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Anionic iron(III) porphyrins immobilized on zinc hydroxide chloride as catalysts for heterogeneous oxidation reactions

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ABSTRACT

This work describes the immobilization of an anionic iron(III) porphyrin (FePor) family on zinc hydroxide chloride (ZHC), a layered hydroxide salt prepared by reacting an aqueous zinc chloride solution with an ammonium hydroxide solution. The FePor immobilization was performed at room temperature under magnetic stirring, under air atmosphere, of each complex ethanol solution and the ZHC solid support suspension. The materials obtained were characterized by X-ray powder diffraction (XRPD), ultraviolet-visible spectroscopy (UV-vis) (solid samples), Fourier transform infrared spectroscopy (FTIR) and electron paramagnetic resonance (EPR). The catalytic activity of the solids was investigated in cyclooctene, cyclohexane and *n*-heptane heterogeneous catalytic oxidation reactions with iodosylbenzene as the oxygen donor. The solid catalyst's reutilization capacity was also investigated and the heterogeneous character of the catalytic process was confirmed. The compounds and the catalytic activity of FePor-ZHC were compared with the synthesis and catalytic activity of the solution were exactly the opposite when the selectivity was analyzed.

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1. Introduction

Inspired by biological systems that have catalytic activity, many different compounds have been synthesized and investigated as oxidation catalysts [1–3]. In this context, synthetic metalloporphyrins are investigated as mimics of cytochrome P-450 [2]. In live organisms the cytochrome P-450 performs oxidation reactions with high selectivity and efficiency [1]. Many different investigations involving metalloporphyrin catalytic activity have been performed, initially in homogeneous media (catalyst and substrate in the same solvent phase) [4–6]. Under these conditions, deactivation of the catalysts has been detected, for example, by dimerization or by destructive auto-oxidation. In the former process, two porphyrin-ring metal μ -oxo bridges are established and in the latter, active catalytic species approach other porphyrin molecule, deactivating both [7]. One of the most significant contributions to obtain efficient, selective and reusable catalysts using metalloporphyrins, seeking possible technological application, was the immobilization of porphyrinic compounds on solids such as clay minerals [7,8], silica [9], and other inorganic-supports [10].

The strategy to obtain and use a solid catalyst for heterogeneous catalysis, where the catalytic species are immobilized, can hinder undesirable approximations between activated and non-activated catalytic species (this species can lead to a deactivating process caused by secondary reactions between porphyrinic rings [7]) and also can create materials that can be reused in several reaction cycles.

In this context, the present work reports the study of a family of anionic iron(III) porphyrins (FePor) (Fig. 1), which were immobilized on zinc hydroxide chloride (ZHC), a non-exchangeable layered hydroxide salt [11]. Layered hydroxide salts have been studied for a great number of applications [11-13], such as intercalation reactions [14,15], catalyst support [12], oxide precursors [16,17], and others [11]. This class of compounds consists of modified brucitelike layers [12], where the Mg²⁺ metallic center, surrounded by hydroxyl groups, is replaced by another M²⁺ metallic center, such as Zn²⁺, Co²⁺ or Cu²⁺ [12,13]. Partial substitution of hydroxyl groups by other anions or water molecules creates a positive charge at the layers, which needs to be compensated by the presence of interlayer anions. In the case of nitrate anions, the compound is an anionic exchanger and in the case of chloride, as these anions are grafted directly to the layers, the compound is neutral [11]. Specifically, zinc hydroxide chloride (ZHC) is represented by the formula Zn₅(OH)₈Cl₂·H₂O [17,18] and the basic structural unit contains a vacancy in a quarter of the octahedral zinc sites coordinated to

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Fig. 1. Structure of the iron porphyrins employed in this study: [Fe(TDFSPP)Na₄]⁺ = [tetrasodium – 5, 10, 15, 20 – tetrakis (2,6-difluoro-3-sulfonatophenyl) porphyrinate iron(III)], [Fe(TCFSPP)Na₄]⁺ = [tetrasodium – 5, 10, 15, 20 – tetrakis (2-chloro-6-fluoro-3-sulfonatophenyl) porphyrinate iron(III)], and [Fe(TDCSPP)Na₄]⁺ = [tetrasodium – 5, 10, 15, 20 – tetrakis (2,6-dichloro-3-sulfonatophenyl) porphyrinate iron(III)], and [Fe(TDCSPP)Na₄]⁺ = [tetrasodium – 5, 10, 15, 20 – tetrakis (2,6-dichloro-3-sulfonatophenyl) porphyrinate iron(III)].

hydroxyl groups, while the upper and lower sides of this vacancy contain tetrahedral zinc sites, originating a positive layer charge [11]. In the tetrahedral zinc site, three vertices are occupied by hydroxyl groups from the octahedral sheet, and in the fourth position the metal is coordinated to chloride ions, building a neutral layered structure. In the ZHC structure, water molecules are also present between the layers [18], generating a solid with basal distance of approximately 7.8 Å (JCPDS card: 07-0155) [17].

The solids obtained after the FePor immobilization on ZHC were investigated as oxidation catalysts for cyclooctene, cyclohexane and *n*-heptane using iodosylbenzene as the oxygen donor.

2. Experimental

2.1. Reagents

All chemicals used in this study were purchased from Aldrich, Sigma, or Merck, and were of analytical grade. Iodosylbenzene (PhIO) was synthesized by hydrolysis of iodosylbenzenediacetate [19]. The solid was carefully dried under reduced pressure and kept at 5 $^{\circ}$ C; its purity was periodically controlled by iodometric titration [20].

2.2. Porphyrins and metalloporphyrins

The anionic free base porphyrins $Na_4[H_2(TDFSPP)]$, $Na_4[H_2(TCFSPP)]$, and $Na_4[H_2(TDCSPP)]$ and their corresponding iron(III) complexes ([Fe(TDFSPP)Na_4]⁺ = [tetrasodium – 5, 10, 15, 20 – tetrakis (2,6-difluoro-3-sulfonatophenyl) porphyrinate iron(III)]; ([Fe(TCFSPP)Na_4]⁺ = [tetrasodium – 5, 10, 15, 20 – tetrakis (2-chloro-6-fluoro-3-sulfonatophenyl) porphyrinate iron(III)] and ([Fe(TDCSPP)Na_4]⁺ = [tetrasodium – 5, 10, 15, 20 – tetrakis (2,6-dichloro-3-sulfonatophenyl) porphyrinate iron(III)] were synthesized, purified, and characterized following a previously described method [21,22]. For the sake of simplification,

these three FePor will be represented in this work by [Fe(TDFSPP)] – FeDF, [Fe(TCFSPP)] – FeCF, and [Fe(TDCSPP)] – FeDC, respectively, so hereafter no mention of the FePor porphyrin charges will be made, to avoid repetition. The Soret bands of the FePors obtained after the metal insertion reaction were the following: FeDF (ethanol) 390 nm ($\varepsilon = 28 \times 10^3 \text{ Lmol}^{-1} \text{ cm}^{-1}$), FeCF (ethanol) 412 nm ($\varepsilon = 73 \times 10^3 \text{ Lmol}^{-1} \text{ cm}^{-1}$), and FeDC (ethanol) 390 nm ($\varepsilon = 74 \times 10^3 \text{ Lmol}^{-1} \text{ cm}^{-1}$).

2.3. Preparation of the solid FePor-ZHC catalysts

A ZnCl₂ solution prepared in distilled water $(0.73 \text{ mol L}^{-1})$ was kept under magnetic stirring and heated to approximately 50–60 °C. Drops of ammonia aqueous solution (28%) were added to the solution and immediately a white cloudy solid precipitate was observed. The total volume addition of 3 mL of NH₄OH drop by drop occurred in the time of 1 h. During the base addition, the pH was verified each 5 min to keep it constant at 7 in order to avoid precipitation of other insoluble zinc hydroxides [12]. The suspension containing the solid ZHC was centrifuged and the supernatant separated. The solid was washed 5 times with distilled water and dried in an oven at 50 °C for 48 h. The reaction's final yield was 38% in relation to the initial amount of zinc.

Although ZHC has a generally neutral structure, the anionic iron porphyrins [Fe(TDFSPP)], [Fe(TCFSPP)] and [Fe(TDCSPP)] were chosen for immobilization on it because they can interact easily with the residual positive charges at the layered crystal edges of the support. The other reason for choosing the anionic complexes is for behavior comparison purposes, since these same FePor were already immobilized on the anionic exchanger zinc hydroxide nitrate (ZHN) [12].

The system used for immobilization consisted of magnetic stirring at room temperature in ethanol solution. This technique does not lead to the collapse of the hydroxide salt structure, as happens when magnetic stirring and reflux conditions were used [12]. For the reaction, 10 mg of each FePor was dissolved in 50 mL of ethanol and kept under magnetic stirring. Then 500 mg of ZHC was added to the solution and the mixture was stirred for 5 h. In the sequence, the suspensions were centrifuged and the supernatant placed in volumetric flasks for posterior analysis by UV–vis spectroscopy. Each solid was washed with a minimum of 5 portions of ethanol, and the used ethanol was also added to volumetric flasks for metalloporphyrin quantification. The solids obtained were dried under air for 48 h.

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

2.4. Heterogeneous catalytic oxidation of cyclooctene, cyclohexane, and n-heptane by PhIO using FePor-ZHC solid as catalyst

The solids obtained by immobilization of the anionic FePor onto the synthetic ZHC matrix were used as catalysts in the oxidation reactions. These reactions were carried out in a thermostatic glass vessel (2 mL) equipped with a magnetic stirrer bar [7,8,23]. The catalyst (20 mg) and PhIO (0.5 mg) were suspended in solvent (0.300 mL of acetonitrile), and the substrate (cyclooctene, cyclohexane or *n*-heptane) was then added to the reaction mixture, resulting in a constant compound/oxidant/substrate molar ratio of 1:20:2000. The oxidation reaction was allowed to proceed for 1 h, under magnetic stirring. Sodium sulfite was added to the reaction mixture to eliminate excess PhIO and to quench the reaction after the experimental time was over. The reaction products were separated from the FePor-ZHC catalyst by centrifugation and transferred to a volumetric flask. Next, the FePor-ZHC solid employed in the reaction was washed several times with methanol and acetonitrile, in order to extract any reaction product that might have been retained in the catalyst. The solution containing the final reaction products and the solvents from the washings of the FePor-ZHC was analyzed by gas chromatography. Product yields were quantified on the basis of PhIO, and high-purity *n*-octanol (99.9%) (acetonitrile solution, 1.0×10^{-2} mol L⁻¹) was employed as internal standard. Control reactions were carried out using the same procedure in the case of (a) the substrate, (b) substrate + PhIO, and (c) substrate + PhIO + ZHC (without FePor).

The corresponding FePor in homogeneous solution were also investigated as catalysts (homogeneous catalysis) using similar reagent molar ratio. The experimental procedure in this case was similar to that used for the heterogeneous catalysis.

Catalyst reuse tests were also performed for all solids with all substrates. At the end of each reaction, the catalytic solid was separated and extensively washed with water, methanol and acetonitrile in sequence. All the solvents used in the washing procedure were analyzed by UV–vis spectroscopy to detect possible lixiviation of the catalyst from the support.

2.5. Characterization of the FePor-ZHC catalysts

For the X-ray powder diffraction (XRPD) measurements, selforiented films were placed on neutral glass sample holders. XRPD patterns were obtained in reflection mode using a Shimadzu XRD-6000 diffractometer operating at 40 kV, 40 mA, using CuK α radiation (λ = 1.5418 Å) and a dwell time of 2°/min.

FTIR spectra were recorded with a Bomem MB spectrophotometer in the range of $400-4000 \text{ cm}^{-1}$, 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.

Ultraviolet-visible (UV-vis) spectra were registered in the 200–800 nm range with a Varian Cary 100 Bio Spectrophotometer. Analyses were accomplished with a 1 cm path length cell or with a Teflon[®] support for solid samples.

Table 1

Degree of FePor immobilization onto the ZHC support.

| FePor | Supported | Immobilization | Loading ^b |
|--------------|-----------|-------------------------|--------------------------------------------------------------------------------------------|
| | FePor | degree ^a (%) | (mol g ⁻¹) |
| [Fe(TDFSPP)] | FeDF-ZHC | 23 | $\begin{array}{c} 5.1\times 10^{-6} \\ 5.3\times 10^{-6} \\ 4.3\times 10^{-6} \end{array}$ |
| [Fe(TCFSPP)] | FeCF-ZHC | 35 | |
| [Fe(TDCSPP)] | FeDC-ZHC | 30 | |

 $^{\rm a}$ Amount of FePor (%) immobilized to the ZHN relative to the initial amount of FePor used in the immobilization process.

^b FePor-ZHC (mol g⁻¹).

Electron paramagnetic resonance (EPR) measurements were performed with a Bruker ESP 300E spectrometer operating in the X-band (approximately 9.5 GHz), at 298 or -196 °C, using liquid N₂.

All the products from the catalytic oxidation reactions were identified using an Agilent 6850 gas chromatograph (flame ionization detector) equipped with a 30 m long DB-WAX capillary column with 0.25 mm internal diameter (J&W Scientific). The oven temperature program used for determination of the oxidation products from cyclooctene and cyclohexane started at 100 °C. Then the temperature was increased to 150 °C at 10 °C min⁻¹, followed by further temperature rise to 200 °C at 50 °C min⁻¹, which was maintained for 1 min. For determination of the products originated from *n*-heptane, the temperature program started at 70 °C, followed by a temperature elevation to 100 °C at 5 °C min⁻¹, maintained for 1 min, and a further temperature increase to 200 °C at 20 °C min⁻¹, kept for 1 min.

3. Results and discussion

3.1. Characterization of FePor-ZHC catalysts

The immobilization process of FePor on the ZHC support occurs probably by electrostatic interaction between the anionic FePor and the positively charged surface edges of ZHC. In comparison to ZHN, the grafted chloride ion in the solid cannot be exchanged as can the nitrate, so the immobilization rates on ZHC are lower, even when the same FePor is immobilized and similar conditions are used.

The degree of FePor immobilization on the support ZHC, determined by UV–vis spectroscopy analysis, and the codes for the synthesized solid catalysts are presented in Table 1.

On the ZHN support, the immobilization degrees were almost 100% [12]. This observation indicates differences between the two matrixes (ZHN and ZHC). Although they have similar structures, they generated distinct immobilization degrees and a possible hypothesis for the immobilization of the porphyrinic complexes in ZHC is shown in Fig. 2.

The basal distance of the layered solid ZHC is approximately 7.8 Å [17] and the sulphonate metalloporphyrin medium size is close to 15 Å [24]. As chloride is covalently bonded to the layer [11], an exchange reaction between this anion and the FePor was not expected, not even at the surface of the layer's crystals. In the present case, the possible location of the porphyrin anions is on the residual positive charges at the layered crystal edges, which can explain the lower immobilization degrees. In the proposed model, only the interaction by two sulphonate groups is proposed since the interaction with the four negative charges would generate an unstable conformation of the porphyrin ring [12]. The outer sulphonate groups are probably compensated by Na⁺/NH₄⁺ or even H⁺.

Fig. 3 shows the XRPD analysis for the synthesized solids. Fig. 3a presents the characteristic pattern of a ZHC solid [17] with a basal distance of 7.78 Å, very close to the reported value of 7.8 Å [11]. Fig. 3b–d shows, respectively, the XRPD patterns of FeDF-ZHC, FeCF-ZHC and FeDC-ZHC. It can be observed that the XRPD patterns are virtually the same and no shift of basal peaks was detected,



Fig. 2. Schematic representation of the FePor immobilized on the solid support ZHC.

suggesting the absence of any porphyrin intercalation between the ZHC layers [12,14]. This finding reinforces the hypothesis of anionic FePor immobilization on the support layered crystal edges. The change of the basal peak's intensity and the overall improvement of the ZHC crystal quality can be explained by the crystal's ripening due to their extensive contact with the solvent during the immobilization process [8].

Fig. 4 depicts the FTIR analysis for the synthesized solids. Fig. 4a shows the pure ZHC spectra, with a characteristic view for these compounds [18,25], the broad band in 3400–3600 cm⁻¹ is attributed to vibration of water molecules [11] and the defined peaks at 3500 and 3454 cm⁻¹ refer to the stretching of the O–H groups from the layer [25]. The band at 1622 cm⁻¹ occurs due to interlayer water angular vibration [12]. The band group at 1045, 906 and 725 cm⁻¹ refers to O–H group deformation [25] and the bands at 576, 532 and 466 cm⁻¹ are attributed to the vibrational modes of Zn–O [12]. A Zn–Cl bound vibration could not be detected, since these vibrations are observed only below 400 cm⁻¹ [18]. Bands at 3200, 1394 and 1250 cm⁻¹ are due to NH₄Cl [26], as this compound



Fig. 3. XRPD patterns of the synthesized ZHC (a), FeDF-ZHC (b), FeCF-ZHC (c) and FeDC-ZHC.

is obtained as a by-product of the ZHC synthesis and was not completely removed by washing.

Fig. 4b–d shows, respectively, the FTIR analysis for the immobilized solids FeDF-ZHC, FeCF-ZHC and FeDC-ZHC. Very small differences between these analyses in comparison to pure ZHC were observed, although these differences are linked to the disappearance or decrease in intensity of bands related to NH_4CI . This can occur as a result of the immobilization process and new material washing procedures. The band groups relative to ZHC are practically the same in the immobilized solids.

For comparison, Fig. 4e presents the analysis for pure [Fe(TDCSPP)], with a characteristic sulphonate porphyrin spectrum, with the band related to the SO₃ group at 1100 cm^{-1} and the aromatic C=C at 1600 cm^{-1} [27]. The analyses for [Fe(TDFSPP)] and [Fe(TCFSPP)] (data not show) are very similar to that reported in Fig. 4e. The bands attributed to FePor were not observed in the immobilized solids, due to the high intensity of support bands and the low amount of porphyrinic complex immobilized [8,23]. Finally,



Fig. 4. FTIR spectra of ZHC (a), FeDF-ZHC (b), FeCF-ZHC (c) and FeDC-ZHC (d) and [Fe(TDCSPP)] (e).



Fig. 5. Solid UV-vis spectra of ZHC (a), FeDF-ZHC (b), FeCF-ZHC (c) and FeDC-ZHC (d).

for the supported solids, a tiny band appears at 1510 cm⁻¹, mainly in FeCF-ZHC and FeDC-ZHC, attributed to carbonate ions adsorbed during the immobilization process, due to the solution's contact with atmospheric carbon dioxide [11].

In order to demonstrate the presence of FePor on the support ZHC, the solids FeDF-ZHC, FeCF-ZHC and FeDC-ZHC were analyzed by UV–vis spectroscopy (Fig. 5b, c and e, respectively). Soret bands were observed at 416, 416 and 434 nm for FeDF-ZHC, FeCF-ZHC and FeDC-ZHC, respectively, and Q bands were observed in the region of 500–600 nm, for each metalloporphyrin.

The Soret band of the immobilized porphyrins, when compared to FePor in ethanol solution, is shifted to the lower spectral energy region [23]. Similar behavior has been reported in other works involving metalloporphyrin immobilization [8,12] and is attributed to interaction between the porphyrinic complex and the solid surface, creating steric limitations to the immobilized metalloporphyrin [28], generating the dislocation to red spectral region [12,29].

Fig. 5a shows the UV-vis spectroscopic analysis of the pure ZHC matrix, where the absence of any band attests that the bands present in the other analyses are due to the immobilized FePor.

EPR analysis was used for solid characterization and also to show the presence of FePor in the ZHC matrix. Fig. 6a shows the analysis for pure ZHC, where an intense signal is observed at g = 1.95, attributed to possible oxygen atoms vacancies in the crystalline solid structure. This behavior is common in zinc oxide [30,31]. For ZHC, some tiny signals near 2800-3300 G region are also present. Signals in that region are observed in materials submitted to electron irradiated ZnO and are assigned to zinc atoms vacancies in the structure [31]. In the case of zinc layered hydroxide salts, according to our knowledge no article describes EPR analysis of pure ZHC, and we suppose that during the solid synthesis, defects are formed in the lattice structure, originating as oxygen atoms so zinc atoms vacancies. In the analysis of ZHN [12], although a radical signal was not detected, signals with minor intensity were also observed, showing this is a typical behavior for the class of zinc hydroxide salt compounds.

The EPR spectra for FePor immobilized solids (Fig. 6b–d, respectively, FeDF-ZHC, FeCF-ZHC and FeDC-ZHC) showed characteristic signals for Fe(III) (S=5/2) high spin in axial symmetry at g=5.8[22,32] and in rhombic symmetry at g=4.3 [12], confirming again the presence of FePor in the synthesized solids. Fig. 6e–g shows, respectively, the EPR analysis of pure [Fe(TDFSPP)], [Fe(TCFSPP)] and [Fe(TDCSPP)], where signals of high spin Fe(III) in axial



Fig. 6. EPR spectra of ZHC (a), FeDF-ZHC (b), FeCF-ZHC (c) and FeDC-ZHC (d), [Fe(TDFSPP)] (e), [Fe(TCFSPP)] (f) and [Fe(TDCSPP)] (g).

symmetry at $g_{\perp} = 5.8$ and at $g_{||} = 2.0$ are observed. This is a common behavior for metalloporphyrin in solid state [22,32], as is also a signal with smaller intensity at g = 4.3. In comparison, the relative signal intensities for Fe(III) in axial and rhombic symmetries have small change after the immobilization process. The immobilization process normally increases the rhombic character of porphyrinic complexes [23,33], consequently increasing the signal intensity at g = 4.3. When the immobilization occurs of a relative uniform and flat surface, as observed for layered double hydroxide [26], the FePor is submitted to a small distortion, but when the immobilization surface is corrugated, as in ZHN [12], the FePor rhombic distortion increases considerably.

The EPR analysis provides more evidence that the metalloporphyrin's immobilization occurred on the edges of the ZHC layers. The distortion in their structure is small, the opposite of what would occur if the immobilization took place at surface tetrahedra [12]. Finally, for the immobilized solids, the free radical present in initial ZHC has smaller intensity, due probably to the increase of crystallinity by the ripening process.

3.2. Investigation of FePor-ZHC solids as catalysts in heterogeneous catalytic oxidation reactions

The first substrate used to investigate the oxidation catalytic activity of the synthesized solids was cyclooctene, a substrate commonly employed for catalytic activity diagnosis [8,23] and frequently cited in the literature [2,24,34,35], in homogeneous and heterogeneous catalysis. In reactions where metalloporphyrins are employed as catalysts for this substrate, only cyclooctenoxide is obtained as a final product. This behavior is attributed to the high stability of intermediate radicals formed during the oxidation reaction [5], where the probably active catalytic species ferryl porphyrin π -cation radical Fe^{IV}(O)P^{•+} shows high reactivity for the double bond of cyclic alkenes, normally generating high catalytic results [4,6,8].

The results obtained for cyclooctene oxidation catalysis with the solids obtained by immobilization of FePor on ZHC can be seem in Table 2. Yields greater than 90% for cyclooctenoxide production were observed when the catalysts containing the supported porphyrinic complexes (Runs 1, 3 and 5) were used; these results are in agreement to other catalysts based on metalloporphyrins [9]. For all synthesized solids, improved reaction yields were observed when compared with homogeneous catalysis (Runs 7–9). This observation can be attributed to different factors, e.g. absence of catalytic

Table 2

Cyclooctenoxide yields achieved in the oxidation of cyclooctene by PhIO catalyzed by FePor and FePor-ZHC. $^{\rm a}$

| Catalyst | Run | Cyclooctenoxide ^b yield (%) |
|-------------------------------|-----|----------------------------------------|
| FeDF-ZHC | 1 | 98 |
| 1st reuse | 2 | 92 |
| FeCF-ZHC | 3 | 91 |
| 1st reuse | 4 | 87 |
| FeDC-ZHC | 5 | 95 |
| 1st reuse | 6 | 93 |
| [Fe(TDFSPP)] | 7 | 85 |
| [Fe(TCFSPP)] | 8 | 70 |
| [Fe(TDCSPP)] | 9 | 78 |
| PhIO only, no catalyst | 10 | 10 |
| ZHC without immobilized FePor | 11 | 11 |

^a Reaction conditions: reactant molar ratio 1:20:2000 (FePor/PhIO/substrate), at room temperature under argon and 1 h of reaction. Homogeneous catalysis were performed under similar conditions to those employed for heterogeneous catalysis (similar reagent molar ratio), using iron porphyrin 1 mg, PhIO 3 mg and about 200 μL of substrate.

^b Yield based on starting PhIO.

solubility factors [7,26] and more catalytic resistance to oxidative degradation.

Another great advantage of heterogeneous systems is avoidance of undesirable approximations between active catalytic species that hinder the product's formation [3,36] and also the possibility of catalyst reuse [7,12,35].

The capacity to reuse the catalyst solids was also investigated in heterogeneous reactions (Runs 2, 4 and 6), where low losses of catalytic activity for the three solids were observed. During the first use of the catalyst, slight leaching of immobilized FePor was observed by UV-vis monitoring of the reaction solution, where approximately 10% of the immobilized complex was lost, contributing to the decrease of the catalytic yield. In the reuse reactions, progressive leaching of the metalloporphyrin from ZHC was not observed. This fact suggests that around 10% of FePor, which left the solid support after the catalyst's first use, was weakly bonded to the ZHC solid. Indeed, in the second and third reuse reactions for FeDF-ZHC, similar catalytic yields of cyclooctenoxide to the first reuse were obtained (data not inserted in Table 2), confirming the stability of the catalyst on the support after the first use. The control reactions, using only iodosylbenzene (Run 10) and pure ZHC (Run 11) showed very low catalytic yields, confirming that the observed catalytic activity can be attributed to the immobilized FePor.

The synthesized solid was also investigated as a catalyst in the oxidation of cyclohexane, a cyclic saturated hydrocarbon. This class of compounds showed less reactive oxidation reactions than the unsaturated substrates, such as cyclooctene [7,24,37]. Cyclohexane is often used by research groups to investigate oxidation reactions [4,12,24,35,37,38]. This substrate is also suitable to investigate the selectivity of the obtained catalysts for a determined product. In the case of cyclohexane oxidation, cyclohexanol and cyclohexanone are obtained as products [7]. Another advantage of using cyclohexane as a substrate for oxidation reaction investigation is the industrial importance of this compound as a precursor for producing many polymers [39].

Table 3 shows the results obtained for cyclohexane oxidation with the prepared catalysts. The catalysts employed in heterogeneous catalysis (Runs 12, 14 and 16) presented very close results for the three immobilized FePor. These results were slightly better than those of homogenous catalysis with the same FePor (Runs 18–20) in relation to the total yield (the final result was very close to homogeneous catalysis only for [Fe(TDFSPP)]), although the selectivity for cyclohexanol production increased considerably for all the catalysts synthesized. These cyclohexane oxidation yield results are lower than the other systems where the same metalloporphyrins are immobilized [7,26]. For example, when the [Fe(TDFSPP)] was

immobilized on synthetic tubular kaolinite [7] 28% of cyclohexanol was obtained and when it was immobilized on a synthetic aluminosilicate [26], 25% of cyclohexanol was produced. Instead of it, in the case of ZHC support, despite of the yield results, it shows an advantage in comparison to the other supports, it is a support with a easiest synthesized route and easier manipulation until the obtation of the solid catalyst with FePor. By contrast, when compared to the same FePor immobilized on a layered double hydroxide [12], only 8% of cyclohexanol is obtained, showing that the catalyst reported in the present work have a better performance.

In general, when FePors are used as oxidation catalysts for cyclohexane, in both homogeneous and heterogeneous reactions, selectivity for cyclohexanol production has been observed [4,7,9,26,36]. This is particularly clear for the catalysts obtained in FePor immobilization on the ZHC support. This behavior can be attributed to the place where FePor immobilization occurs, since FePor interact with the layered crystal edges on a relative uniform surface, presenting low distortion in the porphyrinic ring, as observed by EPR. When the same FePor were immobilized on ZHN support [12], an unusual selectivity for cyclohexanone was observed, where the FePor probably interact with the corrugated surface tetrahedra of the layered crystals, generating an increase in the rhombic character of the immobilized FePor, modifying the catalytic reaction mechanism [12].

In catalytic studies of the reaction of intermediate species, it has been noted that the active catalytic species of oxidation reactions using FePor is the mentioned ferryl porphyrin π -cation radical Fe^{IV}(O)P^{•+} [1–6,12]. Fig. 7 illustrates the reaction mechanism. After the active catalytic species formation by interaction between the FePor with PhIO, a hydrogen atom from the C–H bond of the substrate was abstracted and originated a new intermediate species [Fe^{IV}–OH+R•](R=Substrate)[35], named as "solvent cage". The production of cyclohexanol and/or cyclohexanone is directly dependent on "cage" stability. If the OH group linked to the iron is rapidly directed to the radical (R• species) formed in the substrate, cyclohexanol is produced. However, if the OH and radical recombination does not occur rapidly, the radicalar species generated can escape from the "cage", originating other products such as cyclohexanone [12,35,40,41].

In the case of FePor immobilized on ZHN, it is possible that the place of complex immobilization hampers maintenance of the [Fe^{IV}–OH + R•] species and the recombination process generating radical escape and causing cyclohexanone production [12]. The ZHC structure showed the same surface tetrahedra as ZHN [11], so it can be supposed that the immobilized FePor on this support also can generate ketone production. However, this was not observed. As described previously, the immobilization does not occur on tetrahedra's tops, but rather on layered crystal edges, contributing to "solvent cage" control, preferentially generating alcohol as the oxidation product. This fact is very common in systems where the support surface is more uniform, as in the case of layered double hydroxides [23,38], synthetic aluminosilicates [26] or silica [9]. When these solids were used in immobilization, the selectivity of the synthesized catalysts was directed to cyclohexanol production. The small amount of cyclohexanone obtained in heterogeneous reactions was possibly generated from a new oxidation of cyclohexanol previously formed [26,41].

The heterogeneous reactions were investigated also in the solvent mixture acetonitrile:dichloromethane (1:1, volume:volume). In these reactions the same behavior for the catalysts was observed: the selectivity for cyclohexanol was maintained, although there was a decrease in the alcohol yield (cyclohexanol: 15, 20 and 17%, respectively for FeDF-ZHC, FeCF-ZHC and FeDC-ZHC), and cyclohexanone yield remained practically constant. Consequently, the solvent system using only acetonitrile was the most effective to evaluate the performance of the synthesized catalysts.

Table 3

| Ovidation of | cyclobeyane | by PhIO cat | talyzed by F | Dor and I | Papar_7HC |
|--------------|-------------|-------------|--------------|-----------|-----------|

| Catalyst | Run | Alcohol yield ^b (%) | Ketone yield ^b (%) | Total yield (%) | Alcohol/ketone ratio ^c |
|-------------------------------|-----|--------------------------------|-------------------------------|-----------------|-----------------------------------|
| FeDF-ZHC | 12 | 18 | 2 | 20 | 9.0 |
| 1st reuse | 13 | 8 | 2 | 10 | 4.0 |
| FeCF-ZHC | 14 | 22 | 3 | 25 | 7.3 |
| 1st reuse | 15 | 11 | 2 | 13 | 5.5 |
| FeDC-ZHC | 16 | 23 | 2 | 25 | 11.5 |
| 1st reuse | 17 | 15 | 2 | 17 | 7.5 |
| [Fe(TDFSPP)] | 18 | 16 | 6 | 21 | 2.7 |
| [Fe(TCFSPP)] | 19 | 14 | 5 | 17 | 2.8 |
| [Fe(TDCSPP)] | 20 | 18 | 4 | 20 | 4.5 |
| PhIO only, no catalyst | 21 | <1 | <1 | 1 | 1 |
| ZHC without immobilized FePor | 22 | 2 | 1 | 3 | 2 |

^a Reaction conditions: reactant molar ratio 1:20:2000 (FePor/PhIO/substrate), at room temperature under argon and 1 h of reaction. Homogeneous catalysis were performed under similar conditions to those employed for heterogeneous catalysis (similar reagent molar ratio), using iron porphyrin 1 mg, PhIO 3 mg and about 150 µL of substrate.

^b Yield based on starting PhIO (it was assumed that 2 mol of PhIO was used for ketone formation).

^c Selectivity for alcohol formation in relation to ketone formation.

The results of the first heterogeneous reuse of the solid catalysts (Runs 13, 15 and 17), like those observed in the reaction using cyclooctene, presented a decrease in the reaction yields, mainly the alcohol yield for the three catalysts. This can also be attributed to the porphyrinic complex leaching from the support during the first use of the solids, and also to deactivation of catalyst molecules due to the more drastic reaction medium generated in alkane oxidations [7,26], although the selectivity for cyclohexanol was maintained in the reuse reactions despite the decrease in that value too. In the case of first reuse of the catalysts based on FePor-ZHN [12], a significant decrease in comparison to the first use was observed, probably due to the complex leaching or catalyst deactivation. In other systems, as the [Fe(TDFSPP)] immobilized on synthetic aluminosilicate [26], only a small deactivation was observed, showing that these reuse capacity is specific to each support.

As observed for cyclooctene oxidation, the second and third reuse reactions using FeDF-ZHC catalyst for cyclohexane oxidation showed maintenance of the yields observed in first reuse, around 7% of cyclohexanol and only 1% of cyclohexanone in all cases (data not shown), indicating the catalyst's stability in reuse reactions.

In order to verify the real heterogeneous character of the catalytic reaction and the contribution of the roughly 10% of FePor leached from the support during the first use for any homogeneous catalysis character, the solid catalyst was removed from the reaction media after 1 h of reaction and the reaction was carried out for 1 and 2 h more. The monitoring of the reaction solution did not show any significant increase of the reaction yields. The same experiment was performed at different reaction times and the same results were observed, confirming that the yield observed in fact can be attributed only to the presence of the solid catalyst in the reaction solution.

The control reactions with only PhIO (Run 21) and pure ZHC (Run 22) showed very low yields, confirming once more that the observed catalytic activity is due to the immobilized FePor.

The linear alkane *n*-heptane was also investigated as a substrate in this work. Linear alkanes have shown higher resistance to oxidation than cyclic alkanes [7,39], so when this class of substrates is used, a great expectation is created in relation to the possible terminal positions of oxo-functionalization [8]. Very few examples are described in the specialized literature regarding efficient catalysts for linear alkane position 1 or position 2 selective oxidation [39,42]. The linear alkane C—H bond dissociation energy decreasing by 104, 95.3 and 91 kcal mol⁻¹, respectively, for primary, secondary and tertiary carbons, this fact justifies in part because the majority of previous works on linear alkane oxidation have shown better results for products at positions 2 and 3 of the carbon chain [8,26,36,43], despite the contribution of the statistic factors [7]. In this sense, the development of an effective method for not activating alkane C—H bond oxidation is very important.

Table 4 presents the results obtained for *n*-heptane oxidation with the synthesized catalysts. In the reactions using immobilized FePor (Runs 23, 25 and 27), there was high selectivity for alcohol production, as observed in the cyclohexane oxidation catalysis. The use of FePor catalysts in linear alkane oxidation commonly produces alcohols [7,39]. In comparison with the same FePor immobilized on ZHN [12], the selectivity was the same. The *n*-heptane linear structure contributes to "solvent cage" maintenance, and indeed with the support surface irregularities in the case of ZHN,



Fig. 7. Cyclohexane oxidation mechanism with FePor as catalyst [12,35].

Table 4

Oxidation of *n*-heptane by PhIO catalyzed by FePor and FePor-ZHC.^a

| Catalyst | Run | n-Heptane oxidation products yield ^b (%) | | | | | | | | | |
|-------------------------------|-----|-----------------------------------------------------|-------------------|-------------------|-------------------|----------|--------------------|--------------------|--------------------|-----------|---------------------|
| | | 1-ol ^c | 2-ol ^c | 3-ol ^c | 4-ol ^c | Total ol | 2-one ^d | 3-one ^d | 4-one ^d | Total one | ol/one ^e |
| FeDF-ZHC | 23 | 4 | 10 | 11 | 4 | 29 | - | - | - | _ | 29 |
| 1st reuse | 24 | 1 | 7 | 8 | 2 | 18 | - | - | - | - | 18 |
| FeCF-ZHC | 25 | 2 | 6 | 7 | 3 | 18 | - | - | - | - | 18 |
| 1st reuse | 26 | - | 4 | 6 | 2 | 12 | - | - | - | - | 12 |
| FeDC-ZHC | 27 | 2 | 6 | 8 | 3 | 19 | - | - | - | - | 19 |
| 1st reuse | 28 | - | 3 | 5 | 2 | 10 | - | - | - | - | 10 |
| [Fe(TDFSPP)] | 29 | - | 17 | - | - | 17 | - | 3 | - | 3 | 5.7 |
| [Fe(TCFSPP)] | 30 | - | 13 | - | - | 13 | - | 3 | - | 3 | 4.3 |
| [Fe(TDCSPP)] | 31 | - | 15 | - | - | 15 | - | 2 | - | 2 | 7.5 |
| PhIO only, no catalyst | 32 | - | - | - | - | - | - | - | - | - | - |
| ZHC without immobilized FePor | 33 | - | - | - | - | - | - | - | - | - | - |
| | | | | | | | | | | | |

^a Reaction conditions: reactant molar ratio 1:20:2000 (FePor/PhIO/substrate), at room temperature under argon and 1 h of reaction. Homogeneous catalysis were performed under similar conditions to those employed for heterogeneous catalysis (similar reagent molar ratio), using iron porphyrin 1 mg, PhIO 3 mg and about 130 μL of substrate. ^b Yield based on starting PhIO.

Held based on starting Philo

^c Heptanol.

^d Heptanone.

^e Selectivity for alcohol formation in relation to ketone formation.

Table 5

Comparative results for *n*-heptane oxidation with immobilized FePor on ZHC and ZHN in first catalyst utilization.

| FePor | ZHC | | | ZHN | ZHN | | |
|--------------|-----------------------|------------------------|---------------------|-----------------------|------------------------|---------------------|--|
| | ol ^a total | one ^b total | ol/one ^c | ol ^a total | one ^b total | ol/one ^c | |
| [Fe(TDFSPP)] | 29 | - | 29 | 22 | 2 | 11 | |
| [Fe(TCFSPP)] | 18 | - | 18 | 13 | 3 | 4.3 | |
| [Fe(TDCSPP)] | 19 | - | 19 | 25 | 3 | 8.3 | |

^a Heptanol.

^b Heptanone.

^c Selectivity for alcohol formation in relation to ketone formation.

the mechanism was directed to cyclohexanol production by the traditional route [12]. For ZHC, the immobilized FePor on the crystal's edges contributed once again to alcohol production via the traditional mechanism [40]. In relation to catalytic activity, the immobilized catalysts on the two supports showed similar results for total reaction yields, although the FePor immobilized on ZHC was more selective than the ZHN support (Table 5).

The FeDF-ZHC presented the best catalytic result for *n*-heptane oxidation, while for cyclohexane oxidation reaction it showed a slightly lower result than for the others. This can be linked to the FePor immobilization mode on the support [7]. The fluoride groups, smaller than chloride atoms of the other two FePors, can allow more effective interaction between the metalloporphyrin and the solid surface, generating an increase in catalytic activity and also 4% yield of 1-heptanol, which is a difficult oxidation product to obtain [39]. We stress that the comments about FeDF-ZHC catalytic activity are hypotheses to explain the catalyst behavior.

The catalysts reuse reactions (Runs 24, 26 and 28) showed, as observed for cyclohexane, a lower yield in relation to that observed in the first use of the solid. The leaching of the immobilized species also contributed to the smaller yields. The selectivity continued to favor alcohol production and ketone formation was not observed. As in the other two substrates, the second and third reuse reactions for FeDF-ZHC catalyst showed small reduction of total alcohol yield (17 and 17%, respectively), indicating the absence of complex leaching from the support after the first use. In ZHN system [12], as already described for cyclohexane oxidation, in the first reuse, considerable decreases were observed, indicating a common behavior to the class of compounds containing metalloporphyrins immobilized on layered hydroxide salts.

In comparison to homogeneous catalysis (Runs 29–31), the supported catalysts presented better catalytic efficiency and excellent selectivity for alcohol production. The homogeneous reactions showed selectivity for alcohol production at position 2 and for ketone at position 3 of the carbonic chain. This can be assigned to more restricted substrate access to the active catalytic species in the metallic center, generated by the bulk and anionic substitutions (sulphonates) on porphyrin aromatic rings [26,36]. With the FePor immobilization on the solid surface, the arrangement leads to a decrease in active catalytic center restriction, exposing the metallic center and altering the previous selectivity for alcohol only at position 2 to alcohol selectivity at all the positions of the carbon chain.

Finally, for *n*-heptane, in the control reactions without the catalysts presence and only with the oxidant PhIO (Run 32) and the pure ZHC support (Run 33), insignificant product formation occurred. Heptaldehyde formation was also not detected in any of the experiments.

4. Conclusions

A family of anionic iron(III) porphyrins (FePor) were immobilized on zinc hydroxide chloride (ZHC), previously obtained by reaction between a ZnCl₂ and NH₄OH solution. The synthesized materials were characterized by X-ray powder diffraction, infrared and UV–vis spectroscopy and electron paramagnetic resonance, with this last analysis evidencing that the FePor was immobilized on ZHC.

The solids obtained were investigated as catalysts for heterogeneous oxidation reactions of cyclooctene, cyclohexane and *n*-heptane. Very good results were observed for cyclooctenoxide production, including in reuse reactions. For cyclohexane and *n*heptane, considerable oxidation results were observed. Despite the great selectivity for alcohol production in these two cases, the reuse reactions showed a higher decrease in comparison to the cyclooctene reuse reaction, possibly attributed to active phase leaching from the support or some catalytic deactivation during the oxidation of these two more inert alkanes. The catalytic yields were compared to the results obtained in the same FePor immobilization on zinc hydroxide nitrate (ZHN) [12]. For this solid, an unusual selectivity for the cyclohexane oxidation toward cyclohexanone was observed. This selectivity can be attributed to the metalloporphyrin immobilization mode on ZHN, which modifies the reaction mechanism by a radicalar route. ZHC and ZHN structures are very similar, although the FePor were immobilized in different modes on ZHC, generating alcohol production in cyclohexane oxidation catalysis.

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