

Modified Silicas Covalently Bounded to 5,10,15,20-Tetrakis(2-hydroxy-5-nitrophenyl) Porphyrinato Iron(III). Synthesis, Spectroscopic and EPR Characterization. Catalytic Studies

Maria Elisa F. Gandini,^a Cláudio R. Neri,^a Fábio S. Vinhado,^a Tatiana Stedile Minorin,^a Otaciro R. Nascimento,^b Osvaldo Antônio Serra^a and Yassuko Iamamoto^{*a}

^aDepartamento de Química, FFCLRP, Universidade de São Paulo, Av. Bandeirantes 3900, 14040-901 Ribeirão Preto-SP, Brazil

^bInstituto de Física de São Carlos, Universidade de São Paulo, São Carlos-SP, Brazil

Neste trabalho estudamos a epoxidação do cicloocteno com PhIO utilizando uma nova porfirina 5,10,15,20-tetraquis(2-hidroxi-5-nitrofenil)porfirinato de ferro(III), suportada em matrizes de sílica via interação eletrostática e / ou ligações covalentes, como catalisador. Estes catalisadores foram obtidos e imobilizados em suporte sólido (sílica propiltrimetilamônio (SiN⁺); sílica propiltrimetilamônio e propilimidazol [SiN⁺(IPG)] e cloropropilsilica (CPS)) via interações eletrostáticas e ligações covalentes. A caracterização do catalisador suportado por UV-Vis e EPR (ressonância eletrônica paramagnética) indicou a presença de uma mistura de espécies de Fe^{II} e Fe^{III} em todos os catalisadores obtidos. No caso da epoxidação do (Z)-cicloocteno por PhIO, os rendimentos observados para o *cis*-epoxiciclooctano foram satisfatórios para as reações catalisadas pelos três materiais (entre 65 e 85%). Estes resultados indicam que a imobilização de metaloporfirinas em suportes sólidos via grupos localizados na posição *orto* de seus anéis *meso*fenil pode promover a catálise eficiente das reações de epoxidação. O catalisador **1**-CPS é menos ativo que **1**-SiN e **1**-SiN(IPG), o que está em acordo com a imobilização destas metaloporfirinas em suportes sólidos via interações eletrostáticas, o que é mais fácil de ocorrer e resulta em um catalisador mais ativo. A atividade do catalisador suportado permaneceu a inalterada, mesmo após três ciclos sucessivos, mostrando que eles são estáveis sob condições oxidantes.

In this work we have studied cyclooctene epoxidation with PhIO, using a new iron porphyrin, 5,10,15,20-tetrakis(2-hydroxy-5-nitrophenyl)porphyrinato iron(III), supported on silica matrices via electrostatic interaction and / or covalent bonds as catalyst. These catalysts were obtained and immobilized on the solid supports propyltrimethylammonium silica (SiN⁺); propyltrimethylammonium and propylimidazole silica [SiN⁺(IPG)] and chloropropylsilica (CPS) via electrostatic interactions and covalent binding. Characterization of the supported catalysts by UV-Vis spectroscopy and EPR (Electron paramagnetic resonance) indicated the presence of a mixture of Fe^{II} and Fe^{III} species in all of the three obtained catalysts. In the case of (Z)-cyclooctene epoxidation by PhIO the yields observed for *cis*-epoxycyclooctane were satisfactory for the reactions catalyzed by the three materials (ranging from 68% to 85%). Such results indicate that immobilization of metalloporphyrins onto solid supports via groups localized on the *ortho* positions of their *meso*phenyl rings can lead to efficient catalysts for epoxidation reactions. The catalyst **1**-CPS is less active than **1**-SiN and **1**-SiN(IPG), this argues in favour of the immobilization of this metalloporphyrin onto solids via electrostatic interactions, which is easier to achieve and results in more active oxidation catalysts. Interestingly, the activity of the supported catalysts remained the same even after three successive recyclings; therefore, they are stable under the oxidizing conditions.

Keywords: iron porphyrin, synthesis, (Z)-cyclooctene epoxidation, recycling, supported catalysts, EPR

Introduction

Different enzymes have a ferric hemin, iron(III) protoporphyrin IX, in their active site. These heme-enzymes

are involved in several oxidation reactions, such as hydrogen peroxide dismutation (catalases), oxidation of substrates with hydrogen peroxide via electron transfer (peroxidases), and insertion of an oxygen atom from molecular oxygen in to several substrates (cytochrome P450). The latter is the only heme-enzyme able to oxidize alkanes.¹

*e-mail: iamamoto@usp.br

The development of several synthetic metalloporphyrins for oxidation reactions with a view to mimicking the action of cytochrome P450-dependent monooxygenases has attracted much interest.² The first system described by Groves *et al.*³ used 5,10,15,20-tetrakis(phenyl)porphyrinato iron(III), [Fe(TPP)]Cl, and iodobenzene (PhIO) in the oxidation of hydrocarbons, and it was able to mimic the reactions of the short catalytic cycle of cytochrome P450. The main problem encountered with the catalyst [Fe(TPP)]Cl was its oxidative self-destruction due to the strongly oxidizing reaction media. Such problem has been solved by introducing electron-withdrawing substituents in the peripheral *meso*- and β -positions of the macrocyclic ring, leading to more robust metal complexes.^{4,5} Moreover, it is often reported that the presence of these substituents in the metalloporphyrin makes the metal-oxo complex (regarded as the active oxidant) more electrophilic and hence more reactive.⁶

Further progress has been made through immobilization of these complexes onto solid supports, since supporting metalloporphyrins can provide site-isolation of the metal centre, minimizing catalyst self-destruction.^{7,8} Furthermore, in the era of “clean technology”, heterogeneous oxidation catalysts are an important target since they enable catalyst recovery and reuse. In this sense, silica gel-based supports can have distinct advantages over organic polymers, since inorganic solids are rigid and stable against oxidative degradation even under extreme conditions. The attachment of metalloporphyrins to solid supports can be classified as being either chemical or physical.⁹ The former uses covalent or coordinative binding,^{10,11} whereas the latter involves adsorption (including electrostatic interaction),¹¹ intercalation,¹² and entrapment.¹³

The most common approach used to prepare metalloporphyrins covalently bound to pre-modified solid supports is reacting one or more substituents on the preformed porphyrin ring with a functional group on the support. Since the role of iron protoporphyrin IX in biological systems is strongly dependent on the axial ligand to the iron centre, a logical approach to the design of models for heme proteins is to attach the metalloporphyrin by coordination to ligands on the surface of the support.¹¹ The coordinative binding thus serves the dual role of anchoring the catalyst and moderating the activity of the metal ion. This approach for preparing supported metalloporphyrins is simpler and, in principle, more versatile than covalent binding. However, it results in reversible binding, which leads to leaching of the metalloporphyrin from the support during the catalyzed reactions.⁹

One physical approach to binding metalloporphyrin to supports occurs via electrostatic interactions between

ionic metalloporphyrins and counterionic groups on the surface of the support (Figure 1).⁹ Although the method is limited to ionic metalloporphyrins, it is very useful and the main advantages of such approach are the strong interactions between the porphyrin and the support, which avoids or at least minimize leaching of the metal complex from the solid matrix during the reactions, and the simplicity of the preparations, since the heterogeneous catalyst is achieved by simply stirring a solution of the ionic metalloporphyrin with a suspension of the counterionic support.^{9,11,14}

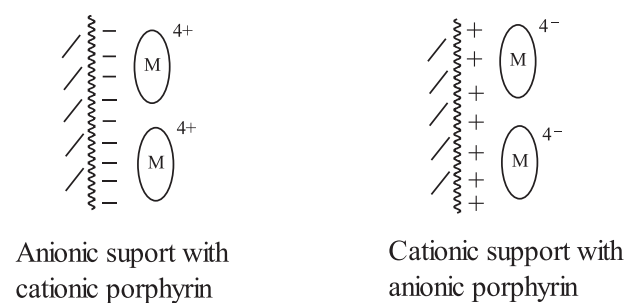


Figure 1. Schematic diagram of electrostatic binding of ionic metalloporphyrins to counterionic supports.

In this report, we have studied the immobilization of iron porphyrin **1** (Figure 2) onto three modified silicas (Figure 3). Iron porphyrin **1** contains electron-withdrawing nitro substituents on its *meso*-phenyl positions, which should make the catalyst more electrophilic and hence more reactive for oxidations.⁴ In addition, iron porphyrin **1** can be made anionic by treatment with a base that is able to remove protons from the *ortho*-hydroxyl positions of the porphyrin ring. The three modified silicas used in this work were (i) chloropropyl silica (CPS), onto which the iron porphyrin should be immobilized by covalent binding; (ii) propyltrimethylammonium silica (SiN⁺) and (iii) propyltrimethylammonium and propylimidazole silica [SiN⁺(IPG)], both of which should allow electrostatic interactions between the anionic iron porphyrin **1** and the cationic supports. Besides, the imidazole group on the solid SiN⁺(IPG) surface can provide an axial ligand, which coordinates to the iron centre and can act like the proximal ligands of heme-enzymes. The preparation of these supported catalysts had two main aims: (a) to investigate the stability of supported catalysts obtained via linkage of the *ortho*-positions of the *meso*-phenyl rings of the porphyrins with the solid supports,¹¹ about which there are few reports¹⁵ and (b) to use the catalysts for the oxidation of hydrocarbons in other solvent systems, preferentially less polar solvents, since [Fe(T2H5NPP)]⁺ requires addition of *N,N*-dimethylformamide as a cosolvent

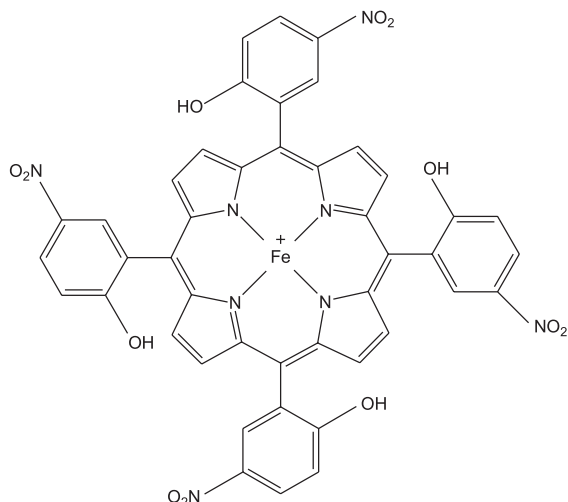


Figure 2. $[\text{Fe}(\text{T2H5NPP})]^+$, (1).

in order to solubilize the iron porphyrin. The solids **1**-CPS, **1**-SiN and **1**-SiN(IPG) were firstly characterized by UV-Vis spectroscopy and EPR. Then, the supported catalysts were used in the catalytic epoxidation of (*Z*)-cyclooctene by PhIO in a first run, and reused in three successive recyclings.

Experimental

Materials

All solvents and reagents were of commercial grade unless otherwise stated and were purchased from Mallinckrodt, Acros, Fluka and Aldrich. HPLC grade 1,2-dichloroethane, *N,N*-dimethylformamide (DMF), and acetonitrile were used as received. (*Z*)-Cyclooctene purity was determined by gas chromatography analysis and it was purified by column chromatographic on basic alumina prior to use. Iodosylbenzene (PhIO) was obtained through hydrolysis of iodosylbenzenediacetate.¹⁶ Samples were stored in a freezer and the purity was checked every 6 months by iodometric assay.

Solid supports

The silica gel 80-230 mesh (Acros Organics) used was previously dried by heating at 60 °C (5 mm Hg) for 4 h. SiN⁺ and SiN⁺(IPG) were prepared as described previously in our laboratory.¹⁷ Chloropropyl silica (CPS) was prepared by refluxing a suspension of silica gel in a solution of 3-chloropropyltrimethoxysilane in toluene according to the method described by Leal *et al.*¹⁸ The solid obtained were dried under vacuum at 100 °C for 8 h. From corresponding elemental analysis the amount of immobilization were estimated: SiN⁺ = 5.3×10^{-4} mol of propyltrimethylammonium/g; SiN⁺(IPG) = 2.3×10^{-4} mol of imidazole/g; CPS = 1.1×10^{-3} mol of chloropropyl/g.

Iron insertion into T2H5NPPH₂

The synthesis of the precursor ligand T2H5NPPH₂, was carried out by the method described by Maestrin *et al.*¹⁹ Iron insertion into T2H5NPPH₂ was achieved in 95% yield by heating the free-base porphyrin and Fe⁰, in excess, at reflux in DMF under inert atmosphere for 48 h. Before the reaction, Fe⁰ was washed several times with hydrochloric acid 0.01 mol dm⁻³, followed by rinsing with deionised water until neutral pH.²⁰ At the end of the reaction, the iron porphyrin solution was isolated from the remaining Fe⁰ by filtration. The product gave rise to one spot by TLC on silica when DMF was used as eluent ($R_f = 1$). UV-VIS spectrum, λ (nm, DMF) 328, 420 ($\epsilon = 3.2 \times 10^4$ dm⁻³ cm⁻¹ mol⁻¹). Electrospray ionization, positive mode, ESI⁺ spectra was recorded for $[\text{Fe}(\text{T2H5NPP})]^+$ (1) and gave [MM] = 11.6 as the major peak.

Preparation of the supported catalysts

$[\text{Fe}(\text{T2H5NPP})]^+$ electrostatically bound SiN⁺(IPG) and SiN⁺

The immobilization of iron porphyrin **1** (soluble in DMF only) onto the cationic supports SiN⁺ and SiN⁺(IPG) requires previous ionization of the iron porphyrin, which

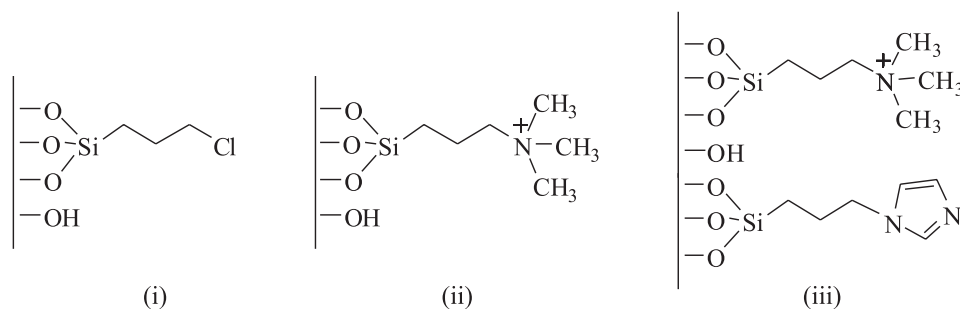


Figure 3. Silica modified with (i) chloropropyl groups (CPS); (ii) propyltrimethylammonium group (SiN⁺); (iii) propylimidazole and propyltrimethylammonium groups [SiN⁺(IPG)].

was achieved by *in situ* deprotonation of the hydroxyl groups of the porphyrin with potassium carbonate, according to the method described by Brulé *et al.*²¹

The procedure for the attachment of **1** by electrostatic interactions require addition of the iron porphyrin (1.71 mg, 1.88 μmol) and potassium carbonate (2.00 mg, 15.0 μmol) to the support (0.25 g) in DMF (3 mL). The mixture was stirred at room temperature until the supernatant liquid became colourless. The supported catalyst was collected by filtration and was washed in a Soxhlet extractor overnight with 1,2-dichloroethane and acetonitrile, in this sequence. Next, the resulting solid materials **1-SiN** and **1-SiN(IPG)** were dried at 100 °C. The supernatant and washings were combined and used to determine the amount of unloaded iron porphyrin by UV-VIS spectroscopy, thus enabling the determination of catalyst loading on the support.

[Fe(T2H5NPP)]⁺ covalently bound to chloropropylsilica

In order to compare possible differences in the catalytic performance promoted by the mode of the binding between the metalloporphyrin and the solid support, **1** was immobilized onto chloropropylsilica (CPS) via covalent binding (Figure 4).

For this purpose, 2.00 mg (2.10 μmol) of metalloporphyrin were dissolved in 5.0 mL DMF, and CPS (0.30 g) was added to this solution. The suspension was magnetically stirred and maintained at 150 °C for 3 h. The resulting solid, **1-CPS**, was washed with 1,2-dichloroethane (24 h) and then with acetonitrile further (24 h) using a Soxhlet extractor and dried at 100 °C. Catalyst loading was obtained using UV-VIS spectroscopy by measuring the amount of iron porphyrin in the combined washings.

(Z)-cyclooctene oxidation

In a typical oxidation, a suspension of the supported catalyst (*ca.* 35 mg, 0.25 μmol) was stirred with the substrate (*ca.* 2.0 mmol) in 1,2-dichloroethane (1.0 mL), and the reaction was started by addition of PhIO (*ca.* 5 mg, 25 μmol). Products were analyzed by gas chromatography using bromobenzene as internal standard; the yields were based on the added oxidant. All solvents and substrates were checked by gas chromatography prior to use to ensure that

they were pure. No reaction occurred in control reactions carried out in the absence of the iron porphyrin, even in the presence of the pure solid support. Furthermore, catalytic activity test with the filtrate of the reactions indicated there was no leaching of the active iron porphyrin from the solid supports during the oxidations.

Recycling of the supported catalysts

At the end of the oxidation reactions, the solid catalysts were recovered by centrifugation and washed four times with methanol (1 mL) to ensure that any remaining PhIO was removed from the surface of the catalyst. Each recovered catalyst was then dried for 3 h at 60 °C, before use in a new reaction.

Instrumentation

UV-Vis spectra were obtained with a Hewlett-Packard 8453, diode array spectrophotometer. The spectra were recorded in 2 mm path length quartz cells (Hellma) as a suspension of the supported catalyst in CCl_4 . A suspension of the corresponding supports SiN⁺, SiN⁺(IPG) and CPS in CCl_4 was used as blank.

The EPR spectra of the supported iron porphyrins were obtained with a Varian E-109 spectrometer operating in the X band frequency (9 GHz) with an amplitude modulation of 4 Gauss, at liquid helium temperature.

Gas chromatographic analyses were performed on a Hewlett-Packard HP 6890 Series GC System coupled to a flame ionization detector using capillary column (HP-INNOWAX, cross linked polyethylene glycol, 30 m length; 0.25 mm i.d., 0.25 μm film thickness) and nitrogen as the carrier gas.

Results and Discussion

Preparation of the supported iron porphyrins

The binding of the iron porphyrin onto SiN⁺ and SiN⁺(IPG) by electrostatic interaction was achieved by the method described by Brulé *et al.*²¹ This method was

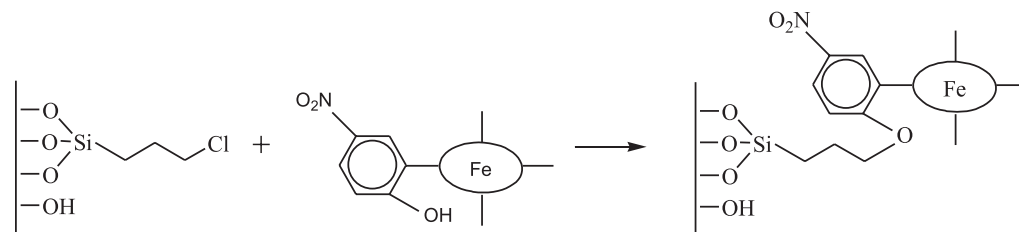


Figure 4. Immobilization of $[\text{Fe}(\text{T}2\text{H}5\text{NPP})]^+$ onto the support CPS.

convenient since the hydroxyl groups of the porphyrin can be deprotonated *in situ* by addition of potassium carbonate, resulting in ionic iron porphyrin and allowing the immobilization of this iron porphyrin onto the cationic supports. The resulting materials, **1**-SiN and **1**-SiN(IPG), were subsequently washed in a Soxhlet extractor with 1,2-dichloroethane and acetonitrile overnight, to remove unbound iron porphyrin. This ensured that the iron porphyrin would not be leached from the support throughout the oxidation reactions, avoiding the concomitant participation of homogeneous catalysis during the reactions with supported catalysts.

Iron porphyrin **1** was also grafted onto chloropropyl silica by nucleophilic aromatic substitution of the *ortho*-hydroxyl group on the *meso*-positions of the porphyrin ring, yielding an ether linkage. The method used to achieve this covalent binding was an adaptation of that previously described for the immobilization of pentafluorophenyl porphyrins onto aminopropyl silica.²² The development of these supported catalysts by different linkages allows the comparison of the effect of the binding modes on the catalytic activity.

Iron porphyrin loadings on the solid materials were quantified by measuring the amount of unloaded iron porphyrin in the solvent washings by UV-Vis spectroscopy (Table 1).

Table 1. Amount of iron porphyrins bound to the solid supports after Soxhlet extraction

Catalyst	mol of 1 per gram of support	Loading (%)
1 -SiN	6.3×10^{-6}	84
1 -SiN(IPG)	7.2×10^{-6}	96
1 -CPS	4.1×10^{-6}	55

It can be observed from Table 1 that the binding of $[\text{Fe}(\text{T}2\text{H}5\text{NPP})]^+$ to the supports SiN^+ and $\text{SiN}^+(\text{IPG})$, which is achieved by electrostatic interactions between the anionic iron porphyrin and the cationic solid supports, displays the highest loadings. Furthermore, the catalyst obtained by immobilization onto the *bis*-functionalized support $\text{SiN}^+(\text{IPG})$ achieved a 96% loading. This can be due to the contribution of two modes of interaction between the iron porphyrin and the support: electrostatic interaction and coordination of Fe^{III} to the imidazole group from the support. On the other hand, **1** bound to CPS by covalent binding led to a lower loading (55%), probably due to the fact that the reaction between the nucleophilic hydroxyl groups in **1** and the chloropropyl groups from the support was not as effective as expected for covalent binding.²² This lower loading suggests that it is necessary to either increase the time of the reaction between **1** and CPS or change some of the reaction conditions.

Characterization of the supported iron porphyrins by UV-Vis spectroscopy

In order to aid the analyses of the supported catalysts, the homogeneous iron porphyrin **1** was also analyzed by this technique. Firstly, the electronic spectra of the supported catalysts confirmed the presence of iron porphyrins only on the solid materials.

All the spectra of **1** shown in Figure 5 exhibit an intense Soret band (λ_{max} ca. 420 nm) and bands at $\lambda < 340$ nm, suggesting the presence of Fe^{II} porphyrin, besides Fe^{III} porphyrin in agreement with a previous report of Evans and Lindsay Smith.²³ It is expected that metalloporphyrins containing electron withdrawing substituents, such as the $-\text{NO}_2$ group, can have the metal centre reduced in the presence of bases (Scheme 1).^{7,23} In this sense, it is likely that the coordinating solvent DMF is responsible for some reduction ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$) seen in the spectrum of the homogeneous complex **1**, the same also occurring for **1**-CPS (Figure 5C) prepared in DMF, in which some amount of Fe^{II} with Fe^{III} coexists. For the supported catalyst **1**-SiN(IPG) (Figure 5B), in turn, the presence of imidazole coordinated to Fe^{III} also facilitates some reduction as already reported previously.⁷ The spectrum of **1**-SiN (Figure 5C) shows a broad band around 580 nm and the absence of the band at 330 nm, which can be explained by the oxygen coordinating to the iron(III) porphyrins⁷ probably from hydroxyl group from the silica matrix or water. It is important to emphasize that in all these systems Fe^{III} is present, since from UV-Vis spectra the intense Soret band is present in the same wavelength for both Fe^{III} and Fe^{II} species.

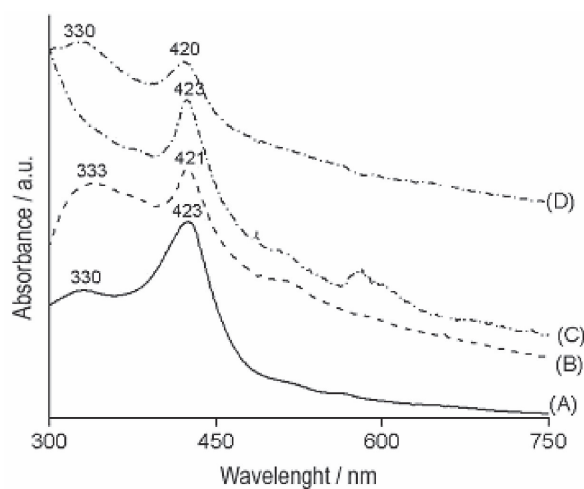
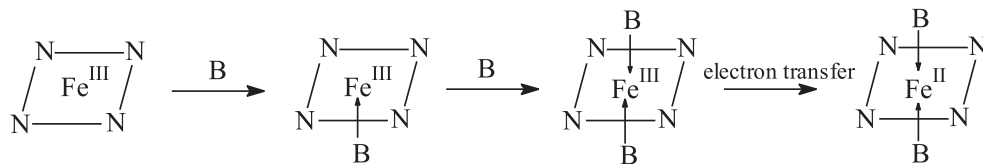


Figure 5. UV-Vis spectra of (A) **1** in DMF; (B) **1**-SiN(IPG); (C) **1**-SiN and (D) **1**-CPS. (B), (C) and (D) were obtained as a suspension in CCl_4 .



B = base

The same is possible with only one B coordinated

Scheme 1.

Characterization of the supported ironporphyrins by EPR

EPR analyses of **1** in solution and immobilized on the solid supports were performed in order to obtain information about the possible presence of Fe^{III} porphyrins in these samples, since the previous UV-Vis analysis had suggested the presence of Fe^{II} species. The EPR analyses indicated that the samples of **1** in DMF solution and **1** immobilized on the solid supports contain a sharp signal in $g = 4.3$, which is consistent with a distorted structure of the metalloporphyrin with high rhombic distortion. Signals in g_{\perp} ca. 6 and g_{\parallel} ca. 2 also appear indicating the presence of high-spin Fe^{III} species with axial symmetry. Typical spectra of supported and homogeneous **1** are shown in Figure 6.

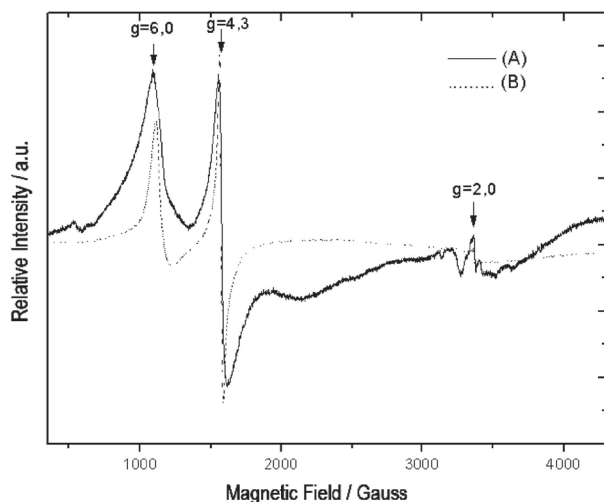


Figure 6. EPR spectra of (A) a solution of **1** in DMF and (B) a suspension of **1-SiN** in 1,2-dichloroethane.

EPR analysis indicates the evidences of Fe^{III} species. Fe^{II} species are EPR “silent” and do not show any signals.

Epoxidation of (*Z*)-cyclooctene with PhIO

Epoxidations of (*Z*)-cyclooctene with PhIO catalyzed by the supported iron porphyrins were initially studied because only the product *cis*-epoxycyclooctane is expected.

In addition, there are various reports in the literature using this substrate, allowing us to compare the efficiency and reactivity of the catalytic systems presented here with those of previously studied systems.^{7,21,24} The three supported catalysts were tested under recycling conditions by carrying out four runs, the first one with fresh catalysts the following ones after recovering the catalysts from the reaction medium for re-use in a new oxidation reaction). The results of these studies are shown in Table 2:

Table 2. (*Z*)-cyclooctene epoxidation with PhIO catalysed by recycled supported catalysts; conditions: 0.25 μ mol of catalyst, molar ratio catalyst/PhIO/*cis*-cyclooctene = 1:100:7000, magnetic stirring for 24 h, solvent = 1,2-dichloroethane; experimental error ca. 8%; ^ayields based on the oxidant added; ^bTON calculated by the ratio between total of product (mols) and amount of catalyst (mol)

Run	<i>cis</i> -epoxycyclooctane yield (%) ^a		
	1-SiN	1-SiN(IPG)	1-CPS
First	74	85	68
Second	53	51	40
Third	54	50	55
Fourth	45	55	41
TON ^b	226	241	204

The yields observed for *cis*-epoxycyclooctane in a first run are satisfactory for the reactions catalyzed by the three materials (ranging from 68% to 85%), being comparable to some results for the epoxidation of (*Z*)-cyclooctene with PhIO catalyzed by supported metalloporphyrins obtained via linkage of *meta* and/or *para* positions of the porphyrin ring to solid materials reported in the literature.^{7,24} Such comparison indicates that the immobilization of metalloporphyrins onto solid supports via groups on the *ortho* positions of the *mesophenyl* rings can also lead to efficient catalysts for epoxidation reactions. It seems that the catalyst **1-CPS** is less active than **1-SiN** and **1-SiN(IPG)**, which could lead us to argue in favour of the immobilizations of metalloporphyrin to solids by electrostatic interactions, that is easier to achieve and yields more active oxidation catalysts. However, two points should be taken into account. Firstly, the difference in yields

and TON is very small if we consider the experimental error (*ca.* 8%). Secondly, the loading of the active catalyst ironporphyrin on the support is lower in the material **1-CPS** than in the materials **1-SiN** and **1-SiN(IPG)** (Table 1). So it is possible presume that the higher the catalyst loading the more active the supported metalloporphyrin.²⁵ The lower yield of **1-CPS** with respect to that of **1-SiN** and **1-SiN(IPG)** can also be due to the nature of immobilization. In the **1-SiN** and **1-SiN(IPG)**, the immobilization occurs through ionic interaction, and normally these ironporphyrins are linked through two or more positions, and are oriented parallel to the surface. For the case of **1-CPS**, the total yield reduction of about 10% can be due to the covalent bonding process that occurs through the flexible propyl group in one position, thus becoming a less available active site than that of **1-SiN**. For **1-SiN(IPG)** the higher additional yield (20%) can be explained by the presence of imidazole coordinating group favouring the formation of the active species $(\text{por}^{*+})\text{Fe}^{\text{IV}}=\text{O}$.⁷

Interestingly, the activity of the supported catalysts is maintained even after three successive recycling steps, showing the stability of the catalysts under the reaction conditions with a decrease of the *cis*-epoxycyclooctane yield only in the first recycling step (second run). The three studied solid catalysts recovered after the first recycling step were clearer brown than the initial catalyst, although leaching of the ironporphyrins from the supports was not observed, once a control of the reaction solution was made and no catalyst was detected by UV-Vis. It seems that there is a little degradation only in the first recycling step, probably due to the fact that some ironporphyrins are immobilized by a certain geometry (random orientation), which favours the degradation attack. On the other hand, the maintenance of the catalytic activity in the epoxidations explains that there is no degradation attack in the subsequent steps.

Concerning the active oxidants operating in these reactions, it is often described that a high-valent intermediate $(\text{por}^{*+})\text{Fe}^{\text{IV}}=\text{O}$ is the key oxidant in hydrocarbon oxidations catalysed by ironporphyrins.²⁶ In this respect, initial assays in the oxidation of cyclohexane catalized by **1-SiN**, **1-SiN(IPG)** and **1-CPS** gave very low yields of the products cyclohexanol and cyclohexanone (Table 3), suggesting that another intermediate is being formed (or stabilized) under the conditions used in this work. In this sense, there are few reports postulating the formation of the $(\text{por})\text{M}^{\text{III}}\text{-OIPh}$ complex as the active oxidant,^{27,28} besides the more electrophilic $(\text{por}^{*+})\text{M}^{\text{IV}}=\text{O}$ species generated in the epoxidation of olefins. The former intermediate would not be able to oxidize alkanes, since it is not as electrophilic as the high-valent $(\text{por}^{*+})\text{M}^{\text{IV}}=\text{O}$.^{29,30} Therefore, we can argue in favour of a $(\text{por})\text{Fe}^{\text{III}}\text{-OIPh}$ complex as the intermediate

stabilized under the reaction conditions used in this work, coexisting with $(\text{por}^{*+})\text{M}^{\text{IV}}=\text{O}$ species.

Table 3. Oxidation of cyclohexane with PhIO catalized by the supported catalysts

Catalyst	Cyclohexanol (%) [*]	Cyclohexanone (%) [*]	Total Yield (%) [*]
1-SiN	4	0	4
1-SiN(IPG)	6	3	9
1-CPS	0	0	0

Conditions: 0.25 μmol of catalyst, molar ratio catalyst/PhIO/cyclohexane = 1:100:7000, magnetic stirring for 24 h, solvent = 1,2-dichloroethane.

^{*}Maximum yields based on the oxidant added.

Conclusions

The development of the ironporphyrin $[\text{Fe}(\text{T2H5NPP})]^+$ allows the formation of the new and stable materials **1-SiN**, **1-SiN(IPG)** and **1-CPS**, via ionic or covalent bonding through the *orto meso*aryl positions of the ironporphyrin. UV-Vis and EPR analyses indicated the presence of Fe^{II} and Fe^{III} on the supported ironporphyrins. The catalytic results confirm the involvement of Fe^{III} species in the oxidative processes. In addition, **1-SiN**, **1-SiN(IPG)** and **1-CPS** showed to be efficient catalysts in the epoxidation of (*Z*)-cyclooctene by PhIO even after three successive recycling steps, making them promising catalysts for selective epoxidations.

Acknowledgments

This work was supported by CAPES, CNPq and FAPESP. We are grateful to Dr. Luiz Alberto Beraldo de Moraes for the mass spectra.

References

- Kadish, K. M.; Smith, K. M.; Guillard, R.; *The Porphyrin Handbook*, Academic Press: San Diego, 2000, vol. 4.
- Feiters, M. C.; Rowan, A. E.; Nolte, R. J. M.; *Chem. Soc. Rev.* **2000**, *29*, 375.
- Groves, J. T.; Nemo, T. E.; Myers, R. S.; *J. Am. Chem. Soc.* **1979**, *101*, 1032.
- Meunier, B.; *Chem. Rev.* **1992**, *92*, 1411.
- Rebelo, S. L. H.; Simões, M. M. Q.; Neves, M. G. P. M. S.; Cavaleiro, J. A. S.; *J. Mol. Catal. A: Chem.* **2003**, *201*, 9.
- Dolphin, D.; Traylor, T. G.; Xie, L. Y.; *Acc. Chem. Res.* **1997**, *30*, 251.
- Prado-Manso, C. M. C.; Vidoto, E. A.; Vinhado, F. S.; Sacco, H. C.; Ciuffi, K. J.; Martins, P. R.; Ferreira, A. G.; Lindsay-Smith, J. R.; Nascimento, O. R.; Iamamoto, Y.; *J. Mol. Catal. A: Chem.* **1999**, *150*, 251; Iamamoto, Y.; Ciuffi, K.; Sacco, H.

- C.; Iwamoto, L. S.; Nascimento, O. R.; Prado-Manso, C. M. C.; *J. Mol. Catal. A: Chem.* **1997**, *116*, 405; Iamamoto, Y.; Ciuffi, K.; Sacco, H. C.; Prado-Manso, C. M. C.; Moraes, M.; Nascimento, O. R.; *J. Mol. Catal. A: Chem.* **1994**, *88*, 167.
8. Poltowicz, J.; Haber, J.; *J. Mol. Catal. A: Chem.* **2004**, *220*, 43.
9. Lindsay-Smith, J. R.; In *Metalloporphyrins in Catalytic Oxidations*; Sheldon, R. A., ed.; Marcel Dekker: New York, 1994, pp. 325.
10. de Faria, A. L.; Airoidi, C.; Doro, F. G.; Fonseca, M. G.; Assis, M. D.; *Appl. Catal. A* **2004**, *268*, 217.
11. Serra, O. A.; Neri, C. R.; Iamamoto, Y.; Nassar, E. J.; Calefi, P. S.; Cicillini, S. A.; Manso, C. M. C. P.; *J. Incl. Phenom.* **1999**, *35*, 271.
12. Barloy, L.; Lallier, J. P.; Battioni, P.; Mansuy, D.; Piffard, Y.; Toumoux, M.; Valim, J.B.; Jones, W.; *New J.Chem.* **1992**, *16*, 71.
13. Skrobot, F. C.; Rosa, I. L.V.; Marques, A. P.; Martins, P.R.; Rocha, J.; Valente, A. A.; Iamamoto, Y.; *J. Mol. Catal. A: Chem.* **2005**, *237*, 86; Serra, O. A.; Nassar, E. J.; Kodaira, C. A.; Néri, C. R.; Calefi, P. S.; Rosa, I. L.V.; *Spectrochem Acta A* **1998**, *54*, 2077.
14. Vinhado, F. S.; Martins, P. R.; Iamamoto, Y.; *Curr. Topics Catalysis* **2002**, *3*, 199.
15. Iamamoto, Y.; Idemori, Y. M.; Nakagaki, S.; *J. Mol. Catal. A: Chem.* **1995**, *99*, 187.
16. Sharefkin, J. G.; Saltzman, H.; *Org. Synth.* **1963**, *5*, 658.
17. Vinhado, F. S.; Martins, P. R.; Masson, A. P.; Abreu, D. G.; Vidoto, E. A.; Nascimento, O. R.; Iamamoto, Y.; *J. Mol. Catal. A: Chem.* **2002**, *188*, 141.
18. Leal, O.; Anderson, D. L.; Bowman, R. G.; Basolo, F.; Burwell Jr., R. L.; *J. Am. Chem. Soc.* **1975**, *97*, 5125.
19. Maestrin, A. P. J.; Tedesco, A. C.; Neri, C. R.; Gandini, M. E. F.; Serra, O. A.; Iamamoto, Y.; *J. Braz. Chem. Soc.* **2004**, *15*, 708.
20. Herrmann, S. H.; Mehdi, S. H.; Corsini, A.; *Can. J. Chem.* **1978**, *56*, 1084.
21. Brulé, E.; Miguel, Y. R.; *Tetrahedron Lett.* **2002**, *43*, 8555.
22. Battioni, P.; Bartolli, J. F.; Mansuy, D.; Byun, Y. S.; Traylor, T. G.; *J. Chem. Soc., Chem. Commun.* **1991**, 1051.
23. Evans, S.; Lindsay-Smith, J. R.; *J. Chem. Soc., Perkin Trans 2* **2001**, *2*, 174.
24. Martinez-Lorente, M. A.; Battioni, P.; Kleemis, W.; Bartoli, J. F.; Mansuy, D.; *J. Mol. Catal. A: Chem.* **1996**, *113*, 343.
25. Cooke, P. R.; Lindsay-Smith, J. R.; *J. Chem. Soc. Perkin Trans 1* **1994**, *1*, 1913.
26. Mclain, J. L.; Lee, J.; Groves, J. T.; In *Biomimetic Oxidations Catalyzed by Transition Metal Complexes*; Meunier, B., ed.; ICP: London, 2000, pp. 91.
27. Nam, W.; Jin, S. W.; Lin, M. H.; Ryu, J. Y.; Kim, C.; *Inorg. Chem.* **2002**, *41*, 3647.
28. Adam, W.; Roschmann, K. J.; Saha-Möller, C. R.; Seebach, D.; *J. Am. Chem. Soc.* **2002**, *124*, 5068.
29. Newcomb, M.; Shen, R.; Choi, S. Y.; Toy, P. H.; Hollenberg, P. F.; Vaz, A. D. N.; Coon, M. J.; *J. Am. Chem. Soc.* **2000**, *122*, 2677.
30. Vinhado, F. S.; Gandini, M. E. F.; Iamamoto, Y.; Silva, A. M. G.; Simões, M. M. Q.; Neves, M. G. P. M. S.; Tomé, A. C.; Rebelo, S. L. H.; Pereira, A. M. V. M.; Cavaleiro, J. A. S.; *J. Mol. Catal. A: Chem.* **2005**, *239*, 138.

Received: September, 5, 2007

Published on the web: February 29, 2008

FAPESP helped in meeting the publication costs of this article.