Review

Electropolymerized manganese porphyrin films as catalytic electrode materials for biomimetic oxidations with molecular oxygen

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Abstract

Some recently published results on the electrocatalytic oxidation of hydrocarbons, olefins and a thioacetamide derivative by molecular oxygen are described. The catalytic process involves electropolymerized manganese porphyrin films as electrode materials in acetonitrile or dichloromethane solution containing 1-methylimidazole and benzoic (or acetic) anhydride, with acceptable catalytic efficiency (up to 500 turnovers of the catalyst per hour) and faradaic yield (up to 98%). Confinement of the catalyst on the electrode surface markedly improves its stability compared with that of homogeneous electrocatalytic systems and makes the supported porphyrin stable and reusable.

Keywords: Manganese; Porphyrins; Electropolymerized films; Polymer films; Biomimetic oxidation; Oxygen; Modified electrodes; Electrocatalysis

Abstract

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1. Introduction

The desire to mimic enzymatic systems has led to an active area of research involving synthetic porphyrin models of enzyme active sites, especially for monooxygenase enzymes of the cytochrome P-450 [1–3]. An analysis of the studies dealing with the selectivity, efficiency and stability for both synthetic porphyrin models and natural systems has shown that efficiency arises from the control of the environment of the enzyme active site [3–6]. Thus, in a first approach, the design of synthetic supramolecular architecture for porphyrin models with an elaborated steric environment (such as picnic basket porphyrins, strapped porphyrins, etc...) has been the subject of intense effort [7]. A similar approach in concept which has been advanced during the past decade involves replacement of the protein envelop of natural enzymes by a mineral or organic polymeric matrix [8–11]. This strategy is based on the fact that a polymeric matrix may provide the best arrangement for a catalytically active centre as well as preventing auto-destruction of the enzyme model during catalysis.

An especially fruitful strategy for modeling the enzymatic systems has been the use of polymeric porphyrins as molecular devices combined with electrochemistry. Therefore, the electroassisted design of modified electrode surfaces by organized porphyrinic structures may play a significant role in achieving biomimetic hydrocarbon oxidations with molecular oxygen. Efficient high-valent metal-oxo porphyrin complexes, the reactive oxygenating intermediates, have been postulated in numerous systems [3,12–30]. Electroassisted formation of the oxo species requires the enzyme model plus molecular oxygen, an activator (such as anhydride or acid) and one or two axial ligands (such as imidazole) as shown in Fig. 1 and as described by several groups [19–24,26,28,30].

In fact, one of the challenges in developing this concept is the necessity to achieve rapid electron transfer to the enzyme model active site

at the electrode surface [31–35]. Conducting polymers such as polypyrrole, polythiophene or polyaniline are attractive as possible materials for this approach [31–34,36–40]. In this review, we address some of the rare and recent published works that have involved electropolymerized metalloporphyrin films in the field of electroassisted biomimetic catalysis.

2. Electrochemical design of the metalloporphyrin film catalysts

Electrochemical polymerization is an elegant, attractive and easy strategy for the immobilization of catalysts [31–33,36–38] and especially for metalloporphyrins on the surface of electrodes. The principle is based on the electrochemical oxidation (or reduction) of a suitably designed monomer to form a polymeric film incorporating the metal complex.

It has been shown that electrooxidative polymerization of pyrrole-substituted cobalt and manganese porphyrins (see Fig. 2) leads to the formation of films having the electrochemical properties of the monomeric complex [28,40–48]. In a typical experiment, the electrochemical polymerization of pyrrole-substituted porphyrins is achieved by cyclic voltammetry of acetonitrile or dichloromethane solutions containing the complex monomer and the supporting electrolyte, through a well-defined potential range. Fig. 3 shows the cyclic voltammograms of the
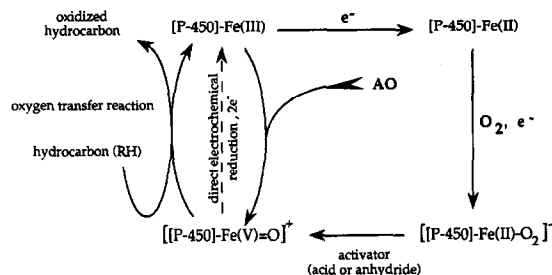

Fig. 1. Simplified catalytic cycle for the oxidation of hydrocarbons (RH) by molecular oxygen (long cycle) or by oxygen atom donors AO (short cycle) and cytochrome P-450 (or its synthetic models).

pyrrole-substituted manganese porphyrin **2b** [43] in acetonitrile + 0.1 M Bu_4NBF_4 solution, at a vitreous carbon disk electrode. They exhibit the redox system corresponding to the Mn(III)/Mn(II) process at $E_{eq} = -0.320$ V/SCE, and two irreversible oxidation steps at $E_{p1} = 0.75$ V/SCE and $E_{p2} = 1.050$ V/SCE. Comparison between the cyclic voltammograms of **2b** and MnTPP suggested that the pyrrole group is oxidized around 1.3 V/SCE. Thus, repeated scanning of the potential over the range -0.8 V to $+1.3$ V may result in the formation

of a polyporphyrin film at the electrode surface via electropolymerization of the attached pyrrole groups. In addition, we can note that with repeated potential scans, the oxidation peak related to the Mn(III)/Mn(II) process is anodically shifted. This indicates that the electrode surface becomes covered by the porphyrin complex.

The electropolymerized manganese porphyrin films are usually characterized by cyclic voltammetry and UV–visible spectrophotometry on optically transparent electrodes [40]. These
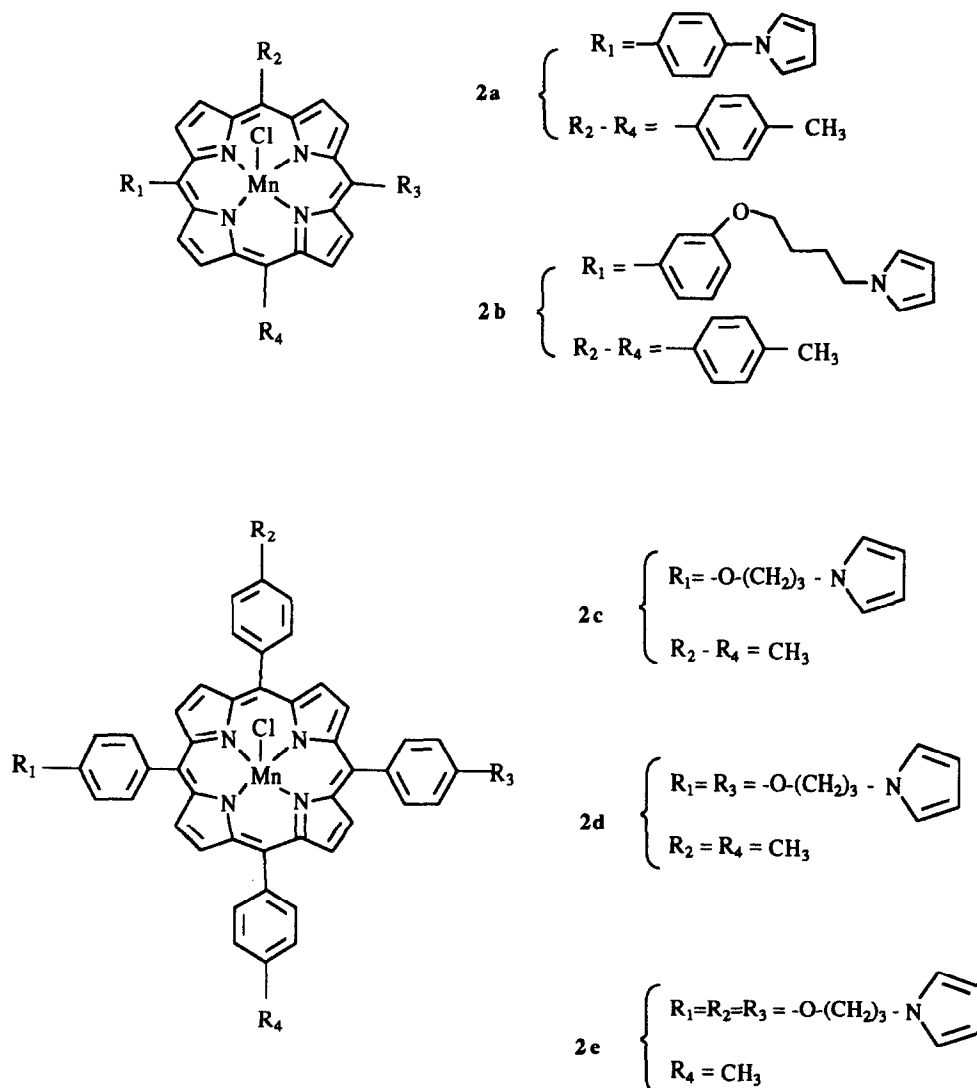

Fig. 2. Structures of various electropolymerizable pyrrole-substituted porphyrins.
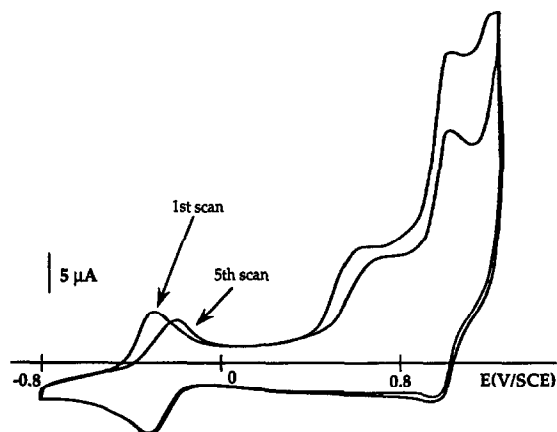
Fig. 3. Electropolymerizing cyclic voltammetry at vitreous carbon disk electrode (area = 0.071 cm^2) of 1 mM Mn–porphyrin **2b** in acetonitrile + 0.1 M Bu$_4$NBF$_4$ solution (scan rate = 100 mV/s, only the 1st and the 5th successive scans are shown).

techniques reveal the formation of supported porphyrin on the electrode surface, and provide evidence for the similarity of the electrochemical (and spectrophotometric) behavior of the polymer porphyrins and the starting monomers. Cyclic voltammetry can also provide useful information on the apparent surface coverage of poly(pyrrole-porphyrin) film electrodes. The thickness of the films can be estimated, as reported previously [45] by calculating the number of the porphyrin layers from the apparent surface coverage of the electrode (by taking into account the shape and size of the porphyrin planar macrocycle) and by estimating the average distance between two layers, Δx, from X-ray studies of tetra-coordinated metalloporphyrin crystals [45]. Thus, a poly(pyrrole-

Table 1

Hydrocarbons and biologically active molecule oxidation by O$_2$ electrocatalyzed by electropolymerized manganese porphyrin films on carbon felt electrodes

Entry	Porphyrin	Amount of Mn porphyrin (10^8 mol)	Axial base [a]	Anhydride (concentration / mM) [b]	Substrate (concentration / mM)	Oxidized products (10^6 mol) [e]	Faradaic efficiency / % [f]	Turnover / h [g]
1	**2a**	5	A	BzAn (100)	Tetralin (400) [c]	tetralol (29) tetralone (29)	98	560
2	**2a**	3.1	A	BzAn (100)	indan (100) [c]	indanone (8.8)	2	81
3	**2a**	2.6	A	BzAn (100)	cyclooctane (100) [c]	cyclooctanol (2.8)	1.5	78
4	**2a**	2.5	A	BzAn (100)	cyclohexene (100) [c]	cyclohexene oxide (6)	13	264
5	**2a**	15	A	BzAn (100)	cis-cyclooctene (20) [c]	cyclooctene oxide (85)	8	162
6	**2c**	2.1	A	BzAn (10)	cis-cyclooctene (10) [d]	cyclooctene oxide (54)	85	520
7	**2c**	1.1	A	AcAn (10)	cis-cyclooctene (10) [d]	cyclooctene oxide (7)	6	–
8	**2c**	1.9	A	BzAn (10)	stilbene (10) [d]	stilbene oxide (38.4)	52	400
9	**2c**	1.6	B	BzAn (10)	cis-cyclooctene (10) [d]	cyclooctene oxide (40)	10	–
10	**2c**	1.6	B	BzAn (10)	stilbene (10) [d]	stilbene oxide (20)	17	–
11	**2c**	0.9	A	BzAn (0.5)	thioacetamide (0.1) [d]	Ta (6); Tb (1.5); Tc (3)	22	290
12	**2d**	3.1	A	BzAn (0.5)	thioacetamide (0.1) [d]	Ta (2.4); Tb (10.9); Tc (0.2)	8	–
13	**2e**	9.1	A	BzAn (0.5)	thioacetamide (0.1) [d]	Ta (1.3); Tb (0.6); Tc (0.1)	5	–

[a] 1-Methyl (A) or 2-methyl (B) imidazole.
[b] Benzoic anhydride (BzAn) or acetic anhydride (AcAn).
[c] Electrolysis carried out in O$_2$- saturated CH$_3$CN + NBu$_4$BF$_4$ (0.1 M), from Ref. [26].
[d] Electrolysis carried out in O$_2$- saturated CH$_2$Cl$_2$ + NBu$_4$ClO$_4$ (0.1 M), from Ref. [28].
[e] HPLC or GC yield after 3 to 5 h reaction.
[f] Expressed as the ratio of moles of product analyzed to the electrochemical charge passed (expressed in moles, assuming a two-electron reaction for the alcohols and epoxides and a four-electron reaction for the ketones).
[g] Number of moles of product per mole of electropolymerized porphyrin, per hour.
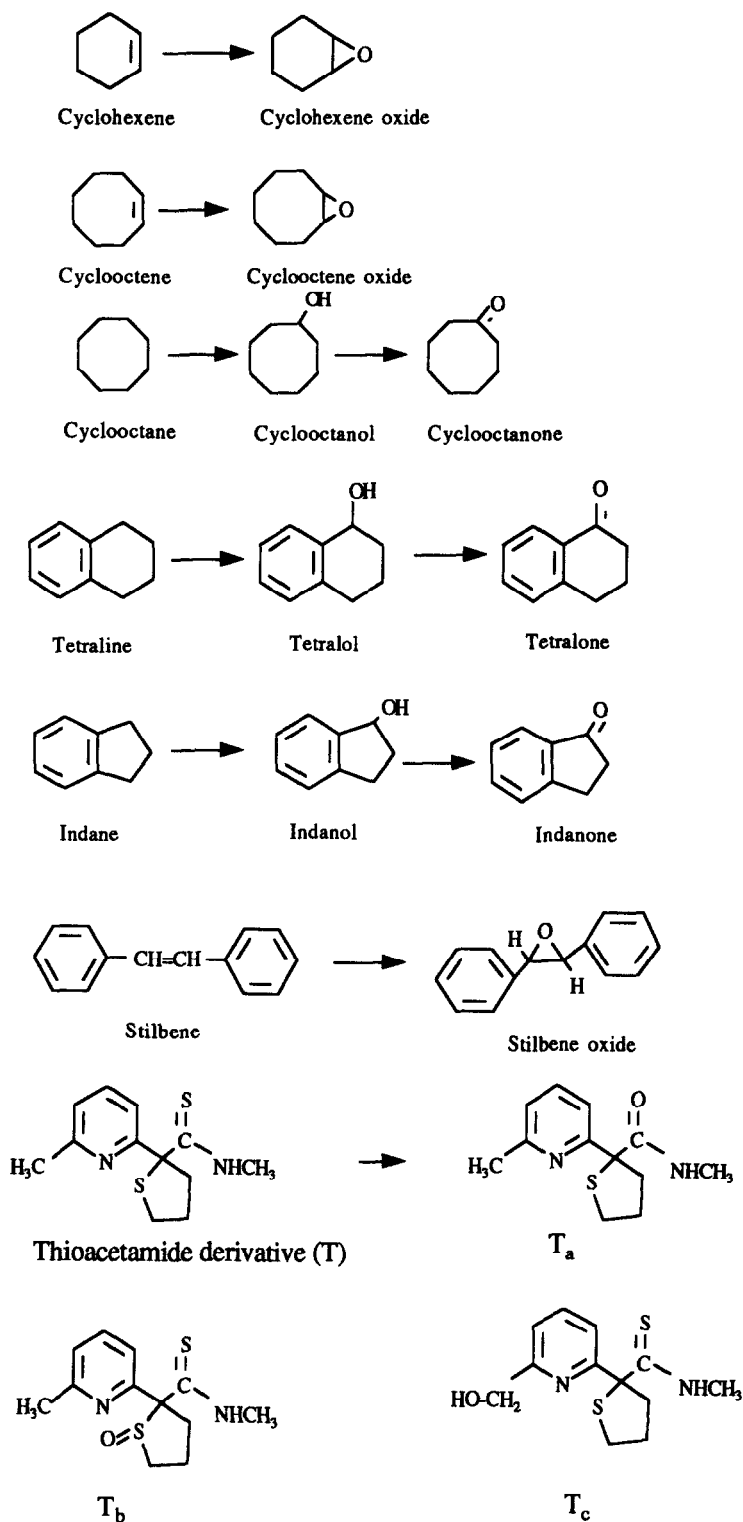
Cyclohexene → Cyclohexene oxide

Cyclooctene → Cyclooctene oxide

Cyclooctane → Cyclooctanol → Cyclooctanone

Tetraline → Tetralol → Tetralone

Indane → Indanol → Indanone

Stilbene → Stilbene oxide

Thioacetamide derivative (T) → T$_a$

T$_b$

T$_c$

Fig. 4. Structures of various oxidizable hydrocarbons.

manganese porphyrin **2b**) film containing 1.1×10^{-9} mol/cm^2 of electroactive porphyrin (or 25 equivalent layers) has a thickness of 10 nm. It was shown that the configuration of the starting pyrrole, mono- or tetra-substituted monomers (with the pyrrole group directly linked on the porphyrin macrocycle or through a flexible tether) induces a cross-linking effect due to the steric hindrance of the macrocomplex. This dramatically affects the efficiency of the electropolymerization reactions and limits the electrode surface coverages by the supported porphyrin [28,40,43–45].

3. Electroassisted biomimetic oxidations using electropolymerized metalloporphyrin films and molecular oxygen

Relatively few examples on electroassisted biomimetic oxidation of hydrocarbons by electropolymerized metalloporphyrins and molecular oxygen have been reported. However, they constitute an important contribution to the development of efficient chemical systems for hydrocarbon oxidation mimicking cytochrome P-450. The catalytic cycle of substrate oxidation by cytochrome P-450, or by its synthetic metalloporphyrin models [29] involves the transfer of an oxygen atom, either directly from oxygen atom donors such as PhIO, H_2O_2, ClO^-, ROOH, $KHSO_5$, ClO_2^-, RCO_3H and R_3NO, or from molecular oxygen after its reduction by two electrons to the porphyrinic catalytic site. This should lead to the formation of a high valent metal-oxo species, formally a $[Fe(V)=O]^+$ or $[Mn(V)=O]^+$ complex (as shown in Fig. 1). This species is highly reactive and is responsible of the hydrocarbons oxidation to alcohols, ketones and epoxides.

We describe here some of the reported results obtained for the oxidation of *cis*-cyclooctene, cyclooctane, Tetralin (1,2,3,4-tetrahydronaphthalene), indan, cyclohexene, stilbene and thioacetamide derivative (a biologically active molecule, noted T) (see Fig. 4) by molecular oxygen. O_2 was electro-activated by a series of electropolymerized films of manganese porphyrin deposited on carbon felt electrodes (10 mm $\times$ 10 mm $\times$ 4 mm). The supported catalyst was regenerated by controlled potential electrolysis at $E = -0.5$ V/SCE, in acetonitrile or dichloromethane solution containing tetrabutylammonium tetrafluoroborate or perchlorate as supporting electrolyte (note that the Mn(III)/Mn(II) redox process of the supported manganese porphyrins is usually taking place in the potential range of -0.20 V/SCE to -0.35 V/SCE). In a typical experiment, the solution contained an axial base (1-methylimidazole or 2-methylimidazole), hydrocarbon and benzoic or acetic anhydride (as the activator) and was kept under atmospheric oxygen pressure for 3 or 6 h at room temperature. The reaction products were usually followed by GLC analysis [26,28].

Table 1 presents these results. They are compared to those previously obtained with the same kind of catalyst in a homogeneous phase (Table 2). The essential observations are that:
- the oxidation products are formed with a very good efficiency by the supported catalyst, up to 500 turnovers of the catalyst per hour.
- the faradaic efficiency expressed as the ratio of moles of oxidation products analyzed to the electrochemical charge passed is poor in some cases, but reached 98% in some other cases.

Comparison of these results (Table 1) with those reported for the homogeneous phase and using different kinds of reducing agents [18,20,21,23,27] (Table 2) clearly show that the catalytic activity of the catalyst (turnover) is largely enhanced when the complex is fixed on the electrode. This is probably due to either a preferred orientation of the supported catalyst for approach of the hydrocarbon to the presumed active manganese site, or to the high local concentration of the catalyst. However, the low faradaic yields obtained in some cases are certainly due to the direct electrochemical reduction of the active oxidant, a high-valent

manganese 'oxo' complex, at the potential of electrolysis according to the electroactivity study of this 'oxo' form of the catalyst previously reported [22,26,30]. Thus, the fixation of the catalyst onto the electrode promotes the electroreductive consumption of the active oxidant. But it is important to note that in these studies, the products are formed using a substrate/catalyst ratio higher than 6000, with similar yields compared with those obtained in homogeneous solution (with a substrate/catalyst ratio up to 400).

From these results it also appears that increasing the surface concentration of catalyst by using manganese porphyrins containing two or three pyrrol groups, and hence having a better polymerizability, gave cross-linked polymers which present a lower activity than a polymer

film prepared from a monomer containing only one pyrrole group [28] (Table 1, entries 11–13). In the same way, it is clear that in the case of the epoxidation reaction of *cis*-cyclooctene, the better turnover (520 per hour) and faradaic yield (85%) (Table 1, entry 6 compared to entry 5) were probably due to the presence of a flexible chain between the pyrrole group and the porphyrinic macrocycle, giving a less dense polymer in which catalytic centers are more active and more easily accessible to substrate molecules. It was also observed that the optimum activity of the polymer porphyrin catalyst was obtained with very thin films [19,24]. Finally, it should be noted that the epoxidation reaction proceeded with difficulty in acetonitrile electrolyte, compared to dichloromethane electrolyte [19,26,28].

Table 2
Behavior of various homogeneous catalytic systems for hydrocarbon oxidations by molecular oxygen

Catalyst and activator	Reducing agent	Hydrocarbon	Product(s)	Turnover	Yield (%) based on the reducing agent
ClMnTPP (0.5 mM) + benzoic anhydride (0.1 M) in dichloromethane [a]	electrolysis at −0.4 V/SCE	*cis*-cyclooctene (0.1 M)	cyclooctene oxide (5.7 mM)	2/h	56
ClMnTPP (1 mM) + acetic acid (0.2 M) in acetonitrile [b]	zinc powder	*cis*-cyclooctene (0.38 M) cyclooctane (0.38 M)	Cyclooctene (75 mM) cyclooctanol + cyclooctanone (22 mM)	150/h 28/h	50 15
ClMnTPP (1 mM) + acetic acid (0.2 M) in acetonitrile [c]	electrolysis at −0.4 V/SCE	*cis*-cyclooctene (0.1 M) cyclooctane (0.1 M)	cyclooctene oxide cyclooctanol + cyclooctanone	1.7/min 0.15/min	45 7.5
ClMn–salen (0.59 mM) + benzoic anhydride (0.1 M) in acetonitrile [d]	electrolysis at −0.45 V/SCE	cyclooctene (0.1 M)	cyclooctene oxide (1.4 mM)	2.4/h	35
ClMnTPP (1 mM) + acetic acid (0.1 M) in acetonitrile + dichloromethane (95:5) [e]	zinc powder	Tetralin (0.4 M)	tetralol + tetralone (27 mM, i.e. μmol)	9/h	36
		indan (0.4 M)	indanol + indanone (27 mM, i.e. 270 μmol)	9/h	37
		cyclohexene (0.4 M)	cyclohexene oxide + cyclohexe-1-ene 2-ol + cyclohexe-1-ene-3-one (70 mM, i.e. 700 μmol)	23/h	50

ClMnTPP is the manganese tetraphenyl porphyrin complex; ClMn–salen is the manganese, N,N'-ethylenebis(salicylaminato) complex.
[a] From Ref. [17], reaction time 6 h.
[b] From Ref. [18], reaction time 1/2 h.
[c] From Ref. [20], reaction time and the chemical yields not given, turnovers are given for the first 10 min.
[d] From Ref. [22], reaction time not given.
[e] From Ref. [27], reaction time is 3 h.

It should also be noted that the substitution of benzoic anhydride by acetic anhydride, which appeared to be a poor activator, produced a dramatic decrease in both the faradaic efficiency and the turnover (Table 1, entries 6, 7). The replacement of 1-methylimidazole by 2-methylimidazole markedly decreased the efficiency of the epoxidation of cis-cyclooctene and cis-stilbene (Table 1, entries 9, 10)

Finally, it was also found that the recovered porphyrin polymer electrodes (stored in air, without precaution) retained 95% of their initial catalytic activity during the second run, and 70% of their initial activity during the third run [26]. It also appears from these results that it is not justified to bring out any valid information on the stereospecificity of the supported catalyst and to draw a firm conclusion regarding this point. More experiments with well-adapted test reactions are needed to reflect the importance of this aspect.

4. Conclusion

The easy-to-build electropolymerized manganese porphyrin film electrodes give an efficient, stable and reusable catalyst for the electroassisted biomimetic oxidation of olefins and hydroxylation of hydrocarbons by molecular oxygen. Comparison between homogeneous phase and supported phase catalytic reactions shows that the confinement of the catalyst in a polymeric film on the electrode surface markedly improves its stability.

Acknowledgements

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