Alkene Epoxidation by Iodosylbenzene Catalysed by Iron(III) 5,10,15,20-Tetra-(2,6-dichlorophenyl)porphyrin† coordinated to Pyridine-modified Silica

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Six silicas, with different surface areas, pore sizes and pore volumes, have been surface modified with pyridine groups and used to support iron(III) 5,10,15,20-tetra(2,6-dichlorophenyl)porphyrin (Fe^{III}TDCPP) by ligation to the metal ion. Comparison of these materials (SiPy–Fe^{III}TDCPP) as catalysts for the epoxidation of (*Z*)-cyclooctene by iodosylbenzene in dichloromethane reveals that all have essentially the same catalytic activity and that the heterogeneous reactions are significantly slower (*ca.* ten-fold) than the homogeneous analogue. In small scale repeat-use experiments the catalysts achieve 2200 catalyst turnovers without loss of activity, however, larger scale reactions (7900 turnovers) lead to catalytic oxidative bleaching and $>50\%$ reduction in activity.

A Hammett study of the epoxidation of styrene and 4-substituted styrenes gives ρ values (*vs.* σ^+) of −0.95 and −0.98 for oxidations catalysed by Fe^{III}TDCPP and a supported catalyst SiPy–Fe^{III}TDCPP, respectively. The similarity of these values to each other and to values from other iron(III) porphyrin-catalysed epoxidations is discussed. A minor pathway in the oxidation of the styrenes in air that leads to benzaldehydes is attributed to dioxygen intercepting an intermediate in the reaction.

Oxidations of (*Z*)- and (*E*)-4-methylpent-2-ene catalysed by Fe^{III}TDCPP and by SiPy–Fe^{III}TDCPP show a marked difference. With the former the relative reactivity of (*Z*)- to (*E*)-alkene is 13:1, whereas the latter fails to catalyse the epoxidation of the (*E*)-alkene and instead is converted into a green material; this is possibly an iron *N*-alkylporphyrin.

Current interest in supported metalloporphyrins[1] is directed towards developing oxidation catalysts that combine the versatility of homogeneous metalloporphyrins[2] with the advantages of heterogeneous systems. To this end, metalloporphyrins have been chemically and physically anchored to both organic polymers and to inorganic solids and the chemistry of the resulting materials compared with those of their homogeneous analogues.[3]

Since the selectivity of metalloporphyrin-catalysed oxidations relies largely on the steric and electronic effects of the groups attached to the macrocycle, for optimum utility, the ideal method of catalyst immobilization should be suitable for a wide range of metalloporphyrins and be simple to carry out. In this way the desired property of a homogeneous catalyst might be transferred to a heterogeneous system.

In principle, immobilizing metalloporphyrins by coordinate binding to ligands attached to a solid support, provided the ligand–metal bond is sufficiently strong to prevent catalyst leaching, might lead to a suitable general method. Furthermore, through selective control of the support and the ligand it should be possible to tailor the catalyst's properties to the needs of the reaction.

In a previous study,[3i] we explored the use of poly(4-vinylpyridine) and imidazole-modified polystyrene and silica supports. We concluded that, for coordinative bonding, the best catalyst supports are rigid and inert, thereby preventing inactivating bis-ligation of the metalloporphyrin and wasteful support oxidation, respectively. It also became evident that the strength of the bond between the metalloporphyrin and the support is very sensitive to the nature of the metal and the substituents on the macrocycle. The best metalloporphyrin was found to be iron(III) 5,10,15,20-tetra(2,6-dichlorophenyl)-porphyrin (Fe^{III}TDCPP).‡

In this study we have modified a selection of silicas with 4-(4-pyridyl)butylsilane groups to provide pyridine ligands for coordinative binding to Fe^{III}TDCPP. Pyridine was selected because it is a good ligand for iron(III) porphyrins[4] and is more oxidatively stable than imidazole used in our previous study. These supported Fe^{III}TDCPPs have been examined and compared as catalysts for alkene epoxidation by PhIO.

Results

Preparation of Pyridine-modified Silica.—Six commercial silica supports (see Table 1 for physical characteristics) were modified by reaction with 3-chloropropyltrimethoxysilane followed by 4-picolyllithium[5] (Scheme 1, 4-picaloyl-4-methylpyridyl). Elemental analysis showed that the chloropropylated silicas typically had surface loadings of two silanes nm^{-2}. Assuming five silanol groups nm^{-2} and bis-ligation of the silanes to the surface,[6] this corresponds to ≈60% coverage of the silica surface. Diffuse reflectance FTIR spectroscopy of the silicas and modified silicas shows the removal of a band at 3400 cm^{-1} (O–H stretch) and the appearance of new bands at 2960 (C–H) and 920 cm^{-1} (C–Cl).

The pyridine coverages of the pyridylbutylated silicas (also obtained from elemental analysis) are given in Table 1. Correlation of the loadings with the physical characteristics of the silicas reveals an approximate linear relationship with surface area (Fig. 1) but no correlations with either pore diameter or pore volume.

Pyridine modified Kieselgel 60 was converted into its *N*-oxide by reaction with excess of H_2O_2 in glacial acetic acid. Cross-polarization magic angle spinning (CPMAS) ^{13}C NMR spectroscopy was used to confirm the presence of the 4-alkylpyridine and its *N*-oxide on the Kieselgel 60 (Fig. 2). In a control experiment 4-picoline was stirred with Kieselgel 60, filtered and washed in an analogous way to the modified silicas and CPMAS ^{13}C NMR spectroscopy of this material showed no evidence of pyridine carbon signals.

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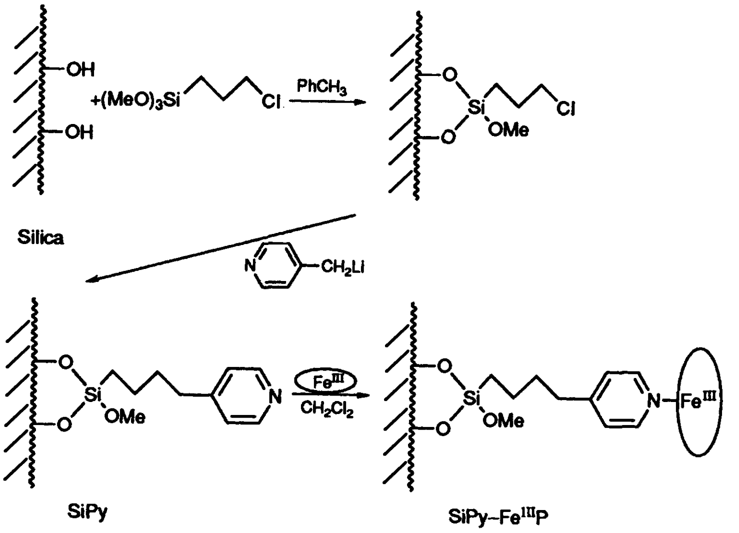
† 5,10,15,20-Tetrakis(2,6-dichlorophenyl)porphyrinato iron(III).

‡ Abbreviations: SiPy, pyridine-modified silica; TDCPP, 5,10,15,20-tetra(2,6-dichlorophenyl)porphyrin ligand; TPP, 5,10,15,20-tetraphenylporphyrin ligand.

Table 1 Physical characteristics, pyridine coverages and Fe^{III}TDCPP loadings of silica supports

	Type of silica gel					
	Kieselgel 60	250 MP	350 MP	1500 MP	350 LP	350 HP
Pore diameter/Å	60	250	350	1500	350	350
Pore volume/cm^3 g^{-1}	0.75	1.2	1.2	1.2	0.85	1.35
Surface area/m^2 g^{-1}	500	175	135	25	95	160
Pyridine coverage/mmol g^{-1} [a]	0.77	0.39	0.29	0.14	0.14	0.29
Fe^{III}TDCPP loading/mg g^{-1} [b]	4	5	3	5	3	3

[a] Pyridine coverages obtained from CHN analyses. [b] Loadings after washing with CH_2Cl_2 followed by MeOH.



Scheme 1 Surface modification of silica with pyridine groups

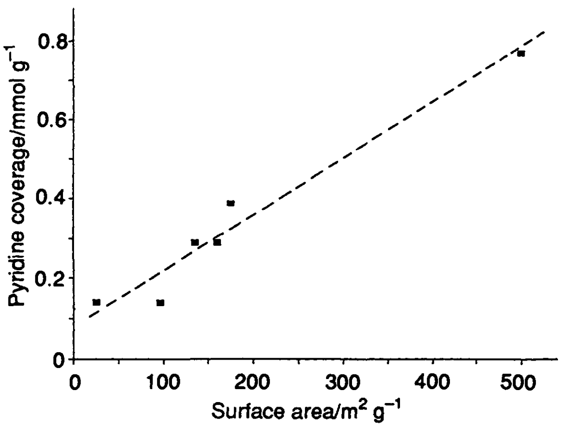


Fig. 1 The relationship between pyridine surface modification and silica surface area

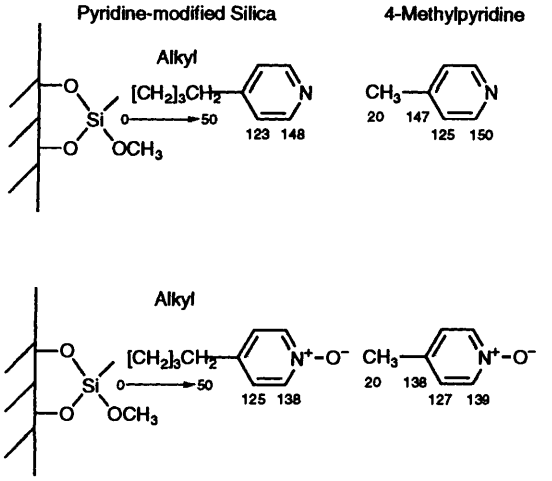


Fig. 2 CPMAS ^{13}C NMR δ-values for pyridine- and pyridine *N*-oxide-modified Kieselgel 60 and the corresponding values for 4-picoline and 4-picoline *N*-oxide in solution

Coordination of Fe^{III}TDCPP to Modified Silicas.—The iron(III) porphyrin ligation was achieved by stirring a dichloromethane solution of a known amount of Fe^{III}TDCPP with a suspension of pyridine-modified silica (SiPy) and the resulting materials were subsequently washed with CH_2Cl_2 and methanol to remove unbound and weakly bound porphyrin (Scheme 1). The loadings were quantified by measuring the amount of unloaded Fe^{III}TDCPP in the combined reaction solvent and washings by UV–VIS spectroscopy (Table 1). It is noteworthy that the Fe^{III}TDCPP loadings on the different modified silicas, after methanol washing, are very similar (2–5 mg g^{-1}) and that the values do not correlate with surface area, pore size or pore volume. Furthermore, two batches of pyridine modified Kieselgel 60, with 33% and 59% of the chloropropylsilane groups modified with pyridine, both gave identical metalloporphyrin loadings.

The *N*-oxide of pyridine-modified Kieselgel 60 failed to load Fe^{III}TDCPP.

Epoxidation of (Z)-cyclooctene with PhIO *catalysed by Fe^{III}TDCPP on SiPy.*—The epoxidations were carried out in CH_2Cl_2 using a molar ratio of catalyst : oxidant : substrate of 1 : 650 : 11 500. The epoxide yields after 24 h from reactions using the six SiPy–Fe^{III}TDCPP catalysts and a homogeneous oxidation for comparison are given in Table 2. Monitoring the

Table 2 Yields of (*Z*)-epoxycyclooctane from the oxidation of (*Z*)-cyclooctene by PhIO catalysed by supported $Fe^{III}TDCPP$ and $Fe^{III}TDCPP$ in homogeneous solution[a]

Catalyst	Yield[b] (%)	
	Epoxide	$PhIO_2$
Kieselgel 60–$Fe^{III}TDCPP$	83	14
250 MP–$Fe^{III}TDCPP$	92	—
350 MP–$Fe^{III}TDCPP$	80	10
1500 MP–$Fe^{III}TDCPP$	87	5
350 LP–$Fe^{III}TDCPP$	90	—
350 HP–$Fe^{III}TDCPP$	90	—
$Fe^{III}TDCPP$	99	1

[a] Catalyst, 2.0 × 10^{-7} mol; PhIO, 1.3 × 10^{-4} mol; substrate 2.3 × 10^{-3} mol; CH_2Cl_2, 3 cm^3. [b] Based on PhIO after 24 h.

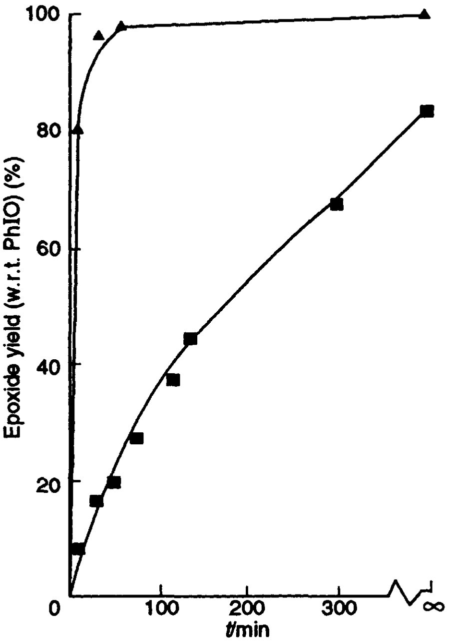


Fig. 3 A comparison of the rates of epoxidation of (*Z*)-cyclooctene by PhIO in CH_2Cl_2 catalysed by $Fe^{III}TDCPP$ (▲) and pyridine-modified Kieselgel 60–$Fe^{III}TDCPP$ (■)

production of epoxide for the first 4 h showed that there are no significant differences in the rates of all the supported $Fe^{III}TDCPP$-catalysed epoxidations. However, the homogeneous reaction is much faster than the heterogeneous analogues (Fig. 3). That $Fe^{III}TDCPP$ was not leached from the SiPy during the epoxidations was confirmed in two ways. First, the UV–VIS spectrum of the filtered reaction mixture did not show the Soret band of $Fe^{III}TDCPP$ and, secondly, when this filtrate was used in a second oxidation (without added catalyst) further epoxidation was negligible.

The epoxidation of (*Z*)-cyclooctene with PhIO catalysed by pyridine-modified Kieselgel 60–$Fe^{III}TDCPP$ was also carried out in methanol, 2,2,2-trifluoroethanol, acetonitrile, Bu^tOMe, neat (*Z*)-cyclooctene and 1% and 10% methanol in Bu^tOMe and in (*Z*)-cyclooctene (Table 3). Of these reactions, only that in acetonitrile gave good yields of epoxide without catalyst leaching and in this respect was very comparable to that in CH_2Cl_2. Although the reactions in Bu^tOMe and in neat (*Z*)-cyclooctene gave no catalyst leaching they proceeded at a very slow rate. Both the alcohols led to significant catalyst leaching even when added as a minor component of a mixed solvent.

Table 3 Epoxidation of (*Z*)-cyclooctene by PhIO catalysed by pyridine modified Kieselgel 60–$Fe^{III}TDCPP$[a]

Solvent	Epoxide yield[b] (%)	Leaching of $Fe^{III}TDCPP$ (%)	Miscellaneous
CH_2Cl_2	83	No	$PhIO_2$ (14%)
CH_3CN	77	No	$PhIO_2$ (20%)
MeOH	80	Yes (< 10)	HCHO (5%)
CF_3CH_2OH	60–70	Yes (10)	—
Bu^tOMe	< 5	No	—
Bu^tOMe–1% MeOH	60	No	—
Bu^tOMe–10% MeOH	70	Yes (1)	—
Neat alkene[c]	45	No	—
Neat alkene[c]–1% MeOH	80	Yes (1)	—
Neat alkene[c]–10% MeOH	100	Yes (3)	—

[a] For conditions see Table 2. [b] Based on PhIO after 24 h. [c] Substrate used as solvent.

Table 4 Repeated oxidation with a large excess of PhIO over pyridine modified Kieselgel 60–$Fe^{III}TDCPP$[a]

PhIO addition	Epoxide yield[b] (%)	Catalyst turnovers[c]
1	90	3850
2	76	7240
3	53	9530

[a] Catalyst, 2.3 × 10^{-6} mol; PhIO, 10 mmol per addition; substrate, 0.17 mol; CH_2Cl_2, 150 cm^3. [b] Yield per PhIO addition, based on PhIO after 48 h. [c] Turnovers calculated on total epoxide yield.

The UV–VIS spectrum of the leached porphyrin, which is identical to that of the $Fe^{III}TDCPP$ dissolved in methanol–dichloromethane, has a Soret peak at 394 nm. By comparison with the reported UV–VIS spectrum of the bis-ethanol complex of $Fe^{III}TPP$,[7] this corresponds to the bis-methanol complex of $Fe^{III}TDCPP$.

Stability of the SiPy-$Fe^{III}TDCPP$ Catalysts in Repeat Oxidations.—The pyridine-modified Kieselgel 60–$Fe^{III}TDCPP$-catalysed epoxidation of (*Z*)-cyclooctene in CH_2Cl_2 was monitored for four additions of PhIO added at 24 h intervals. This reveals the first oxidation to be slower and to give a lower final yield of epoxycyclooctane (75%) than the subsequent reactions, all of which were essentially identical (final yield ≈ 90%). After the four oxidations the catalyst had achieved 2200 turnovers and showed no sign of degradation. The repeat oxidation was also carried out with pyridine modified Grace silica 350 LP–$Fe^{III}TDCPP$ and a very similar rate and yield enhancement, following the first reaction, was observed.

The effect of catalyst particle size on the epoxidation was investigated by grinding up the catalyst before use. A comparison of the performance of the ground and unground materials in otherwise identical reactions shows the former to be more active.

The repeat oxidation of (*Z*)-cyclooctene was also carried out on a larger scale using 150 cm^3 of CH_2Cl_2, 10 mmol of oxidant and a catalyst : oxidant : substrate ratio of 1 : 4300 : 73 500 (Table 4). Under these conditions the catalyst gave a total of 9530 turnovers, but it became less active with each addition of PhIO and a white solid ($PhIO_2$) was formed. When the used catalyst was washed with 5% aqueous NaOH (to remove $PhIO_2$), water, dried and reused in a small scale epoxidation, it gave a 29% yield of epoxycyclooctane. Comparison of the diffuse reflectance UV–VIS spectrum of the supported catalyst, before and after use in the large scale repeat oxidation, shows that this sequence of reactions leads to a significant amount of catalyst oxidative bleaching (Fig. 4).

Following the reactions of (*Z*)-cyclooctene, described above, the epoxidation of all the other alkenes used pyridine-modified Kieselgel 60–Fe^{III}TDCPP.

Epoxidation of Styrene and 4-*Substituted Styrenes by* PhIO *Catalysed by Fe^{III}TDCPP and SiPy-Fe^{III}TDCPP.*—The yields of epoxides from the homogeneous and heterogeneous Fe^{III}TDCPP-catalysed epoxidations of styrenes are given in Table 5, together with the comparable results from an earlier study in which Fe^{III}TPP was used as the catalyst.[8] In the oxidations of styrene and 4-chloro, 4-methyl- and 4-methoxystyrene a further minor product, not present after 4 h, was detected after 24 h reaction. This was identified, by GC–MS and retention time comparison with authentics, as benzaldehyde or the corresponding 4-substituted benzaldehyde. When the reaction of 4-chlorostyrene with PhIO and Fe^{III}TDCPP was repeated under nitrogen the yield of 4-chlorobenzaldehyde decreased from 15% to 2% and that of the epoxide correspondingly increased from 80% to 90%. Control reactions showed that the benzaldehydes are not formed from the epoxide and that their formation requires both PhIO and Fe^{III}TDCPP.

A further problem encountered in the oxidation of all the styrenes using the supported-Fe^{III}TDCPP, which was not observed during the epoxidation of (*Z*)-cyclooctene, was the leaching of a small proportion of the metalloporphyrin from the support. UV–VIS spectroscopy showed this to be typically 0.5% to 3%. When these reactions were filtered and the filtrates were used in a second oxidation epoxide, yields were 4% to 30%. Control experiments showed that both oxidant and substrate were required for leaching to occur.

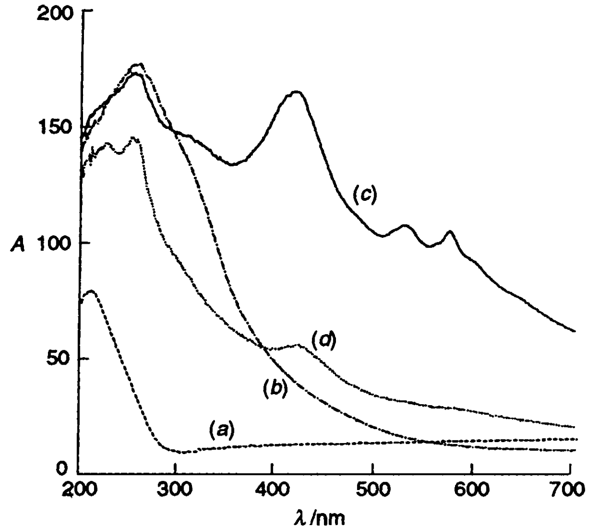


Fig. 4 Diffuse reflectance UV–VIS spectrum of Kieselgel 60 (*a*), modified with pyridine (*b*), with coordinated Fe^{III}TDCPP before use (*c*), with coordinated Fe^{III}TDCPP after use in repeat oxidation and 9350 catalyst turnovers (*d*)

Competitive Epoxidations of Styrene and 4-*Substituted Styrenes.*—The competitive oxidations used equimolar amounts of the two substrates, each in a 20-fold excess over the oxidant and the relative yields of the two epoxides were monitored during the course of the reaction. For each competitive experiment the product ratio remained essentially constant throughout the reaction (two typical sets of results are shown in Table 6). To eliminate problems that might have arisen from the formation of benzaldehyde during long reactions and consequently to avoid the necessity of having to carry out the competitive reactions under N_2, the relative reactivities were obtained from aerobic reactions using data obtained in the first 60 min. Table 7 gives the relative reactivities of the five substrates measured in this way.

Epoxidation of (Z)- *and* (E)-4-*Methylpent*-2-*ene.*—The conditions used to epoxidize the 4-methylpent-2-enes were identical to those described above for the styrenes and the product yields obtained are recorded in Table 8. It is noteworthy, in contrast to the homogeneous oxidations of (*Z*)-4-methylpent-2-ene, that that catalysed by SiPy–Fe^{III}TDCPP is not completely stereospecific; a small amount of the (*E*)-epoxide was formed.

The reaction of the (*E*)-4-methylpent-2-ene reveals two further differences between SiPy–Fe^{III}TDCPP and Fe^{III}TDCPP.

Table 5 Epoxide yields from styrene and 4-substituted styrenes with PhIO in CH_2Cl_2 catalysed by Fe^{III}TDCPP,[a] SiPy–Fe^{III}TDCPP[a] and Fe^{III}TPP[b]

Substrate 4-X–$C_6H_4CH{=}CH_2$	Catalyst[c]	Epoxide yield[d] (%)
X = MeO	Fe^{III}TDCPP	99
MeO	SiPy–Fe^{III}TDCPP	90
MeO	Fe^{III}TPP	71
Me	Fe^{III}TDCPP	96
Me	SiPy–Fe^{III}TDCPP	90
Me	Fe^{III}TPP	45
H	Fe^{III}TDCPP	78
H	SiPy–Fe^{III}TDCPP	89
H	Fe^{III}TPP	32
Cl	Fe^{III}TDCPP	90
Cl	SiPy–Fe^{III}TDCPP	83
Cl	Fe^{III}TPP	30
NO_2	Fe^{III}TDCPP	37[e]
NO_2	SiPy–Fe^{III}TDCPP	23
NO_2	Fe^{III}TPP	16

[a] For conditions see Table 2. [b] From ref. 8: catalyst, 4.2 × 10^{-5} mol; PhIO, 4.5 × 10^{-4} mol; substrate, 5.0 × 10^{-3} mol; CH_2Cl_2 5 cm^3 at room temperature. [c] SiPy–Fe^{III}TDCPP is pyridine-modified Kieselgel 60–Fe^{III}TDCPP. [d] Yield based on PhIO. [e] Substrate, 2 × 10^{-4} mol.

Table 6 Time dependence of epoxide yields and relative reactivities in the competitive oxidation of styrene and 4-methylstyrene by PhIO in CH_2Cl_2 catalysed by Fe^{III}TDCPP and SiPy–Fe^{III}TDCPP[a]

	Fe^{III}TDCPP			SiPy–Fe^{III}TDCPP		
	Epoxide yield[b] (%)			Epoxide yield[b] (%)		
Reaction time/min	Styrene	Me–Styrene	Reactivity relative to styrene[c]	Styrene	Me–Styrene	Reactivity relative to styrene[c]
5	10	23	2.30	1.1	2.7	2.45
10	23	51	2.22	2.1	5.3	2.52
35	27	63	2.33	4.7	11.8	2.51
1440	29	64	2.21	29.0	59.0	2.03

[a] Catalyst, 2 × 10^{-7} mol; PhIO, 1.3 × 10^{-4} mol; styrene = 4-methylstyrene, 2.3 × 10^{-3} mol; CH_2Cl_2, 3 cm^3. [b] Based on PhIO. [c] Yield of styrene epoxide/4-methylstyrene epoxide.

Table 7 Relative reactivities of styrene and 4-substituted styrenes obtained from competitive epoxidations by PhIO in CH_2Cl_2 catalysed by $Fe^{III}TDCPP$, SiPy–$Fe^{III}TDCPP$[a] and $Fe^{III}TPP$

Substrate	Reactivity relative to styrene		
4-X–$C_6H_4CH{=}CH_2$	$Fe^{III}TDCPP$	SiPy–$Fe^{III}TDCPP$[a]	$Fe^{III}TPP$[b]
X = MeO	6.61 ± 0.7	3.66 ± 0.45	6.61
Me	2.27 ± 0.16	2.50 ± 0.10	2.38
H	1.00	1.00	1.00
Cl	1.27 ± 0.05	0.83 ± 0.05	0.98
NO_2	0.20 ± 0.15	0.11 ± 0.07	0.24

[a] Pyridine modified Kieselgel 60–$Fe^{III}TDCPP$. [b] Data from ref. 8.

Table 8 Epoxide yields from the reaction of (*Z*)- and (*E*)-4-methylpent-2-ene with PhIO in CH_2Cl_2 catalysed by $Fe^{III}TDCPP$,[a] SiPy–$Fe^{III}TDCPP$[a] and $Fe^{III}TPP$[b]

4-Methylpent-2-ene isomer	Catalyst	Epoxide product	Yield[c] (%)
Z	$Fe^{III}TDCPP$	*Z*	100
Z	SiPy–$Fe^{III}TDCPP$	*Z*	97
		E	2
Z	$Fe^{III}TPP$	*Z*	51
E	$Fe^{III}TDCPP$	*E*	66
E	$Fe^{III}TDCPP$[d]	*E*	64
E	SiPy–$Fe^{III}TDCPP$	[e]	—
E	$Fe^{III}TPP$	*E*	13

[a] For conditions see Table 2. [b] For conditions see Table 5 and ref. 8. [c] Yields based on PhIO. [d] Reaction under N_2. [e] Some very small yields of allylic oxidation products and the catalyst turned a pale green colour.

The supported iron(III) porphyrin, unlike $Fe^{III}TDCPP$, is unable to catalyse the (*E*)-alkene epoxidation and is instead converted into an inactive green species.

In competitive epoxidations of the isomeric 4-methylpent-2-enes, $Fe^{III}TDCPP$ gives a relative reactivity of (*Z*) to (*E*) of 13:1. This should be compared with the ratio of 14:1 reported for the $Fe^{III}TPP$-catalysed epoxidation.[8] Although the competitive oxidation catalysed by SiPy–$Fe^{III}TDCPP$ could not be used to obtain the relative reactivities of the two isomers, it is noteworthy that the presence of the (*E*)-alkene in the reaction reduced the yield of (*Z*)-epoxide from (*Z*)-alkene from 97% to 60% and the catalyst became green coloured.

Discussion

Supported-catalyst Preparation.—The method used to prepare the pyridine-modified silicas used in this study was essentially the same as that reported by Allum *et al.*[5] The silicas were selected to provide a range of surface areas, pore sizes and pore volumes (Table 1) to investigate the influence of these properties on catalyst behaviour. As expected, the extent of pyridine modification was dependent on the surface areas of the silicas (Fig. 1) and was insensitive to the pore size and pore volume, since with none of the silicas are the latter sufficiently small to restrict the access of the silanizing agent or 4-picolyl anion.

DRIFT spectroscopy shows small changes following surface modification which can be accounted for in terms of the expected changes to the surface groups. However, CPMAS ^{13}C NMR spectroscopy is much more informative. The covalently bound butylpyridine groups give clear signals with the expected δ-values (Fig. 2).

The $Fe^{III}TDCPP$ loadings on the pyridine-modified silicas do not show any correlation with surface area, pore size, pore volume or pyridine coverage. Indeed two samples of Kieselgel 60 modified to very different extents with pyridine groups gave identical $Fe^{III}TDCPP$ loadings. This suggests that the porphyrin loading depends on the availability of pyridine groups on the surface and not on their total number. The first pyridine groups to bind to the silica probably do so on the most accessible surface sites and subsequently it is these ligands that bind most readily to $Fe^{III}TDCPP$. The corollary is, the less accessible pyridines are poor ligands.

Pyridine *N*-oxide groups on the surface of the silica, by comparison with pyridine, are very poor ligands for $Fe^{III}TDCPP$. This agrees with our previous finding that whereas poly(4-vinylpyridine) ligates $Fe^{III}TDCPP$ very well, its *N*-oxide does not.[3i]

Optimization of the Epoxidation by Supported $Fe^{III}TDCPP$–PhIO *Systems.*—The epoxidizing systems were compared and optimized using (*Z*)-cyclooctene as the standard substrate. This is a reactive alkene that has been widely used in previous studies both with homo- and hetero-geneous catalysts[3d,3i,9] and which generally gives one oxidation product, epoxycyclooctane.[10] The choice of solvent is critical since it should be oxidatively stable, at least partially dissolve the PhIO and, to prevent catalyst leaching, it should not be a competitive ligand for $Fe^{III}TDCPP$. In this study CH_2Cl_2 and CH_3CN fulfilled these requirements and the former was selected for all subsequent studies. Although methanol dissolves PhIO[11] it is oxidized to HCHO during the reactions and through competitive ligation it leaches $Fe^{III}TDCPP$ from the supports as the bis-methanol complex.[3i] 2,2,2-Trifluoroethanol has been used previously as a solvent or in a mixed solvent for metalloporphyrin–iodosylarene oxidations[12] and we argued that the electron-withdrawing CF_3 group should reduce its ligand donor properties and make it less readily oxidized than methanol. However, it gave rise to catalyst leaching making it unsuitable as a solvent in these systems. *tert*-Butyl methyl ether did not cause catalyst leaching and should be relatively stable to oxidation, however, it is a very poor solvent for PhIO. The latter problem also occurs in the solvent-free system. Unfortunately the addition of small amounts of methanol, to improve the solubility of the oxidant, resulted in catalyst leaching. It is noteworthy that 1% methanol in the solvent in the oxidation regime used in this study is approximately 4000-fold excess over $Fe^{III}TDCPP$ and 50-fold excess over the pyridine ligands.

Comparison of the catalytic activity of $Fe^{III}TDCPP$ supported on the six modified silicas reveals that the epoxidation of (*Z*)-cyclooctene with each of the catalysts occurs at very comparable rates. Thus, differences in surface area and structure of the support do not lead to differences in the rate of reaction. As a consequence of this observation, in all subsequent studies with other alkene substrates, the readily available Kieselgel 60 was used as the catalyst support material.

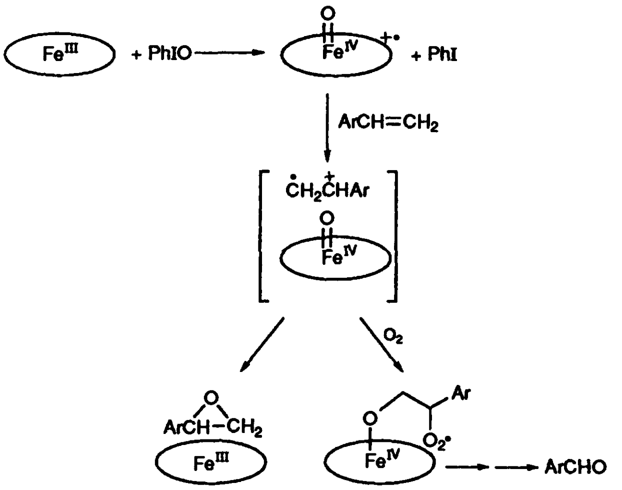
The rate of (*Z*)-cyclooctene epoxidation with homogeneous $Fe^{III}TDCPP$ is approximately ten-times faster than that with SiPy–$Fe^{III}TDCPP$. A very similar difference in the rate of epoxidation was observed when $Fe^{III}TDCPP$ was supported on imidazole-modified silica.[3i] However, axial ligation of a nitrogen base to metalloporphyrins is reported to increase the rate of catalytic epoxidation,[13] so that the reduced rate observed in these studies must arise from the local environment of the catalyst molecules. This will be significantly more polar than $Fe^{III}TDCPP$ in CH_2Cl_2 solution and consequently, as we have proposed previously,[3i] this may disfavour the approach of the non-polar (*Z*)-cyclooctene and may also slow down the diffusion of product epoxide into the reaction medium.

The stability of SiPy–$Fe^{III}TDCPP$ to oxidative self-oxidation was examined by reusing the catalysts in small and larger scale repeat oxidations (catalyst:oxidant ratio 1:650 and 1:4300, respectively). In the former, the catalyst showed no sign of degradation after four cycles and 2200 catalyst turnovers. On the contrary, there was a significant rate enhancement for the second oxidation compared with the first. In our previous studies of epoxidations catalysed by Fe^{III}TDCPP on poly(4-vinylpyridine), although not on imidazole-modified silica, we observed a similar effect on repeat use of the catalyst.[3i] We attribute this to the consumption of some of the first batch of PhIO in the oxidation of organic groups on the silica surface close to the active oxidant. This could involve the *N*-oxidation of some of the pyridine groups, although CPMAS ^{13}C NMR spectroscopy of the used catalyst did not show any evidence of pyridine *N*-oxide groups on the surface. Another cause for the rate enhancement could be the grinding up of the catalyst by the magnetic stirrer to produce smaller particles and a larger surface area of active catalyst. Comparison of used and unused catalyst by scanning electron microscopy confirms the extensive fragmentation of the silica particles.

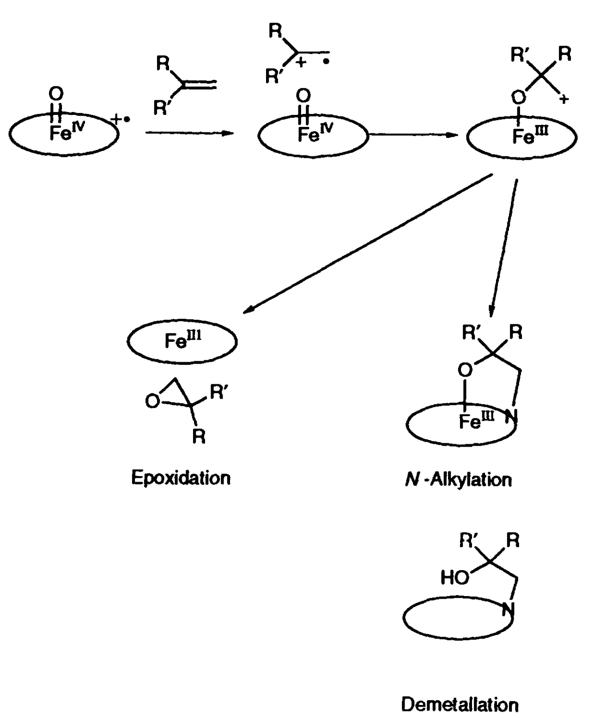
In the larger scale reuse experiments the activity of the system was significantly reduced after three cycles and 9530 catalyst turnovers; any initial catalyst activation was hidden in the first cycle. Examination of recovered catalyst, that had been washed with dilute NaOH to remove $PhIO_2$, by diffuse reflectance UV–VIS spectroscopy identifies the cause of the catalyst deactivation as oxidative bleaching of Fe^{III}TDCPP (Fig. 4), although the choking of the catalyst by precipitated $PhIO_2$ may also be a contributory factor. These experiments show that even in the presence of a large excess of a reactive alkene the supported Fe^{III}TDCPP undergoes self-oxidation. A further problem with this oxidizing system is the catalysed disproportionation of the iodosylbenzene which generates insoluble and unreactive iodoxybenzene.

Epoxidation of Styrene and 4-*Substituted Styrene*.—We have attempted to characterize the active oxidant in the SiPy–Fe^{III}TDCPP/PhIO system by investigating the influence of substituents on the rate of epoxidation of styrenes and the results are compared with those from homogeneous Fe^{III}TDCPP and from an earlier study using Fe^{III}TPP.[8] One potential measure of the relative reactivities of the alkenes towards the active oxidant is the overall percentage yield of epoxide from single substrate experiments. This relies on the fact that epoxidation competes with other reactions of the active oxidant (*e.g.* catalyst, PhIO and solvent oxidation). Although this approach gives good qualitative information for the Fe^{III}TPP–PhIO system (Table 5), it cannot be used with either of the Fe^{III}TDCPP systems. The explanation for this difference is that Fe^{III}TDCPP is much more stable towards oxidative destruction than Fe^{III}TPP,[14] hence competitive catalyst oxidation is much less significant and epoxide yields are consequently almost all very high (Table 5). Two complications, however, were noted in the present study. The first is the formation of minor quantities of benzaldehydes. These were shown to arise from a slow aerobic oxidation which requires the presence of both Fe^{III}TDCPP and PhIO. Similar observations have been reported by others who have attributed them to an autoxidation route possibly involving the reactive intermediate alkene radical cation with dioxygen, which initiates a free-radical chain process (Scheme 2).[15] Since, however, the epoxidation is fast relative to the autoxidation, product analyses during the first 4 h are free of this complication.

The second complication, not encountered in the epoxidation of (*Z*)-cyclooctene is a small amount of catalyst leaching in reactions of the styrenes. Interestingly, this requires both PhIO and a styrene to be present. A possible explanation involves the formation of iron *N*-alkyl porphyrin derivatives which are less tightly bound to the supports. In this respect terminal alkenes, including styrene, are known to bring about *N*-alkylation of iron porphyrins as a minor side reaction during alkene epoxidation (Scheme 3).[16]



Scheme 2 Possible autoxidation route to the formation of substituted benzaldehydes from styrenes in parallel with epoxidation by iron(III) porphyrin–PhIO systems



Scheme 3 Proposed mechanisms for alkene epoxidation and *N*-alkylation in homogeneous reactions of alkenes with oxoiron(IV) porphyrin π-radical cations

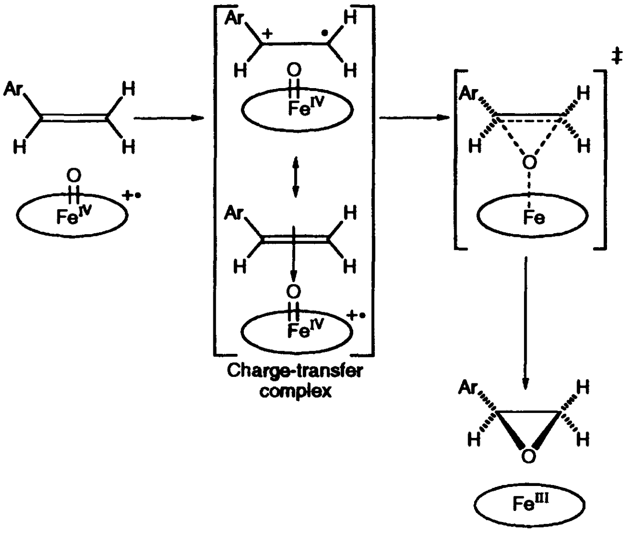
To obtain meaningful substituent effects relative rate data from competition experiments between pairs of styrene substrates were measured. When these are analysed by a Hammett treatment using σ^+ they give ρ values of -0.95 ± 0.24 and -0.98 ± 0.48 for the homogeneous Fe^{III}TDCPP and heterogeneous SiPy–Fe^{III}TDCPP systems, respectively. It is interesting that these systems give the same ρ value and that this is essentially the same as that obtained using the Fe^{III}TPP–PhIO system (-0.93 ± 0.05).[8]

The results from the present study show that the support and the substituents on the aryl groups of the porphyrin macrocycle (*e.g.* phenyl *vs.* 2,6-dichlorophenyl) have a negligible effect on the reactivity of the active oxidant. The latter observation

Table 9 A comparison of the ρ values for the epoxidation of styrenes by metalloporphyrin-catalysed oxidation systems

Catalyst	Oxidant	Solvent	T/°C	ρ-Value[a]	Reference
Fe$^{\text{III}}$TPP	PhIO	CH_2Cl_2	Room temp.	−0.93	8
Fe$^{\text{III}}$TDCPP	C_6F_5IO	CH_2Cl_2–MeOH–H_2O	Room temp.	−0.84	18
Fe$^{\text{III}}$TDCPP	PhIO	CH_2Cl_2	20	−0.95	This study
SiPy–Fe$^{\text{III}}$TDCPP	PhIO	CH_2Cl_2	20	−0.98	This study
Fe$^{\text{III}}$TMP[b]	3-Cl-$C_6H_4CO_3H$	CH_2Cl_2	−50	−1.9	19
—	OCr$^{\text{V}}$TDBPP[c]	CH_2Cl_2	30	−1.9	20
Mn$^{\text{III}}$TMP[d]	NaOCl	CH_2Cl_2–H_2O	Room temp.	−0.46	17
—	$PhCO_3H$	C_6H_6	30	−1.3	21

[a] ρ-Values obtained using σ^+ correlations. [b] Iron(III) 5,10,15,20-tetra(mesityl)porphyrin. [c] Oxochromium(V) 5,10,15,20-tetra(2,6-dibromophenyl)porphyrin. [d] Manganese(III) 5,10,15,20-tetra(mesityl)porphyrin.



Scheme 4 Mechanism of alkene expoxidation by oxoiron(IV) porphyrin π-radical cations

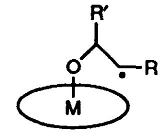
has been noted previously by Bortolini and Meunier for manganese(III) porphyrin–OCl$^-$ epoxidizing systems.[17]

Table 9 compares the results from the present investigation with those from some related metalloporphyrin catalysed epoxidations reported in the literature. The ρ values for all these reactions are negative as would be expected for electrophilic high valent oxometalloporphyrin active oxidants. Although a variety of mechanisms have been proposed for alkene epoxidation by oxoiron(IV) porphyrin π-radical cations, the recent work by Ostovic and Bruice[22] indicates that the most likely mechanism involves the rate determining formation of a charge-transfer complex followed by a concerted addition of the oxygen into the double bond (Scheme 4). The ρ values obtained in this investigation are in agreement with this mechanism.

Epoxidation of (Z)- *and* (E)-4-*Methylpent*-2-*ene*.—The epoxidation of alkenes by iron(III) porphyrin–PhIO systems almost invariably occurs by a stereospecific *syn*-addition, as the mechanism in Scheme 4 indicates and (*Z*)-alkenes react much more readily than their (*E*)-isomers.[8,23] The stereoselectivity of the (*Z*)- over (*E*)-alkenes has been accounted for by the preferred direction of approach of the alkene to the oxoiron group of the active oxidant which is more sterically hindered for the (*E*)-alkene. In agreement with previous studies with iron(III) porphyrin–PhIO systems the homogeneous Fe$^{\text{III}}$TDCPP catalyst shows the expected preference for epoxidation of (*Z*)-4-methylpent-2-ene both in single substrate and in competitive reactions. Somewhat surprisingly, however, the (*Z*) : (*E*) relative reactivity (13 : 1) is virtually identical to the value obtained with the less hindered Fe$^{\text{III}}$TPP–PhIO system (14 : 1).[8]

The SiPy–Fe$^{\text{III}}$TDCPP–PhIO system shows two distinct differences from the homogeneous analogue. First, it does not epoxidize (*E*)-4-methylpent-2-ene. Ostovic and Bruice[23c] have observed a similar total lack of epoxidation of (*E*)-stilbene by the very hindered iron(III) 5,10,15,20-tetra(2,6-dibromophenyl)-porphyrin–PhIO system which, by the use of computer graphics, they attributed to severe steric hindrance. With SiPy–Fe$^{\text{III}}$TDCPP, it is likely that the 2,6-dichlorophenyl substituents will be more constrained by the support and less able to move out of the way of the approaching (*E*)-alkene than those on the homogeneous Fe$^{\text{III}}$TDCPP. This may effectively prevent epoxidation and allow an alternative competitive catalyst degradation process to dominate. Although the nature of this reaction is unclear, it does not involve oxidative bleaching of the iron(III) porphyrin. From the observed green colouration of the used catalyst we suspect *N*-alkylation of the porphyrin occurs. Although *N*-alkylation of iron(III) porphyrins most commonly occurs with terminal alkenes,[16] it has also been observed with non-terminal alkenes and the resulting products are green coloured.[12,24]

The second difference is the formation of a small amount of (*E*)-2,3-epoxy-4-methylpentane from (*Z*)-4-methylpent-2-ene. This lack of stereospecificity is unusual with iron(III) porphyrin–PhIO systems. However, there is a precedent from the work of Castellino and Bruice[15b] who observed a similar small yield of (*E*)-stilbene epoxide from the epoxidation of (*Z*)-stilbene by iron(III) 5,10,15,20-tetra(pentafluorophenyl)porphyrin with PhIO. They suggest that this isomerization might occur *via* C–C bond rotation in an intermediate such as **1** in a minor non-concerted reaction.



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Conclusions

(*i*) Fe$^{\text{III}}$TDCPP has been coordinatively bound to pyridine modified silica and used as a catalyst for alkene epoxidation by PhIO.

(*ii*) The supported Fe$^{\text{III}}$TDCPP catalyses a large number of epoxidation turnovers with (*Z*)-cyclooctene although some catalyst destruction occurs in the largest scale reactions.

(*iii*) The rates of epoxidation catalysed by the supported Fe$^{\text{III}}$TDCPP are not influenced by the surface properties of the silica, however, they are slower than the analogous homogeneous reactions.

(*iv*) Based on the relative reactivities of styrene and 4-substituted styrenes, the mechanisms of epoxidation catalysed by Fe$^{\text{III}}$TDCPP and SiPy–Fe$^{\text{III}}$TDCPP are the same and the support has no detectable electronic influence on the active oxidant.

(*v*) Steric effects of the support are apparent in the epoxidation of (*Z*) and (*E*)-4-methylpent-2-ene. SiPy–Fe^{III}TDCPP is unable to catalyse the epoxidation of the (*E*)-isomer and competitive catalyst degradation (possibly *N*-alkylation) occurs.

Experimental

Materials.—Unless otherwise stated the reagents were commercially available. Kieselgel 60 was from Merck and the other samples of silica (250 MP, 350 MP, 1500 MP, 350 LP and 350 HP) were from Grace GmbH. The preparation of iodosylbenzene, iron(III) 5,10,15,20-tetra(2,6-dichlorophenyl)-porphyrin, 4-nitrostyrene and epoxides of (*Z*)-4-methylpent-2-ene, styrene and 4-substituted styrenes have been reported previously.[8] The epoxides were all purified by distillation on a high vacuum Schlenk line to >98% purity by GC and structures confirmed by ^{1}H NMR spectroscopy.

Pyridine-modified silicas were prepared by refluxing the silica (2.5 g) with distilled 3-chloropropyltrimethoxysilane (14 mmol) in sodium dried toluene (20 cm^3) following the method of Allum *et al.*[5] The resulting material was filtered, washed with toluene and dried under vacuum (0.05 mmHg/100 °C); Diffuse reflectance FTIR (DRIFT) ν(KBr)/cm^{-1} 2975 (propyl-C–H) and 920 (C–Cl). The percentage loading of silane was calculated from carbon analyses.[3i,6] The silanized silica (2.08 silanes nm^{-2}) was suspended in dry toluene and a five-fold excess of 4-picolyllithium in tetrahydrofuran (THF)[25] was added slowly under nitrogen with stirring. Following addition of methanol to remove excess of 4-picolyllithium the modified silica was filtered, washed with methanol and the resulting cream coloured solid was dried under vacuum. Cross-polarization magic angle spinning (CPMAS) ^{13}C NMR; δ 0–50 (5 peaks, alkyl), 123 and 148 (pyridine).

Pyridine *N*-oxide-modified silica was obtained by heating pyridine-modified silica (0.2 g) in glacial acetic acid with a ten-fold excess of H_2O_2 at 90 °C for 6 h. The solid was recovered by filtration, washed with 5% aq. Na_2CO_3 and water and dried under vacuum. CPMAS ^{13}C NMR; δ 0–50 (5 peaks, alkyl), 125 and 138 (pyridine *N*-oxide).

The Fe^{III}TDCPP (10 mg) was loaded onto the modified silicas (1 g) by stirring in CH_2Cl_2 (50 cm^3). The material was subsequently washed with CH_2Cl_2 and methanol and the loading determined by measuring (UV–VIS spectroscopy) the unloaded Fe^{III}TDCPP in the solvent and washings. The supported catalyst was dried under vacuum (0.05 mmHg/100 °C).

Methods.—*Instrumentation.* UV–VIS spectra were recorded using a Hewlett Packard 8452A Diode array spectrometer. Diffuse reflectance UV–VIS spectra were recorded by Dr. H. Herman, BP Chemicals, Sunbury, using a Perkin-Elmer Lambda 9 UV–VIS spectrometer fitted with a powder attachment. Fixed wavelength determinations (412 nm) for the Nash test for formaldehyde were recorded with a Pye-Unicam SP 1750 spectrometer.[25]

^{1}H and ^{13}C NMR spectra were recorded on a Bruker MSL 300 spectrometer (300 MHz). For CPMAS ^{13}C NMR spectra, adamantane was used as a reference to assign ^{13}C chemical shifts.

IR spectra as KBr discs or KBr powders were recorded using a Perkin-Elmer 1720 FT spectrometer.

Mass spectra were recorded on a V.G. Analytical Autospec instrument. For GC–MS the mass spectrometer was coupled to a Hewlett Packard 5890 GC.

GC analysis was performed using an AMS 94 or a Pye-Unicam GCD chromatograph with a flame ionization detector. Columns were packed with Celite with the following liquid phases: 10% w/w carbowax 20 M [(*Z*)-cyclooctene reactions], 2% w/w DEGA (4-chloro, 4-methoxy- and 4-nitro-styrene reactions), 10% w/w DEGA (styrene, 4-chloro- and 4-methyl-styrene reactions) and 20% SE30 [(*Z*)- and (*E*)-4-methylpent-2-ene reactions].

Electron micrographs of solid supports were obtained using a Hitachi Model S-2400 scanning electron microscope.

Elemental analyses were carried out by Butterworth Laboratories Analytical Services.

Alkene Oxidations.—In single substrate oxidations, catalyst (2.0×10^{-7} mol), either as Fe^{III}TDCPP or SiPy–Fe^{III}TDCPP, was mixed with alkene (2.3×10^{-3} mol) in the solvent (3 cm^3) and the oxidation was initiated by the addition of iodosylbenzene (30 mg). The mixture was stirred and aliquots were removed at appropriate time intervals for GC analysis. At the end of the reactions in methanol an aliquot of the solvent (250 mm^3) was removed for colourimetric determination of formaldehyde.[26] The iodoxybenzene in the reaction mixture was determined iodometrically.

Competitive substrate oxidations were carried out as for single substrates using equimolar amounts (2.3×10^{-3} mol) of each alkene.

Repeat use oxidations were carried out as for single substrate oxidations above with fresh iodosylbenzene (30 mg) being added after at 24 h intervals. In the larger scale repeat use oxidations the catalyst (2.3×10^{-6} mol) and alkene (0.17 mol) were reacted with PhIO (1×10^{-2} mol) in dichloromethane (150 cm^3). Fresh PhIO (1×10^{-2} mol) was added after 48 and 96 h.

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