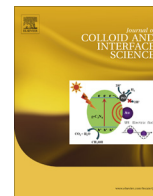




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Metalloporphyrins immobilized in Fe₃O₄@SiO₂ mesoporous submicrospheres: Reusable biomimetic catalysts for hydrocarbon oxidation



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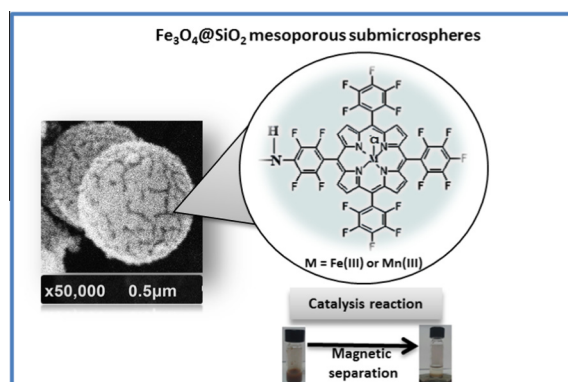
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HIGHLIGHTS

- Recyclable biomimetic catalysts.
- Metalloporphyrins inside magnetic core@shell mesoporous silica.
- Selective hydrocarbon hydroxylation and excellent epoxidation performance.

GRAPHICAL ABSTRACT



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ABSTRACT

We successfully immobilized metalloporphyrins (MeP) in mesoporous silica coating magnetite spheres. In this sense, we prepared two different classes of core@shell supports, which comprise aligned (Fe₃O₄-AM-MeP, MeP = FeP or MnP) and non-aligned (Fe₃O₄-NM-MeP, MeP = FeP or MnP) mesoporous magnetic structures. X-ray diffractometry and energy dispersive X-ray spectroscopy confirmed the mesoporous nature of the silica shell of the materials. Magnetization measurements, scanning and transmission electron microscopies (SEM/TEM), electrophoretic mobility (ζ -potential), and infrared spectroscopy (FTIR) also confirm the composition and structure of the materials. The catalysts maintained their catalytic activity during nine reaction cycles toward hydrocarbon oxidation processes without detectable catalyst leaching. The catalysis results revealed a biomimetic pattern of cytochrome P450-type enzymes, thus confirming that the prepared materials are can effectively mimic the activity of such groups.

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1. Introduction

Synthetic metalloporphyrins (MePs) have been used as biomimetic catalysts of Cytochrome P450 enzymes and raise great

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interest [1–6], particularly in the case of Fe(III) and Mn(III) complexes [7]. Several authors have extensively studied MeP-catalyzed alkene epoxidation and alkane hydroxylation in homogeneous medium [4,8]. Although these studies revealed highly efficient systems [9], researchers pointed that homogeneous catalysts possess some critical drawbacks. For example, they can undergo self-destruction during the reaction, not to mention the difficult catalyst recovery at the end of the reaction for further reuse [10,11].

A common strategy to overcome the aforementioned limitations was the development of heterogeneous catalysts, which comprise MePs attached to a variety of solid supports. Several research groups have worked with various types of supports, namely clays [12], mesoporous silica [13–15], and zeolites, among others [16]. In this context, magnetic core@shell structures have currently drawn an increasing attention as supports for the achievement of heterogeneous catalysts and also for other applications. For instance, researchers usually synthesize the silica-coated Fe_3O_4 particles (Scheme 1, I and II) and the MePs are immobilized by electrostatic interaction [17,18] or by means of organofunctionalization, commonly with the use of 3-aminopropyltriethoxysilane (APTES) [19].

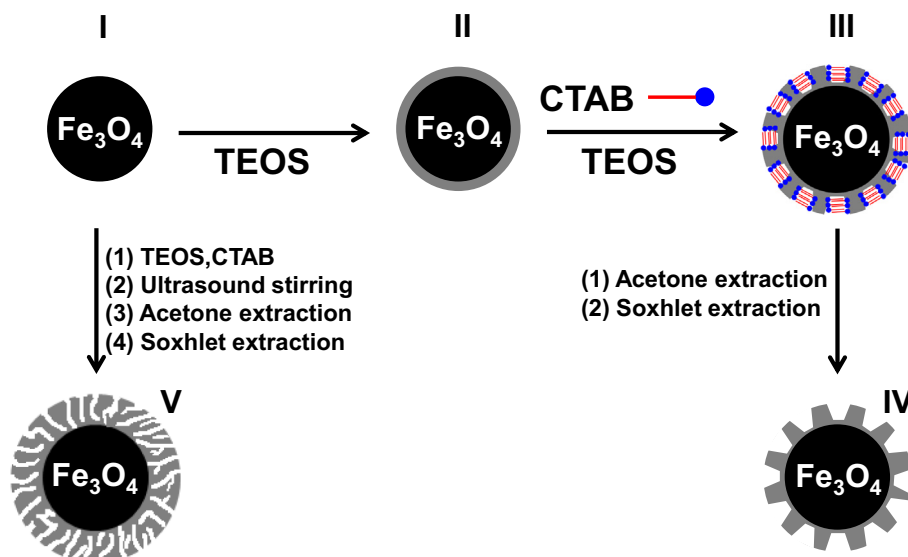
Currently, various types of novel core@shell magnetic mesoporous silica composites (Scheme 1, I–IV and I–V) have gained much attention for applications in catalysis [20,21]. These materials must display several adequate characteristics, mainly a large surface area that can undergo chemical modification to enable the immobilization of countless types of complexes [20–22], usually inside the silica mesopores. Accordingly, these systems provide a convenient method to remove the catalyst from the reaction medium, since it is only necessary to apply an appropriate magnetic field [20–23].

In this sense, core@shell magnetic mesoporous silica composites are interesting supports for MePs since, according to Mansuy [4], progress is still required to further improve these metalloporphyrin-based systems, mainly in the sense of the amelioration of the selectivity of substrate recognition by the catalyst or the support of the catalyst.

In the last decade metalloporphyrins have been highlighted as responsible for oxidation reactions using oxygen donors as PhIO and molecular oxygen, among others [16,24,25]. In this context, Huang et al. [24] reported iron meso-*tetrakis*(pentafluorophenyl)porphyrin immobilized on zinc oxide as catalyst for cyclohexane

oxidation in aerobic condition. This study therefore reinforces that preliminary studies are still necessary to evaluate the influence of different supports in catalysis performance of the MePs aiming at possible industrial applications of these ecofriendly catalyst systems [24,25].

Recently [19], we described the preparation of ordered mesoporous materials loaded with magnetic spheres inside the porous cages, which consist in Fe_3O_4 particles embedded into micrometric-sized silica structures. In such systems, manganese metalloporphyrins were immobilized via the post-synthesis methodology and the effect of pore expansion was investigated with regard to the catalytic properties of MePs in hydrocarbon oxidation. However, such report and other related papers do not discuss catalytic properties considering the different contributions of porphyrin groups inside pores and in the outer surface of the silica particles. Moreover, descriptions concerning the effects of pore ordering in the catalytic hydrocarbon oxidation by MePs and clear comparisons among covalently bound and electrostatically immobilized porphyrins in such systems are rather scarce in the literature. Therefore, in this paper we describe the synthesis of the new mesoporous magnetic catalysts and the support influence on the biomimetic behavior of metalloporphyrins as catalysts in the oxidation of hydrocarbons. Different $\text{Fe}_3\text{O}_4/\text{SiO}_2$ sub-micrometric structures were prepared, where isolated Fe_3O_4 particles were individually coated by silica layers (Scheme 1). This, in turn, enables the obtainment of catalysts that are readily dispersible both in water and organic solvents, presenting an improved colloidal stability, as confirmed by ζ potential measurements. Hence, cyclohexane hydroxylation and (*Z*)-cyclooctene epoxidation by iodosylbenzene (PhIO) were evaluated, as well as the potential reuse of the synthesized systems. Iron(III) or manganese(III) complexes of 5,10,15,20-*tetrakis*(pentafluorophenyl)porphyrin (FeP and MnP, respectively) were covalently bonded in mesoporous silica layers coating magnetite spheres by means of APTES using the co-condensation method. Complementarily, cationic manganese (III) complexes of 5,10,15,20-*tetrakis*(4-*N*-methylpyridyl)porphyrin (MnTMPyP) were immobilized in mesoporous silica layers by electrostatic interaction for further comparison. Magnetic catalysts involving distinct silica arrays were prepared, namely (i) aligned mesoporous silica (Fe_3O_4 -AM-MeP, Scheme 1, IV), (ii) non-aligned mesoporous silica (Fe_3O_4 -NM-MeP, Scheme 1, V) and (iii) a control consisting in MePs immobilization only at the silica



Scheme 1. Synthesis of the core@shell magnetic materials consisting in magnetite particles coated by aligned and non-aligned mesoporous silica.

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