

Manganese porphyrins covalently bound to silica and montmorillonite K10 as efficient catalysts for alkene and alkane oxidation by hydrogen peroxide

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Abstract

New supported Mn^{III}-porphyrin-based catalysts were prepared by covalent binding of *meso*-tetrakis-(2,6-dichlorophenyl) porphyrin derivatives bearing NH₂ or SO₃H functions on their *meso*-aryl rings to either silica or montmorillonite K10. All these supported metalloporphyrins efficiently catalysed the epoxidation of alkenes with PhIO. The Mn^{III}-porphyrin covalently bound to montmorillonite K10 gave remarkably good results for the hydroxylation of linear alkanes such as heptane with PhIO, the obtained yields (54%) being much better than those observed with corresponding homogeneous catalysts. The Mn^{III}-porphyrin covalently bound to silica was an efficient catalyst for epoxidation of alkenes with H₂O₂ (yields between 65 and 95% under conversion conditions). In the presence of an excess of substrate, this supported catalyst was found to be able to catalyse alkene epoxidation with yields based on H₂O₂ between 67% and 88%, as well as alkane hydroxylation with yields between 21% (for heptane) and 90% (for cyclooctane).

Keywords: Manganese porphyrin; Silica; Montmorillonite; Alkene oxidation; Alkane oxidation; Hydrogen peroxide

1. Introduction

Several systems based on Fe^{III}- and Mn^{III}-porphyrins that are able to mimic cytochrome P450-dependent monooxygenases have been reported during these last fifteen years (For reviews see Ref. [1]). In order to construct systems useful for selective oxidation in organic chemistry, it would be particularly interesting to associate H₂O₂, an inexpensive, readily available oxidant which should give H₂O as the only

by-product and a supported metalloporphyrin catalyst easier to handle and to recycle than corresponding homogeneous catalysts. However, the use of H₂O₂ in the presence of Fe^{III}- and Mn^{III}-porphyrins leads to several problems linked to the easy dismutation of H₂O₂ by these metalloporphyrins and the fast destruction of these catalysts by H₂O₂ and/or ·OH. This is presumably why only few systems efficient for metalloporphyrin-catalysed oxidation of alkanes with H₂O₂ have been reported in literature. Fe^{III}-porphyrins bearing many electron-withdrawing substituents catalyse alkene epoxidation by H₂O₂ in good yields, in the absence

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of any cocatalyst [2], but they appear as ineffective catalysts for alkane hydroxylation by H_2O_2 . On the contrary, several systems based on Mn^{III} -porphyrins have been shown to be able to perform both alkene epoxidation and alkane hydroxylation by H_2O_2 , provided that a cocatalyst is used to facilitate the heterolytic cleavage of the O–O bond of H_2O_2 . Most of these systems use the robust catalyst $\text{Mn}(\text{TDCPP})\text{Cl}$ [H_2TDCPP = *meso*-tetrakis-(2,6-dichlorophenyl)porphyrin] and either a nitrogenous base such as imidazole [3], an imidazole and a carboxylic acid such as benzoic acid [4], a soluble base and a tertiary amine-*N*-oxide [5], or simply ammonium acetate [6], as cocatalysts. The role of the cocatalyst in such systems is to facilitate the formation of the active oxygen species of the $\text{Mn}^{\text{V}}=\text{O}$ type from reaction of Mn^{III} with H_2O_2 . It may be involved in several steps of this reaction [3,4]. In the removal of a proton from H_2O_2 before formation of intermediate $\text{Mn}^{\text{III}}-\text{OOH}$, it should act as a base. In order to facilitate the heterolytic cleavage of the O–O bond of this intermediate, it may act as a Mn-ligand in *trans* position of the OOH ligand; moreover, its acid conjugate may protonate the appropriate oxygen atom of $\text{Mn}^{\text{III}}-\text{OOH}$ which is necessary for the departure of H_2O as a leaving group [3]. Finally, in the particular case of ammonium acetate or benzoic acid in the presence of imidazole, it could catalyse the formation of $\text{Mn}^{\text{V}}=\text{O}$ via a $\text{Mn}^{\text{III}}-\text{OOCOR}$ species in which the heterolytic cleavage of the O–O bond should be much easier [4].

In the presence of H_2O_2 , the use of a supported metalloporphyrin catalyst instead of an homogeneous one, leads to supplementary problems related to a possible oxidative degradation of the support in the case of organic polymer supports, or to a possible dismutation of H_2O_2 by the support in the case of inorganic supports. All these considerations would explain why only very few systems based on supported metalloporphyrin catalysts and H_2O_2 have been reported for the oxidation of alkenes and alkanes [7].

This paper describes the preparation of two supported catalysts obtained by covalent binding of two derivatives of $\text{Mn}(\text{TDCPP})$ either to montmorillonite or to silica. One of them gives particularly good results in the hydroxylation of linear alkanes by PhIO, whereas the second one is efficient for the epoxidation of alkenes and hydroxylation of alkanes by H_2O_2 itself.

2. Results

2.1. Preparation of metalloporphyrins bearing appropriate functions

Two inorganic supports were used in this study. The first one was silica bearing a carboxylic acid function; it was covalently bound to a TDCPPH_2 derivative bearing an amine function. The second one was montmorillonite K10. This material was functionalised with a $-(\text{CH}_2)_3 \text{NH}_2$ group and covalently bound to a TDCPPH_2 derivative involving a SO_2Cl function.

2.1.1. Preparation of silica-bound catalysts 6 and 7 (Fig. 1)

Porphyrin **2**, $\text{TDCmNO}_2\text{PPH}_2$, was prepared by condensation of stoichiometric amounts of 2,6-dichloro-3-nitrobenzaldehyde, **1**, and pyrrole according to a previously described procedure [8]. Reduction of the nitro groups with SnCl_2 at 70°C followed by metallation with $\text{Mn}(\text{OAc})_2$ afforded $\text{Mn}^{\text{III}}(\text{TDCmNH}_2\text{PP})\text{OAc}$, **4**, in very good yields. Complex **4** was covalently bound to silica CBA bearing $-\text{CH}_2\text{COOH}$ groups, after activation of their COOH functions upon treatment with thionyl chloride. After formation of the amide bonds (CH_3CN at reflux), the insoluble material obtained, **6**, was washed with CH_2Cl_2 , CH_3CN , then extensively extracted with acetone in a Soxhlet system and dried at 80°C for 24 h. Finally, supported catalyst **7** was obtained after acetylation of the residual NH_2 functions of the metalloporphyrin in order to avoid any secondary reactions at the

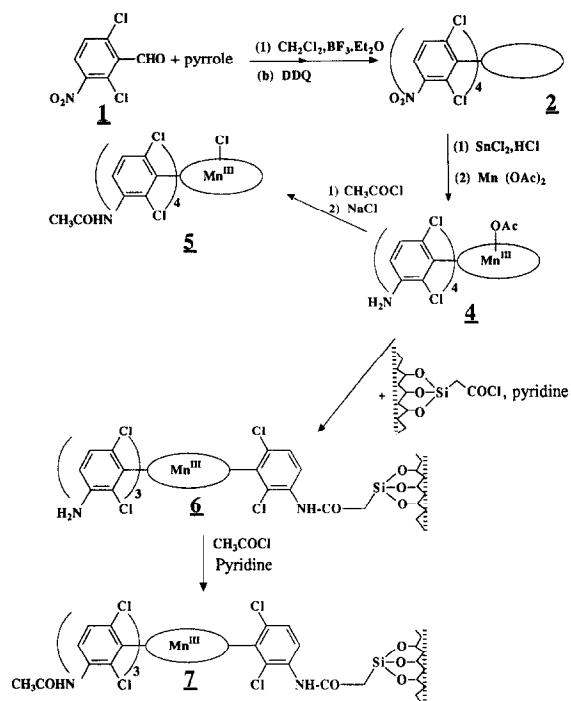


Fig. 1. Synthesis of a Mn^{III} -porphyrin covalently bound to silica. The oval symbol represents the tetrapyrrole porphyrin ring. Only the *meso*-aryl substituents are indicated in the figure.

level of those functions during oxidation catalysis (treatment with CH_3COCl and pyridine at 0°C and extensive washing of the solid as described above).

The UV-vis. spectra of **6** and **7** were similar to those of **4**, with a Soret peak at 474 nm, indicating that no demetallation has occurred during the preparation and that the porphyrin ring was not modified. Elemental analysis of Mn showed that compounds **6** and **7**, respectively contained 6.6% and 2.6% (m/m) of Mn-porphyrin.

2.1.2. Preparation of montmorillonite-bound catalyst **11** (Fig. 2)

The precursor Mn^{III} -porphyrin **10** was prepared by treatment of the previously described [14] complex **9** with PCl_5 at 150°C and extraction of the resulting paste with CH_2Cl_2 . Then **10** was made to react in refluxing pyridine with a clay, montmorillonite K10 bearing $-(\text{CH}_2)_3\text{NH}_2$ functions, which has been pre-

pared by reaction of commercially available montmorillonite K10 with aminopropyltriethoxy-silane according to a previously described procedure [15]. Extensive washing of the resulting solid with several solvents as for compounds **6** and **7** afforded the supported catalyst **11** which contained 3.5% (m/m) Mn-porphyrin and exhibited a UV-vis. spectrum very similar to those of compounds **6** and **7**. The homogeneous catalyst **12** equivalent to **11** was prepared by treatment of complex **10** with propylamine in refluxing pyridine (Fig. 2).

2.2. Catalytic properties of **6**, **7** and **11**

2.2.1. Oxidations with PhIO

Epoxidation of cyclooctene with PhIO, an easy oxidation, was first studied in order to have an idea of the accessibility of the Mn^{III} centres of the supported catalysts towards substrates and oxidants. As shown in Table 1, the homogeneous Mn^{III} catalyst **4** led to a good yield of cyclooctene epoxide (86%). This yield was even slightly higher (90%) when using

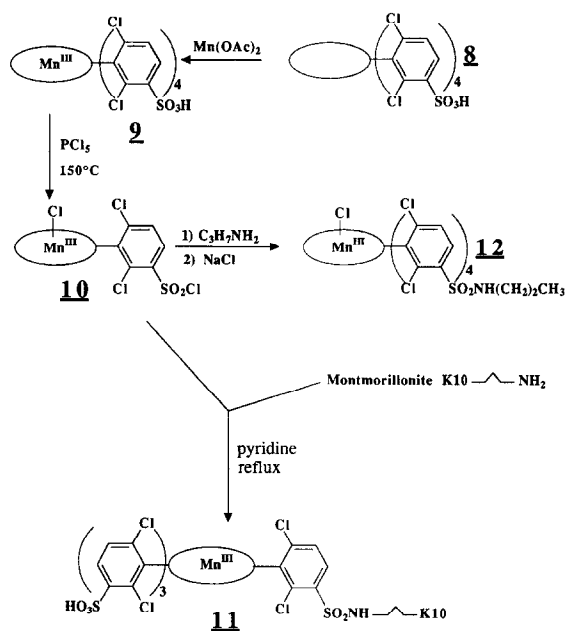





Fig. 2. Synthesis of a Mn^{III} -porphyrin covalently bound to montmorillonite.

Table 1

Epoxidation of cyclooctene with PhIO catalyzed by various homogeneous and supported Mn^{III}-porphyrins ^a.

Catalyst		Epoxide yield ^b (%)
Mn(TDCmNH ₂ PP)Cl	4	86
Mn(TDCmNHCOCH ₃ PP)Cl	5	90
Mn(TDC-mNH ₂ PP)-  -SiO ₂	6	60
Mn(TDC-mNHCOCH ₃ PP)-  -SiO ₂	7	88
Mn(TDCSPP)-  -K10	11	98

^a Molar ratio of catalyst: PhIO: cyclooctene = 1:20:800; 'equivalent concentration' of catalyst: 10⁻³ M in CH₃CN/CH₂Cl₂ (2:1).

^b Yields based on starting PhIO after 2 h at room temperature.



catalyst **5** in which the NH₂ groups have been acetylated. Such high yields were also observed with supported catalyst **7** (88%) whereas they were markedly lower with catalyst **6** containing free and potentially reactive NH₂-functions. Finally, the Mn^{III}-porphyrin bound to montmorillonite, **11**, was highly active and led to an almost quantitative epoxidation of cyclooctene (98%).

Hydroxylation of linear alkanes such as heptane is a much more difficult reaction [1]. This is shown by the low yields that were observed for heptane hydroxylation with PhIO in the presence of catalysts **5** and **9** (21% and 10%, respectively, Table 2). Interestingly, supported catalysts **7** and **11** gave much better results, the

54% yield obtained with **11** being quite remarkable for such a difficult reaction. It is noteworthy that this good overall oxidation yield was accompanied with a heptanols:heptanones ratio remarkably higher than those observed with the other catalysts (13 instead of 2–4). Another difference between supported catalysts **7** and **11** and their homogeneous analogues **5** and **9** concerns the regioselectivity of heptane hydroxylation. The regioselectivity observed with homogeneous catalysts **5** and **9** is very much in favour of hydroxylation at position 2 (mean value of 5:63:22:10 for the ratio of the oxidation products on positions 1, 2, 3 and 4, respectively, Table 2). Such a regioselectivity has been reported previously for metalloporphyrins of the TDCPP series. It has been explained by a restricted access of heptane to the high-valent metal-oxo species due to the bulky *ortho*-chloro substituents of the porphyrin *meso*-aryl groups [1]. The regioselectivity obtained with the two supported catalysts **7** and **11** was slightly but significantly different; it was less in favour of heptane hydroxylation at position 2 (mean value of 4:52:30:14 for the regioselectivity index). This phenomenon is not easy to explain; it would correspond to a less restricted access to the metal-oxo species in the supported catalysts. This could be caused by a different position of

Table 2

Hydroxylation of heptane by PhIO catalyzed by homogeneous and supported Mn-porphyrins ^a

Catalyst		Total yield ^b (%)	Alcohols yield ^c (%)	Ketones yield ^d (%)	Alcohols/ ketones ratio	Regioselectivity ^e (%)			
						1	2	3	4
Mn(TDCSPP)	9	10	6	2	3	4	62	22	12
Mn(TDCSPP)-  -K10	11	54	47	3.5	13.4	5	51	30	14
Mn(TDCmNHCOCH ₃ PP)Cl	5	21	11	5	2.2	6	65	21	8
Mn(TDC-mNHCOCH ₃ PP)-  -SiO ₂	7	36	24	6	4	3	53	30	13

^a Conditions: ratio of catalyst: PhIO: alkane = 1:20:800; concentration of soluble catalyst: 1.5 mM or eq. of supported Mn-porphyrin = 1.5 μmol in 1 ml CH₃CN:CH₂Cl₂ (2:1) at 20°C under argon. In reaction using water soluble Mn(TDCSPP) **9** alone 10% CH₃OH was added in order to solubilize it.

^b Yields based on starting PhIO obtained after 2 h reaction. It was assumed that 2 mol of PhIO are necessary for the ketone formation.



^c Total yields of 1-, 2-, 3- and 4-heptanols.

^d Total yields of 2-, 3- and 4-heptanones.

^e Relative proportions of products coming from oxidation at position 1, 2, 3 and 4 of heptane.

Table 3

Oxidation of cyclooctene by H₂O₂ catalyzed by Mn^{III}-porphyrins in the presence of imidazole (Im), pyridine (Py) or CH₃COONH₄ (AA) ^a

Catalyst		Cocatalyst	Epoxide yields ^b (%)
Mn(TDCmNH ₂ PP)Cl	4	Im	60
		AA	70
Mn(TDCmNHCOCH ₃ PP)Cl	5	Im	60
		Py	18
		AA	81
Mn(TDC-mNHCCH ₃ PP)-  -SiO ₂	7	Im	60
		Py	62
		AA	70
Mn(TDCSPP)-  -K10	11	Im	15

^a Conditions: ratio of catalyst: H₂O₂: cocatalyst: cyclooctene = 1:20:10 (Im or AA) or 50 (Py):800; eq. of supported Mn-porphyrin = 1 μmol in 1 ml CH₃CN: CH₂Cl₂ (2:1) at room temperature.

^b Yields based on starting H₂O₂.

the *meso*-aryl rings in the homogeneous and supported catalysts. These rings should be in a mean position perpendicular to the porphyrin plane in the former [1], whereas they could make an angle inferior to 90° in the latter because of interactions with the inorganic matrix.

2.2.2. Oxidations with H₂O₂

In the presence of either imidazole or ammonium acetate, the Mn^{III} complexes **4** and **5** catalysed the epoxidation of cyclooctene (in large excess) with diluted H₂O₂ in yields between 60 and 80% (based on H₂O₂) (Table 3). The supported Mn-porphyrin **7** led to very simi-

Table 4

Oxidation of alkenes and alkanes by H₂O₂ catalyzed by compound **7** in the presence of CH₃COONH₄, under conversion conditions ^a

Substrate	Products	eq. of H ₂ O ₂ necessary ^b	Yield	Total yield
Cyclooctene	epoxide	2		91
Cyclohexene ^c	epoxide	4		95
non-1-ene	epoxide	4		95
<i>cis</i> -Stilbene	<i>cis</i> -Epoxide ^d	4		65
Cyclooctane	ol	3	26	36
	one		10	
Cyclohexane	ol	5	14	20
	one		6	
Heptane	ols ^e	5	5	7
	ones		2	
Adamantane	1-ol	3	34	46
	2-ol		12	
	-one		< 1	

^a Conditions: progressive addition of H₂O₂ (30% in H₂O, diluted 10 times in CH₃CN) to a substrate: cocatalyst: catalyst mixture (40/100/1) in CH₂Cl₂/CH₃CN (1:2) under aerobic conditions. Yields based on starting substrate.

^b Number of molar eq. of H₂O₂ necessary for maximum conversion of the substrate.

^c Cyclohex-2-en-1-ol and cyclohex-2-en-1-one were formed with yields lower than 5%.

^d *trans*-Stilbene oxide was also formed with a yield of 2% (ratio *cis* / *trans* = 97:3).

^e %Regioisomers at positions 1, 2, 3 and 4 around 3:60:25:12.

lar results (60–70% yield), while **11** acted as a much poorer catalyst (Table 3). It is noteworthy that, when pyridine was used as a cocatalyst instead of imidazole or ammonium acetate, the epoxide yield obtained with **7** was much higher than that obtained with **5** (62% instead of 18%). Therefore, catalyst **7** was used in the following studies on alkene and alkane oxidations.

Data of Table 4 allow one to compare the efficacy of the system to convert alkenes of different reactivity into the corresponding epoxides. They show results obtained upon progressive additions of H₂O₂ to an alkene: CH₃COONH₄: **7** mixture (40:100:1 molar ratio) in CH₃CN:CH₂Cl₂ (2:1), until complete alkene conversion. Complete conversion of cyclooctene occurred after addition of only 2 eq. of H₂O₂ to that system, the cyclooctene oxide yield being 91%. Complete conversion of cyclohexene and non-1-ene occurred after addition of 4 eq. of H₂O₂, and led to epoxide yields of 95%. Under identical conditions, *cis*-stilbene was oxidized to a 97:3 mixture of the corresponding *cis* and *trans* epoxides with an overall yield of 65%. The necessary consumption of 4 eq. of H₂O₂ for complete conversion of cyclohexene, non-1-ene and *cis*-stilbene, corresponding to a low selectivity towards H₂O₂ (25%), could be due to the well-known 'catalase-like' reaction in which the (porphyrin) Mn^V=O species reacts with H₂O₂ with formation of O₂ and H₂O [1]. In the case of supported catalyst **7**, one cannot exclude that H₂O₂ could also be consumed by secondary reactions with metal ions possibly present in montmorillonite K10.

The same system oxidized cyclooctane to cyclooctanol and cyclooctanone in yields of 26% and 10% after addition of 3 eq. of H₂O₂ (Table 4). Under identical conditions, adamantane was oxidized to adamantan-1-ol and -2-ol (respective yields of 34% and 12%). In the case of the less reactive alkanes, cyclohexane and heptane, lower yields were obtained (20% and 7%, respectively) even after addition of 5 eq. of H₂O₂ (Table 4).

During the course of this study, it was found

Table 5

Oxidation of alkenes and alkanes by H₂O₂ catalyzed by compound **7** in the presence of CH₃COONH₄, using an excess of substrate vs. H₂O₂^a

Substrate	Products	Yield ^b	Total yield ^c
Cyclooctene	epoxide		88
Cyclohexene ^c	epoxide		75
non-1-ene	epoxide		67
Cyclooctane	ol	72	90
	one	9	
Cyclohexane	ol	48	62
	one	7	
heptane	ols ^d	15	21
	ones	3	
adamantane	1-ol	44	56
	2-ol	12	
	-one		

^a Conditions: ratio of catalyst: H₂O₂: CH₃COONH₄: substrate = 1:20:100:800; eq. of supported Mn-porphyrin = 1 μmol in 1 ml CH₃CN:CH₂Cl₂ (2:1) at room temperature under aerobic conditions.

^b Yields based on starting H₂O₂ after 2 h.

^c Total yields calculated by assuming that 1 and 2 mol of H₂O₂ were used for alcohol and ketone formation, respectively.

^d %Regioisomers at positions 1, 2, 3, 4 = 3:60:25:12.

that an increase of the cocatalyst (CH₃COONH₄):catalyst ratio from 10 to 100 led to a dramatic increase of the oxidation yields. Table 5 shows that oxidation of hydrocarbon substrates in large excess with H₂O₂ in the presence of CH₃COONH₄ and **7** (hydrocarbon: H₂O₂: CH₃COONH₄: **7** molar ratio = 800:20:100:1) led to good yields of oxidized products relative to H₂O₂. Cyclooctene, cyclohexene and non-1-ene were epoxidised with yields between 67% and 88%, and cyclooctane, cyclohexane and adamantane were hydroxylated with yields between 56% and 90%. These results are quite remarkable as they show that there is only a slight loss of H₂O₂, by dismutation for instance, in these reactions using a Mn^{III}-porphyrin bound to an inorganic support. Only in the case of the poorly reactive alkane, heptane, was the yield much lower (21%), indicating an increasing contribution of secondary reactions consuming H₂O₂.

Kinetic experiments performed in order to determine initial rates of epoxidation of cy-

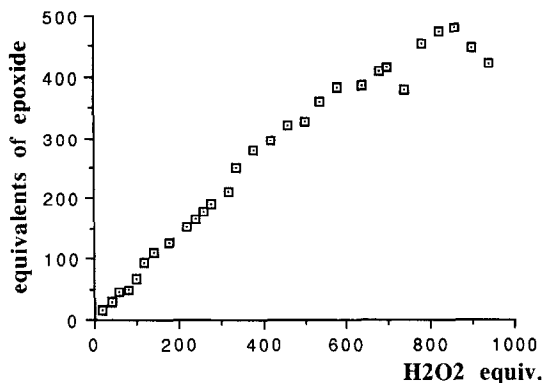


Fig. 3. Epoxidation of cyclooctene upon progressive addition of H_2O_2 to a $\text{CH}_3\text{COONH}_4$ -catalyst **7** mixture. Conditions: progressive addition of H_2O_2 and cyclooctene (20 eq. relative to the catalyst every 30 min) to a cyclooctene: $\text{CH}_3\text{COONH}_4$: **7** (1000:100:1) mixture in $\text{CH}_3\text{CN}:\text{CH}_2\text{Cl}_2$ (2:1); 'equivalent concentration' of catalyst: 10^{-3} M.

clooctene with H_2O_2 (catalyst **7**: $\text{CH}_3\text{COONH}_4$: H_2O_2 : cyclooctene = 1:100:400:200) gave a value of $10 \text{ cycles min}^{-1}$ (data not shown).

Finally, the efficiency and stability of catalyst **7**, under operating conditions, was studied by progressive addition of H_2O_2 to a cyclooctene: $\text{CH}_3\text{COONH}_4$: **7** (1000:100:1) mixture in $\text{CH}_3\text{CN}:\text{CH}_2\text{Cl}_2$ (2:1). Fig. 3 shows a linear formation of cyclooctene oxide as a function of the amount of H_2O_2 added (up to 800 eq.). After addition of 800 eq. of H_2O_2 (relative to **7**), 50% of starting cyclooctene was oxidized to the corresponding epoxide. Further additions of H_2O_2 did not increase epoxide formation presumably because of a great decrease of the amounts of cyclooctene and possible inactivation of the catalyst. However, after filtration, washing with acetone and drying (at 80°C) of the catalyst, epoxidation of cyclooctene under identical conditions occurred with identical rates and yields.

3. Conclusion

The two supported catalysts, **7** and **11**, which were prepared by covalent binding of $\text{Mn}(\text{TDCPP})$ derivatives to either silica or mont-

morillonite, exhibited different behaviours as catalysts for hydrocarbon oxidation. Compound **11** was a remarkable catalyst for the hydroxylation of linear alkanes such as heptane with PhIO ; it gave higher yields (54%) than corresponding homogeneous catalysts and supported catalyst **7**. However, **11** was a poor catalyst for hydrocarbon oxidation with H_2O_2 . When using this oxidant, **7** appeared as a good catalyst slightly more efficient than corresponding homogeneous catalysts for the epoxidation of alkenes with H_2O_2 . Interestingly, supported catalyst **7** was able to transfer an oxygen atom from H_2O_2 to a substrate (used in excess) with yields (based on H_2O_2) between 65 and 95% in the case of alkenes, and between 21% to 90% in the case of alkanes. This result is interesting as it shows that it is possible to build up metalloporphyrin-based supported catalysts for alkene and alkane oxidation with H_2O_2 , not leading to an important non-productive H_2O_2 decomposition.

Epoxidation of alkenes and hydroxylation of alkanes by H_2O_2 have been performed under similar conditions (temperature between 20 and 100°C) in the presence of heterogeneous catalysts such as titanosilicates [16]. Further studies are necessary to compare the respective advantages and drawbacks of the two systems, i.e., supported metalloporphyrins such as **7** and redox molecular sieves or metal complexes encapsulated in molecular sieves [16]. In that respect, one of the main interest of supported Fe^{III} - or Mn^{III} -porphyrins remains their oxidation mechanisms which closely mimic cytochrome P450-dependent enzymes.

4. Materials and methods

4.1. Physical measurements

UV-vis. spectra of Mn^{III} -porphyrins were recorded on a CARY 210 spectrophotometer. For the supported Mn^{III} -porphyrins a Beckman

5270 spectrophotometer was used. Microanalyses were carried out by the Service de Microanalyses du CNRS (Vernaison, France). Mass spectra of metalloporphyrins were performed on a Ribermag apparatus at the Ecole Normale Supérieure de Paris. Gas chromatography analyses were carried out using an Intersmat IG 120FL chromatograph equipped with a hydrogen flame ionization detector. The glass column (length 3 m, internal diameter 3 mm) was packed with 10% FFAP on chromosorb WAW (80/100 mesh). The products formed were analyzed by comparison of their retention time with those of authentic samples. Yields were determined by using an internal standard.

$^1\text{H-NMR}$ spectra were recorded at 20°C on a Bruker WM250 spectrometer operating at 250 MHz. The IR spectra were measured on a Perkin Elmer 783 spectrophotometer using KBr pellets.

4.2. Materials

Acetonitrile and dichloromethane HPLC grade (SDS, Peypin, France) were used as received. All alkene or alkane substrates were purchased from Janssen in their highest commercial purity, stored at 5°C and purified by passage through a column of basic alumina (Aldrich) prior to use.

Iodosylbenzene was prepared as described previously [9], carefully dried under reduced pressure and kept at 5°C. Hydrogen peroxide (H_2O_2 , 30% in H_2O , Prolabo) was stored at 5°C and titrated every month [10]. 2,6-Dichloro-3-nitrobenzaldehyde was prepared by direct nitration of 2,6-dichlorobenzaldehyde (Janssen) according to a classical procedure [11].

Meso-tetrakis-(dichlorophenyl)porphyrin (H_2TDCPP) was prepared by the method of Lindsey and Wagner [12].

Silica CBA (Bondesil 40 μm , containing 0.9 mmol g^{-1} of $-\text{CH}_2\text{COOH}$ functional groups) from Analytichem, was dried by heating at 150°C for 8 h under reduced pressure. Montmorillonite K10 (Südchemie) was Na^+ -exchanged by stirring its suspension in water containing 5

M NaCl (2 g of montmorillonite for 100 ml NaCl solution). The solid was washed with 1 l water until no NaCl was detectable in the filtration and dried for 24 h at 80°C.

4.3. Synthesis of Mn^{III} -porphyrins

4.3.1. *Meso*-tetrakis-(2,6-dichloro-3-nitrophenyl)porphyrin **2**

Porphyrin **2** was prepared according to a previously described procedure [8] using 4.4 g (20 mmol) of 2,6-dichloro-3-nitrobenzaldehyde **1**, 1.39 ml (20 mmol) of pyrrole and 3×0.244 ml (2 mmol) of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in 1 l of CH_2Cl_2 (freshly distilled from CaH_2). The resulting porphyrinogen was oxidized by addition of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (10 g, 44 mmol) in 200 ml of toluene. Column chromatography (alumina, CH_2Cl_2) and recrystallisation from a CH_2Cl_2 -cyclohexane mixture afforded 2 g (38% yield) of porphyrin **2**.

$^1\text{H-NMR}$ (CDCl_3), δ : -2.5 (s, 2H); 7.96–8.27 (2d, 8H, $J = 9$ Hz); 8.65 (s, 8H) ppm. MS (Cl , NH_3) m/z : 1071 ($M^+ + 1$, 100), 1035 ($M^+ - \text{Cl}$, 5). UV-vis. (CH_2Cl_2), λ_{max} (ϵ , $10^4 \text{ M}^{-1} \text{ cm}^{-1}$): 420 (Soret) (36.9); 511 (2.1); 587 (0.8) nm.

4.3.2. *Meso*-tetrakis-(2,6-dichloro-3-aminophenyl)porphyrin **3** and its Mn^{III} complex **4**

0.5 g (0.47 mmol) of porphyrin **2** was dissolved in 30 ml of concentrated HCl and 1.8 g (8 mmol) of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was added to the solution. The solution was stirred at 70°C for 30 min. After cooling in an ice bath, the mixture was slowly neutralized with 32% aqueous ammonia. The reaction temperature was kept below 10°C. An excess of ammonia was then added and the mixture was stirred for 12 h at 20°C. The solvent was eliminated by distillation under vacuum and the solid residue was extracted with acetone. After filtration, the organic phase was chromatographed on a silica gel column using CH_2Cl_2 as eluent. Recrystallization from a CH_2Cl_2 -pentane mixture afforded 0.43 g of pure **3** (98% yield).

$^1\text{H-NMR}$ (acetone- d_6) δ : -2.41 (s, 2H); 5.49 (s, 8H); 7.61–7.40 (2d, 8H, $J = 9$ Hz); 8.80 (s, 8H) ppm. MS (Cl, NH_3) m/z : 951 ($M^+ + 1$, 100), 915 ($M^+ - \text{Cl}$, 5), 879 ($M^+ - 2\text{Cl}$, 1). UV-vis. (acetone), λ_{max} (ϵ , $10^4 \text{ M}^{-1} \text{ cm}^{-1}$): 419 (Soret) (30.9); 511 (3.5); 549 (2.4); 593 (3.2) nm.

Metallation of **3** was performed according to a classical technique [13]. The crude Mn^{III} -porphyrin was purified by recrystallization from an acetone-cyclohexane mixture. This procedure afforded pure **4** in a 86% yield.

MS (Cl, NH_3) m/z : 1003 ($M^+ - \text{OAc}$, 100). UV-vis. (CH_2Cl_2), λ_{max} (ϵ , $10^4 \text{ M}^{-1} \text{ cm}^{-1}$): 371 (8.37); 400 (5.72); 477 (Soret) (16.00); 579 (1.30); 610 (0.69) nm. Elemental Analysis: Calculated for $\text{MnC}_{46}\text{H}_{27}\text{N}_8\text{Cl}_8\text{O}_2 \cdot 4.5\text{H}_2\text{O}$: C, 48.32; H, 3.17; N, 9.80; Cl, 24.81; Mn, 4.80. Found: C, 48.39; H, 3.17; N, 10.07; Cl, 24.70; Mn, 4.62.

4.3.3. Mn^{III} [meso-tetrakis-(2,6-dichloro-3-acetylaminophenyl)porphyrin]Cl **5**

97 mg (0.09 mmol) of porphyrin **4** was suspended in 5 ml of dry THF and 150 μl of anhydrous pyridine was added. The reaction mixture was cooled at 0°C and then, 150 μl (2.1 mmol) of acetyl chloride (Fluka) was added dropwise under magnetic stirring. After stirring overday at room temperature, the solvent was eliminated by distillation under vacuum and the crude product washed with Et_2O . After recrystallization from CH_2Cl_2 -pentane, 0.05 g of **5** was obtained (46% yield).

MS (FAB $^+$) m/z : 1171 ($M^+ - \text{Cl}$, 100); 1206 (M^+ , 10). UV-vis. (acetone), λ_{max} (ϵ , $10^4 \text{ M}^{-1} \text{ cm}^{-1}$): 370 (10.6); 477 (Soret) (17.5); 523 (3.5); 582 (4.1); 615 (3.3) nm. IR (KBr): 1670 ($\nu_{\text{C}-\text{O}}$) cm^{-1} .

4.3.4. Mn^{III} [meso-tetrakis-(2,6-dichloro-3-sulfonatophenyl)porphyrin] **9**

Porphyrin **8** and its Mn^{III} complex **9** were prepared as described previously [14]. UV-vis. of **9**, λ_{max} (H_2O): 464 (Soret), 565, 600 nm.

4.3.5. Mn^{III} [meso-tetrakis-(2,6-dichloro-3-N-propylsulfonamidophenyl)porphyrin] **12**

0.2 g (0.15 mmol) of porphyrin **9** and 0.8 g (3.8 mmol) of PCl_5 (Aldrich) were mixed in a mortar. The reaction mixture was introduced in a flask and heated at 150°C for 20 h. After cooling to room temperature, the resulting paste was extracted with CH_2Cl_2 , dried over NaCl and filtered. After evaporation of the solvent, this procedure afforded porphyrin **10**. 0.1 g (0.077 mmol) of porphyrin **10**, 8 ml of propylamine and 2 ml of pyridine were refluxed overnight with magnetic stirring and argon. The reaction mixture was concentrated by distillation under vacuum and the solid residue was washed with water and extracted with CH_2Cl_2 . The organic phase was chromatographed on a silica gel column using CH_2Cl_2 - CH_3OH (90:10) as eluent. **12** was obtained (90% yield) after evaporation of the solvents to dryness, dissolution of the Mn-porphyrin in CH_2Cl_2 , filtration on a short NaCl column and recrystallization from a CH_2Cl_2 -pentane mixture.

MS (MALDI-TOF) m/z : 1428 ($M^+ - \text{Cl} + 1$, 100). UV-vis. (acetone), λ_{max} (ϵ , $10^4 \text{ M}^{-1} \text{ cm}^{-1}$): 368 (6.5); 371 (6.5); 477 (Soret) (11); 580 (2.1); 615 (1.4) nm.

Elemental analysis for the free base porphyrin of **12**: Calculated for $\text{C}_{56}\text{H}_{50}\text{N}_8\text{Cl}_8\text{S}_4\text{O}_8 \cdot 2\text{H}_2\text{O}$: C, 47.67; H, 3.83; N, 7.95. Found: C, 47.59; H, 4.03; N, 7.62.

4.4. Synthesis of the supported Mn^{III} -porphyrins

4.4.1. Supported catalyst **6**

5 g of silica CBA (Bondesil, 40 μm , containing 0.9 mmol g^{-1} of $-\text{CH}_2\text{COOH}$ functional groups) from Analytichem, was dried by heating at 150°C for 8 h under reduced pressure. Then, 50 ml of thionyl chloride was added. The resulting suspension was refluxed for 7 h under magnetic stirring and argon. Then, thionyl chloride was eliminated by distillation under vacuum and the solid obtained was dried at 150°C for 3 h under reduced pressure. 0.95 g (0.91

mmol) of porphyrin **4** was dissolved in 200 ml anhydrous CH_3CN and added, under argon, to the flask containing the modified silica. The reaction mixture was refluxed for 10 h. After cooling and filtering, the solid was washed with CH_2Cl_2 , CH_3CN , extracted with acetone using a Soxhlet system and dried at 80°C for 24 h.

UV-vis., λ_{max} (dilution in $\gamma\text{-Al}_2\text{O}_3$): 411, 473 (Soret), 511, 567 nm.

4.4.2. Supported catalyst **7**

Supported catalyst **7** was prepared from 0.5 g of supported catalyst **6**, 5 ml dry THF, 250 μl anhydrous pyridine and 250 μl of acetylchloride, as described for porphyrin **5**. The solid was washed with CH_3OH , $\text{CH}_2\text{Cl}_2/\text{HCl}(\text{g})$, acetone and Et_2O and dried at 80°C for 24 h.

UV-vis., λ_{max} (Al_2O_3): 416, 474 (Soret), 512, 580 nm.

4.4.3. Supported catalyst **11**

4.4.3.1. Preparation of montmorillonite K10 bearing $-(\text{CH}_2)_3\text{NH}_2$ groups according to [15].

Montmorillonite K10- Na^+ was H^+ -exchanged by stirring its suspension in 10^{-2} M HCl (10 g K10- Na^+ for 300 ml HCl solution) at room temperature for 2 h. Then, the clay was washed with pure water until pH (floaty solution) = 7, with EtOH, anhydrous Et_2O and dried for 24 h at 80°C . 5 g K10- H^+ montmorillonite were suspended in anhydrous toluene (20 ml) and stirred under argon for 15 min. Then, 1.4 ml (5 mmol) aminopropyltriethoxysilane were added. The mixture was refluxed under argon for 48 h and, after cooling, the resulting solid was filtered, washed with toluene, Et_2O and dried for 24 h at 80°C .

4.4.3.2. Covalent binding of porphyrin **9** to montmorillonite K10- $(\text{CH}_2)_3\text{NH}_2$.

0.2 g (0.15 mmol) of porphyrin **9** and 0.8 g (3.8 mmol) of PCl_5 (Aldrich) were mixed in a mortar. The reaction mixture was introduced in a flask and heated at 150°C for 20 h. After cooling to room temperature, the resulting paste was extracted

with CH_2Cl_2 , dried over NaCl and filtered. After evaporation of the solvent, this procedure afforded porphyrin **10**. 0.2 g (0.15 mmol) porphyrin **10** was dissolved in 20 ml anhydrous pyridine and added, dropwise, under magnetic stirring, to a flask containing 1 g functionalised montmorillonite suspended in 5 ml anhydrous pyridine. The reaction mixture was refluxed overnight and filtered. The obtained solid was washed with CH_2Cl_2 , until no porphyrin was detectable in the filtrate, then by CH_3CN , CH_3OH and dried for 24 h at 80°C . UV-vis., λ_{max} (Nujol): 476 (Soret), 585, 628 nm. Elemental analysis of Mn indicated that **11** contained 27 μmol of Mn-porphyrin bound per g of support (3.5% m/m).

4.5. Procedure for catalytic oxidations

All substrates were checked by gas chromatography to ensure that no oxidation products were present before reaction. Reactions were carried out in a 5 ml tube equipped with a septum cap and a stirring bar at room temperature.

Catalyst, cocatalyst, substrate and internal standard (acetophenone) were dissolved in a $\text{CH}_3\text{CN}:\text{CH}_2\text{Cl}_2$ mixture (650 $\mu\text{l}:\text{350 } \mu\text{l}$) and the oxidant added last. Quantitative analysis was performed on aliquots directly withdrawn from the reaction medium. Yields were determined by GC by comparison with authentic samples using calibration curves with acetophenone as an internal standard. No reaction occurred in the absence of the catalysts in reactions performed under identical conditions.

References

- [1] T.J. McMurry and J.T. Groves, In: ed. P.R. Ortiz de Montelano, Cytochrome P-450, Structure, Mechanism and Biochemistry (Plenum Press, New York, 1986) 1; T.C. Bruice, Acc. Chem. Res. 24 (1991) 243; M.J. Gunter and P. Turner, Coord. Chem. Rev. 108 (1991) 115; T.G. Traylor, Pure Appl. Chem. 63 (1991) 265; B. Meunier, Chem. Rev. 92 (1992) 1411; D. Mansuy, Coord. Chem. Rev. 125 (1993) 129; R.A.

- Sheldon, ed., *Metalloporphyrins in Catalytic Oxidations* (Marcel Dekker, New York, 1994).
- [2] T.G. Traylor, W.P. Fann and D. Bandyopadhyay, *J. Am. Chem. Soc.* 111 (1989) 8009; T.G. Traylor, S. Tsuchiya, Y.S. Byun and C. Kim, *J. Am. Chem. Soc.* 115 (1993) 2775; J.F. Bartoli, P. Battioni, W.R. De Foor and D. Mansuy, *J. Chem. Soc., Chem. Comm.* (1994) 23.
- [3] P. Battioni, J.P. Renaud, J.F. Bartoli, M. Reina-Artiles, M. Fort and D. Mansuy, *J. Am. Chem. Soc.* 110 (1988) 8462.
- [4] F. Montanari, S. Banfi and S. Quici, *Pure Appl. Chem.* 61 (1989) 1631; S. Banfi, F. Legramandi, F. Montanari, G. Pozzi and S. Quici, *J. Chem. Soc., Chem. Comm.* (1991) 1285; S. Banfi, F. Montanari, G. Pozzi and S. Quici, *Tetrahedron* 50 (1994) 9025.
- [5] A.M. d'A Rocha Gonsalves, R.A. W. Johnstone, M.M. Pereira and J. Shaw, *J. Chem. Soc., Perkin Trans. 1* (1991) 645.
- [6] A. Thellend, P. Battioni and D. Mansuy, *J. Chem. Soc., Chem. Comm.* (1994) 1035.
- [7] J.R. Lindsay Smith, In: ed. R.A. Sheldon, *Metalloporphyrins in Catalytic Oxidations* (Marcel Dekker, New York, 1994) p. 325.
- [8] S. Banfi, A. Maiocchi, A. Moggi, F. Montanari and S. Quici, *J. Chem. Soc., Chem. Commun.* (1990) 1794; S. Banfi, R. Mandelli, F. Montanari and S. Quici, *Gazz. Chim. Ital.* 123 (1993) 409.
- [9] B.S. Furniss, A.J. Hannaford, P.W.G. Smith and A.R. Tatchell, *Vogel's Textbook of Practical Organic Chemistry*, 5th Ed. (Longman, Wiley, New York, 1989) p. 869.
- [10] P.C. Bonet-Maury, *C.R. Acad. Sci. Fr.* 217 (1944) 127.
- [11] J. Lock, *Chem. Ber.* 62 (1935) 1505.
- [12] J.S. Lindsey and R.W. Wagner, *J. Org. Chem.* 54 (1989) 828
- [13] H. Kobayashi, T. Higuchi, Y. Kaizu, H. Osada and H. Aoki, *Bull. Soc. Chim. Jpn.* 48 (1975) 3137.
- [14] D. Dolphin, T. Nakano, T. Kirk, R. Maione, R. Farrell and T. Wijesekera, *PCT Int. Appl. WO 88/07988* (1988); H. Turk and W.T. Ford, *J. Org. Chem.* 56 (1991) 1253; L. Barloy, J.P. Lallier, P. Battioni and D. Mansuy, *New. J. Chem.* 16 (1992) 71; S. Camperstrini and B. Meunier, *Inorg. Chem.* 31 (1992) 1999.
- [15] W.F. Spender and J.E. Gieseking, *J. Phys. Chem.* 56 (1952) 751; K. Mikkanti, Y.V. Subba Rao and B.M. Choudary, *Tetrahedron Lett.* 30 (1989) 251.
- [16] R.A. Sheldon and J. Dakka, *Catal. Today* 19 (1994) 215; R. Hutter, D.C.M. Dutoit, T. Mallat, M. Schneider and A. Baiker, *J. Chem. Soc., Chem. Comm.* (1995) 163; K.A. Koyano and T. Tatsumi, *J. Chem. Soc., Chem. Comm.* (1996) 145.