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

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Abstract

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

Keywords: Iron porphyrin; Supported catalysts; Leached chrysotile; Grafting; Oxidation; Catalysis

1. Introduction

Metalloporphyrins are important examples of macrocyclic complexes and have attracted much interest in the study of various oxygenation reactions of hydrocarbons under mild conditions [1–4]. This class of compounds is used in solution or following immobilization in organic amorphous polymers and crystalline inorganic materials, such as silica [5–7], zeolites [8,9], montmorillonite clay [10,11] and others [12–16]. The use of metalloporphyrins substituted with electron-withdrawing groups (the so-called second generation porphyrins [17]) and their immobilization has resulted in efficient and selective catalysts for oxidation reactions since the support can impose shape selectivity and promote a special environment, favoring the approach of the substrate to the active catalytic species [5–7,12,13,18]. In addition, the immobilization may prevent molecular aggregation or bimolecular self-destruction reactions, which leads to deactivation of catalytically active metalloporphyrin species. The immobilization of metalloporphyrins is also associated with an easily recyclable solid, which can be reused [19].

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

Silica gel is an example of inorganic solid that present siloxanes groups (Si–O–Si) in the bulk and a high population of silanols groups (Si–OH) at the surfaces [24], being the surface groups available for grafting reactions. The silane coupling agents (general formula $(R'O)_3SiR$)) covalently bonded to inorganic supports, are one interesting alternative to immobilize catalysts, including metalloporphyrins [16,23].

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

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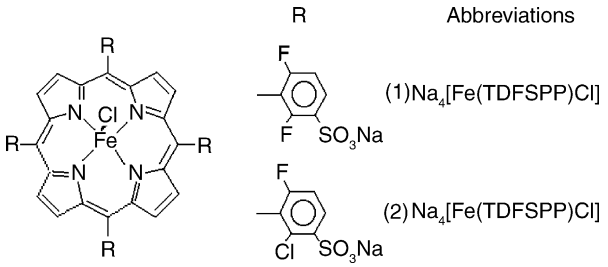

Fig. 1. Schematic representation of iron(III) porphyrins.

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

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

2. Experimental

2.1. Physical measurements

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

2.2. Materials

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

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

(3-Aminopropyl)triethoxysilane-3-APTS), $NH_2(CH_2)_3Si(CH_2CH_2O)_3$ (Aldrich), toluene (Synth) and ethanol (Nuclear) were all reagent grade. Deionized water was used in all experimental procedures.

2.2.1. Porphyrins

Free base porphyrins $Na_4[H_2(TDFSPP)]$ and $Na_4[H_2(TCFSPP)]$ were synthesized, purified and characterized following the methodology previously described [25–28].

2.2.2. Iron(III) porphyrins

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

2.2.3. Oxidant

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

2.2.4. Catalyst preparation

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

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