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Alkene Epoxidation Catalysed by Ligand-Bound Supported Metalloporphyrins

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Abstract: *Iron(III) and manganese(III) tetra(2,6-dichlorophenyl)porphyrin bound to surface imidazole and pyridine groups on solid supports are efficient catalysts for the epoxidation of cyclooctene by iodosylbenzene.*

Tetraarylmetalloporphyrins catalyse the oxidations of a wide range of organic compounds,[1] and several studies have shown how the shape-,[2] regio-[3] and stereo-selectivity[4] of these reactions can be controlled by structural features on the catalyst. However, their full potential will only be realised if the catalysts can be made stable towards self-oxidation and can be recovered and reused. Recent work indicates that the stability of the catalysts is greatly enhanced by halogenation of the β-pyrrole carbons and of the ortho positions of the aryl groups on the porphyrin ring.[5] An alternative approach is to use site-isolation[6] on a solid support to prevent porphyrin degradation by intermolecular reactions between the active oxidant and other porphyrin molecules. The challenge remains to develop methods for the recovery and reuse of these catalysts.

One method we have used is to ligate the metalloporphyrin to the surface of a solid. This approach has been employed in studies on reversible oxygen binding with iron(II) porphyrins[7] but has found only limited applications in metalloporphyrin-catalysed oxidations.[8] Here we report the use of iron(III) and manganese(III) tetra(2,6-dichlorophenyl)porphyrin [Fe(III)TDCPP and Mn(III)TDCPP], bound to surface imidazole and pyridine groups, as catalysts in alkene epoxidation.

Fe(III)TDCPP has been bound to three supports, (1-imidazolyl)methylated polystyrene (1% crosslinked) (PS-Im),[9] poly-4-vinylpyridine (6% crosslinked) (PVP) and silica gel modified with 3-(1-imidazolyl)propyl groups (Si-Im),[10] and Mn(III)TDCPP to PS-Im and Si-Im. The iron porphyrin binds more strongly, in particular to the organic polymer ligands, than the Mn(III) analogue and it seems likely that Fe(III)TDCPP is bis-ligated to the flexible organic polymers. Iron(III) porphyrins have a strong tendency to form bis-complexes with nitrogen ligands,[11] by contrast manganese(III) porphyrins form stable mono-ligated pentacoordinated species.[12] Thus, Fe(III)TDCPP is not leached from PS-Im by washing with dichloromethane, acetone or methanol, although it can be displaced by the competitive ligand imidazole in methanolic solution. By contrast Mn(III)TDCPP is removed from PS-Im by methanol. With Si-Im, washing with CH_2Cl_2 and MeOH removes some Fe(III)TDCPP leaving a residue (4 mg per g of silica gel) of bound catalyst. The Si-Im-Mn(III)TDCPP was only washed with CH_2Cl_2 since methanol displaces the metalloporphyrin.

All the supported Fe(III)TDCPPs catalyse the oxidation of cyclo-octene by iodosylbenzene (PhIO) in methanol[13] and the yields of epoxycyclo-octane and formaldehyde are comparable to those from the equivalent homogeneous reaction (Table 1), although the heterogeneous reactions are slower (Figure).

Table 1 Yields of epoxycyclooctane and formaldehyde from the oxidation of cyclooctene by iodosylbenzene in methanol catalysed by Fe(III)TDCPP on PS-Im, PVP and Si-Im.[a]

Support (loading)[b]	Yield (%)[c]		Unused oxidant[d] (%)	Oxidant accountability (%)	Catalyst turnovers[e]
	epoxide	HCHO			
PS-Im (10)	78	14	3	95	104
PVP (10)	79	12	7	98	108
Si-Im (4)	90	10	4	104	308
none[f]	92	4	0	96	123

[a] Supported catalyst, 100 mg; cyclooctene, 0.3 cm^3; iodosylbenzene, 30 mg; methanol 3.0 cm^3; [b] mg of Fe(III)TDCPP per g of support; [c] Based on oxidant; [d] PhIO/PhIO$_2$ estimated by iodometric titration; [e] based on amount of Fe(III)TDCPP and yield of epoxide; [f] Fe(III)TDCPP, 1.0 mg.

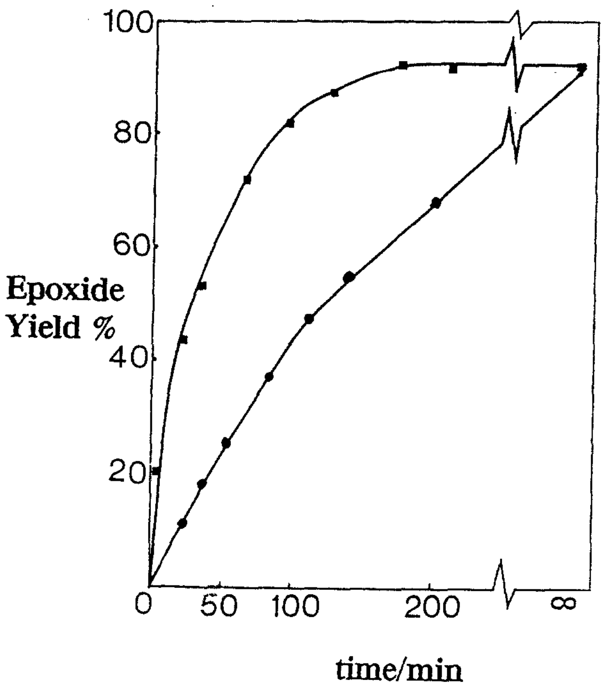

Figure: Change of yield of epoxycyclooctane with time in the epoxidation of cyclooctene by iodosylbenzene catalysed by Fe(III)TDCPP (■) and Si-Im-Fe(III)TDCPP (●) in dichloromethane.

The stability of the catalysts were investigated in repeat oxidations by the step-wise addition of PhIO to a suspension of catalyst in a solution of cyclo-octene. The best catalysts, Fe(III)TDCPP and Mn(III)TDCPP on Si-Im, gave large catalyst turnovers without loss of catalytic activity (Table 2). Fe(III)TDCPP on PVP was also a very effective catalyst although there was a measurable reduction in its catalytic activity on prolonged use. By contrast the catalytic efficiency of Fe(III)TDCPP on PS-Im fell away rapidly with repeated use. Interestingly, in none of the oxidations was there any apparent oxidative bleaching of the supported metalloporphyrins.

Table 2 Yield of epoxycyclooctane from the epoxidation of cyclooctene by iodosylbenzene (repeated addition) catalysed by ligand-bound supported Fe(III)TDCPP and Mn(III)TDCPP.[a]

Catalyst (loading)[b]	Solvent	Additions of PhIO[c]	Yield (%)[d]	Catalyst Turnovers[e]
PVP-Fe(III)TDCPP (10)	MeOH	8	63[f]	5,100
Si-Im-Fe(III)TDCPP (6)	CH_2Cl_2	8	93	7,900
Si-Im-Mn(III)TDCPP (10)	CH_2Cl_2	28	86	24,700

[a] Initial conditions: supported catalyst, 50 mg; cyclooctene, 1.3 cm^3; iodosylbenzene, 110 mg (70 mg with Si-Im-Fe(III)TDCPP), solvent, 50 cm^3; [b] mg of Fe(III)TDCPP per g of support; [c] 1000-fold excess of PhIO over Fe(III)TDCPP in each addition; [d] based on total PhIO added; [e] based on total yield of epoxide and Fe(III)TDCPP; [f] Oxidant consumed to give HCHO not measured.

Table 3 Yield of epoxycyclooctane from the epoxidation of cyclooctene by hydrogen peroxide catalysed by Mn(III)TDCPP.[a]

Catalyst	Yield of epoxide (%)	
	based on H_2O_2	based on alkene
Mn(III)TDCPP [b]	2	16
Mn(III)TDCPP/imidazole [c]	10	78
Si-Im-Mn(III)TDCPP [d]	9	67

[a] Mn(III)TDCPP, 0.5 mg; cyclooctene, 10 μl; solvent, CH_2Cl_2/CH_3CN (1 : 1) 3 cm^3; H_2O_2, eight separate additions of 30% aqueous H_2O_2, 7 μl; [b] Mn(III)TDCPP in free solution; [c] Mn(III)TDCPP/imidazole (1 : 20) in free solution; [d] 10 mg of Mn(III)TDCPP per g of Si-Im.

Si-Im-Mn(III)TDCPP is also an effective catalyst for epoxidation by H_2O_2 and gives comparable results to the metalloporphyrin and imidazole in homogeneous solution. This contrasts with the ineffective catalysis by Mn(III)TDCPP in the absence of imidazole (Table 3). Imidazole, by acting as a base and an axial ligand is thought to encourage the heterolytic, rather than the homolytic, cleavage of H_2O_2 to give an oxomanganese(V) active oxidant.[14] With the supported catalyst the imidazole is clearly acting as a ligand, however, whether or not the cleavage of the peroxide bond involves a base remains unclear.

These studies show the potential of ligand-bound supported metalloporphyrins as oxidation catalysts. This approach to developing useful catalytic systems has the advantages that preparing the catalysts is simple, it should also be generally applicable and by careful choice of the surface ligand it should be possible to control the selectivity of the oxidations. We are currently exploring the scope of these reactions.

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