# An Easy Access to Polyhalogenated Metalloporphyrins Covalently Bound to Polymeric Supports as Efficient Catalysts for Hydrocarbon Oxidation

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Reaction of silica, montmorillonite and polystyrene bearing amino functions with several polyhalogenated metalloporphyrins gave an easy one-step access to new supported catalysts, owing to a selective nucleophilic substitution of the *para*-halogen atoms of the porphyrin *meso*-aryl groups by the polymer amine function; these catalysts were very active for cyclooctene epoxidation and alkane hydroxylation by PhIO.

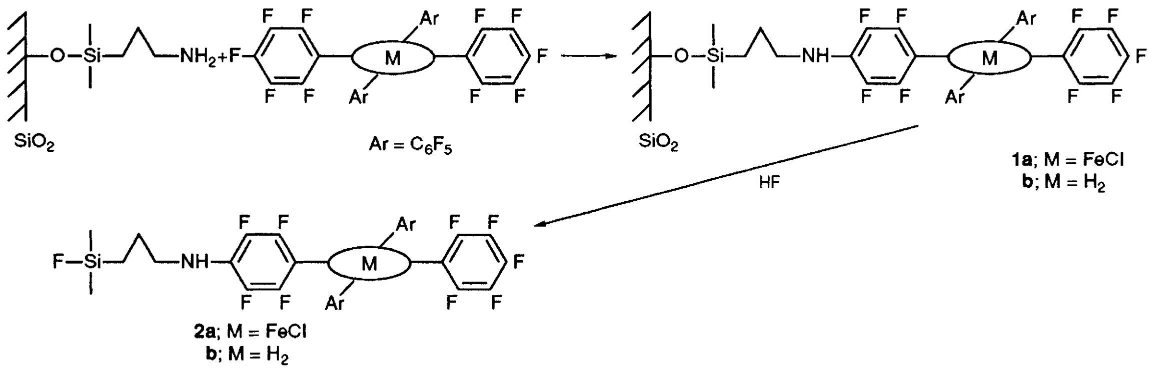
Efficient biomimetic systems based on metalloporphyrins have been developed during the last decade and used for hydrocarbon oxidation.[1] The use of perhalogenated porphyrins on the one hand[1] and supported metalloporphyrins[1,2] on the other has greatly improved the efficiency of the catalysts. Recently, it was shown that nucleophiles react very easily with *meso*-tetra(pentafluorophenyl) porphyrin, $H_2$tfpp, with selective substitution of the *para*-F substituent of the *meso*-aryl groups.[3] This reaction was applied to the polymerisation of tfpp derivatives in the presence of sodium sulfide.[4]

This communication describes another application of this substitution reaction, the preparation of new supported oxidation catalysts by covalent binding of $H_2$tfpp derivatives onto various supports bearing an amino group as a nucleophile. These supported polyhalogenated metalloporphyrins were found to be good catalysts for alkane hydroxylation and alkene epoxidation.

In a typical experiment, a mixture of $Fe^{III}$(tfpp)Cl (70 μmol) and a modified silica (500 mg) bearing Si–$[CH_2]_3$–$NH_2$ groups (1.1 mmol $g^{-1}$) in diglyme was heated at 140 °C under argon for 3 h. The resulting solid was thoroughly washed with a large variety of solvents [$CH_2Cl_2$, cyclohexane, dimethylformamide (DMF), MeCN, EtOH, $Et_2O$] extracted with $CH_2Cl_2$ by a Soxhlet procedure and dried at 80 °C for 24 h. Elemental analysis (Fe and F) of solid **1a** indicated that it contained 90 μmol of iron porphyrin bound per gram of support (9.7% m/m). A similar reaction performed with the same iron porphyrin and with silica not bearing aminopropyl groups, under identical conditions, led to a minor retention of the metalloporphyrin in the final solid (<1% m/m).

The supported porphyrin **1a** showed a Soret band at 419 nm similar to that of the starting Fe(tfpp)Cl indicating that the porphyrin ring was not modified during the anchoring procedure.

The nature of the covalent bond between $H_2$tfpp and the aminopropylsilica was established by a $^1$H NMR study of the soluble porphyrin obtained by solubilization of **1b** (the demetallated form of **1a**) in HF[5] (Scheme 1). The resulting soluble porphyrin **2b** exhibited UV–VIS and $^1$H NMR characteristics [λ/nm (ε) 417 (253 000), 510 (12 000), 548 (2200) and 587 (3800); δ($CD_2Cl_2$, $D_2O$, HF) 9.03 and 8.93




**Scheme 1**

**Table 1** Catalytic activities of polyhalogenated metalloporphyrins covalently bound to polymeric supports, for cyclooctene epoxidation and cyclohexane and heptane hydroxylation by PhIO[a]

| Supported catalyst | Loading of porphyrin µmol $g^{-1}$ | Loading of porphyrin (% m/m) | Cyclooctene oxide yield (%) | Cyclohexanol + cyclohexanone Yield[g] (%) | Cyclohexanol + cyclohexanone (ol/one)[e] | Heptanols + heptanones[f] Yield (%)[g] | Heptanols + heptanones[f] (ols/ones)[f] |
|---|---|---|---|---|---|---|---|
| {**Si**–O–Si-$[CH_2]_3NHC_6F_4$}$(C_6F_5)_3$**P** FeCl[b] | 90 | (9.7) | 98 | 62 | (10) | 44[h] | (14) |
| {**MT**–O–Si-$[CH_2]_3NHC_6F_4$}$(C_6F_5)_3$**P** FeCl[c] | 20 | (2.1) | 82 | 44 | (7) | 44[h] | (16) |
| {**P**–$CH_2$–$NHC_6F_4$}$(C_6F_5)_3$**P** FeCl[d] | 25 | (2.7) | 85 | 27 | (25) | 23[h] | (16) |
| {**Si**–O–Si-$[CH_2]_3NHC_6F_4$}$(C_6F_5)_3$**P** MnCl | 51 | (5.5) | 99 | 64 | (6) | 50[h] | (5.5) |
| {**Si**–O–Si-$[CH_2]_3NHC_6Cl_4$}$(C_6Cl_5)_3$**P** FeCl | 66 | (7.1) | 88 | 39 | (24) | 20[i] | (15) |
| {**Si**–O–Si-$[CH_2]_3NHC_6F_4$}$(C_6F_5)_3Br_8$**P** FeCl | 55 | (5.9) | 79 | 46 | (11) | 42[h] | (10) |

[a] Conditions: molar ratio of catalyst : PhIO : hydrocarbon = 1 : 20 : 800; 'equivalent concentration' of supported catalyst: 2 mmol $dm^{-3}$ in $CH_2Cl_2$ (0.5 $cm^3$) at 20 °C during 1 h. Yields based on starting PhIO were found unchanged after 24 h. [b] Aminopropyl-silica (Bondesil, 1.1 mmol $g^{-1}$, Analytichem). [c] Aminopropyl-montmorillonite (prepared as described previously[8] from MT K10, Fluka, 0.7 mmol $g^{-1}$). [d] Aminomethyl-polystyrene beads cross-linked with 1% divinylbenzene (Pierce, 0.3–0.7 mmol $g^{-1}$). [e] Alcohol to ketone ratio. [f] Heptan-2-, 3- and 4-ol; heptan-2-, 3- and 4-one. [g] For total yields, it was assumed that 2 mol of PhIO were necessary for ketone formation. [h] Relative ratios of products arising from oxidation at positions 2, 3 and 4 of heptane = 40 : 40 : 20. [i] Regioselectivity for heptane oxidation different from that given in [h] and equal to 57 : 29 : 14.

(8H), 3.74 (2H), 2.0 (2H) and 1.25 (2H)] very similar to those of the porphyrin **3b**, *meso*-(tris-pentafluorophenyl)(4-propylaminotetrafluorophenyl)porphyrin, prepared by monosubstitution of a *para*-F of $H_2$tfpp by propylamine.† In particular, the presence in the spectrum of **2b** of a signal at δ 3.74 which was almost identical to that of the N–$CH_2$ moiety of porphyrin **3b** (and at a very similar chemical shift; δ 3.67 for **3b**) showed the formation of a covalent bond between an $NH_2$ group of functionalized silica and a *para*-carbon of the *meso*-aryl group of $H_2$tfpp, as expected for nucleophilic reaction of aminopropylsilica with $H_2$tfpp.

This anchoring method allowed an easy one-step preparation of supported catalysts by reaction between various polyhalogenated metalloporphyrins and functionalized supports. Thus, reactions of Fe(tfpp)Cl with aminopropylmontmorillonite or aminomethylpolystyrene led to supported catalysts containing respectively 2.1 and 2.7% (m/m) metalloporphyrin (Table 1). Reaction of aminopropyl-silica with Mn(tfpp)Cl and Fe(tfpBr$_8$p)Cl [tfppBr$_8$p = *meso*-tetra(pentafluorophenyl)-β-octabromoporphyrin][6] led to the incorporation of about 6% (m/m) metalloporphyrin to the support. The nucleophilic substitution was found to be more difficult with Fe(tCl$_5$pp)Cl [tCl$_5$pp = *meso*-tetra(pentachlorophenyl) porphyrin],[7] its reaction with aminopropylsilica requiring 24 h reflux in diglyme to give 7% (m/m) of porphyrin binding.

All the supported $Fe^{III}$ (or $Mn^{III}$) porphyrins catalysed the epoxidation of cyclooctene and the hydroxylation of cyclohexane and heptane by PhIO (Table 1). Epoxidation yields varied from 80 to 100%, the best ones being obtained with Fe(tfpp)Cl and Mn(tfpp)Cl bound to silica. These catalysts were also very efficient for the hydroxylation of cyclohexane and heptane (respective yields around 60 and 50%). Fe(tfpp)Cl bound to montmorillonite gave lower yields for cyclooctene epoxidation and cyclohexane hydroxylation but was one of the best catalysts for heptane hydroxylation (44% yield). This particular ability of metalloporphyrins supported on montmorillonite to catalyse linear alkane hydroxylation has previously been reported.[2f] The iron porphyrin bound to polystyrene was the least efficient catalyst. Finally, it is noteworthy that Fe(tCl$_5$pp)Cl and Fe(tfpBr$_8$p)Cl bound to silica are clearly less efficient than Fe(tfpp) bound to the same support.

The aforementioned results describe a new easy access to good oxidation catalysts bound to various supports, by a one-step reaction between organic and mineral polymers bearing an amine function and polyhalogenated metalloporphyrins. This reaction appears rather general and does not require the difficult preparation of polyhalogenated porphyrins bearing a functional group. In fact, most of the metalloporphyrins and polymers used are commercially available.

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† Prepared according to ref. 3(*b*) except for the use of a propylamine to $H_2$tfpp molar ratio of 1 : 1.

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## References

1 For recent reviews: T. J. McMurry and J. T. Groves, in *Cytochrome P-450, Structure Mechanism and Biochemistry*, ed. P. R. Ortiz de Montellano, Plenum Press, New York, 1986, p. 1; B. Meunier, *Bull. Soc. Chim. Fr.*, 1986, II, **4**, 578; D. Mansuy, *Pure Appl. Chem.*, 1987, **59**, 759; D. Mansuy, P. Battioni and J. P. Battioni, *Eur. J. Biochem.*, 1989, **184**, 267; D. Mansuy, *Pure Appl. Chem.*, 1990, **62**, 741; M. J. Gunter and P. Turner, *Coord. Chem. Rev.*, 1991, **108**, 115.

2 (*a*) A. W. Van der Made, J. W. H. Smeets, R. J. M. Nolte and W. Drent, *J. Chem. Soc., Chem. Commun.*, 1983, 1204; (*b*) J. A. S. Razenberg, A. W. Van der Made, J. W. H. Smeets and R. J. M. Nolte, *J. Mol. Catal.*, 1985, **31**, 271; (*c*) T. Mori, T. Santa and M. Hirobe, *Tetrahedron Lett.*, 1985, **26**, 555; (*d*) P. Battioni, J. P. Lallier, L. Barloy and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, 1989, 1149; (*e*) T. Tatsumi, M. Nakamura and H. Tominaga, *Catalysis*, 1989, **6**, 163; (*f*) L. Barloy, P. Battioni and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, 1990, 1365; (*g*) D. R. Leanord and J. R. Lindsay Smith, *J. Chem. Soc., Perkin Trans. 2*, 1991, 25.

3 (*a*)K. M. Kadish, C. Araullo-Mc-Adams, B. C. Han and M. M. Franzen, *J. Am. Chem. Soc.*, 1990, **112**, 8364; (*b*) P. Battioni, O. Brigaud, H. Desvaux, D. Mansuy and T. G. Traylor, *Tetrahedron Lett.*, 1991, **32**, 2893.

4 T. G. Traylor, Y. S. Byun, P. S. Traylor, P. Battioni and D. Mansuy, *J. Am. Chem. Soc.*, 1991, **113**, 7821.

5 According to a previously described method for cleavage of the Si–O–Si bonds of silica and analysis of groups covalently bound to silica: C. Gaget, D. Morel, M. Traore and J. Serpinet, *Analusis*, 1984, **12**, 386. Porphyrin **2b** was extracted from the solubilization medium (40% HF in $H_2O$ in the presence of $H_2SO_4$[5]) by $CD_2Cl_2$ containing HF, and directly characterized by $^1H$ NMR spectroscopy. Under these conditions it mainly exists as a porphyrin–$NH[CH_2]_2CH_2SiF_3$ moiety because of the presence of HF. Further isolation and characterisation is difficult because of the fast reaction of its Si–F bonds with nucleophiles including $H_2O$.

6 P. E. Ellis and J. E. Lyons, *Coord. Chem. Rev.*, 1990, **105**, 181.

7 P. S. Traylor, D. Dolphin and T. G. Traylor, *J. Chem. Soc., Chem. Commun.*, 1984, 279.

8 K. Mukkanti, Y. V. Subba Rao and B. M. Choudary, *Tetrahedron Lett.*, 1989, **30**, 251.