# The oxidation of ethylbenzene by dioxygen catalysed by supported iron porphyrins derived from iron(III) tetrakis(pentafluorophenyl)porphyrin

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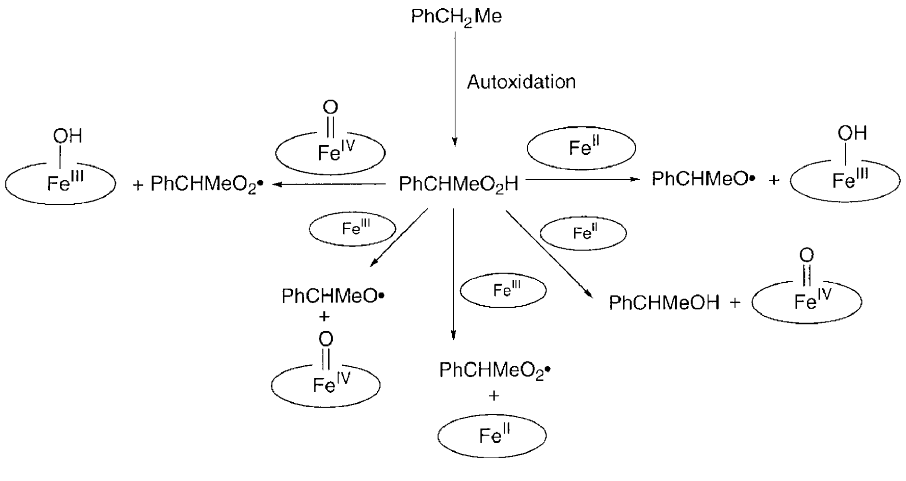
Chloromethylated poly(styrene) and chloropropylated silica gel have been reacted with α,ω-diamines to give diamine modified catalyst supports which have then been covalently attached to iron(III) tetrakis(pentafluorophenyl)porphyrin ($FeTF_5PP$). In this way the diamino groups provide a simple linker/spacer unit between the support and the catalyst. The diamino-silica has been further modified using trimethylsilyl chloride and by acetylation or acid washing. The polarities of the modified inorganic and organic supports have been measured using Reichardt's dye. Spectroscopic studies reveal that with all the supported catalysts, except that on acid washed diamino-silica where the amines are protonated, the diamino groups reduce the iron(III) porphyrin to iron(II). The supported iron porphyrins have been used to catalyse the oxidation of ethylbenzene by dioxygen. These reactions give the same three products, 1-phenylethyl hydroperoxide, 1-phenylethanol and acetophenone, as the analogous homogeneous oxidation using $FeTF_5PP$, suggesting that they proceed by the same mechanism, however, in general they are slower. The overall product yields are limited by the stability/activity of the iron porphyrin and these in turn are very dependent on the length of the linker, the catalyst loading and the microenvironment provided by the support. The role of the diamino groups in the oxidations is discussed.

## Introduction

The work of Ellis and Lyons[1] and more recently that of Gray and Labinger and their co-workers[2] has identified the potential of metalloporphyrin-catalysed oxidations of alkanes by dioxygen which function at relatively low temperatures in the absence of an external reducing agent. Although the mechanism of these reactions has been a matter of some debate over a number of years, it is now generally agreed that oxygen-centred free radicals bring about the oxidations in these systems. Thus, although oxometal species are present in the reaction mixtures, their role is in one-electron redox reactions and free radical chemistry rather than in two-electron oxygen-transfer processes.

In an earlier paper, we described our extensive studies on the homogeneous oxidation of ethylbenzene and some other alkylbenzenes with dioxygen catalysed by $FeTF_5PP$ and related iron porphyrins.[3] We chose $FeTF_5PP$ as the principal catalyst because it is readily available, it has been reported to be effective for alkane oxidation by dioxygen[1f,2c] and it can easily be modified to generate a selection of related catalysts. A further advantage is that it can also, by nucleophilic substitution of the *para*-fluorines on the *meso*-pentafluorophenyls, be grafted by covalent bonding to solid supports.[4]

The mechanism of the ethylbenzene oxidation was investigated over the temperature range 30–110 °C. The reaction profiles and products obtained are wholly consistent with a typical free radical autoxidation in which the redox chemistry of the iron porphyrin species in the system catalyses the formation of and maintains the flux of radical chain carriers derived from the primary autoxidation product, 1-phenylethyl hydroperoxide (Scheme 1). The overall yields of the products are determined by the rate of the reaction and the reactivity and stability of the catalyst towards oxidative degradation by oxyl, and in



**Scheme 1** Reactions of iron porphyrins with 1-phenylethyl hydroperoxide.

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**Table 1** Properties of supports and supported $FeTF_5PP$ catalysts

| Support | Polarity ($E_T^N$) | Support surface modification[a]/ mmol g$^{-1}$ | Catalyst loading[b]/ mg g$^{-1}$ | UV–Vis $\lambda_{max}$/nm[c] | Fe oxidation state |
|---|---|---|---|---|---|
| Silica | 0.91 | — | — | — | — |
| 3-Chloropropylated silica | 0.65 | 1.38 | 0 | — | — |
| $DA_{1,6}$-Si | 0.69 | 0.54 | 10 | 324, 424 | 2 |
| $DA_{1,6}$-Si | 0.69 | 0.54 | 85 | 336, 422 | 2 |
| $DA_{1,6}$-Si | 0.69 | 0.54 | 172 | 422 | 2 |
| Trimethylsilylated $DA_{1,6}$-Si | 0.63 | 0.51 | 10 | 322, 424 | 2 |
| Acetylated $DA_{1,6}$-Si | 0.61 | 0.54 | 10 | 422 | 2 |
| Acid washed $DA_{1,6}$-Si | — | 0.54 | 10 | 358, 418 | 3 |
| Chloromethylated poly(styrene) | 0.26 | 1.6 | — | — | — |
| $DA_{1,3}$-PS | 0.64 | 1.10 | 10 | — | — |
| $DA_{1,6}$-PS | 0.64 | 0.92 | 10 | 430 | 2 |
| Acid washed $DA_{1,6}$-PS | — | 0.92 | 10 | 350, 412 | 3 |
| $DA_{1,9}$-PS | 0.60 | 0.64 | 1.1 | — | — |
| $DA_{1,12}$-PS | 0.60 | 0.45 | 0.9 | — | — |
| None ($FeTF_5PP$–hexylamine)[d] | — | — | — | 322, 420 | 2 |
| None ($FeTF_5PP$)[e] | — | — | — | 350, 410 | 3 |
| None ($FeTF_4NMe_2PP$)[f] | — | — | — | 350, 418 | 3 |

[a] mmol of surface modification per g of silica or poly(styrene). [b] mg of $FeTF_5PP$ per g of support. [c] Spectra recorded as suspensions in $CH_2Cl_2$. [d] Homogeneous solution of iron(II) porphyrin obtained by reduction of $FeTF_5PP$ with hexylamine in $CH_2Cl_2$. [e] Homogeneous solution of $FeTF_5PP$ in $CH_2Cl_2$. [f] Homogeneous solution of $FeTF_4NMe_2PP$ in $CH_2Cl_2$.

particular, alkoxyl radicals. Electron-withdrawing substituents, as has been reported previously,[1f] enhance the rate of oxidation. However, in general the least active catalysts give the highest overall yields. The latter advantage clearly has to be weighed against the disadvantages of long induction periods and reaction times.

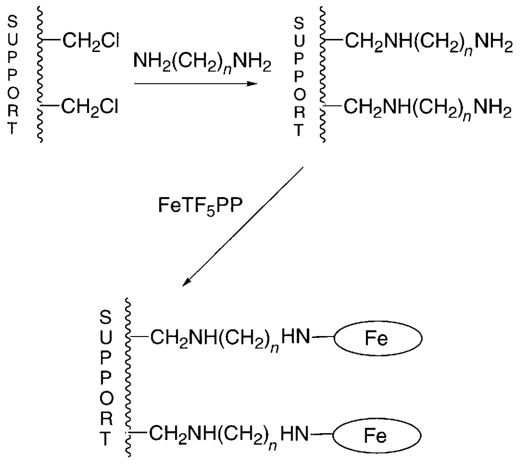
Although supported iron porphyrins have been widely employed as catalysts in systems, using single oxygen donors, that mimic the oxygen-transfer reactions of cytochrome P450 monooxygenases and electron-transfer processes of peroxidases,[5] there are few reports of their use with dioxygen as the terminal oxidant.[6] The potential advantages of using a solid catalyst include the ease of its removal from the oxidation mixture and subsequent reuse, and control of its reactivity through the microenvironment created by the support. This paper reports our studies on ethylbenzene oxidation by dioxygen using iron porphyrin catalysts, derived from $FeTF_5PP$, covalently bound to silica gel and poly(styrene) *via* an α,ω-diamine linker. The results are compared with those from our earlier study using homogeneous systems.

## Results and discussion

### Supports and supported catalysts

The catalysts selected for this study were all derived from $FeTF_5PP$ and were covalently bound *via* a spacer to the solid supports. Covalent binding was used to ensure that the iron porphyrin was firmly attached to the support to minimise problems arising from catalyst leaching. α,ω-Diamines were chosen as spacer/linker units since they provide a synthetically simple means of varying the distance between the catalyst and the support. It was hoped that by increasing the length of the spacer it might be possible to move the metalloporphyrin away from the surface so that it behaved more like a homogeneous catalyst in the bulk solution.

The catalyst-supports used in this study were derived from chloropropylated silica gel (Si) and chloromethylated poly(styrene) (PS). These were reacted in *p*-xylene with the α,ω-diamine spacer prior to attaching the iron porphyrin (Scheme 2). For some experiments the chloropropylated silica gel was reacted with trimethylchlorosilane, to remove unreacted silanol groups, prior to the reaction with the diamine. The extent of surface modification of the supports was obtained by elemental analysis (Table 1).



**Scheme 2** The covalent attachment of $FeTF_5PP$ to diamine-modifed supports.

Iron(III) tetrakis(pentafluorophenyl)porphyrin ($FeTF_5PP$) was covalently bound to the diamine-modified inorganic and organic supports by nucleophilic substitution of the *para*-fluorines on the *meso*-pentafluorophenyl groups (Scheme 2). This was achieved by heating a suspension of the support in a solution of the iron porphyrin in diglyme. The resulting silica-based catalysts were dark brown and those on poly(styrene) were orange coloured. Some of the supported catalysts were subjected to a further reaction (acetylation or treatment with acid) to modify the unreacted surface amino groups.

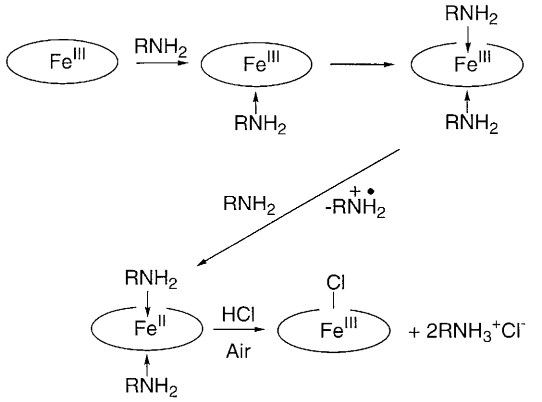
The loadings of the iron porphyrin on the supports were determined by using UV–Vis spectroscopy to measure the total amount of unloaded $FeTF_5PP$ in the reaction solution and washings from the work-up procedure (Table 1).

DRIFT spectroscopy is a simple method for the detection of key functional groups on the support and provides evidence for the surface modification in this study. Reaction of silica gel with (3-chloropropyl)trimethoxysilane resulted in the disappearance of a band at 983 cm$^{-1}$ which has been assigned to highly reactive, isolated Si–OH[7] and the appearance of three peaks at 2867, 2950 and 700 cm$^{-1}$. The first two new peaks arise from the C–H stretching frequencies of the propyl chain and the last is characteristic of the C–Cl group. 1,6-Diaminohexane-modification of the chloropropylated silica, to give $DA_{1,6}$-Si, led to a decrease in the intensity of the 700 cm$^{-1}$ band and the appearance of two new bands at 3300 and 3367 cm$^{-1}$ characteristic of an N–H group. Acetylation of $DA_{1,6}$-Si resulted in the appearance of a new band at 1625 cm$^{-1}$ from the amide carbonyl group.

$^{13}$C CP-MAS NMR analysis of the chloropropylated silica gave peaks at $\delta$ 49.7 ($CH_3O$-Si), 46.4 ($CH_2$*$CH_2$*-Cl), 26.8 ($CH_2$*$CH_2$*$CH_2$) and 10.3 (Si-*$CH_2$*$CH_2$). These were assigned by comparison with data reported by Vrancken *et al.*,[8] from other studies at York[9] and from the solution $^{13}$C NMR spectrum of (3-chloropropyl)trimethoxysilane. Further modification with trimethylchlorosilane led to the appearance of a peak at $\delta$ 0.0 from the Si–$CH_3$ groups. However, because the diamine loadings were very low (~0.5 mmol g$^{-1}$), no clear peaks from 1,6-diaminohexane could be detected.

As a further check that the diamine was bound to the silica, the chloropropylated silica and $DA_{1,6}$-Si were each reacted with $FeTF_5PP$ in diglyme. The catalyst only loaded on to the latter.

The supported iron porphyrins were characterised by UV–Vis spectroscopy as suspensions in dichloromethane and the data, together with those from selected iron porphyrin solution spectra, are recorded in Table 1. The iron(III) porphyrins, $Fe(TF_5PP)Cl$ and $Fe(TF_4NMe_2PP)Cl$[3] in dichloromethane each have a strong absorption at 350 nm and their Soret peaks are at 410 and 418 nm respectively, whereas the iron(II) tetrakis(pentafluorophenyl)porphyrin bis(hexylamine) complex has bands at 322 and 420 nm. Based on these data, all the catalysts on diamine-modified supports are iron(II) porphyrins. This is not surprising since iron(III) porphyrins with electron-withdrawing groups, such as $FeTF_5PP$, are known to be readily reduced by amines to give low spin bis-ligated iron(II) compounds.[9a,10] The mechanism for this process involves first forming the low spin iron(III) complex, followed by an electron-transfer from the ligand to give the iron(II) porphyrin and an aminium radical cation (Scheme 3).[10] With the supported catalysts, some of the large excess of amino groups on the surface can presumably ligate to the iron(III) porphyrins enabling the electron-transfer to occur. To confirm this conclusion, the supported catalysts were washed with acid to protonate the surface amino groups and disrupt any ligation; this brought about the reoxidation of the catalyst by air to give back the iron(III) porphyrin. Interestingly acetylation of $DA_{1,6}$-Si-$FeTF_4$-PP with acetic anhydride did not bring about the reoxidation of the iron(II) porphyrin. It is possible that either the ligated amino groups are not acetylated or that the amido groups are capable of stabilising the iron(II) porphyrin sufficiently to prevent reoxidation.



**Scheme 3** The reduction of an iron(III) porphyrin by a primary amine.

The polarities ($E_{\mathrm{T}}^{\mathrm{N}}$ values) of the supports were measured using the method of Tavener *et al.*[11] This involved adsorbing 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (Reichardt's dye),[12] which has a polarity-dependent charge-transfer (CT) band in its visible spectrum, on to the support and measuring the CT $\lambda_{max}$ by diffuse reflectance UV–Vis spectroscopy. The CT $\lambda_{max}$ values were used to calculate the standardised $E_{\mathrm{T}}^{\mathrm{N}}$ polarities (Table 1).[12] The results show that, although the polarities of support backbones, Kieselgel 60 silica and chloromethylated poly(styrene), are widely different ($E_{\mathrm{T}}^{\mathrm{N}}$, 0.91 and 0.26, respectively; *cf.* water, 1.0 and tetramethylsilane, 0.0), all the diamine-modified supports have very similar polarities ($E_{\mathrm{T}}^{\mathrm{N}}$, 0.60–0.69).

The high polarity of silica gel arises from the polar silanol groups and surface-bound water molecules. Surface modification with relatively non-polar amines and silanes ($E_{\mathrm{T}}^{\mathrm{N}}$ values in the range 0.2–0.3) would, as observed, be expected to decrease the polarity of the surface. However, the relatively high polarities of the modified poly(styrene)s were unexpected since the polarities of both chloromethylated poly(styrene) and the diamine are low ($E_{\mathrm{T}}^{\mathrm{N}} < 0.3$). This suggests that on $DA_{1,6}$-Si the polar terminal amino groups of the hexanediamine are probably directed back towards the polar silica surface whereas on $DA_{1,6}$-PS they are directed away from the non-polar poly(styrene) backbone. The net result is that the measured polarities of both are very similar. Further modification of the supports by acetylating the amino groups and trimethylsilylating the surface silanols led to small decreases in polarity.

We argued that an ideal support might be expected to have a low polarity to favour the approach of the substrate to the supported catalyst and to encourage the diffusion of the products into the bulk solution. Unfortunately in this study all attempts to generate a very non-polar support were unsuccessful.

## Ethylbenzene oxidation

**The method.** The oxidations were carried out at 100 °C, under one atmosphere of dioxygen, with ethylbenzene acting as both the substrate and the reaction medium. The three major products obtained from all the oxidations were the same as those observed in the homogeneous iron(III) porphyrin-catalysed reactions, namely 1-phenylethyl hydroperoxide, 1-phenylethanol and acetophenone. The hydroperoxide was the main product in each oxidation except those using the more active catalyst, acetylated $DA_{1,6}$-Si-$FeTF_4PP$, where acetophenone predominated.

As described in our earlier paper,[3] the hydroperoxide is thermolysed during GC analysis to acetophenone and its yield has to be measured indirectly making use of the quantitative reduction of hydroperoxides to alcohols by triphenylphosphine.[13] Thus GC analysis of the reaction mixtures before and after $PPh_3$ treatment allowed the yields of all three products to be determined. A typical reaction product time profile is illustrated in Fig. 1. This shows an induction period, as was observed in low temperature homogeneous reactions. The reaction comes to a halt when all the catalyst has been destroyed. However, unlike the equivalent reaction profiles from the homogeneous oxidations, the disappearance of the iron porphyrin is not shown in Fig. 1. The absorbances from the UV–Vis spectra of the catalyst suspensions are very variable so that, although the spectra provide $\lambda_{max}$ values, they cannot easily be used to obtain quantitative data on the concentrations of the heterogeneous species present.

**Optimum length of diamine linker.** Four α,ω-diamine linkers, with 3, 6, 9 and 12 carbon atoms, were examined with poly(styrene) as the support (Table 2). Increasing the length of the linker led to a >50% decrease in the amount of diamine on the support and to a ten-fold decrease in the $FeTF_5PP$ that could be covalently attached to $DA_{1,9}$-PS and $DA_{1,12}$-PS. We attribute this to an increase in back-biting, where both amino groups react with the surface chloromethyl groups, with the long chain linkers. As a consequence fewer diamines react with the support and significantly fewer primary amino groups are available to bind the catalyst.

**Table 2** Influence of diamine linker and support backbone on catalyst activity/stability in ethylbenzene oxidations at 100 °C

| Catalyst | Induction period/h | Catalyst lifetime/h | Yield (catalyst turnovers)[a] |
|---|---|---|---|
| $DA_{1,3}$-PS-$FeTF_4PP$ | 55 | 20 | 4200 |
| $DA_{1,6}$-PS-$FeTF_4PP$ | 5 | 16.5 | 7400 |
| $DA_{1,9}$-PS-$FeTF_4PP$ | 3 | 26 | 250 |
| $DA_{1,12}$-PS-$FeTF_4PP$ | 1.5 | 23 | 350 |
| $DA_{1,6}$-Si-$FeTF_4PP$ | 60 | 15 | 4300 |
| $FeTF_5PP$ | 0 | 1.5 | 2900 |
| $FeTF_4NMe_2PP$ | 0 | 20 | 14000 |

[a] Total yield of products, 1-phenylethyl hydroperoxide, 1-phenylethanol and acetophenone, as catalyst turnovers.

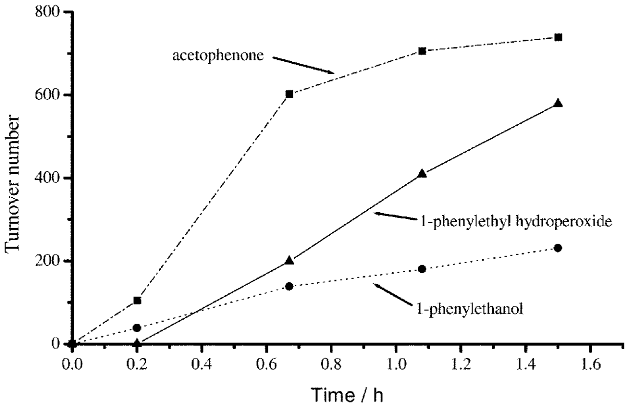


**Fig. 1** Product turnover *versus* time in the oxidation of ethylbenzene with dioxygen catalysed by $DA_{1,6}$-Si-$FeTF_4PP$ at 100 °C; ■ acetophenone, ▲ 1-phenylethyl hydroperoxide, ● 1-phenylethanol.

In the oxidation of ethylbenzene, increasing the linker length led to a large reduction in the induction period, possibly because, as suggested by Montanari and co-workers,[14] the catalyst's environment becomes more like the bulk solution than that of the support. The equivalent homogeneous reactions of $FeTF_5PP$ and $FeTF_4NMe_2PP$ at 100 °C do not show a detectable induction period.[3] However, the highest oxidation yields were obtained using the $DA_{1,6}$-PS-$FeTF_4PP$ (7400 turnovers) which was much more efficient than those using the 1,9- and 1,12-diamine linkers (250 and 350 turnovers, respectively). This may be the result of the low loading of the catalyst (see below). $DA_{1,3}$-PS-$FeTF_4PP$ gave a very long induction period and the overall oxidation yield (4200 turnovers) was lower than that of $DA_{1,6}$-PS-$FeTF_4PP$. Based on these results, the 1,6-diaminohexane linker was selected for all the subsequent studies described below.

**Comparisons of oxidations with heterogeneous and homogeneous catalysts.** In all the reactions, the overall oxidation yields (total catalyst turnovers) were limited by the destruction of the iron porphyrin. As discussed previously, the catalyst degradation is brought about by oxygen-centred radicals, formed during the oxidation of ethylbenzene, reacting with the porphyrin ligand.[3] In general, the heterogeneous oxidations at 100 °C showed moderate to long induction periods whilst, with the homogeneous systems, these were only detectable at temperatures <80 °C. Furthermore the rates of the former systems, once initiated, tended to be lower than those of the analogous homogeneous oxidations using iron(III) tetrakis-(4-dimethylamino-2,3,5,6-fluorophenyl)porphyrin ($FeTF_4NMe_2PP$) or $FeTF_5PP$.

To investigate the influence of the support in these catalysed oxidations, we made a series of changes to the surface groups and the support backbone and compared the performances of the resulting catalysts.

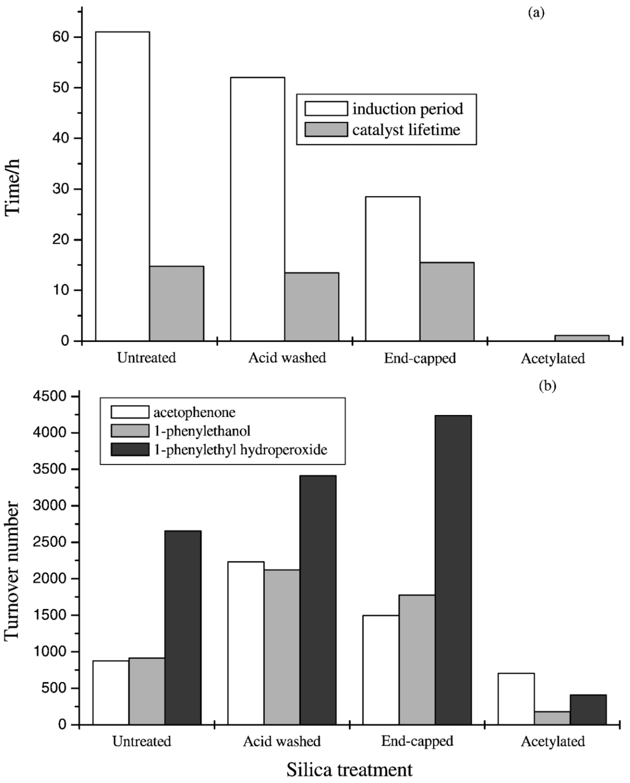


**Fig. 2** The effect of acid washing, trimethylsilylation and acetylation of $DA_{1,6}$-$SiFeTF_4PP$ on (a) catalyst lifetime and reaction induction period, and (b) product turnovers, in the oxidation of ethylbenzene with dioxygen at 100 °C.

Acetylation of the excess amino groups on $DA_{1,6}$-Si-$FeTF_4PP$ had a dramatic effect on the catalyst's activity. The induction period was eliminated and the rate of oxidation increased, however, the catalyst's lifetime and the overall product yield (1300 turnovers) were reduced (Fig. 2). The reaction profile became very similar to that observed in the homogeneous oxidation of ethylbenzene using $FeTF_5PP$, showing that the excess amino groups are clearly responsible for the long induction period with the catalyst on the unacylated support. It was hoped, by analogy with the homogeneous reactions of $FeTF_5PP$,[3] that lowering the reaction temperature would improve the performance of the catalyst on acetylated $DA_{1,6}$-Si. However, although it resulted in the expected increase in the induction period and catalyst lifetime, these were not accompanied by an increase in product yield (Fig. 3).

Acid treatment of the catalyst supported on $DA_{1,6}$-Si, interestingly, had little effect on the induction period or catalyst lifetime although it led to a significant improvement in activity and consequently to an increase in the overall turnovers (7500 *vs.* 4300) (Fig. 2).

Trimethylsilylation of the surface silanols on $DA_{1,6}$-Si-$FeTF_4PP$ reduces the polarity of the support without affecting the surface amino groups. This capping procedure resulted in a decrease in the induction period for the ethylbenzene oxidation and an increase in yield of products (7500 *vs.* 4300 turnovers) (Fig. 2).

The effect of changing the catalyst loading on the oxidation of ethylbenzene was investigated using four catalyst loadings (5, 10, 85 and 172 mg $g^{-1}$) on $DA_{1,6}$-Si. Assuming that each iron porphyrin is attached to the surface by only one diamine linker, these loadings correspond to 114-, 57-, 7- and 3-fold excesses of diamine over iron porphyrin, respectively (Fig. 4). The lowest loaded catalyst was inactive under the conditions used, presumably because the large excess of diamine suppressed the oxidation (see below). Increasing the loading (reducing the excess of diamine) resulted in a decrease in both the induction period and the catalyst's lifetime. The overall product yield

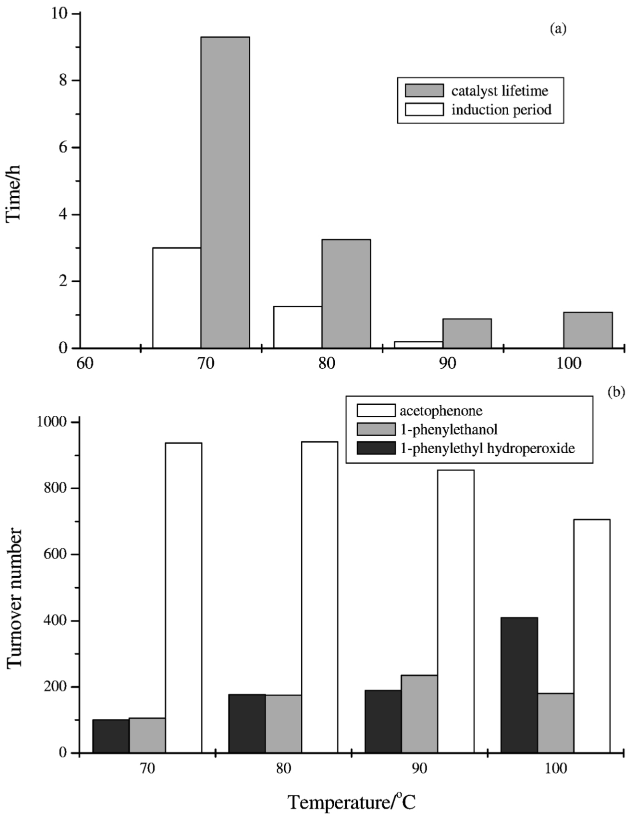


**Fig. 3** The effect of temperature on (a) catalyst lifetime and reaction induction period, and (b) product turnovers, in the oxidation of ethylbenzene with dioxygen catalysed by acetylated $DA_{1,6}$-$SiFeTF_4PP$.

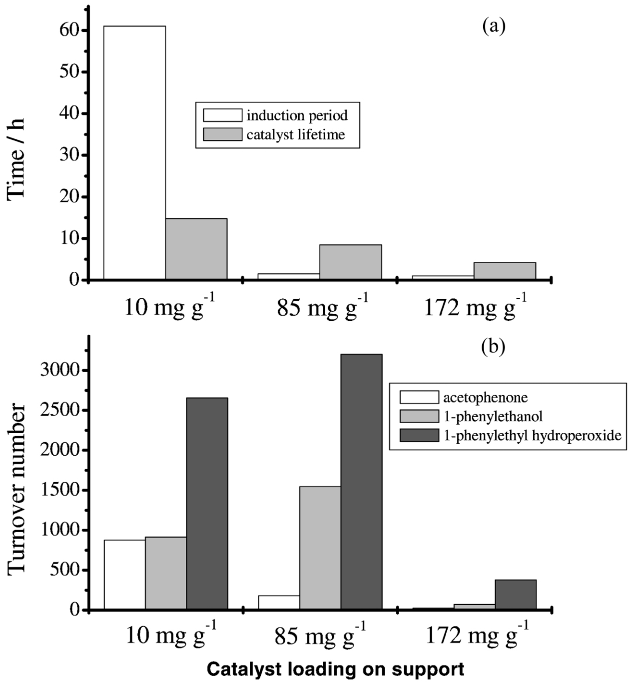


**Fig. 4** The effect of catalyst loading on (a) catalyst lifetime and reaction induction period, and (b) product turnovers, in the oxidation of ethylbenzene with dioxygen catalysed by $DA_{1,6}$-$SiFeTF_4PP$ at 100 °C.

from the oxidation of ethylbenzene was also sensitive to the catalyst loading, increasing to a maximum (4900 turnovers) with 85 mg $g^{-1}$ of catalyst. It is likely that, at the highest loading, inter-porphyrin interactions are significant and these reduce the oxidation yield by encouraging oxidative self-destruction of the catalyst.

Changing the support from $DA_{1,6}$-Si to $DA_{1,6}$-PS resulted in a shorter induction period and, surprisingly, a higher overall yield of oxidation products (4300 and 7400 turnovers, respectively) (Table 2). We interpret these effects as arising from the involvement of the tertiary benzylic C–H bonds of the poly(styrene) backbone in these reactions.[15] These C–H bonds should be very prone to radical autoxidation, which would in turn shorten the induction period and, by helping to maintain the flux of radicals, would increase the yield of oxidation products. Overall the oxidation of the poly(styrene) makes it an unsuitable support for these oxidations since ultimately it will result in the degradation of the polymer backbone.

The polarities of the two supports are very comparable ($E_T^N$: $DA_{1,6}$-Si, 0.69 and $DA_{1,6}$-PS, 0.64) but the organic support was only lightly cross-linked (2% divinylbenzene) and consequently it swells in ethylbenzene and is very flexible compared with the rigid silica-based material. The support flexibility may result in a more accessible and reactive catalyst. This difference in flexibility of the two supports is also evident from the brown and orange colours of $DA_{1,6}$-Si-$FeTF_4PP$ and $DA_{1,6}$-PS-$FeTF_4PP$, respectively, the latter is typical of an iron(II) porphyrin diamine complex. As noted previously, flexible organic polymers accommodate the formation of the diamine complexes much more readily than rigid inorganic supports.[5b,16]

During the early stages of the reactions the orange colour of $DA_{1,6}$-PS-$FeTF_4PP$ changes to dark brown whereas $DA_{1,6}$-Si-$FeTF_4PP$ starts and remains brown during the course of the oxidation. This we attribute to the formation of iron(III) porphyrin from the initial bis-ligated iron(II) species on the organic support. Acid washing of $DA_{1,6}$-PS-$FeTF_4PP$, which would be expected to give the supported iron(III) complex (see above), brings about an identical colour change and the UV–Vis spectrum shows the characteristic absorptions of an iron(III) porphyrin.

Possible reasons for the differences between catalysts on supports and in solution include:

(i) the excess amines on the support's surface which lead to the formation of mono- and bis-ligated iron(II) porphyrins; (ii) the amines on the support surface participating in the radical oxidation. They could either have a beneficial effect by protecting the catalyst from oxidative destruction, as observed with the $NMe_2$ groups in homogeneous oxidations catalysed by $FeTF_4$-$NMe_2PP$,[3] or have a deleterious effect acting as inhibitors by reacting with the autoxidation chain carriers; (iii) the polarity of the catalyst's microenvironment arising from the support's backbone, which in turn affects rates of diffusion of reactants, intermediates and products to and from surface-bound catalysts.

To investigate further the role of the amino groups in these oxidations, the effect of adding 1,3-diaminopropane, $DA_{1,6}$-Si and acid washed $DA_{1,6}$-Si to the standard homogeneous oxidation of ethylbenzene with $FeTF_5PP$ at 70 °C was studied.[3] In each reaction the amount of diamine used was equivalent to that present on $DA_{1,6}$-Si-$FeTF_4PP$ (catalyst loading, 10 mg $g^{-1}$, *i.e.* 57-fold excess of diamine over $FeTF_5PP$). The presence of 1,3-diaminopropane led to the rapid formation (<1 min) of bis-ligated iron(II) porphyrin and the reaction was totally inhibited. The influence of added $DA_{1,6}$-Si was much less dramatic, although it resulted in a significant decrease in product yields, and acid treated $DA_{1,6}$-Si was effectively inert (Fig. 5). These results show that free amino groups clearly interfere with the $FeTF_5PP$-catalysed oxidation of ethylbenzene by dioxygen; the possible causes being points (i) and (ii) above, the inactivation of the catalyst as a bis-ligated complex and/or the diamine acting as an autoxidation inhibitor.

The above results show that the amino groups have a large effect on the performance of the iron porphyrin catalyst in these oxidations and it is likely that the activity of $DA_{1,6}$-Si-$FeTF_4PP$ is markedly affected by the excess diamine groups on the support. The induction period, rate of oxidation and catalyst stability are all sensitive to a complex interplay of effects arising

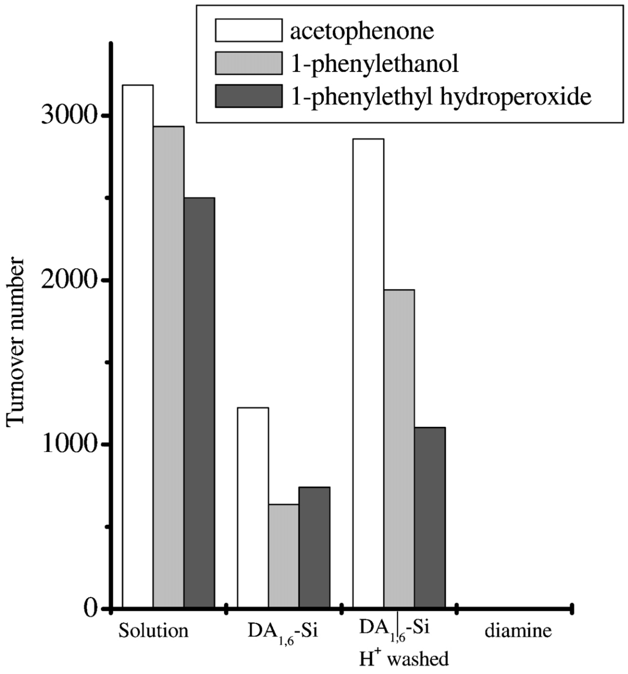


**Fig. 5** The effect, on product turnovers, of adding 1,3-diaminopropane, $DA_{1,6}$-Si or acid washed $DA_{1,6}$-Si to the homogeneous $FeTF_5PP$-catalysed oxidation of ethylbenzene by dioxygen at 70 °C.

from the surface groups and the polarity provided by the support's microenvironment. Thus surface amines affect the reactivity of the iron porphyrin by mono- and bis-ligation, by acting as competitive substrates and by behaving as antioxidants and these effects can be moderated or eliminated by protonation or acetylation. The surface amines, ammonium ions, amides and trimethylsilyl groups also exert their influence on the reactions by modifying the support's polarity: this will affect the rates of the reactions by controlling the diffusion of substrate, intermediates and products between the solution and solid phases.

## Experimental

### Instrumental methods

UV–Vis spectra of solutions and suspensions were recorded on a Hewlett Packard 8452A diode array spectrometer using 1 cm quartz cuvettes. Diffuse reflectance UV–Vis spectra were recorded on a Perkin-Elmer Lambda 15 instrument using a 1 mm path length quartz cuvette. $^1H$ and $^{19}F$ NMR spectra of solutions were recorded on a JEOL JNM-EX270 spectrometer using TMS and $CFCl_3$ as the respective internal standards. $^{13}C$ CP-MAS NMR spectra of supports were obtained using a Bruker MSL 300 MHz spectrometer using adamantane as the external standard. Diffuse reflectance IR Fourier transform (DRIFT) spectra were recorded at ambient temperature and pressure on a Perkin-Elmer 1720 infrared spectrometer. Gas chromatography was carried out with a glass column (3 m × 2.5 mm) packed with 10% w/w carbowax 20M on GasChrom Q (80–120 mesh) in a Pye Unicam GCD chromatograph equipped with a flame ionisation detector. The results were analysed with a JCL6000 for windows programme (Jones Chromatography Ltd.) using 1,3-dichlorobenzene as the internal standard. C,H,N Elemental analysis was performed by Butterworths Laboratories Ltd.

### Reagents

All the reagents were commercially available and used without purification unless otherwise stated. All the alkyl aromatic substrates were passed through a short activated alumina column (UGI) (Phase Sep) and screened by GC to ensure the absence of autoxidation products.

Iron(III) tetrakis(pentafluorophenyl)porphyrin was prepared as described previously.[3]

### Support materials

3-Chloropropylated silica gel was prepared by refluxing a suspension of silica gel (13 g, Kieselgel 60, 230–400 mesh) in a solution of freshly distilled 3-chloropropyltrimethoxysilane (12 $cm^3$, 0.065 mol) in toluene (100 $cm^3$). After 14 h, the mixture was cooled and filtered to give a white solid that was washed sequentially with toluene (50 $cm^3$), acetone (24 $cm^3$) and water (15 $cm^3$) and dried in a vacuum pistol (100 °C, 1 mmHg, 2.5 h). DRIFT, $\nu_{max}/cm^{-1}$ (KBr) 700, 800, 1100, 1633, 1850, 3500 (the Si–OH stretching frequency at 967 $cm^{-1}$ of the silica gel was absent following surface modification); $^{13}C$ CP-MAS NMR $\delta$ 10.3, 26.8, 46.4 ($CH_2CH_2CH_3$), 49.7 (MeO); CH analysis (C 6.58 and H 1.41%) gives a loading of 1.38 mmol $g^{-1}$.

Trimethylsilylation of 3-chloropropylsilica gel was achieved by refluxing the modified silica (5.31 g) in trimethylchlorosilane under argon. After 4 h the mixture was cooled and the solvent was removed under vacuum. The white residue was washed with deionised water until the washings were neutral and then dried under vacuum (100 °C, <0.1 mmHg, 2.5 h). $^{13}C$ CP-MAS NMR $\delta$ 0.0 ($SiMe_3$), 10.3, 26.5, 45.9 ($CH_2CH_2CH_3$), 49.9 (MeO); CH analysis (C 7.55 and H 1.67%) gives a loading of $SiMe_3$ groups of 0.25 mmol $g^{-1}$.

Synthesis of 1,6-diaminohexane-modified silica gel ($DA_{1,6}$-Si) was carried out by heating a suspension of chloropropylated silica (1 g) in a solution of 1,6-diaminohexane (5.9 g, 46 mmol) in *p*-xylene (30 $cm^3$) under nitrogen at 75 °C. After 3.75 h, the mixture was cooled, filtered and washed with *p*-xylene (30 $cm^3$), acetone (30 $cm^3$) and water (until the washings were neutral) and dried under vacuum (100 °C, <0.1 mmHg, 2.5 h). DRIFT, $\nu_{max}/cm^{-1}$ (KBr) 800, 1100, 1450, 1633, 1850, 2867, 2950, 3300, 3367; the nitrogen content from CHN analysis (C 8.62, H 2.06 and N 1.48%) gives a diamine loading of 0.54 mmol $g^{-1}$.

Trimethylsilylated 1,6-diaminohexane-modified silica gel was obtained by the method above using trimethylsilylated 3-chloropropylsilica. The nitrogen content from CHN analysis (C 8.25, H 1.98 and N 1.44%) gives a diaminohexane loading of 0.51 mmol $g^{-1}$.

The diamine-modified poly(styrene)s were prepared from 2% cross-linked chloromethylated poly(styrene) (5.0 g) and diamine (46 mmol) in *p*-xylene by the method described above for $DA_{1,6}$-Si. After filtration, the product was washed with *p*-xylene (90 $cm^3$), methanol (90 $cm^3$) and water (until the washings were neutral) and dried under vacuum. The nitrogen content from CHN analyses gave the diamine loadings (C 85.53, H 7.92 and N 3.08%) for $DA_{1,3}$-Ps, 1.10 mmol $g^{-1}$; (C 86.43, H 7.96 and N 2.58%) for $DA_{1,6}$-Ps, 0.92 mmol $g^{-1}$; (C 84.94, H 7.87 and N 1.80%) for $DA_{1,9}$-Ps, 0.64 mmol $g^{-1}$ and (C 86.38, H 7.93 and N 1.25%) for $DA_{1,12}$-Ps, 0.45 mmol $g^{-1}$.

A typical procedure for loading the catalyst on to diamine-modified supports involved heating a suspension of the support (500 mg) in a solution of $FeTF_5PP$ (5 mg) in freshly distilled diglyme (40 $cm^3$) under nitrogen at 135 °C. After 3.25 h the mixture was cooled, filtered and washed with methanol (50 $cm^3$) followed by dichloromethane (50 $cm^3$). Finally the solid was washed, for 13 h, with dichloromethane in a Soxhlet extractor and dried (100 °C, <0.1 mmHg, 2.5 h).

Acetylation of excess amino groups on $DA_{1,6}$-Si-$FeTF_4PP$ required heating a suspension of the supported catalyst (451 mg) in freshly distilled acetic anhydride (40 $cm^3$) at 90 °C. After 20.5 h the reaction was cooled and the suspension was filtered and washed consecutively with water (until the washings were neutral), methanol (40 $cm^3$) and dichloromethane (40 $cm^3$) before it was subjected to Soxhlet extraction overnight with dichloromethane. Drying under vacuum (100 °C, <0.1 mmHg, 2.5 h) gave a brown solid. DRIFT $\nu_{\mathrm{max}}$/cm$^{-1}$ (KBr) 800, 1100, 1625, 1633, 1850, 2867, 2950.

### Measurement of support polarities

The procedure used to measure support polarities was that of Tavener *et al.*[11] and involved suspending the support (300–400 mg) in a solution of 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (Reichardt's dye) in dichloromethane (20 cm$^3$). The solvent was removed under vacuum and the process was repeated until the support was visibly coloured, at which point the solid was dried under vacuum for 30 min to remove the dichloromethane. A diffuse reflectance UV (DRUV) spectrum of the solid, relative to that of a non-dye coated sample, was recorded and the measured $\lambda_{\mathrm{max}}$ was used to calculate the polarity ($E_{\mathrm{T}}^{\mathrm{N}}$ value).

### Oxidation methods

In a typical oxidation, the supported iron porphyrin ($6.6 \times 10^{-7}$ mol) was mixed with 1,3-dichlorobenzene (0.25 cm$^3$) and the alkyl aromatic (25 cm$^3$) (for homogeneous reactions the iron porphyrin was dissolved in the dichlorobenzene) and analysed by GC prior to being heated in a slow stream of dioxygen at the required temperature. The course of the reaction was followed by removing small samples for GC analysis (0.4 cm$^3$). These were analysed twice, before and after treatment with $PPh_3$. The latter involved adding $PPh_3$ (~30 mg) to the sample at room temperature and stirring for a few minutes before GC analysis.

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