Manganese- and iron-porphyrins embedded in a polydimethylsiloxane membrane: a selective oxidation catalyst

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Abstract

The use of [5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato] Mn(III) and Fe(III) chloride [TDCPP(Mn)Cl and TDCPP(Fe)Cl] encapsulated in a polydimethylsiloxane (PDMS) membrane is reported for the oxidation of cyclic alcohols to ketones with *t*-butylhydroperoxide from an aqueous solution. Two major conclusions can be drawn from the comparison with carbon black (CB) supported complexes. Firstly, both hydrophobic carriers enhance the turnover numbers (TON) of the reaction by sorption of the reagents near the active site. Secondly, the support material requires a specific morphology to promote reaction selectivity. Indeed, the CB-supported complexes can be considered as an improved version of the homogeneous catalyst, whereas PDMS adds an extra dimension—selectivity—to the heterogeneous catalyst. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the past, a wide spectrum of supports has been used for the immobilization of metallo-porphyrins [1]. The heterogeneous systems using a hydrophobic support performed particularly well [2–6] as they change the polarity of the active site in such a way that the sorption of apolar molecules is favored. As a consequence, both the turnover numbers (TON) of oxygena-

tion reactions with peroxide as mono-oxygen atom donor and the peroxide efficiency increase [3–5]. Polydimethylsiloxane (PDMS) [3,6,7] and carbon black (CB) [4,5] are two support materials that are extremely interesting from this point of view. In addition to their hydrophobic properties, both supports are chemically stable and have proven to be useful in the immobilization of metallo-complexes.

Research in aqueous catalysis is timely, because of the attractive features of water as an environmentally friendly and non-flammable solvent, and the occurrence of recalcitrant organic pollutants in wastewater [8,9]. Especially

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for heterogeneously catalyzed reactions in aqueous solutions, the use of an hydrophobic support is indispensable [10,11]. In previous work, the properties of manganese-porphyrins encapsulated in PDMS were briefly reported for the oxidation of water-soluble cyclic alcohols. For the first time, a catalytically active membrane was designed in which the catalyst support induced selectivity based on its affinity for the substrates [6]. Further research is reported here on the characterization of these catalytic membranes, i.e., PDMS occluded complexes and on the comparison between PDMS and CB as support for [5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato] Mn(III) chloride [TDCPP(Mn)Cl] porphyrins. Finally, the potential of PDMS–[5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato] Fe(III) chloride [TDCPP(Fe)Cl] is explored in the oxidation of cyclic alcohols.

2. Experimental

2.1. Materials

Cyclopentanol (99%), cyclohexanol (99.5%) and cycloheptanol (> 97%) from Fluka and dichloromethane (99.5%), tertiary butylhydroperoxide (t-BHP; 70% in water) from Janssen Chimica were used as received.

Synthesis procedure for PDMS membranes with and without encapsulated Mn- and Fe-TDCPP(Cl) porphyrins: prepolymer (General Electric; RTV 615A) and crosslinker (General Electric; RTV 615B) in a ratio of 10:1 are stirred in dichloromethane (90 vol.%) for 1 h at 40°C (prepolymerization step). A solution of TDCPP(Mn)Cl or TDCPP(Fe)Cl [1] in dichloromethane with a loading of 0.37, 0.0185 or 0.0925 wt.% relative to PDMS is then added

to the prepolymer mixture, while stirred at room temperature for 1 h. The suspension is cast on a petri dish and kept overnight at room temperature. Finally, the polymerizing mixture is cured under vacuum at 150°C for 1 h. The thickness of the membrane is 150 μm, except for the sorption measurements where unfilled PDMS membranes with a thickness of 750 μm are prepared.

Preparation procedure for CB adsorbed porphyrin (CB-TDCPP(Mn)Cl):TDCPP(Mn)Cl complexes were deposited onto the CB carrier of the type Corax N326 (Degussa) by impregnation (CB-TDCPP(Mn)Cl). Some 36 mg of TDCPP(Mn)Cl was dissolved in a minimal volume of the solvent dichloromethane ($\pm$ 20 ml). Subsequently, 1 g of the CB was added. The solvent was evaporated under continuous stirring of the mixture at room temperature.

2.2. Spectroscopic characterization of encapsulated complexes

UV-Vis spectra were recorded on a Perkin Elmer lambda 12 UV-Vis spectrophotometer. The catalytic membranes were fixed on the outside of the sample holders, while an unfilled PDMS membrane was used as reference. The spectra of the complexes in solution were recorded in dichloromethane, using a quartz cell with 10 mm path length.

ESR spectra were recorded at 120 K and 160 K on a Bruker ESP 300E spectrometer operating in X-band (9.5 GHz). The g-values were calculated by taking the frequency indicated on a Hewlett Packard 5342 A microwave frequency meter and the measured field.

2.3. Reaction set-up and conditions

The catalytic reactions were carried out at room temperature in a batch reactor, using dichloromethane and water for the homogeneous and heterogeneous catalysts, respectively. The reaction conditions were the following: 1

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[1] Synthesis procedure for TDCPP(Mn)Cl according to Ref. [12].

Table 1
The UV-Vis bands for TDCPP(Fe)Cl in dichloromethane and for
PDMS–TDCPP(Fe)Cl

Catalyst	CT-band	Soret band	Q-band
TDCPP(Fe)Cl	352	417	573
PDMS–TDCPP(Fe)Cl	326	414	578

mmol substrate, 2 mmol *t*-BHP, 5 μmol TD-CPP(Mn)Cl (Table 1, run 1 + 7), 0.2 g PDMS–TDCPP(Mn)Cl (Table 1, run 3 + 8) or 0.02 g CB-TDCPP(Mn)Cl (Table 1, run 5). For the competitive reactions, 1 mmol of each alcohol, 6 mmol *t*-BHP, 5 μmol TDCPP(Mn)Cl (Table 1, run 2 + 8), 0.2 g PDMS–TDCPP(Mn)Cl (Table 1, run 4 + 9) or 0.02 g CB-TDCPP(Mn)Cl (Table 1, run 6) were mixed. Sampling was usually done after 27 h of reaction.

In certain experiments membrane, loading and cyclopentanol concentration were varied. The reaction conditions were the following: 1, 2.5, 5, 7.5 or 10 mmol cyclopentanol, 20 mmol *t*-BHP, 0.20 g PDMS–TDCPP(Mn)Cl (complex loading of 0.37, 0.185 or 0.0925 wt.%) in 30 ml of bidistilled water in a batch reactor. Sampling is done after 24 h.

2.4. Procedure for the sorption measurements

Some 1.5 mmol of the alcohol in the non-competitive sorption (runs 1 and 3) and 0.5 mmol of each alcohol in the competitive sorption (runs 2 and 4) is dissolved in 30 ml water. Around 1 g of PDMS (750 μm thickness) or 1 g CB is added to the mixture after a pretreatment at 150°C for 1 h under vacuum to remove the sorbed water. For each experiment, a reference mixture without adsorbent is prepared with the same composition. The mixtures are allowed to stand for 24 h under constant stirring. After removing the adsorbent from the sorption mixtures, *t*-butanol (0.65 mmol) is added to both sorption and reference mixtures as an internal standard for GC analysis. Subtracting the values

of the sorption mixture from those found in the reference gives the sorbed amounts corrected for evaporation.

3. Results and discussion

3.1. Characterization of PDMS–TDCPP(Mn)Cl and PDMS–TDCPP(Fe)Cl

The UV-Vis spectrum of PDMS–TDCPP(Mn)Cl and PDMS–TDCPP(Fe)Cl show the characteristic bands of the Mn- respectively Fe-porphyrin, suggesting that the porphyrin structure is kept intact during immobilization (Fig. 1, Table 2). However, the peaks are broader and the Q-band and the Soret band are shifted. These observations indicate a variable distortion of the phenyl substituents on the porphyrin ring, depending on their contact with the polymer chain.

TDCPP(Fe)Cl is further characterized by ESR spectroscopy. Both TDCPP(Fe)Cl and PDMS–TDCPP(Fe)Cl present signals at $g_{\perp} = 5.7$ and $g_{\parallel} = 1.9$, which correspond to a high spin Fe(III) species. The similarity of the ESR spectra of TDCPP(Fe)Cl in solution and embedded in PDMS rules out the existence of strong electronic interactions between iron and the support. The spectrum of PDMS–TDCPP(Fe)Cl is

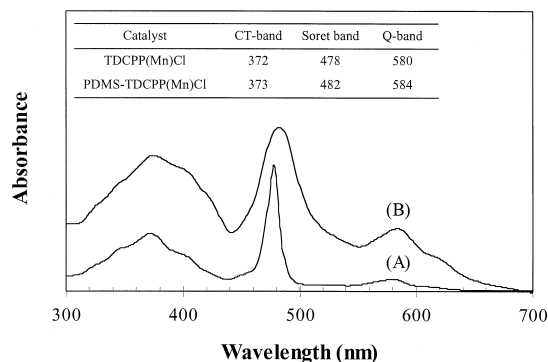| Catalyst	CT-band	Soret band	Q-band
TDCPP(Mn)Cl	372	478	580
PDMS-TDCPP(Mn)Cl	373	482	584

Fig. 1. The UV-Vis spectra of (A) TDCPP(Mn)Cl and (B) PDMS–TDCPP(Mn)Cl. Inset: the wavelength at which the characteristic bands of the Mn-porphyrin appear.

Table 2
The oxidation of cyclopentanol, cyclohexanol and cycloheptanol by *t*-BHP catalyzed by TDCPP(Mn)Cl and TDCPP(Fe)Cl, homogeneously or supported on PDMS or CB

Run	Catalyst	TON (mol. alcohol/mol. complex)		
		Cyclopentanol	Cyclohexanol	Cycloheptanol
1[a]	TDCPP(Mn)Cl	5.5	5.0	10.0
2[b]	TDCPP(Mn)Cl	3.4	4.3	11.0
3[a]	PDMS–TDCPP(Mn)Cl	10.7	29.0	72.9
4[b]	PDMS–TDCPP(Mn)Cl	16.2	27.6	49.4
5[a]	CB-TDCPP(Mn)Cl	43.2	62.1	79.3
6[b]	CB-TDCPP(Mn)Cl	20.3	27.1	75.6
7[a]	TDCPP(Fe)Cl	36.1	28.0	92.5
8[a]	PDMS–TDCPP(Fe)Cl	12.4	18.9	34.0
9[b]	PDMS–TDCPP(Fe)Cl	–	12.7	31.5

[a]Separate oxidation of the respective alcohols.
[b]Competitive oxidation reaction.

recorded at a temperature (160 K) above the PDMS glass transition temperature (150 K) to ensure that the polymer retains its flexibility.

3.2. PDMS vs. CB as support for the TDCPP(Mn)Cl catalyst (Table 1)

TDCPP(Mn)Cl impregnated on CB is used as a reference for the performance of PDMS–TDCPP(Mn)Cl. The TON for the oxidation of cycloheptanol is comparable in both systems (runs 3, 5). For the separate oxidation of cyclopentanol and cyclohexanol, much higher activities are observed using CB-TDCPP(Mn)Cl. The higher TON reached with both heterogeneous systems compared to the homogeneous system (run 1) can be ascribed to the sorption exercised by the hydrophobic supports. In the case of PDMS, the enhancement is more pronounced as the carbon number of the alcohol increases (runs 1, 3). These catalytic results are supported by sorption measurements, which show a preferable uptake of cycloheptanol by the unfilled PDMS membrane (Table 3) [6]. The different behaviour of PDMS–TDCPP(Mn)Cl and CB-TDCPP(Mn)Cl results from the different mode of supply of the reagents to the active site. With CB, the sorption values of the substrates are more balanced (Table 3). Thus, the

relative values for the TON of the three alcohols with CB-TDCPP(Mn)Cl correspond with the difference in intrinsic reactivity, as shown in the homogeneous experiment (runs 1, 5). In the case of PDMS, a consecutive diffusion step is necessary for the molecules before they reach the complexes after their sorption in the membrane phase. The transport of the various substrates through the polymer matrix is based on mutual affinity, which induces a specific selectivity in the catalyst. For the competitive reactions, it is clear that CB-TDCPP(Mn)Cl behaves according to the rules of the homogeneous system. When the CB-catalyst is used in a competitive reaction, the TON of cyclopentanol and

Table 3
The relative values, with regard to cyclopentanol, for the sorption of the cyclic alcohols by PDMS and CB

Run	Support	Sorption (μl g^{-1})		
		Cyclopentanol[a]	Cyclohexanol	Cycloheptanol
1[b]	PDMS	1 (1.9)	1.3	3.5
2[c]	PDMS	1 (1.3)	1.6	2.6
3[b]	CB	1 (29.0)	1.1	1.7
4[c]	CB	1 (9.8)	1.5	2.3

[a]The number in parentheses is the absolute sorption value in microliter per gram adsorbent.
[b]Separate sorption of the respective alcohols.
[c]Competitive sorption.

cyclohexanol decreases, while the activity level of the separate reaction is maintained for cyclo- heptanol (runs 5, 6). This is not the case for PDMS–TDCPP(Mn)Cl (runs 3, 4) where 'cou- pling phenomena' diminish the differences be- tween the TONs of the alcohols with respect to the individual reactivity. Both at the level of sorption in the membrane and diffusion through it, the behaviour of one alcohol is influenced by the presence of the other alcohols.

3.3. Comparison between Mn and Fe porphyrin complexes

Table 2 (runs 7, 9) shows the TON for the oxidation of cyclopentanol, cyclohexanol and cycloheptanol with the iron porphyrin complex. In a homogeneous reaction, TDCPP(Fe)Cl is a significantly better catalyst than the Mn-com- plex (runs 1, 7). On the contrary, when the Fe-porphyrin is embedded in the PDMS mem- brane, the TONs drop in comparison to PDMS–TDCPP(Mn)Cl (runs 3, 8 and 4, 9). The decreased performance of PDMS–TDCPP(Fe)Cl can be the result of a decreased rate of supply of reagents to the active sites. To verify whether transport [2] of the reagents is rate limiting, the amount of complex loaded in the membrane is varied. Figs. 2 and 3 show the influence of the complex loading on the TOF of cyclopentanol for PDMS–TDCPP(Fe)Cl and PDMS– TDCPP(Mn)Cl, respectively. When the amount of complex in the membrane decreases, the TOF increases. This observation points to a hindered supply of the reagents to the active site. The substrate/oxidant ratio at which the constant TOF value is reached decreases as the complex loading diminishes. However, even at a low complex loading of 0.0925 wt.% the reaction is still transport controlled. As shown
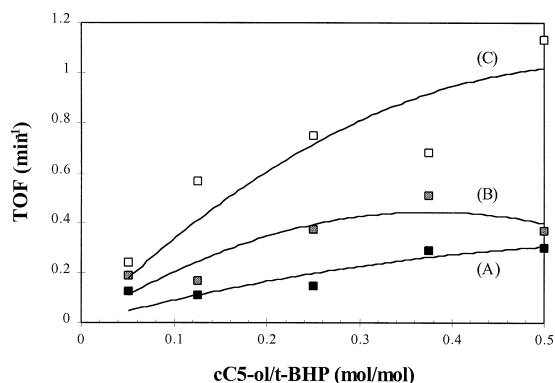

Fig. 2. TOF (mol. alcohol/(mol. complex min)) against the molar ratio of substrate vs. oxidant for the oxidation of cyclopentanol by *t*-BHP with PDMS–TDCPP(Fe)Cl with a complex loading of (A) 0.37 wt.%, (B) 0.185 wt.% and (C) 0.0925 wt.%. The line is a polynomial fit of the second order through the experimental points (A)■, (B)▨ and (C)□.

in Fig. 3, the transport of the alcohol towards the porphyrins can not keep up with its conver- sion, not even for the low activity catalysts. Thus, there has to be an additional explanation for the unexpectedly low TON of the PDMS– TDCPP(Fe)Cl catalyst. Indeed, as iron com- plexes lead to a higher peroxide decomposition than their manganese counterparts (unpublished results), it is straightforward that when an ex- cess of oxidant is used, the activity of
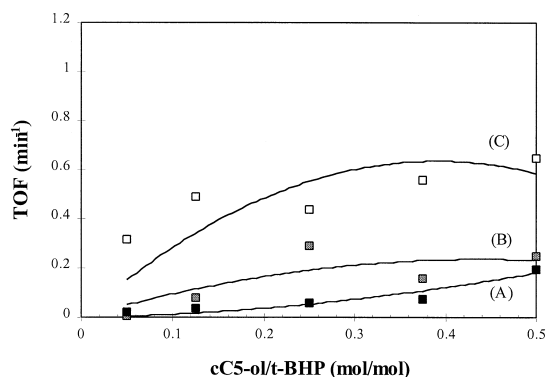

Fig. 3. TOF (mol. alcohol/(mol. complex min)) against the molar ratio of substrate vs. oxidant for the oxidation of cyclopentanol by *t*-BHP with PDMS–TDCPP(Mn)Cl with a complex loading of (A) 0.37 wt.%, (B) 0.185 wt.% and (C) 0.0925 wt.%. The line is a polynomial fit of the second order through the experimental points (A)■, (B)▨ and (C)□.

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[2] We speak of transport problems in general and do not distin- guish yet between sorption in the membrane phase and diffusion through it.

TDCPP(Fe)Cl incorporated in PDMS will be lower than that of the manganese analogue.

4. Conclusion

The PDMS–porphyrin system is very promising for oxidation reactions in aqueous solution especially by selective sorption of some components from the reaction mixture.

The spectroscopical characterization of the PDMS–porphyrin system indicates that the metallo-porphyrin in the membrane is in a pseudo-homogeneous state.

From the comparison of PDMS with CB, it is clear that a hydrophobic support is necessary to reach acceptable TON, although this is insufficient to create a selective catalyst. The property of PDMS to induce selectivity can be attributed to the fact that it belongs to the class of elastomers, a group of polymers which discriminates among molecules on the basis of mutual affinity.

Iron-porphyrins are known to be better oxidation catalysts than the manganese-complexes. Upon incorporation in the PDMS membrane, the activity order is reversed. Firstly, a hindered supply of the reagents to the active site has a more crucial effect on the more active Fe-complex. Secondly, iron-complexes have a higher decomposition rate for the oxidant.

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