

Catalytic activity of anionic iron(III) porphyrins immobilized on grafted disordered silica obtained from acidic leached chrysotile

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Abstract

Hydrated disordered silica obtained by leaching chrysotile with hydrochloric acid was grafted with 3-APTS and reacted with aqueous iron porphyrins solutions of [Fe(TDFSPP) and Fe(TCFSP)]. The obtained materials were characterized by powder X-ray diffraction (PXRD), UV–vis, FTIR and electron paramagnetic resonance (EPR) spectroscopies and investigated as catalysts in oxidation reaction of cyclohexane using iododisylbenzene as oxidant. The catalytic activities obtained in heterogeneous media for Fe(TDFSPP) was superior to the results obtained in homogeneous conditions but the opposite effect was observed for the Fe(TCFSP), indicating that instead of the structural similarity of both iron porphyrins (second generation porphyrins), the immobilization way produced different catalysts. The best catalytic activity of the Fe(TDFSPP)/Si-3-APTS (65%) compared to Fe(TCFSP)/Si-3-APTS (33%) can be explained by the easy access of the oxidant and the substrate to the catalytic sites in the former. A schematic representation for the immobilization and a mechanism for the oxidation reaction have been presented.

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1. Introduction

Metalloporphyrins are important examples of macrocyclic complexes and have attracted much interest in the study of various oxygenation reactions of hydrocarbons under mild conditions [1–4]. This class of compounds is used in solution or following immobilization in organic amorphous polymers and crystalline inorganic materials, such as silica [5–7], zeolites [8,9], montmorillonite clay [10,11] and others [12–16]. The use of metalloporphyrins substituted with electron-withdrawing groups (the so-called second generation porphyrins [17]) and their immobilization has resulted in efficient and selective catalysts for oxidation reactions since the support can impose shape selectivity and promote a special environment, favoring the approach of the substrate to the active catalytic species [5–7,12,13,18]. In addition, the immobilization may prevent molecular aggregation or bimolecular self-destruction reactions, which leads to deactivation of catalytically active metalloporphyrin species. The immobilization of metalloporphyrins is also

associated with an easily recyclable solid, which can be reused [19].

Chrysotile, one of the alternative source of highly hydroxylated silica, is classified in the kaolin/serpentine mineral 1:1 group with tri-octahedral site occupancy [20–22]. This solid displays substitution of aluminum atoms, which form a compact brucite-like layer [20]. The mismatch of the brucite-like octahedral sheet with the silica tetrahedral sheet causes the curvature of the layers, which can roll into tight tubes, the characteristic chrysotile fibers [21]. A drastic leaching of concentrated acid on chrysotile fibers transform this natural polymer by removing the brucite-like layer, resulting in an excellent source of hydrated disordered silica [23], with physico-chemical characteristics similar to silica gel.

Silica gel is an example of inorganic solid that present siloxanes groups (Si–O–Si) in the bulk and a high population of silanols groups (Si–OH) at the surfaces [24], being the surface groups available for grafting reactions. The silane coupling agents (general formula (R'O)₃SiR) covalently bonded to inorganic supports, are one interesting alternative to immobilize catalysts, including metalloporphyrins [16,23].

To test the performance of the new silica, we report in this paper the immobilization of a second generation iron porphy-

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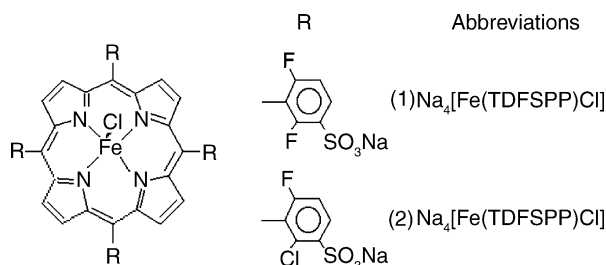


Fig. 1. Schematic representation of iron(III) porphyrins.

rin, 5,10,15,20-tetrakis(2-fluor-6-chloro-3-sulfonatophenyl) porphyrinate] iron(III) [Fe(TCFSPP)] and the already used also second generation iron porphyrin 5,10,15,20-tetrakis(2,6-difluor-3-sulfonatophenyl) porphyrinate] iron(III), (Fe(TDFSPP) (Fig. 1) at the surface of the grafted disordered hydrated silica derived from the chrysotile structure.

The solid materials were investigated in the oxidation reaction of cyclohexane using iodossylbenzene as oxidant and the results compared to the immobilization and catalytic behavior of the iron porphyrins systems previously reported [19].

2. Experimental

2.1. Physical measurements

UV–vis spectra of the solids obtained after the immobilization process were recorded from CCl_4 suspension and the porphyrins and metalloporphyrins were recorded in deionized water solutions, using a Hewlett Packard-8452 A diode array spectrophotometer. FTIR spectra were recorded on a Biorad 3500 GX spectrophotometer in the range of $400\text{--}4000\text{ cm}^{-1}$, using KBr pellets. KBr was crushed with a small amount of the solids and the spectra were collected with a resolution of 4 cm^{-1} and accumulation of 32 scans. For the X-ray diffraction measurements, self-oriented films were placed on neutral glass sample holders. The measurements were performed in reflection mode using a Shimadzu diffractometer XRD-6000 operating at 40 kV and 40 mA (Cu $\text{K}\alpha$ radiation, $\lambda = 1.5418\text{ \AA}$) with a dwell time of $1^\circ/\text{min}$. Electron paramagnetic resonance (EPR) measurements were performed with a Bruker ESP 300E spectrometer at X-band (approximately 9.5 GHz) at 293 or 77 K, using liquid N_2 . Products from catalytic oxidation reactions were identified using a Shimadzu CG-14B gas chromatograph (flame ionization detector) with a DB-WAX capillary column (J&W Scientific). Elemental analysis was made using a EUROVECTOR equipment, model EA 3000 CHNS.

2.2. Materials

All solvents and reagents were of commercial grade (Merck and Aldrich) unless otherwise stated. Authentic samples (alcohol and ketone) were purchased at their highest commercial purity (Aldrich) and used as-received. All substrates were stored at 5°C and purged with argon just before use. After use, all the reagents were discarded in an appropriate container for later treatment for reuse when it was possible or for final disposal.

The chrysotile sample with a fiber length below 2.0 mm (SAMA7ML) was supplied by SAMA-Mineração de Amianto Ltda, mined in Uruaçu, state of Goiás, Brazil. The white solid of disordered silica was obtained by treating chrysotile with hydrochloric acid, as previously described [21,22].

(3-Aminopropyl)triethoxysilane-3-APTS), $\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{CH}_2\text{CH}_2\text{O})_3$ (Aldrich), toluene (Synth) and ethanol (Nuclear) were all reagent grade. Deionized water was used in all experimental procedures.

2.2.1. Porphyrins

Free base porphyrins $\text{Na}_4[\text{H}_2(\text{TDFSPP})]$ and $\text{Na}_4[\text{H}_2(\text{TCFSPP})]$ were synthesized, purified and characterized following the methodology previously described [25–28].

2.2.2. Iron(III) porphyrins

Iron(III) porphyrins (FePor) were obtained by metallation of the free ligand with ferrous chloride tetrahydrate in DMF following the method described by Adler et al. [29,30]. The iron porphyrins were purified by column chromatography on exchange resin (Sephadex), using deionized water as eluent. The products were characterized by UV–visible and EPR spectrometry and the data were consistent with the expected compound after the metallation reaction $[\text{Fe}(\text{TDFSPP})\text{Cl}]^{4-}$ (deionized water): 390 nm ($\epsilon = 37 \times 10^3\text{ L mol}^{-1}\text{ cm}^{-1}$), 504 nm ($\epsilon = 3 \times 10^3\text{ L mol}^{-1}\text{ cm}^{-1}$); $[\text{Fe}(\text{TCFSPP})\text{Cl}]^{4-}$ (deionized water): 390 nm ($\epsilon = 15 \times 10^3\text{ L mol}^{-1}\text{ cm}^{-1}$). The negative charges and the chlorine counter ion will be omitted in the text for simplification purposes [31].

2.2.3. Oxidant

Iodossylbenzene (PhIO) was prepared as previously described [19,31]. It was obtained through the hydrolysis of iodossylbenzenediacetate following the methods described by Saltzman and Sharefkin [32,33]. The purity was measured by iodometric assay.

2.2.4. Catalyst preparation

Silica derived from chrysotile (700 mg) was activated at 100°C for approximately 8 h. The organo-functionalization reaction consisted in refluxing (at 110°C) the suspension of silica (under mechanical stirring) in toluene (150 mL), under inert argon atmosphere. After starting the reflux, 4.5 mL of (3-aminopropyl)triethoxysilane (3-APTS) were added dropwise (1.0 mL/h) to the suspension and the reaction maintained for 10 h. After cooling, the product was centrifuged and washed with toluene, ethanol and a large volume of deionized water and dried at 70°C for 24 h (Si-3-APTS).

The iron porphyrin [Fe(TDFSPP)] immobilization was conducted in a typical experiment, by suspending Si-3-APTS (500 mg) in 20 mL of deionized water, under magnetic stirring. Drops of a 1% (w/w) hydrochloric acid were added to the solution until pH 5–6 and the stirring was maintained for 15 min. Following, $1.2 \times 10^{-5}\text{ mol}$ of iron(III) porphyrin was dissolved in 5 mL of deionized water ($1.5 \times 10^{-3}\text{ mol/L}$), which was added dropwise to the grafted silica acidic suspension. The reaction was conducted under reflux conditions for 5 h at

100–110 °C following by a rest of 15 h at 5 °C. Finally, the green solid obtained was recovered by centrifugation (10 min at 3000 rpm), washed thoroughly with deionized water and dried at 70 °C for 24 h. The iron porphyrin Fe(TCFSP) immobilization, product purification and characterization were done following the same procedure. The amount of iron porphyrin retained within the Si-3-APTS support (solids Fe(TCFSP)/Si-3-APTS and Fe(TDFSP)/Si-3-APTS), after the end of the immobilization process, was determined by the UV–visible spectroscopy analyses of the amount of iron porphyrins in the reaction solutions and all extracts obtained in the washing processes. The content of 2.3×10^{-5} and 1.3×10^{-5} mol of FePor/g functionalized silica for Fe(TDFSP) and Fe(TCFSP), respectively, were determined. The immobilization processes were also carried out for both iron porphyrins in the absence of hydrochloric acid and similar percentage of iron porphyrin retention in the silica support were observed. When raw silica derived from chrysotile was used as support to immobilize the iron porphyrin, no significant retention of the metallocomplexes was observed as only a white solid was obtained and no traces of iron porphyrin Soret band were detected by UV–vis analyses. The molar absorptivities (ϵ) of the iron porphyrins Soret band were determined by analyzing a solution of Fe(TDFSP) or Fe(TCFSP) in deionized water using the UV–vis measurement of successive dilutions.

2.2.5. Catalytic oxidation reaction

Catalytic oxidation reactions were carried out in a 2 mL thermostatic glass reactor equipped with a magnetic stirrer inside of a dark chamber [10]. In a standard experiment within the reactor, solid catalyst and iodobenzene (in different FePor:PhIO molar ratios—1:5, 1:50, 1:100 and 1:500) were suspended in 0.350 mL of solvent (dichloromethane–acetonitrile 1:1 mixture, v/v) and degassed with argon during 10 min. The substrate (cyclohexane, FePor:substrate molar ratio = 1:1000) was added and the oxidation reaction was carried out during 1–24 h, under magnetic stirring. To eliminate the excess of iodobenzene, sodium sulfite was added and the products of the reaction were separated from the solid catalyst by exhaustive washing and centrifugation of the solid with an acetonitrile–dichloromethane mixture. The extracted solution was analyzed by capillary gas chromatography and the amount of the products was determined by using the internal standard method. No products were detected when the catalyst used was grafted silica without any iron porphyrins or in solutions set up without catalyst. After the first catalytic run for each catalyst solid, the supported catalysts were recovered from the solution reaction by filtration and washed thoroughly in Soxhlet extractor with different solvents and finally dried to be reused.

3. Results and discussion

The infrared spectroscopy was used as a tool to provide information from the surface silanol group region of the hydrated silica (Fig. 2).

The main characteristic of the spectrum of hydrated disordered silica (Fig. 2a) is the complete absence of a band in 3686 and 3644 cm^{-1} attributed to typical inner surface

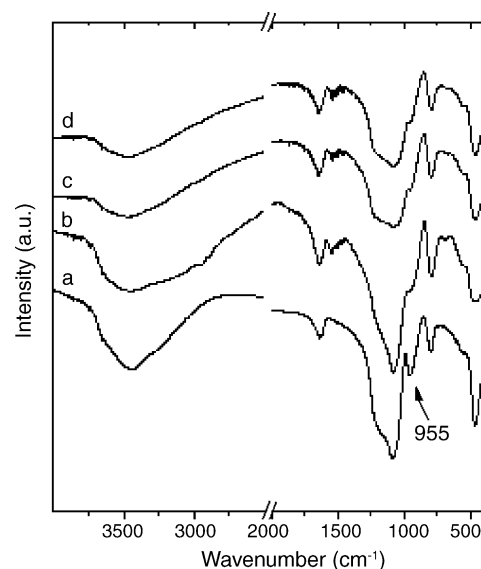


Fig. 2. FTIR spectra of hydrated disordered silica (a), Si-3-APTS (b), Fe(TDFSP)/Si-3-APTS (c) and Fe(TCFSP)/Si-3-APTS (d).

Mg–OH bond on the inorganic structural layer [21,23]. The broad bands at 3447 and 1640 cm^{-1} are attributed to stretching modes of hydrogen-bonded silanol groups and trapped water molecule on the structure. The broad band at 1088 cm^{-1} can be attributed to the Si–O–Si symmetric stretching vibrations [23]. The spectrum relating to the precursor silica shows the band at 955 cm^{-1} , which is attributed to the surface Si–OH, being the band at 463 cm^{-1} , associated to deformation of Si–O. The result for modified silica (Fig. 2b) was characterized by the reduction of the intensity of the band at 955 cm^{-1} and presence of small bands in the region of 2800–3000 cm^{-1} , attributed to typical CH_2 stretching modes, both characterizing the effective reaction of the coupling agent to the surface of hydrated silica (Fig. 2a).

Fig. 2 presents also the spectra of Fe(TDFSP)/Si-3-APTS (c) and Fe(TCFSP)/Si-3-APTS (d). The bands attributed to the ironporphyrin are absent, due to the low concentration of the complexes in the matrix [19].

The silica derived from chrysotile present almost 50% of the silicon atoms bonded to hydroxide group ($\text{SiO}_{1.75}(\text{OH})_{0.5}$) [22]. According to the chemical analysis (Table 1), after the grafting reaction, almost 25% of the reactive hydroxide groups were reacted to 3-APTS, where the silicon atoms have 1.7 OH and 0.3 ethoxyde group (1 bonding to the surface). After the addition of the acid and immobilization of the iron porphyrin, partial

Table 1
Percentages of hydrogen (H), carbon (C) and nitrogen (N), C/N ratio observed and calculated on the samples

| Sample | Found | | | | Calculated C/N |
|---------------------|-------|-------|-------|------|-------------------|
| | C (%) | N (%) | H (%) | C/N | |
| Silica (Si) | 0.10 | 0 | 1.48 | 0 | 0 |
| Si-3-APTS | 6.80 | 2.21 | 2.06 | 3.08 | 3.09 |
| Fe(TCFSP)/Si-3-APTS | 5.04 | 1.70 | 1.67 | 2.97 | 2.72 |

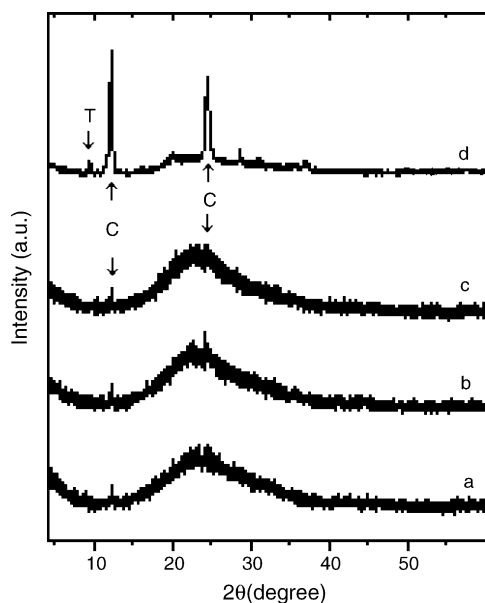


Fig. 3. Powder X-ray diffraction patterns of hydrated disordered silica (a), Si-3-APTS (b) and Fe(TCFSP)/Si-3-APTS (c) and raw chrysotile (d). C, chrysotile; T, talc.

hydrolysis occur and the amount of immobilized iron porphyrin is about 0.2%. The same behavior was already described for the immobilization of metalloporphyrins in kaolinite grafted with 3-APTS [16].

Fig. 3 shows the powder X-ray patterns of hydrated disordered silica (a), Si-3-APTS (b), Fe(TCFSP)/Si-3-APTS (c) (the result of this analysis for the Fe(TDFSP)/Si-3-APTS was the same) and raw chrysotile (d). In all the cases, it was observed the typical diffraction pattern of amorphous samples, with only two sharp peaks of low intensity near 12° and 24° (2θ) denoted by “C”, attributed to main diffraction peaks of the residual chrysotile. Chrysotile shows a small contamination of talc (T), removed during the acid leaching process in the form of a cloudy suspension. It can also be seen that the functionalization and immobilization process do not change the crystallinity of silica.

EPR spectrum of the starting Fe(TCFSP) shows a signal with $g = 6.0$, typical of iron(III)porphyrin high spin 5/2 complex (Fig. 4d) [8]. Hydrated disordered silica (Fig. 4a) and Si-3-APTS (Fig. 4b), shows a very small contamination of high spin Fe(III) in rhombic symmetry ($g = 4.3$) and low spin Fe(III) in $g = 1.95$. Fig. 4c shows the presence of the typical Fe(III) EPR signal in the solid Fe(TCFSP)/Si-3-APTS ($g = 6.0$ to the Fe(III)), confirming the immobilization and excluding the demetallation in the process [10,11].

The EPR results to the Fe(TDFSP)/Si-3-APTS were similar to the EPR results obtained to the solid Fe(TCFSP)/Si-3-APTS, showing the same peaks (not shown). The FePor/Si-3-APTS spectra show that some distortion from the planarity is possible for the porphyrin ring, suggesting that the iron porphyrins are immobilized at the surface of the grafted silica. It is proposed that electrostatic interaction of the positive charged protonated amino terminal groups provided from the functionalization groups and the sulfonated negative charged porphyrin ring. In this case, the acid media would be necessary to the immobilization pro-

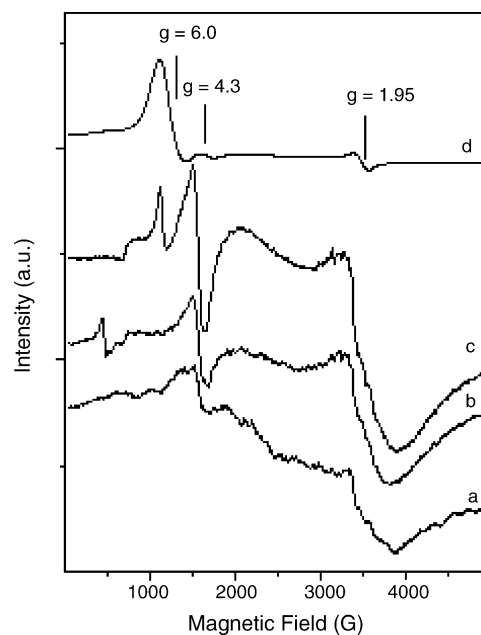


Fig. 4. EPR spectra of hydrated disordered silica (a), Si-3-APTS (b), Fe(TCFSP)/Si-3-APTS (c) and Fe(TCFSP) (d).

cess. On the other hand, coordinative interaction by the terminal amino groups and iron from the complexes is also possible since substantial iron porphyrin immobilization was also observed in the absence of hydrochloric acid. In both cases, the distortion of the porphyrin ring is expected, characterized by the $g = 4.3$ signal [16].

The presence of the iron(III) porphyrins in the solid FePor/Si-3-APTS was also confirmed by UV–vis spectra (in CCl_4 suspension; Fig. 5). The measurements suggest that no demetallation (characterized by a blueshift of the Soret band that is associated

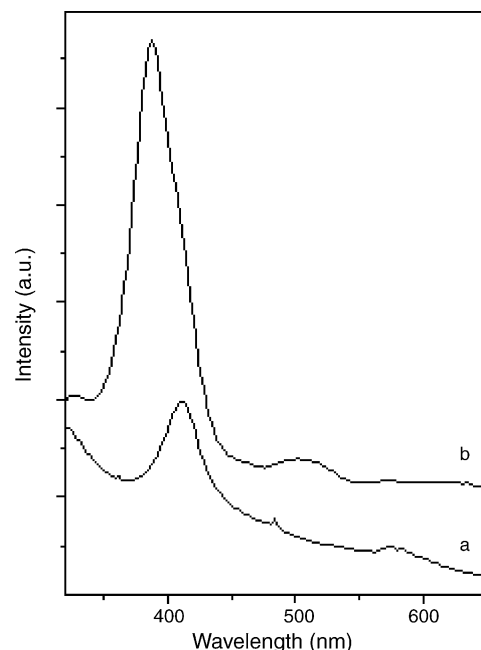


Fig. 5. UV–vis spectra of Fe(TCFSP)/Si-3-APTS (a) and methanol solution of Fe(TCFSP) (b).

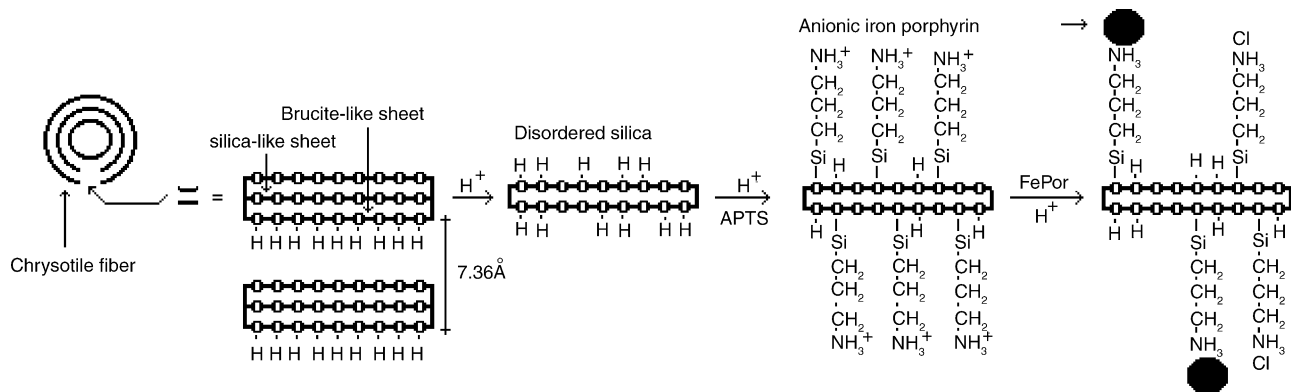


Fig. 6. Schematic representation of the support preparation, surface modification and immobilization of the iron porphyrin in acid media.

with a significant amount of free base porphyrin [12–14]) or significant exchange of the Fe(III) ion with the supports occurred during the preparation process. The Soret peaks at 412 nm for Fe(TDFSPP)/Si-3-APTS (Fig. 5a) and for Fe(TCFSP)/Si-3-APTS (not shown) were red-shifted when compared to those of iron porphyrins in solution (methanol water), 388 nm for Fe(TCFSP) (Fig. 5b) and 386 nm for Fe(TDFSPP) (not shown). A similar behavior was observed previously [19], when metalloporphyrins were immobilized in different inorganic supports [10,12–14,34]. This behavior was attributed to steric constraints caused by the support, which modified the iron porphyrin structure substantially in these supported catalysts [34].

Fig. 6 shows schematically the possible process of the support preparation by leaching the brucite like sheet from the chrysotile structure, surface modification by grafting and immobilization of the porphyrin, in acid media.

3.1. Catalytic properties of the supported iron(III) porphyrins

The catalytic activity of the both iron porphyrin supported catalysts, Fe(TDFSPP)/Si-3-APTS and Fe(TCFSP)/Si-3-APTS, was investigated on the oxidation of weakly reactive alkanes, such as cyclohexane. It is a very useful substrate and frequently used for the Fe(III) porphyrin-catalyzed hydroxylation by iodosylbenzene (PhIO) [6,10,35,36] and was used as test reaction to compare the catalyst activity of the iron porphyrins. The results are presented in Table 2 (Fe(TDFSPP)/Si-3-APTS) and Table 3 (Fe(TCFSP)/Si-3-APTS). When using 1.4 mmol of substrate in the solvent mixture CH₃CN:CH₂Cl₂ (1:1, v/v, ratio), the supported catalysts do not release their iron porphyrin and different proportions of PhIO relative to the iron porphyrin supported catalyst led to selective formation of alcohol (based

Table 2
Hydroxylation of cyclohexane by PhIO catalyzed by iron(III) porphyrin, Fe(TDFSPP) (homogeneous catalysis) and supported iron(III) porphyrin, Fe(TDFSPP)/Si-3-APTS (heterogeneous catalysis)^a

| Catalyst | Run | FePor:PhIO ^b | Time (h) | Alcohol yield (%) ^{c,d} | Yield/time (%) ^e |
|-------------------------|-------------------|-------------------------|----------|----------------------------------|-----------------------------|
| Fe(TDFSPP) ^f | 1 | 1:50 | 1 | 13 | |
| Fe(TDFSPP)/Si-3-APTS | 2 | 1:50 | 1 | 36 | |
| | 3 | 1:50 | 3 | 57 | 7.0 |
| | 4 | 1:50 | 6 | 63 | 2.0 |
| | 5 | 1:50 | 24 | 61 | |
| | 6 | 1:100 | 1 | 25 | |
| | 7 | 1:100 | 3 | 48 | 7.0 |
| | 8 | 1:100 | 6 | 50 | 0.3 |
| | 9 | 1:100 | 24 | 48 | |
| | 10 | 1:500 | 1 | 8 | |
| | 1st Reutilization | 11 | 1:50 | 24 | 22 |
| 12 | | 1:100 | 24 | 9 | 0 |
| Si-3-APTS | 13 | | 1 | <1 | |

^a Typical conditions: purged argon, catalyst:oxidant:cyclohexane molar ratio = 1 mmol:10 mmol:1000 mmol; solvent mixture dichloromethane/acetonitrile (1:1, v/v) (350 μL) at room temperature. When high FePor:PhIO molar ratio was used (>1:100), proportional increase of the solvent and substrate was used. Homogeneous catalyses were made under identical conditions as heterogeneous catalyses.

^b Iron porphyrin:iodosylbenzene = FePor:PhIO molar ratio (mol:mol).

^c Yields based on starting PhIO obtained after 1, 3, 6, 12 or 24 h of reaction. It was assumed that two mols of PhIO are necessary for ketone formation. Trace yields of cyclohexanone gave results smaller than 5% in all reactions.

^d Total yields of cyclohexanol.

^e Ratio % yield product/time of the reaction. E.g. to run 2 and 3: 57% – 36% = 21% / 3 h = 7.0% / h.

^f Homogeneous catalysis performed in dichloromethane/acetonitrile solvent mixture (1:1, v/v).

Table 3

Hydroxylation of cyclohexane by PhIO catalyzed by iron(III) porphyrin, Fe(TCFSP), (homogeneous catalysis) and supported iron(III) porphyrin, Fe(TCFSP)/Si-3-APTS (heterogeneous catalysis)^a

| Catalysts | Run | FePor:PhIO ^b | Time (h) | Alcohol yield (%) ^{c,d} | Yield/time (%/h) ^e |
|------------------------|-------------------|-------------------------|----------|----------------------------------|-------------------------------|
| Fe(TCFSP) ^f | 1 | 1:50 | 1 | 48 | |
| Fe(TCFSP)/Si-3-APTS | 2 | 1:50 | 1 | 15 | |
| | 3 | 1:50 | 3 | 25 | 3.0 |
| | 4 | 1:50 | 6 | 30 | 0.8 |
| | 5 | 1:50 | 24 | 33 | |
| | 6 | 1:100 | 1 | 6 | |
| | 7 | 1:100 | 3 | 16 | 3.0 |
| | 8 | 1:100 | 6 | 20 | 0.8 |
| | 9 | 1:100 | 24 | 26 | 0.5 |
| | 10 | 1:500 | 1 | 1 | |
| | 1st Reutilization | 11 | 1:50 | 24 | 8 |
| 12 | | 1:100 | 24 | 8 | 0.3 |
| Si-3-APTS | 13 | | 1 | <1 | |

^a Typical conditions: purged argon, catalyst:oxidant:cyclohexane molar ratio = 1 mmol:10 mmol:1000 mmol; solvent mixture dichloromethane/acetonitrile (1:1, v/v) (350 μ L) at room temperature. When high FePor:PhIO molar ratio was used (>1:100) proportional increase of the solvent and substrate was used. Homogeneous catalyses were made under identical conditions as heterogeneous catalyses.

^b Iron porphyrin:iodosylbenzene = FePor:PhIO molar ratio (mol:mol).

^c Yields based on starting PhIO obtained after 1, 3, 6, 12 or 24 h of reaction. It was assumed that two mols of PhIO are necessary for ketone formation. Trace yields of cyclohexanone gave results smaller than 5% in all reactions.

^d Total yields of cyclohexanol.

^e Ratio % yield product/time of the reaction. E.g. to run 2 and 3: 25% – 15% = 10% / 3 h = 3.0% / h.

^f Homogeneous catalysis performed in dichloromethane/acetonitrile solvent mixture (1:1, v/v).

on PhIO) within 1, 3, 6, 12 and 24 h (the results obtained for 12 h reaction was omitted in Tables 2 and 3 because they were similar to the results for 24 h). The consumption of PhIO in all reactions was monitored by the presence of iodobenzene (PhI).

For the catalyst Fe(TDFSPP)/Si-3-APTS (Table 2) in the best condition, 63% of conversion to the alcohol was observed (run 4). This catalyst presented better oxy-functionalization results (run 2) than the iron(III) porphyrins in solution in the same amount of oxidant (run 1), indicating that the immobilization favors the catalytic activity of these metalloporphyrins. The low solubility of the iron porphyrins in a CH₂Cl₂:CH₃CN (1:1, v/v, ratio) solvent mixture in homogeneous catalysis certainly is an important factor responsible for the low yields of the iron porphyrin itself. The possibility of the molecular interaction of the Fe(TDFSPP) species in solution could be another reason for the low catalytic activity observed in the homogeneous catalysis because it can be accompanied by μ -oxo complex formation [17,35,36]. The catalyst oxidative degradation in solution is frequently responsible for the low yield in catalytic reaction using metalloporphyrins [17] but not to second generation iron porphyrins and in FePor/oxidant molar ratio low like the used in run 1 (1:50).

Table 3 presents the results of the catalytic activity of Fe(TCFSP) (run 1) and Fe(TCFSP)/Si-3-APTS. It can be observed that the best yield for immobilized system was obtained in run 5 (33% of alcohol). In opposite behavior to Fe(TDFSPP) catalyst, Fe(TCFSP) present substantially better yield in homogeneous catalysis (run 1) when compared with this iron porphyrin immobilized, under same reaction condition (run 2).

For Fe(TDFSPP), the heterogeneous catalytic results presented superior yield of alcohol than the homogeneous catalysis (run 1, Table 2) and the opposite behavior was observed for Fe(TCFSP) (run 1, Table 3). In homogeneous catalysis, one *ortho*-chlorine substituent in each *meso*-phenyl porphyrin groups in the Fe(TCFSP) can avoid molecular interactions, which can deactivate (by destruction of the iron porphyrin or dimerization) and/or avoid the catalytic active species formation [8,24,37]. So, higher yields of oxidation reaction are expected to this iron porphyrin in comparison to Fe(TDFSPP). On the contrary, after immobilization, the best catalytic results observed for Fe(TDFSPP) could be due to an easy access of PhIO and substrate to the iron site, based on the small size of the two *ortho*-fluorine substituent in comparison to *ortho*-chlorine substituent from Fe(TCFSP) [24]. Besides, the immobilization process avoids any molecular interaction possible in homogeneous catalysis, mainly when low percentage of iron porphyrin immobilized in the Si-3-APTS solid is used.

For both catalysts, the increase of the alcohol yield was accompanied by a modest increase of ketone, (yields below 5% in all of the runs) suggesting a good selectivity to alcohol, for both immobilized iron porphyrins for all conditions (Tables 2 and 3). Besides, the best results were observed when the iron porphyrin–iodosylbenzene molar ratio was 1:50 and worst for 1:500, suggesting that the high amount of PhIO could be blocking the access of the reactants to the catalytic site and/or destruction of the catalyst. This phenomenon is more dramatic to the Fe(TCFSP), which have a structure with bulk chlorine atom substituents (Fig. 1). This result also suggests that the access of

the reactants to the catalytic site is an important factor to the catalytic activity when the iron porphyrins are immobilized in Si-3-APTS.

On the other hand, instead of the fact that the so-called second generation iron porphyrin are able to resist to some extent to the oxidative destruction, because of the steric and electronic structure [15–17,19], some destruction of the catalyst can be occurring in high molar ratio. This destruction can explain the observed drastic yields reduction in the proportions 1:500 FePor/oxidant (runs 10, Tables 2 and 3).

In general, it was observed that the yield of the conversion of cyclohexane to alcohol increases with the increase of the reaction time from 1 to 24 h for both the iron porphyrins (runs 2–5, Tables 2 and 3). The same behavior was observed in the high FePor:PhIO molar ratio conditions 1:100 (runs 6–9, Tables 2 and 3). In general, the yield of alcohol became constant after 6 h. The observation that in high molar ratio, increase the alcohol yield (1:100 at 6 h or more time reaction) suggests that the access to the iron is an effective factor to the catalytic performance of the ironporphyrin immobilized. Normally, in this high oxidant molar ratio, a decrease of the yield could be expected with the increase of the reaction time, as a consequence of the some iron porphyrin destruction.

It is noteworthy that reactions using the Si-3-APTS support itself without iron porphyrin gave very low hydroxylation yields (under 1% of alcohol), indicating that the catalytic effect in the hydroxylation of the cyclohexane can be attributed to the presence of the adsorbed iron porphyrin.

The results of the catalyst reuse in a second reaction showed lower yields than the first reaction, suggesting that the catalysts can be detached from the surface after the first use by simple filtration and washing process in Soxhlet extractor.

4. Conclusions

Two tetra-anionic iron porphyrins were immobilized on disordered hydrated silica grafted with 3-APTS. The grafting process occurred establishing covalent bonds between the silanol groups and 3-APTS, releasing ethanol. After the acidification and immobilization of the iron porphyrins, part of the organic moieties were removed and only 0.2% of TCFSP remains immobilized at the surface mainly through electrostatic interactions between the protonated amino terminal groups and the negatively charged sulfonate groups from the porphyrin ring.

The obtained materials, which do not release the ironporphyrin from the support after washing with different organic solvent (as expected with iron(III) porphyrins bearing four negative charges [6,8]), show the main characteristic desirable for a good catalyst.

The immobilization process seemed to favor the catalytic ability of the Fe(TDFSP) metalloporphyrin probably because the immobilized catalyst had lower susceptibility to inactivation by molecular interaction process than this metalloporphyrin in solution but the inverse behavior was observed to the Fe(TCFSP), suggesting that the steric hindrance is an important factor to be considered to design immobilized catalysts.

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