

Iron porphyrin immobilized into natural clays and silica prepared by the Stober method as mimics of cytochrome P450.

Thais E. Cintra¹ (IC), Emerson H. de Faria¹ (PQ), Eduardo J. Nassar¹ (PQ), Katia J. Ciuffi¹ (PQ), Miguel A. Vicente² (PQ), Raquel Trujillano² (PQ), Vicente Rives² (PQ)

¹Universidade de Franca, Franca, Brazil

²GIR QUESCAT, Universidad de Salamanca, Salamanca, Spain

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Introduction

Synthetic ironporphyrins, FeP, behave as successful biomimetic catalysts in many oxidation reactions in homogeneous media. However, their high cost and difficult recovery from the reaction medium make their large-scale application unfeasible. Catalyst heterogeneization is an alternative approach to overcome the typical problems of homogeneous catalysis: heterogeneous catalysts are easy to recover and reuse, which reduces the costs and environmental impact. This work reports on two new biomimetic heterogeneous ironporphyrin catalysts consisting of: (a) a naturally occurring Brazilian kaolinite functionalized with the organosilane precursor 3-chloropropyltrimethoxysilane (3-CIPTMS), grafted with iron(III)-5,10,15,20-tetrakis(4-hydroxyphenyl) porphyrin, FeTHPP, and (b) a catalytic system synthesized by the Stöber methodology based on the hydrolysis and condensation of tetraethylorthosilicate (TEOS) and 3-CIPTMS, in the presence of FeTHPP, in a mixture of alcohol, water, and ammonia, designated as Ka-FeTHPP and Si-FeTHPP, respectively. UV-Vis spectroscopy, X ray diffraction, thermogravimetric analysis, FTIR, texture analysis, electron paramagnetic resonance (EPR), and scanning electron microscopy (SEM) aided to the characterization of the materials. The catalyst performance was evaluated and compared in the degradation of the dye Orange II by hydrogen peroxide in aqueous solution, at room temperature.

Results and Discussions

The UV-Vis spectra of both materials displayed Soret band at 422 nm, but red-shifted as compared to the position for FeTHPP in solution (414 nm). This indicated that FeP was distorted in the matrixes, as confirmed by EPR. SEM revealed that Ka-FeTHPP consisted of characteristic hexagonal particles. SEM also showed that the clay particles agglomerated after FeTHPP insertion, which evidenced that clay interacted with FeTHPP. As for Si-FeTHPP, the different H₂O/silane molar ratios and ammonia concentration used during the synthesis resulted in spherical particles. For both Ka-FeTHPP and Si-FeTHPP, thermal analyses confirmed that

heterogeneization enhanced the FeP thermal stability: whilst FeTHPP usually underwent degradation around 250°C, Ka-FeTHPP and Si-FeTHPP started to degrade at 475 and 329°C, respectively. X-ray diffraction of the clay revealed the intensification of the 001 reflection after FeP immobilization, indicating that FeTHPP improved the structural organization. The opposite phenomenon occurred in the case of Si-FeTHPP: FeP insertion into the latter matrix did not affect silica crystallinity or organization, and the material remained amorphous. Both Ka-FeTHPP and Si-FeTHPP promoted dye degradation after 24 h (37 and 84 %, respectively). The dye underwent complete mineralization, and no new UV-Vis bands arose during reaction with hydrogen peroxide. Factors such as FeP arrangement in the matrix, specific surface area, acidity, and surface anionic or cationic charge accounted for the different activities of Ka-FeTHPP and Si-FeTHPP. The presence of radical traps decreased the efficiency of the dye degradation (17% for Ka-FeTHPP and 38% for Si-FeTHPP).

Conclusions

The results reported herein evidenced that heterolytic and homolytic cleavage of hydrogen peroxide occurred simultaneously, and that the active iron(IV)-oxo porphyrin π -cation radical and hydroxyl radical species underlay dye degradation. Factors such as FeP arrangement in the matrixes, specific surface area, acidity, and surface anionic or cationic charge accounted for the different activities of Ka-FeTHPP and Si-FeTHPP.

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