dioxygen to yield ketone. This fact together with the high oxygen uptake found for this porphyrin lead to the conclusion that the encapsulation in the zeolite micropores creates favourable conditions for oxygen binding and maintaining the high oxidation state of the cobalt centre. It is a well known fact that cobalt(II) porphyrins bind and activate dioxygen to its superoxo form which is quite stable when
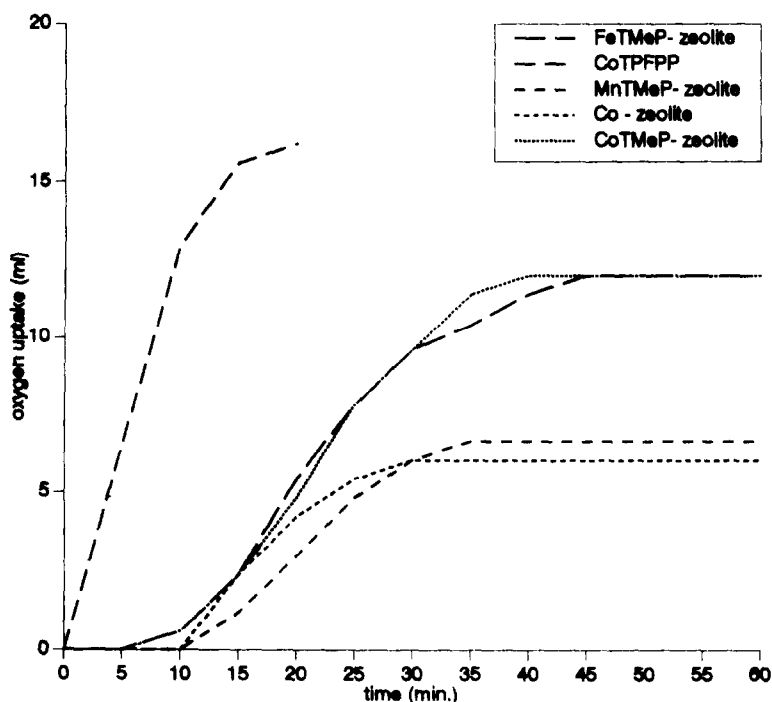

Fig. 2. Consumption of dioxygen during the course of the reactions.

compared with oxygenated adducts of the iron or manganese porphyrins.

Fig. 2 shows the oxygen uptake during the reactions catalyzed by the encapsulated metalloporphyrins. For the sake of comparison the oxygen uptake curves obtained for not encapsulated Co(TPFPP) as well as for the zeolite sample containing only cobalt ions are shown. It can be seen that the curves obtained for the zeolite samples show an induction period presumably needed for diffusion of the substrates into the catalyst centres involved in the zeolite micropores. Oxygen consumption for the encapsulated iron porphyrin is similar to that of the cobalt complex, however, lower yields of alcohol and ketone together with the high amount of carbon dioxide evolved indicate that ineffective decomposition of peroxy acid is the predominant pathway of the reaction. Contrary to cobalt(III) porphyrin, the iron(III) complex, due to its low oxidation potential, is not capable of abstracting a hydrogen atom from the hydrocarbon molecule and the oxo-iron species, even if generated, are not efficient in this system. Similar behaviour is observed for manganese porphyrin. The oxygen uptake observed for the encapsulated cobalt porphyrin is evidently higher than that found for the encapsulated cobalt ions.

It is noteworthy that while in the purely homogeneous systems the amount of the oxygen consumed was almost quantitatively recovered in the oxidation products, in the reactions with zeolite-encapsulated catalysts the oxygen uptake was lower than the amount found in the products. It should be noted, however, that the zeolite contains oxygen absorbed inside the micropores which becomes replaced by the liquid components of the system at the beginning of the reaction being simultaneously consumed in the reaction with substrates. As estimated on the basis of the gas absorption ability of the zeolite used, the missing amount of oxygen is covered by oxygen present in the zeolite micropores. Also, a large amount of CO_2 evolved perturbs the oxygen uptake: its partial pressure adds to the oxygen pressure in the reactor and blocks its
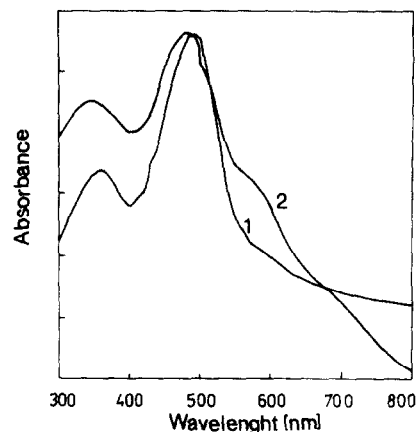

Fig. 3. Diffuse reflectance spectra: effect of TPP binding to Mn- (spectrum 1) and Co- (spectrum 2) exchanged zeolite.

supply from the pump. Such was the case with the ClFe(III)TDCPP catalyzed reaction (Table 1).

The porphyrin-free zeolite samples which were colourless at the beginning of the reaction became coloured as the reaction proceeded, indicating the migration of the metal ions from the zeolite into the reacting solution. This was not the case with the samples containing porphyrin complexes.

Manganese and cobalt tetraphenylporphyrins have also been synthesized in the zeolite micropores as shown by the reflectance spectra shown in Fig. 3. However, no products of cyclohexane oxidation were found, and small amounts of peroxy acid detected correspond to the negligible amounts of the oxygen consumed. This lack of activity may be related to the steric hindrance created by large phenyl rings impeding access of substrates to the metal centres in zeolites.

4. Concluding remarks

Diffuse reflectance spectra, X-ray analysis and the course of the oxygen uptake curves indicate that the described porphyrin complexes have been encapsulated in the zeolite micropores.

Cobalt(III) porphyrins give similar turnovers and product distributions for both, the strictly homogeneous and the heterogenized systems. This fact may be explained in terms of great affinity of Co(II) complexes towards dioxygen and the properties of the oxygenated adduct. It seems that the encapsulation creates favourable conditions for binding dioxygen and stabilizing a high oxidation state of the cobalt centre, allowing abstraction of hydrogen from the hydrocarbon molecule and giving rise to the oxidation reaction. A similar effect is obtained with the electron-withdrawing TDCPP ligand, which stabilizes a high oxidation state of the metal and increases its oxidation potential. In contrast, encapsulation of manganese and iron porphyrins yielded rather poor results when compared with the homogeneous systems employing TDCPP or TPFPP ligands. The oxidation potentials of manganese(III) and iron(III) porphyrins are much lower than that of cobalt(III) porphyrin and therefore these porphyrin complexes are not effective in splitting C–H bonds. Catalytic oxidations are effected by high-valent oxo-metal species, which even if generated, are not very effective in the zeolite catalysts.

Of all the catalysts investigated here, the manganese porphyrin carrying sixteen chloride substituents at its periphery appeared the most active. This is due to its high stability, enhanced electron deficiency at the metal centre and easy access of the reagents to the catalytic site.

Acknowledgements

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