

Anionic iron(III) porphyrin immobilized on silanized kaolinite as catalyst for oxidation reactions

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Abstract

Kaolinite (KGa-2, standard poorly crystallized) was reacted with 3-aminopropyltriethoxysilane (3-APTS) (silanization reaction) after intercalation with urea and delamination under ultrasonic treatment. The silane groups were grafted partially on the layered kaolinite outer surface and aqueous treatment could hydrolyze the remaining ethoxy groups. The silanized kaolinite (compound **4**) was used as a new inorganic support for immobilization of the anionic iron(III) porphyrin: 5,10,15,20-tetrakis(2,6-difluoro-3-sulfonatophenyl) porphyrinato iron(III) chloride $[(\text{FeTDFSPP})\text{Cl}]^{4-}$ (compound **3**). It was found that compound **4** was an appropriated structure to immobilize the $[(\text{FeTDFSPP})\text{Cl}]^{4-}$ by electrostatic interactions. The obtained material (kaolinite-iron(III) porphyrin, compound **5**) was characterized by different techniques such as UV-Vis and infrared (FTIR) spectroscopy, electron paramagnetic resonance (EPR), proton nuclear magnetic resonance ($^1\text{H NMR}$), atomic absorption spectrometry (AAS) and thermal analysis (simultaneous TG/DSC). Compound **5** was investigated in brand oxidation reactions using cyclooctene, heptane and cyclohexane. Iodosylbenzene (PhIO) was used as oxygen atom donor in different molar ratios of iron(III) porphyrin:PhIO. It was observed that compound **5** was an efficient and highly selective catalyst system for epoxidation of cyclooctene (97% of cyclooctene oxide) and hydroxylation of cyclohexane (90% cyclohexanol) after 1 h. The heptane hydroxylation gave 50% of heptanols. The hydrogen peroxide was also used as oxidant but moderate results were obtained. After reuse (3–5 times) the catalyst showed a higher conversion than the primary reactions.

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1. Introduction

Metalloporphyrins are known to perform alkane hydroxylation and alkene epoxidation in a biomimetic catalytic way. In order to recover the catalyst from the reaction media for future reuse or recycling, heterogenization methods of the catalyst have been intensively investigated [1–7]. Main aim of these studies has been to obtain a solid compound that can stabilize the metalloporphyrin for reuse in the reactions and at the same time, promote the catalytic reaction in a selective and desirable stereo-specific manner. To achieve this, many different inorganic materials such as silica, zeolite, alumina, glasses, natural and synthetic layered material (clays and layered double hydroxides) have been used [8–12].

Kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ is a dioctahedral layered hydrated aluminosilicate of the 1:1 type with two distinct in-

terlayer surfaces. One side of the layer is gibbsite-like with aluminum atoms coordinated octahedrally to corner oxygen atoms and hydroxyl groups. The other side of the layer is constituted by a silica-like structure, where the silicon atoms are coordinated tetrahedrally to oxygen atoms. The adjacent layers are linked by hydrogen bonds involving aluminol (Al–OH) and siloxane (Si–O) groups. These binding forces hinder the intercalation processes, but the hydroxyl groups on the aluminum side of the layer are passive to solvation and covalent grafting reactions [13,14]. In the case of large molecules, it is expected that only the surface would be grafted. In this sense, a delamination process would be helpful to provide a small number of stacked layers producing crystals with a large basal surface area [15]. Mechanochemical intercalation of urea and treatment with water under ultrasound stirring is a very easy way to promote the delamination of kaolinite and produce high surface basal area crystals, ideal for the grafting reaction and subsequent immobilization of anionic porphyrins.

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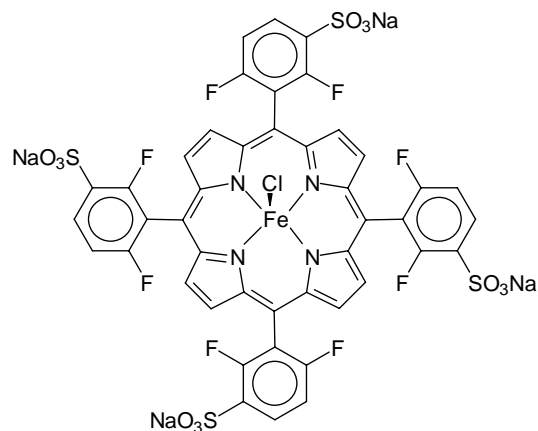


Fig. 1. Structure representation of the iron porphyrin $\text{Na}_4[\text{Fe}(\text{TDFSPP})\text{Cl}]$.

Although kaolinite has a neutral structure and belongs to the same category of clay minerals, no report has been found so far for its use as support for the immobilization of molecules with catalytic activity. Hence in this work, we report the immobilization of the anionic iron(III) porphyrin $\text{Na}_4[\text{Fe}(\text{TDFSPP})\text{Cl}]$ (Fig. 1) in silanized kaolinite and its use as catalyst to oxidation reaction.

2. Experimental

2.1. Materials and synthesis

All chemicals used in this study were purchased from Aldrich, Sigma or Merck and were of analytical grade. Chloroform and toluene were treated with small portions of concentrated sulfuric acid, neutralized with NaOH solution to pH 7, dried with anhydrous CaCl_2 , bidistilled and stored in 4 Å molecular sieves. Ethanol or methanol was refluxed over magnesium–iodine mixture and after distillation stored over 3 Å molecular sieves. Pyrrole was bidistilled under reduced pressure and used immediately after distillation or stored over night in 4 Å molecular sieves. The 2,6-difluorobenzaldehyde (98%), boron trifluoride diethyl etherate (BF_3 etherate), *p*-chloranil (previously powdered) were used under nitrogen atmosphere and without treatment. Dichloromethane of analytical grade was distilled and stored over 4 Å molecular sieves. Distilled water was purified by the Millipore filtration system. NaHCO_3 anhydrous was dried. Pre-activated Silica gel (Merck) 60/70-230 mesh was used in the chromatographic purifications.

Standard poorly crystallized kaolinite (KGa-2) purchased from the Clay Minerals Society (Source Clay Minerals Repository, Columbia, MO), was activated at 60 °C under vacuum (chemical analysis was negative to carbon). The 3-aminopropyltriethoxysilane was reagent grade and used under nitrogen atmosphere. Sephadex resin SP-C25 was hydrated with aqueous HCl solution ($1 \times 10^{-5} \text{ mol l}^{-1}$) for 2 h before use. Urea was powdered in a mortar before its

use. Cyclohexane, heptane and cyclooctene were treated under argon atmosphere before use. Iodosylbenzene was prepared following the methods described by Sharefkin and Saltzmann [16] through hydrolysis of iodosylbenzenediacetate. The solid was carefully dried under reduced pressure and kept at 5 °C. Hydrogen peroxide (30% in water) was stored at 5 °C and titrated before use [17].

After use, all the reagents were discarded in an appropriate container for later treatment for reuse, or for final disposal.

2.1.1. 5,10,15,20-Tetrakis(2,6-difluorophenyl)porphyrin— $\text{H}_2(\text{TDFPP})$ (1)

Compound **1** was synthesized following by the classical procedure described by Lindsay for preparation of meso-substituted porphyrin [18]. Stoichiometric amounts of 2,6-difluorobenzaldehyde and pyrrole were condensed in CHCl_3 , catalyzed by BF_3 etherate, followed by the oxidation with powdered *p*-chloranil. The solvent mixture was evaporated to dryness resulting in a great quantity of deep purple solid material. The solid powder was analyzed by preparative thin layer chromatography on silica gel in pure CH_2Cl_2 . The crude solid was dissolved in a minimal amount of CH_2Cl_2 and purified on silica gel chromatographic column (45 cm \times 1.5 cm) eluted with dichloromethane. The first deep dark purple band of porphyrin **1** was separated and dried under vacuum at 35–45 °C, which yielded 63% of a thin deep red-purple solid **1**.

UV-Vis (chloroform), λ_{max} (nm) (ϵ , $\text{mol}^{-1} \text{ cm}^{-1}$): 416 (Soret band) (2.48×10^5), 508 (1.37×10^4), 538 (2.43×10^3), 584 (5.22×10^3), 638 (4.52×10^2). Chem. anal. calcd. for $\text{C}_{44}\text{H}_{22}\text{N}_4\text{F}_8$ (FW 758.65): C 69.66%, H 2.92%, N 7.38%. Found: C 68.5%, H 2.81%, N 7.02%. IR (KBr, cm^{-1}): 3427 (N–H stretch), 3333, 3110 (=C–H stretch), 1587 (C=C stretch), 1463, 1342, 1234, 1000, 817, 783, 711. ^1H NMR performed in CDCl_3 (signal values in ppm): 8.95 (s, 8H, β -pyrrole-H), 7.82 (m, 4H, *p*-Ph-H), 7.41 (d, $J = 8.5$ Hz, 8H, *m*-Ph-H), -2.73 (s, 2H, internal NH ring).

2.1.2. Anion of 5,10,15,20-tetrakis(2,6-difluoro-3-sulfonatophenyl)porphyrin— $[\text{H}_2(\text{TDFSPP})]^{4-}$ (2)

The sulfonation of **1** was made following the method of Turk and Ford [19,20]. The porphyrin **1** (0.39 mmol) and concentrated H_2SO_4 (0.21 mol) were magnetically stirred inside a single-long-neck round bottom flask under reflux at 185 °C for 7 h in a silicon oil bath. The mixture was cooled at room temperature, and stirred for 38 h. The sulfonation reaction was accompanied by a porphyrin color change from red to light green. A small portion of the green mixture was neutralized with solid NaHCO_3 followed by addition of CH_2Cl_2 and both phases were analyzed by UV-Vis spectroscopy. The sulfonation reaction was completed when no more porphyrin was present in CH_2Cl_2 . The excess of H_2SO_4 was neutralized with NaHCO_3 resulting in the porphyrin **2** bearing $-\text{SO}_3\text{Na}$ or $-\text{SO}_3\text{H}$ groups and Na_2SO_4 . The mixture was dried under vacuum, which resulted in impure crude solid. The porphyrin **2** was extracted with methanol and the

extraction process was repeated several times until no more porphyrin could be detected in the crude solid. The solvent was evaporated at 40 °C under vacuum and the residual Na₂SO₄ was removed twice by column chromatography in silica gel eluted with methanol. After drying the pure porphyrin **2** was obtained (85% yield based on porphyrin bearing four SO₃⁻ groups).

UV-Vis (methanol), λ_{max} (nm) (ε, mol⁻¹ cm⁻¹): 412 (Soret band) (2.22 × 10⁵), 510 (1.40 × 10⁴), 540 (2.70 × 10³), 586 (4.60 × 10³), 642 (8.60 × 10²). Chem. anal. calcd. (considering four SO₃⁻ groups and four H₂O molecules per porphyrin ring) for C₄₄H₃₄N₄F₈S₄O₂₈Na₄ (FW 1454.53): C 36.33%, H 2.35%, N 3.6%, S 10.97%. Found: C 36.99%, H 2.56%, N 3.22%, S 11.98%. IR (KBr, cm⁻¹): 3425 (N–H stretch), 3097 (=C–H stretch), 1614 (C=C aromatic stretch), 1429 (C–N stretch), 1107 (SO₃⁻), 1055–1000 (C–F multiple bands). ¹H NMR performed in D₂O (signal values in ppm): 9.05 (m, 8H, β-pyrrole-H), 8.30 (m, 4H, *p*-Ph-H), 7.45 (m, 4H, *m*-Ph-H).

2.1.3. Anion of 5,10,15,20-tetrakis(2,6-difluoro-3-sulfonatophenyl) porphyrinato iron(III) chloride—[Fe(TDFSPP)Cl]⁴⁻ (**3**)

Porphyrin **2** (0.220 mmol) and FeCl₂·4H₂O (2.20 mmol) were refluxed in 20 ml of *N,N'*-dimethylformamide (DMF) under argon atmosphere for 8 h. The solvent was evaporated under vacuum and the dark solid was dissolved in a minimal amount of bidistilled water and purified by column chromatography packed with a cationic ion-exchange resin Sephadex SP-C25 (hydrogen form) to remove the excess of iron salt. The solution was evaporated and the porphyrin **3** solid was stored in desiccator under dried conditions.

UV-Vis (H₂O), λ_{max} (nm) (ε, mol⁻¹ cm⁻¹): 390 (Soret band) (3.78 × 10⁴), 504 (2.55 × 10²), 578 (1.00 × 10³), 656 (7.12 × 10⁴). The EPR analysis showed an intense signal at *g* = 6.0. IR spectrum showed similar bands of porphyrin **2** except the 3425 cm⁻¹ band characteristic of internal N–H stretching.

2.1.4. Preparation of compound **4** by the functionalization of kaolinite with 3-aminopropyltriethoxysilane

Kaolinite (6.0 g) and urea (20%, m/m, 1.2 g) were mixed in a agate mortar by grinding for 2 h, transferred to 150 ml of boiled hot water and treated in an ultrasound bath until a colloidal suspension of a delaminated kaolinite was obtained (about 0.5 h after) [15]. The suspension was centrifuged at 4500 rpm to remove the supernatant; the solid was washed several times with water to remove the excess of urea, and then dried under vacuum at 60 °C for 12 h. The dried solid (3.7 g) was suspended in 95 ml of toluene under magnetic stirring (argon atmosphere) and 3-aminopropyltriethoxysilane (12 mmol) was added in drops and was refluxed for 48 h. The suspension was filtered and washed in Soxhlet with toluene, ether, dichloromethane, methanol and acetone for 48 h in order to remove the residual 3-aminopropyltriethoxysilane. The solid **4** was dried

Table 1

Previous test to determinate the ideal immobilization conditions of iron porphyrin (compound **3**) on silanized kaolinite (compound **4**)

Test number	Reagents ^a	Percent of iron porphyrin immobilized after washing process (%) ^b
1	(4) + (3) + H ₂ O	52
2	(4) + (3) + methanol	40
3	(4) + (3) + H ₂ O + HCl	63
4	Delaminated kaolinite + (3) + H ₂ O	0
5	Delaminated kaolinite + (3) + methanol	0

^a (**4**) = 10–20 mg of silanized kaolinite; (**3**) = 5.0 ml of iron porphyrin [Fe(TDFSPP)Cl]⁴⁻ solution (4.0 × 10⁻⁵ mol l⁻¹); 1.0 of HCl aqueous solution (1.0 × 10⁻⁵ mol l⁻¹); test volume 6.0 ml.

^b %Fe_{por}: total iron porphyrin added – total iron porphyrin quantitatively determined by UV-Vis analyzed in all supernatants resulted from the washing of the solid resulted by the immobilization process (percent results based on the difference of the quantity of iron porphyrin added and the quantity removed or no immobilized after the reaction).

under vacuum at 65 °C for 24 h. The TG–DSC analyses and EA (chemical analysis) result suggested that there were 4.2 mmol of 3-APTS groups per gram of kaolinite. IR spectroscopy showed characteristic bands of 3-APTS groups at 692 (Si–C), 2933 (as C–H) and 3292 cm⁻¹ (s N–H).

2.1.5. Preparation of compound **5** by the immobilization of iron(III) porphyrin (**3**) on compound **4**

Initially four experiments were performed to find the ideal condition to immobilize the Fe(TDFSPP) on inorganic support. All the tests reactions were carried out at same conditions and proportions of reagents (Table 1). General conditions to tests 1 and 2 were as follows: silanized kaolinite (compound **4**) (10 mg) was suspended in 1.0 ml solvent (water or purified methanol) to which 5.0 ml of Fe(TDFSPP) solution were added (solution prepared in the same solvent of the suspension, 4.0 × 10⁻⁵ mol l⁻¹). The suspension was magnetic stirring at room temperature during 1 h. The system was air-tightly closed and again stirred magnetically for 1 h in a water bath. The suspension was centrifuged and the solid was thoroughly washed with water and methanol. All the supernatant was transferred to a volumetric flask for quantitative UV-Vis analysis. For test 3 (Table 1) aqueous HCl solution (1.0 ml, 1.0 × 10⁻⁵ mol l⁻¹) was added. For tests 4 and 5, pure delaminated kaolinite instead of silanized kaolinite (**4**) was used as inorganic support. From the tests described in Table 1, the best conditions of test 3 were chosen for the synthesis of compound **5**. Compound **4** (800 mg) was suspended in 15 ml of pure water under magnetic stirring and 1.5 ml of 10⁻⁵ mol l⁻¹ HCl solution was added followed by the addition of iron(III) porphyrin (**3**) (11 μmol). The system was closed with air tightness and stirred magnetically for 1 h in a water bath. The suspension was centrifuged and the solid obtained (compound **5**) was thoroughly washed with water and methanol. All the supernatant was transferred to a volumetric flask for quantitative UV-Vis analysis.

The green solid compound **5** was refluxed in methanol, kept for 14 h in order to observe, if any iron(III) porphyrin was removed. The solid was again centrifuged and thoroughly washed. The supernatant was monitored by UV-Vis analysis in order to observe a possible leaching of Fe(TDFSPP) from the support (no iron(III) porphyrin was detected). The solid recovered was dried at 60 °C for 72 h. The TG–DSC and AAS results indicated 12 μmol iron/g of compound **5**, EA (chemical analysis, 1.56% C) and the quantitative UV-Vis analysis showed 13 μmol Fe(TDFSPP)/g of compound **5**.

2.1.6. Treatment of compound **5** with 2-(dimethylamino)pyridine (DMAP)

Compound **5** (0.1 g) was suspended in 10 ml of DMF under magnetic stirring at 60 °C. The organic base 2-(dimethylamino)pyridine (DMAP, 0.18 mmol), dissolved in a minimal amount of DMF was added in drops (DMAP:FeTDFSPP molar ratio was 10:1). The mixture was heated under magnetic stirring for 8 h at 45 °C. The solid was once again thoroughly washed with methanol and dichloromethane and the supernatant was stored and analyzed by UV-Vis spectroscopy with a view to quantify the iron(III) porphyrin removed from the matrix.

2.1.7. Oxidation of cyclooctene, heptane and cyclohexane by iodosylbenzene (PhIO) or H_2O_2 catalyzed by compound **5**

Catalytic oxidation reactions were carried out in a 2 ml thermostatic glass reactor equipped with a magnetic stirrer inside a dark chamber. In a typical reaction of heterogeneous catalysis, compound **5** (20 mg) and iodosylbenzene solid were degassed with argon during 30 min inside a 2 ml vial. The solid mixture was suspended in 0.3 ml of solvent (dichloromethane) and the substrate cyclooctene, heptane or cyclohexane (1.1 mmol) were added resulting in a Fe(TDFSPP):oxidant:substrate constant molar ratio. The oxidation reaction was carried out during a controlled time interval (1, 3 and 6 h) under magnetic stirring. Sodium sulfite was added in order to eliminate the excess of iodosylbenzene. The reaction products in solution were separated from the solid by centrifugation and the catalyst solid was washed with dichloromethane and acetonitrile solvents. All the extracted solution and supernatant were transferred to a volumetric flask and analyzed by gas chromatography. Product yields were determined based on PhIO with the internal standard method. The solid catalyst was thoroughly washed and dried for its reuse in another reaction. With a view to check the reproducibility of the determinations, all the reactions were repeated 3–5 times since a micro method was used to measure catalytic activities and only average results are reported. The same procedure was followed in the control reactions using: (a) only the substrate, (b) substrate + PhIO and (c) substrate + PhIO + compound **4**. The procedure for homogeneous catalysis reactions was similar to that for heterogeneous catalysis reaction. Fe(TDFSPP) solution was prepared using a acetonitrile:dichloromethane (1:1) solvent

mixture ($8.0 \times 10^{-5} \text{ mol l}^{-1}$). Hydrogen peroxide was used in the same way as PhIO with the addition of required amount of 30% aqueous solution. 1-Methylimidazole (Imi) solution also prepared in CH_3CN :dichloromethane mixture ($8.0 \times 10^{-4} \text{ mol l}^{-1}$) was added to the iron(III) porphyrin solution before the substrate and oxidant.

2.2. Techniques used

UV-Vis spectra were recorded in the 200–800 nm range in a HP 8452A Diode Array Spectrophotometer. All analysis were obtained with a 0.5 cm path length cell for 10^{-5} and $10^{-6} \text{ mol l}^{-1}$ of porphyrin solution. Spectra of solid samples were recorded in a 0.1 cm path length quartz cell (Hellma) in nujol mull.

Infrared spectra were obtained using a Bomem Michelson MB-100 spectrophotometer on powdered samples mixed with dried KBr and measured over the 4000–400 cm^{-1} region, with 65 scans and a resolution of 4 cm^{-1} .

Electron paramagnetic resonance (EPR) measurements of the powder materials were made with a Bruker ESP 300E spectrometer at X-band (ca. 9.5 GHz) at 293 or 77 K using liquid N_2 .

Proton nuclear magnetic resonance (^1H NMR) measurement was made using INOVA 500-Varian 500 MHz in CDCl_3 or D_2O .

Atomic absorption spectroscopic (AAS) studies were carried out in a Perkin Elmer 4100-1319 Spectrophotometer using a conventional air–acetylene flame, after acid (HF) dissolution of known amounts of clay material in PARR digest pump.

Chemical analysis (CA) measurements (CHN) were carried out with a Perkin Elmer 240C instrument.

Thermogravimetric and differential scanning calorimetric (TG and DSC) measurements were performed with a Netzsch-STA 409EP series equipment. Samples were heated under air static atmosphere from 20 to 1000 °C at a rate of 8 °C/min, using 0.065 ml alumina crucibles.

X-ray diffraction study of powdered samples was performed with a Rigaku diffractometer using the Bragg–Bretano geometry (radiation $\text{Co K}\alpha$ ($=1.7902 \text{ \AA}$, 40 kV and 20 mA, Ni filter, scan speed of 1° min^{-1}). Silicon powder was added to the samples and used as internal standard (denoted by an asterisk in the X-ray powder diffraction patterns).

Products from organic oxidation were identified using a Shimadzu CG-14B gas chromatograph (flame ionization detector) with a DB-WAX capillary column (J&W Scientific).

3. Results and discussion

3.1. Synthesis of porphyrins and iron(III) porphyrin

The required porphyrin ligand **1** was prepared following the general procedure developed by Lindsay based on thermodynamic equilibrium conditions [18]. The UV-Vis anal-

ysis of compound **1** shows an intense Soret band at 416 nm and four Q-bands at 500–700 nm region characteristic of the porphyrin free base. Compound **1** was sulfonated with concentrated sulfuric acid added at 185 °C to give compound **2** [6,19,21]. Chemical analysis showed four SO_3^- groups per porphyrin ring and ^1H NMR showed 100% of sulfonation in *m*-phenyl ring position. The UV-Vis spectrum of the water soluble compound **2** showed a large Soret band at 412 nm.

Metallation of compound **2** with iron(II) chloride produced compound **3** and the UV-Vis spectrum showed the characteristic reduction of Q-bands number (from 4 to 2) for metallated porphyrin [22–24] and the Soret band blue shifted to 390 nm. The EPR analysis of compound **3** showed an intense signal related to $S = \frac{5}{2}$ Fe(III) high spin in axial symmetry at $g = 6.0$ [25].

It is expected that the halogen-substituted iron(III) porphyrin Fe(TDFSPP) would be a robust and efficient catalyst for oxidation reactions mediated by oxidants like PhIO. The resistance of the porphyrin ring against oxidation degradation can be explained by the introduction of highly electron-withdrawing fluorine substituents in the *ortho* positions of the meso phenyl porphyrin groups that can increase the acceptor character of the porphyrin ring in comparison with the classic tetraphenyl porphyrin (TPP) or other porphyrins with electron donor methyl groups to the meso-phenyl moieties [26,27]. In order to explore the full catalytic potential of the $\text{Na}_4[\text{Fe}(\text{TDFSPP})\text{Cl}]$, the ways to graft it in solid supports are investigated in this study.

3.2. Preparation of compound **5** (kaolinite **4** bound catalyst **3**)

With a view to look for efficient immobilization condition of iron(III) porphyrin **3** to modified kaolinite **4**, first five tests were performed (Table 1). Better results of iron(III) porphyrin immobilization were observed in water than in methanol as reaction solvent (tests 1 and 2, Table 1). The presence of acid increased the percent of immobilization

in water from 52 to 63% (tests 1 and 3). The delaminated kaolinite showed no immobilization capacity in water or methanol, suggesting that the functional groups 3-APTS from compound **4** is necessary to the immobilization process (tests 4 and 5). Since the best results of iron(III) porphyrin immobilization were observed in test 3, compound **5** was synthesized in these conditions.

Compound **5** was thoroughly washed and no removal of iron(III) porphyrin was observed by UV-Vis analysis suggesting that a strong interaction between the iron(III) porphyrin and the silanized kaolinite (compound **4**) had taken place. Possible electrostatic bond could explain the success of the immobilization process since no new covalent bond was expected to be formed by the interaction of the anionic iron(III) porphyrin and the solid matrix. In fact, strong electrostatic bond is possible if one considers that the anionic iron(III) porphyrin is attracted by cationic amine generated by the protonation of the 3-APTS amine groups present in the silanized kaolinite **4** (Fig. 2b). The nature of electrostatic interaction between iron(III) porphyrin and the kaolinite matrix was indirectly confirmed by reaction of compound **5** with the organic base 2-(dimethylamino)pyridine DMAP. The addition of a weak base such as DMAP could remove the iron(III) porphyrin immobilized exclusively by electrostatic interactions. After the reaction at mild conditions, the solid was thoroughly washed and the resulting supernatant analyzed by UV-Vis spectroscopy. The 98% of the iron(III) porphyrin was removed from the matrix confirming that the organic compound substituted the charged iron(III) porphyrin in the charged matrix.

The presence of the Fe(TDFSPP) immobilized on silanized kaolinite (compound **5**) was confirmed by UV-Vis spectra (Fig. 3c in nujol mull). The UV-Vis spectrum results suggested that no demetallation occurred during the preparation process, since the characteristic metalloporphyrin Soret peak was observed for supported porphyrins compound **5** at 412 nm and no characteristic blue shift of

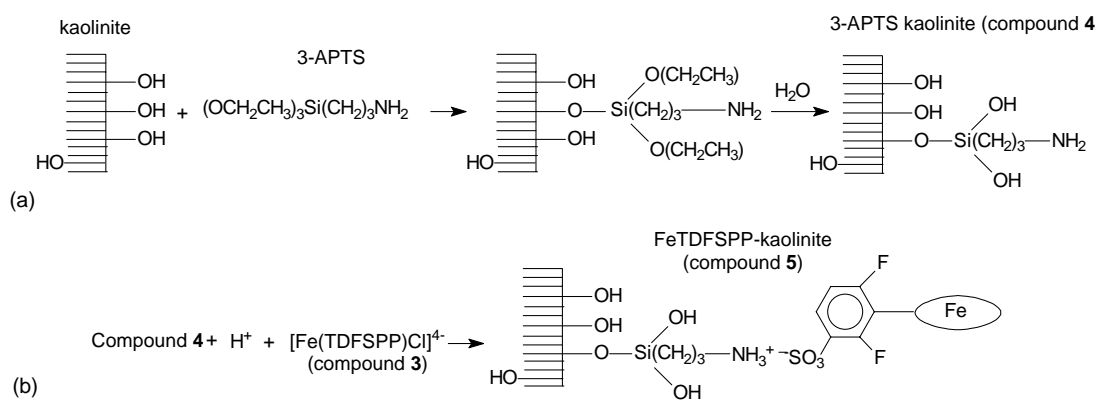


Fig. 2. (a) Synthesis of compound **4** by 3-APTS grafting process in delaminated kaolinite followed by the ethoxy groups hydrolysis (based on CA, CHN and TG–DSC results); (b) schematic representation of the immobilization reaction of the iron porphyrin (compound **3**) in pre-silanized kaolinite (compound **4**) to obtain compound **5**.

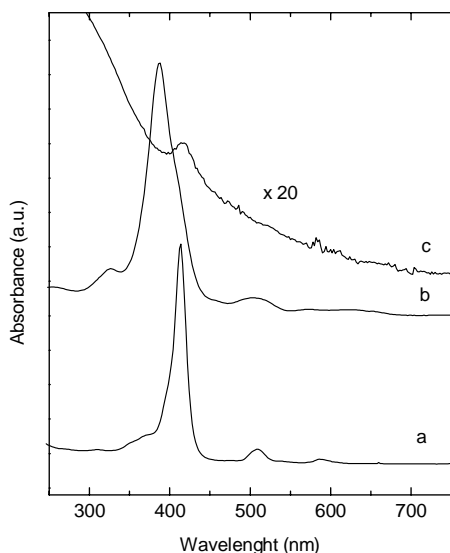


Fig. 3. UV-Vis spectra of: (a) $\text{Na}_4[\text{Fe}(\text{TDFSPP})\text{Cl}]$ (compound **3**); (b) H_2TDFSPP (compound **2**); (c) FeTDFSPP bound to 3-APTS-kaolinite (silanized kaolinite) in nujol mull (compound **5**).

Soret band associated with a significant amount of free base porphyrin (Fig. 3b) was observed [22,24,27,28]. The UV-Vis spectrum for iron(III) porphyrin in solution shows the Soret band in the range of 390 nm (Fig. 3a).

It can be observed from the X-ray diffraction analysis that kaolinite is intercalated with urea where a mixture of kaolinite ($d = 7.2 \text{ \AA}$), urea intercalated kaolinite ($d = 10.8 \text{ \AA}$) and an excess of urea, characterized by a sharp peak at $2\theta = 26^\circ$, Fig. 4a–c. By the intensities of the basal peaks, an interca-

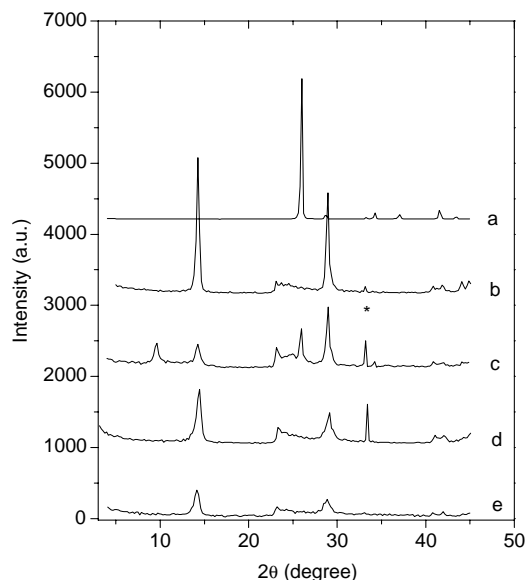


Fig. 4. Powder X-ray diffraction patterns of the entire procedure to delaminate kaolinite, after mechanochemical intercalation of urea: (a) pure urea; (b) raw kaolinite; (c) K-urea; (d) kaolinite after the delamination process and grafting of silane (silanized kaolinite compound **4**); (e) compound **5** (iron porphyrin bound to silanized kaolinite compound **4**); (*) silicon used as internal standard.

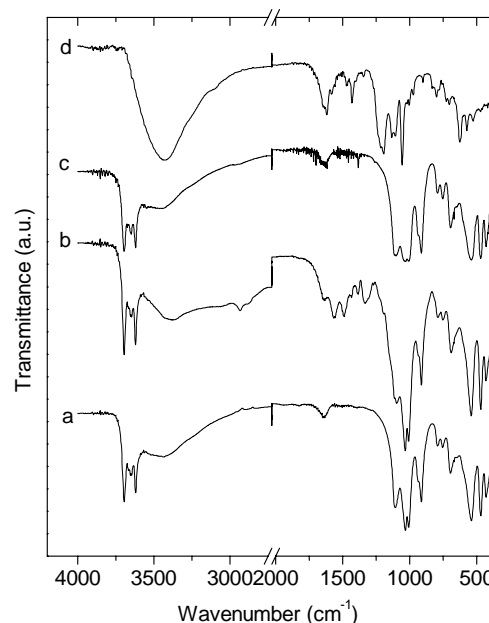


Fig. 5. FTIR spectra of: (a) kaolinite; (b) silanized kaolinite (compound **4**); (c) FeTDFSPP bound to silanized kaolinite (compound **5**); (d) FeTDFSPP (compound **3**).

lation ratio of ca. 50% was obtained [29]. After the intercalation and delamination process (Fig. 4b), the basal peaks of kaolinite became broad and with low intensities, showing that the delamination process was efficient, urea totally being removed by the washing procedure. The crystals were very small with low stacking coherence along the basal direction. After the washing procedure, grafting (Fig. 4d) and immobilization process (Fig. 4e), the same basal spacing was obtained, indicating that the reactions proceeded on the surface of the layered kaolinite crystals. The FTIR spectra of: (a) the raw kaolinite, (b) silanized kaolinite (compound **4**), (c) after reaction with the iron(III) porphyrin (compound **5**) and (d) pure iron(III) porphyrin (compound **3**) are shown in Fig. 5. The interpretation of the FTIR spectra of the raw kaolinite has been reported earlier [30a] with the common band at 1635 cm^{-1} being attributed to adsorbed water OH bending [30b]. After the grafting of the silane, new characteristic bands were observed at 1310, 1333, 1386, 1434, 1492, 1563, 1637, 2870 and 2938 cm^{-1} , which could be attributed to the organic grafted molecules [30b]. In the silanized kaolinite and reaction with the iron(III) porphyrin (**5**) (c) the FTIR spectra resembles that for pure kaolinite. One important characteristic distinction can be made between raw kaolinite, grafted kaolinite (**4**) and grafted kaolinite after the immobilization of the iron(III) porphyrin (**5**) as follows: the bands in 3696 , 3667 and 3650 cm^{-1} , attributed to the surface OH groups have the intensities progressively reduced in comparison to the band at 3621 cm^{-1} , attributed to inner OH groups. This confirms that surface hydroxyl groups are involved in the grafting and immobilization of the porphyrin. The concentration of the porphyrin and the

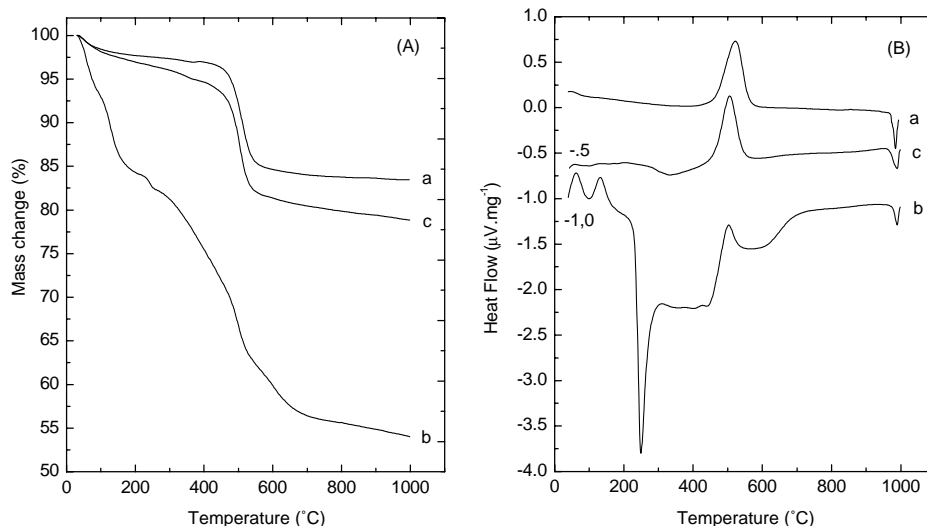


Fig. 6. TG (A) and DSC (B). Measurements of the raw kaolinite (a); kaolinite after the delamination and grafting reaction (compound **4**) (b); after immobilization of the iron porphyrin (compound **5**) (c).

silane is too low to be detected in the FTIR spectra of the grafted and porphyrin immobilized kaolinite (**5**) (Fig. 5c).

Fig. 6 shows the TG (A) and DSC (B) measurements on: (a) the raw kaolinite, (b) kaolinite after the delamination and grafting reaction (compound **4**) and (c) after immobilization of the iron(III) porphyrin (compound **5**).

For raw kaolinite, the 2% mass loss observed at temperatures below 200 °C could be attributed to the loss of moisture. The dehydroxylation of kaolinite was observed at 515 °C and the crystallization of metakaolinite was observed as an exothermic peak centered at 984 °C [31]. This process generated a mass loss of 14.8% (in dry weigh basis) and this was in good agreement with the predicted value of 13.96% [30a] from the theoretical formula of pure kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$).

After the grafting process (Fig. 6b), two endothermic peaks were observed at 62 and 132 °C related to the elimination of adsorbed/absorbed and coordinated water molecules, respectively. An exothermic peak was observed at 249 °C followed by a broad band in the region of 400 °C, both related to the combustion of the organic matter of the sample. The peaks related with the dehydroxylation of the matrix and the crystallization of the oxide as observed earlier for raw kaolinite, were observed at 507 and 987 °C, respectively. A broad band was observed in the region of 550 °C, related to the oxidation of the remaining organic matter of the sample. The mass loss between 200 and 1000 °C was 35.7%, on dry weight basis. The two curves showed clearly that kaolinite was grafted with the silane, as proposed. After the process of the iron(III) porphyrin immobilization (Fig. 6c), the sample resembled the decomposed raw kaolinite. The difference could be characterized by a broad low intensity band centered at 330 °C and a different mass loss of 3% up to 200 °C and 18.7% between 200 and 1000 °C (on dry weight basis). This result suggested that almost all the organic matter (grafted silane) was eliminated and only a small amount of

iron(III) porphyrin remained immobilized as confirmed by quantitative UV-Vis analysis.

The EPR spectra of the kaolinite and compounds **3–5** are shown in Fig. 7. There are five main lines in the spectra at magnetic fields below 2500 G, which are characteristic of kaolinites with g -values of 9.0, 5.0, 4.3, 3.5 and 2.8. Those lines are due to absorptions of the cation Fe(III) in both Fe(I) and Fe(II) sites of kaolinites resulting from spin resonance arising from the three Kramer's doublets, whose energies are separated by crystal fields of rhombic symmetry. Fe(I) and Fe(II) are two inequivalent crystal sites in which Fe(III) can occupy the octahedra in kaolinite [32]. The EPR spectrum of compound **5** shows one signal at $g = 6.0$ characteristic of

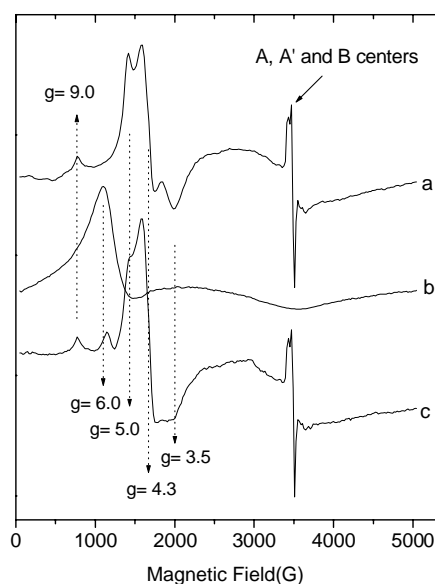


Fig. 7. EPR spectra of: (a) $\text{Na}_4[\text{Fe}(\text{TDFSPP})\text{Cl}]$ bound to 3-APTS-kaolinite (compound **5**); (b) $\text{Na}_4[\text{Fe}(\text{TDFSPP})\text{Cl}]$ (compound **3**); (c) silanized kaolinite (compound **4**).

$\text{Na}_4[\text{Fe}(\text{TDFSPP})\text{Cl}]$, indicating the presence of the iron(III) porphyrin in the catalyst.

3.3. Oxidation reactions

The most common systems for heterogeneous catalysis are based on metalloporphyrins immobilized inside porous materials or in the interlayer space of clays. The oxygen atom donors such as PhIO or organic peroxides have slow diffusion in these supports, hindering the access of these reagents to iron(III) porphyrin sites. Therefore, catalysts immobilized on the surface of inorganic matrix can be the solution to this problem imposed by the support [3].

There is a growing interest in using supported porphyrin as a catalyst: oxygen carriers mimicking biological systems as cytochrome P-450. In general, supports are used to replace the protein cavity of natural enzymes by a size- and shape-selective framework of the mineral matrix, preventing the complexes from undergoing dimerization, self-aggregations through π – π interactions and degradation mainly due to the immobilization opening the opportunity to the reuse of the catalyst [5,8–12,19,20,33].

The catalytic activity of compound **5** was investigated on the oxidation of cyclooctene and in the oxidation of weakly reactive alkanes such as cyclohexane and heptane.

Epoxidation of cyclooctene with PhIO was first studied in order to investigate the efficiency and stability of the iron(III) porphyrin as a catalyst for alkene oxidation and also to have an idea of the accessibility of the iron(III) sites of the supported catalyst towards substrate and oxidant PhIO. Table 2 shows the epoxide yields from the oxidation reaction after one hour. The heterogeneous catalyst compound **5** led to a good yield of cyclooctene epoxide (63%, run 1) when the 1:10 molar ratio of Fepor:PhIO was used. The yield and turnover number were even slightly higher (90%) when the ratio increased to 1:50, 1:100, 1:1000 and 1:10000 (in the same ratio of substrate as shown in runs 2, 3, 9 and 15). These results indicated that the immobilization process did not hinder the access of the reagents to the iron(III) centers to generate the catalytic species. The high resistance of the catalyst is illustrated by the observation that the increase of the oxidant concentration (1:10–1:10000) led to higher yields of epoxide and turnover number for all reactions.

Compound **5** also assisted the catalytic activity in the oxidation reaction of cyclohexane, a more inert substrate (runs 1–5, Table 3). When compared with the oxidation of cyclooctene, the high molar ratio of iron(III) porphyrin:PhIO favored the oxidation reaction and high selectivity was observed in the alcohol than ketone for all conditions studied.

Oxidation of linear alkanes, such as heptane is a much more difficult reaction to take place in a controlled condition at lower temperature. In fact, linear alkanes are very resistant to attack by strong oxidizing agents [34]. The catalyst (compound **5**) has shown moderate efficiency to convert the heptane to the oxidation products (runs 1–5, Table 4). In the best condition of heterogeneous catalyst (run 5, Table 4), the

Table 2
Oxidation of cyclooctene catalyzed by compound **5**/PhIO system

Run ^a	Molar ratio of Fepor:PhIO	Cyclooctene oxide (%)	Turnover number ^b
1	1:10	63	110
2	1:50	92	152
3	1:100	94	153
4	1:1000	93	149
5	1:10000	97	488
Recycling run ^c			
6–10	1:100	99	152
11–15	1:1000	95	200
16–20	1:10000	97	490
21 ^d	1:100	12	21
22	1:1000	21	39
Molar ratio of Fepor:H ₂ O ₂ :Imi			
23 ^e	1:100	16	29
24	1:1000	17	29
25 ^f	1:100:1	28	46
26	1:1000:1	36	54

^a Runs 1–20: heterogeneous reactions performed with compound **5**. Yield based on starting PhIO.

^b Turnover number = moles of product (epoxide) per mole of iron porphyrin.

^c Groups of five recycling reactions performed with the same solid catalyst (compound **5**) in the same molar ratio conditions.

^d Runs 21 and 22: homogeneous reactions performed with compound **3** in dichloromethane/acetonitrile solvent mixture (1:1 v/v).

^e Runs 23 and 26: using H₂O₂ as oxidant instead of PhIO.

^f Runs 25 and 26: addition of 1 equiv. of 1-methylimidazole per equivalent of iron porphyrin.

catalyst presented 48% to total alcohol conversion (alcohol in positions 2 and 3). Instead, good selectivity to the alcohol was observed (ketones yield was inferior to 2%), but negligible products were observed resulting in terminal oxidation (position 1) [34,35]. This tendency of low oxidation yields to catalytic oxidation of linear alkanes agrees with previous reports observed in the literature in manganese(III) porphyrin immobilized in silica and montmorillonite clay [4,7]. However, no oxidation product was observed quantitatively on position 1 of the linear alkene in compound **5** [34,35]; there was a remarkable position selectivity favoring the oxidation in position 2 followed the 3 to heptanols products. These results can be justified by the ease or difficulty posed by the support structure in obtaining active iron(III) porphyrin species through the use of linear substrates.

The iron(III) porphyrin immobilized in kaolinite presented better oxy-functionalization results than the iron(III) porphyrin in solution (homogeneous catalysis, compound **3**, runs 21 and 22, Tables 2–4) indicating that the immobilization favors the catalytic ability of this metalloporphyrin.

As observed in Tables 2–4 (runs 6–20 in different molar ratios), the catalyst's activity can be restored after the first use by simple filtration and washing the immobilized iron(III) porphyrin (compound **5**) with dichloromethane and acetonitrile to reuse again. The results of the catalyst re-using in a new second reaction showed similar or higher

Table 3
Oxidation of cyclohexane catalyzed by compound **5**/PhIO system

Run ^a	Molar ratio of Fepor:PhIO	Cyclohexanol yield (%)	Cyclohexanone yield (%)	Turnover number ^b
1	1:10	33	8	19
2	1:50	47	7	22
3	1:100	74	3	64
4	1:1000	85	3	367
5	1:10000	90	3	504
Recycling run ^c				
6–10	1:100	82	2	69
10–15	1:1000	87	4	372
16–20	1:10000	92	4	510
21 ^d	1:100	23	–	11
22	1:1000	14	–	35
Molar ratio of Fepor:H ₂ O ₂ :Imi				
23 ^e	1:100	24	<1	47
24	1:1000	21	–	52
25 ^f	1:100:1	25	–	50
26	1:1000:1	33	–	60

^a Runs 1–20: heterogeneous reactions performed with compound **5**. Yield based on starting PhIO.

^b Turnover number = moles of product (1 × alcohol + 2 × ketone) per mole of iron porphyrin.

^c Groups of five recycling reactions performed with the same solid catalyst (compound **5**) in the same molar ratio conditions.

^d Runs 21 and 22: homogeneous reactions performed with compound **3** in dichloromethane/acetonitrile solvent mixture (1:1 v/v).

^e Runs 23 and 26: using H₂O₂ as oxidant instead of PhIO.

^f Runs 25 and 26: addition of 1 equiv. of 1-methylimidazole per equivalent of iron porphyrin.

yield than the first reaction for all substrates (cyclooctene, heptane and cyclohexane), suggesting that the first reaction and the recovering process could activate the iron(III) site for the subsequent reactions [3]. This fact can be an indicative of the probable resistance of iron(III) porphyrin to the harsh reaction conditions and that there is strong interac-

tion between the iron(III) porphyrin and the support and it does not release from the surface after the first use. In fact, all reaction solutions analyzed after catalytic reactions did not show the characteristic iron(III) porphyrin Soret band at 390 nm. After the second use, the catalyst was recovered again and reused which showed similar results (runs

Table 4
Oxidation of heptane catalyzed by Fepor-kaol (compound **5**)/PhIO system

Run ^a	Molar ratio of Fepor:oxidant	Alcohol yield (%)	Turnover number ^b	Regioselectivity (%) (carbon position 1)
1	1:10	14	12	0
2	1:50	16	17	0
3	1:100	18	21	2
4	1:1000	41	51	1
5	1:10000	48	65	2
Recycling run ^c				
6–10	1:100	30	40	2
11–15	1:1000	45	62	1
16–20	1:10000	53	75	1
21 ^d	1:100	1	<1	1
22	1:1000	2	4	2
Molar ratio of Fepor:H ₂ O ₂ :Imi				
23 ^e	1:100	3	4	1
24	1:1000	4	6	3
25 ^f	1:100	6	8	2
26	1:1000	14	10	2

^a Runs 1–20: heterogeneous reactions performed with compound **5**. Yield based on starting PhIO.

^b Turnover number = moles of product (1 × total moles of alcohol + 2 × total moles of ketones) per mole of iron porphyrin.

^c Groups of five recycling reactions performed with the same solid catalyst (compound **5**) in the same molar ratio conditions.

^d Runs 21 and 22: homogeneous reactions performed with compound **3** in dichloromethane/acetonitrile solvent mixture (1:1 v/v).

^e Runs 23 and 26: using H₂O₂ as oxidant instead of PhIO.

^f Runs 25 and 26: addition of 1 equiv. of 1-methylimidazole per equivalent of catalyst.

7, 12 and 17 from Tables 2–4). This fact was also observed in three more subsequent reactions (runs 8–10, 13–15 and 18–20 from Tables 2–4).

It is noteworthy that reactions using silanized kaolinite support (**4**) themselves (without iron(III) porphyrin) were the oxidation reaction of all the substrates and gave very low oxidation yields (under 2%) under identical conditions, indicating that the catalytic effect in the oxidation of the substrates could be attributed to the presence of the immobilized iron(III) porphyrin.

The low solubility of $\text{Na}_4[\text{Fe}(\text{TDFSPP})\text{Cl}]$ in CH_2Cl_2 or in $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{CN}$ (1:1 ratio) solvent mixture in homogeneous catalysis (runs 21 and 22 in Tables 2–4) could be one of the reasons for the low yields obtained on homogeneous catalysis. The dimerization of the iron(III) porphyrin in solution could be another one because it is accompanied by μ -oxo complex formation [36]. Dimeric iron(III) porphyrins are frequently associated to low catalytic activity of porphyrin in homogeneous catalysis [27,28]. In fact, the structure of compound **3** does not have bulk groups that can avoid dimerization process in the porphyrin solution [27].

The catalyst oxidative degradation in solution is frequently responsible for the low yield in catalytic reaction using metalloporphyrins [5b]. In reaction using $\text{Na}_4[\text{Fe}(\text{TDFSPP})\text{Cl}]$, no significant catalyst Soret band decay was quantitatively detected on the homogeneous oxidation reaction solution by UV-Vis analysis.

Attempts were made to use H_2O_2 with compound **5** but the products were obtained lower than PhIO results (run 23 and 24, Tables 2–4). This phenomenon could probably be caused by a dismutation of the H_2O_2 or another secondary reac-

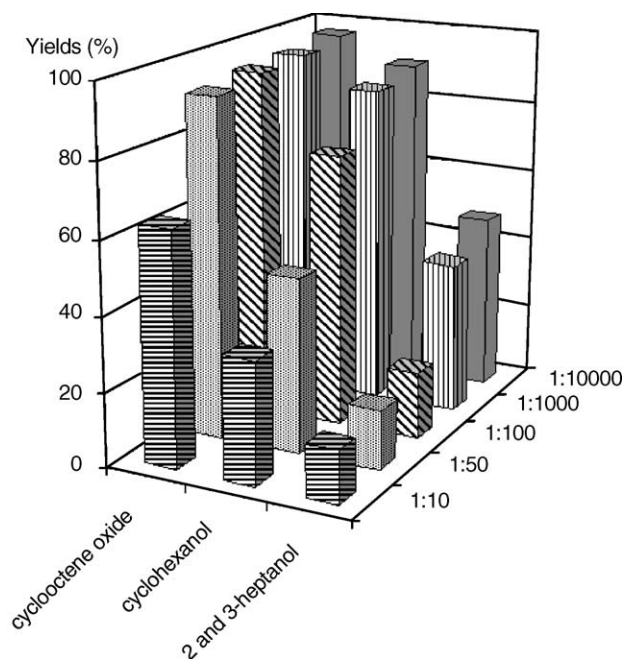


Fig. 8. Schematic representation of catalytic selectivity results of compound **5**. PhIO: iodossylbenzene; Imi: 1-methylimidazole; H_2O_2 : hydrogen peroxide.

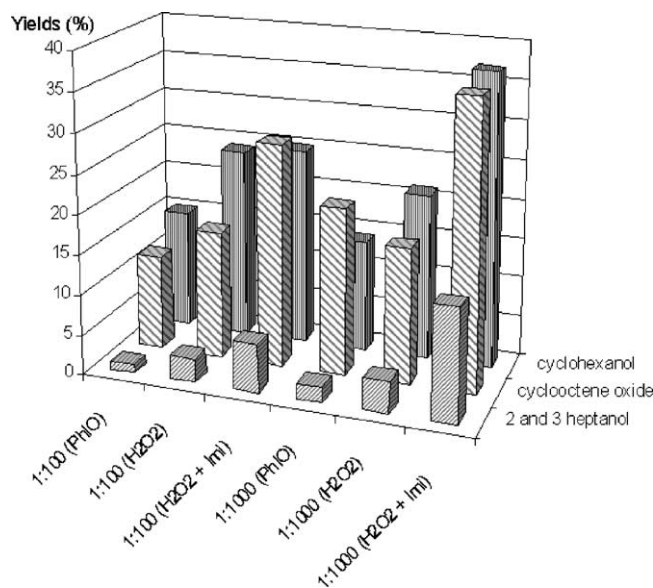


Fig. 9. Schematic representation of catalytic selectivity results of $\text{Na}_4[\text{Fe}(\text{TDFSPP})\text{Cl}]$ (compound **3**) in homogeneous reactions. PhIO: iodossylbenzene; Im: 1-methylimidazole; H_2O_2 : hydrogen peroxide.

tion in the presence of iron or other trace quantities of metal present in the supports [7]. The well-known catalase-like reaction in which the catalytically active species formed by the reaction of iron(III) porphyrin and iodossylbenzene could be involved in the transformation of hydrogen peroxide in molecular oxygen and water by the described O–O homolysis, resulting in lower yields of products [27]. This problem was partially solved with the addition of 1-methylimidazole to the porphyrin solution (runs 25 and 26, Tables 2–4). The nitrogen atom of 1-methylimidazole was able to coordinate an axial position of iron(III) center, mimicking the histidine amino acid residue axially bound in cytochrome P-450 porphyrin site. This axial coordination made the redox cycling of the iron(III) porphyrin more favorable [37,38].

In summary, the catalytic ability of the immobilized iron(III) porphyrin (compound **5**) and the iron(III) porphyrin $\text{Na}_4[\text{Fe}(\text{TDFSPP})\text{Cl}]$ (compound **3**) could be compared as observed in Figs. 8 and 9. The immobilization process seemed to favor the catalytic ability of this metalloporphyrin probably because the immobilized catalyst had lower susceptibility to inactivation by molecular interaction process than the metalloporphyrin in solution.

4. Conclusions

The functionalization of kaolinite showed a suitable hybrid organic–inorganic matrix for $\text{Fe}(\text{TDFSPP})$ immobilization by electrostatic interactions. Grafting the catalyst on the surface of kaolinite allowed the easy access of substrates and simple removal of products after short time reactions (1 h). The present catalytic system is stable, safe to operate and can be recovered several times with negligible catalyst deactivation or leaching from the support.

The iron(III) porphyrin is a very versatile and robust catalyst for alkene epoxidation and alkanes hydroxylation using PhIO. The Fe(TDFSPP) bound to kaolinite promotes a great conversion of products in high and fast turnover numbers. The use of three different substrates is possible to get an interesting view of efficiency and selectivity of compound **5**. The comparative homogeneous reactions performed with H₂O₂ supplies low yields of products stimulated probably by hydrogen peroxide dismutation. The use of 1-methylimidazole increases the product yields showing an alternative way to improve catalytic results.

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