Manganese porphyrin functionalized on $Fe_3O_4@nSiO_2@MCM$-41 magnetic composite: Structural characterization and catalytic activity as cytochrome P450 model

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ABSTRACT

This study reports on the preparation of heterogeneous catalysts with two different pore sizes, the $Fe_3O_4@nSiO_2@MCM$-41-MnP and $Fe_3O_4@nSiO_2@MCM$-41(E)-MnP catalysts. Such systems ally the catalytic properties of metalloporphyrins (MeP) with the magnetic properties of magnetite nanoparticles (Fe_3O_4) in a mesoporous MCM-41 silica matrix. The synthesis of Fe_3O_4 nanoparticles was followed by the surface coating with a thin silica layer ($Fe_3O_4@nSiO_2$). Then, an MCM-41-type ordered mesoporous silica structure was grown over the initial particles in the presence of CTAB as surfactant and TEOS as the silica precursor, to yield the $Fe_3O_4@nSiO_2@MCM$-41 solid. In this step, mesitylene can also be incorporated as a structure expanding agent for the production of larger pores, thus yielding the $Fe_3O_4@nSiO_2@MCM$-41(E) solids. The resulting composites were further functionalized with aminopropyl groups by the silylating agent APTES. This enabled the covalent immobilization of manganese(III)-5,10,15,20-*tetrakis*(penta-fluorophenyl)porphyrin ($Mn(TPF_5PP)$) onto the composites via a aromatic nucleophilic substitution reaction, to afford the $Fe_3O_4@nSiO_2@MCM$-41-MnP and $Fe_3O_4@nSiO_2@MCM$-41(E)-MnP catalysts. Characterization of the catalysts by XRD, UV–Vis, DR UV–vis, FTIR, SEM, TEM, VSM and N_2 adsorption/desorption isotherms, aided understanding the catalyst structure and morphology. The catalytic activity of the catalysts in hydrocarbon oxidation ((Z)-cyclooctene and cyclohexane) was evaluated; iodosylbenzene (PhIO) was used as the oxygen donor agent. The catalytic tests demonstrated higher yields of epoxide for $Fe_3O_4@nSiO_2@MCM$-41(E)-MnP than $Fe_3O_4@nSiO_2@MCM$-41-MnP catalyst, which can be attributed to the larger pore sizes. Both catalysts were selective for the cyclohexanol product, thus indicating a P450-type biomimetic behavior.

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1. Introduction

Many catalytic processes that occur in living organisms are controlled by redox enzymes named oxidoreductases, which mainly comprise the monooxygenases and dioxygenases. Among monooxygenases, the enzymes belonging to the cytochrome P450 superfamily are noteworthy, because they exert important roles in a number of metabolic processes [1,2]. This class of enzymes bears heme units as prosthetic groups, which contain iron(III) protoporphyrin-IX ($Fe^{III}P$-IX) as the active center. The $Fe^{III}P$-IX

macrocycle displays a number of specific activities in biosystems, among which the ability to functionalize C–H bonds and to promote selective oxidations are the most important ones [3,4]. To take advantage of the catalytic potential of $Fe^{III}P$-IX-based systems, a number of studies have focused the preparation of several synthetic metalloporphyrins (MePs) in the second half of the twentieth century, which allowed them to mimic the reactions catalyzed by P450 enzymes in laboratory conditions [5–8]. This motivated deeper investigation into the mechanisms underlying the activity of P450 enzymes and encouraged application in different areas, such as the chemical and pharmaceutical industry.

P450 biomimetic systems can catalyze important industrial reactions such as hydroxylation of alkanes and epoxidation of olefins, regio- and stereoselective reactions such as regioselective

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hydroxylation of aromatic compounds and stereoselective oxidation of alkenes [4,9]. Furthermore, P450 systems can be applied in drug metabolism studies [10—13], toxicity studies of compounds (e.g. herbicides) [11,14,15] and preclinical studies of new bioactive substances [11,16].

However, catalytic studies normally involve the use of MePs in homogeneous media (i.e., substrate, catalyst, and products exist in the same liquid phase), which poses challenges regarding catalyst recovery and reuse, as well as porphyrin aggregation in solution. One strategy to overcome these difficulties, has been to design heterogeneous catalysts through immobilization of MePs on inorganic solid supports [17—22]. Immobilization facilitates catalyst recovery and reuse, minimizes MeP oxidative self-oxidation, and prevents loss of MeP catalytic efficiency due to formation of dimers [23]. Such systems allow for versatile control of MeP activity through the intrinsic characteristics of the metalloporphyrin binding site, the structure of the inorganic matrix, the nature of the interaction between the support and the catalyst, and the properties of the medium in which the catalytic reaction occurs [24]. In other words, the inorganic support enables tailoring of the catalytic performance of the immobilized MePs through creation of a controllable microenvironment for the target reactions.

Among the different classes of supports available for this kind of catalysis, matrices that integrate the properties of mesoporous materials with the characteristics of nanosized solids have attracted great attention in recent years [25—28]. In this context, $Fe_3O_4@SiO_2$ composites are quite promising supports in heterogeneous catalysis, since they combine the magnetic properties of magnetite (Fe_3O_4) nanoparticles with the structural tunability of silica structures, which can present different pore sizes and arrangements; besides, the reactivity of the silanol groups (Si—OH) enables modification and functionalization of the surface of these materials, thereby allowing anchoring of a variety of molecules, such as MePs [29,30].

Particularly, MCM-41 (Mobil Composition of Matter No. 41) is an important class of silica materials with applications in countless fields. These materials consist of mesoporous-structured SiO_2 formed by a hexagonal array of unidirected mesopores [31]. Compared to amorphous silica, the MCM-41 mesoporous silica have high surface area and have relatively uniform pore sizes, allowing a better efficiency and reproducibility of results. Moreover, the synthetic approaches applied to obtain MCM-41 structures can afford a wide range of pore dimensions (15—100 Å), which is highly attractive if one wishes to control the catalytic microenvironment [32].

In addition to the advantageous properties of MCM-41, the magnetic properties of the Fe_3O_4 nanoparticles present as a core for the silica structure can optimize the operations of separation, recycling, and reuse of the heterogeneous catalyst. Hence, these nanoparticles make catalyst recovery more practical and faster than conventional separation methods, and reduce solvent consumption, favoring a green chemistry strategy [33,34].

In this sense, the current work reports on the steps involved in the synthesis of $Fe_3O_4@nSiO_2@$MCM-41 and $Fe_3O_4@nSiO_2@$MCM-41(E) composites (in which "(E)" denotes an expanded porous structure) and their further modification with manganese(III)-5,10,15,20-*tetrakis*(pentafluorophenyl) porphyrin (Mn(TPF₅PP)) via covalent binding, to obtain the $Fe_3O_4@nSiO_2@$MCM-41-MnP and $Fe_3O_4@nSiO_2@$MCM-41(E)-MnP heterogeneous catalysts, respectively. They are systems that ally the catalytic properties of metalloporphyrins (MeP) with the magnetic properties of magnetite nanoparticles (Fe_3O_4) in a structured matrix of MCM-41 mesoporous silica. X-ray diffractometry (XRD), UV—vis, diffuse reflectance and infrared spectroscopies (UV—vis, DR UV—vis and FTIR, respectively), scanning and transmission electron microscopies (SEM and TEM, respectively), vibrating sample magnetometer (VSM) and nitrogen adsorption/desorption isotherms, aided structural and morphological characterization of the synthesized solids. Hydrocarbon oxidation tests employing the (Z)-cyclooctene and cyclohexane as starting materials and iodosylbenzene (PhIO) as oxygen donor, helped to assess the catalytic activity of the composites, as well as to evaluating the accessibility of the substrate and oxidant molecules to the catalytic sites. This, in turn, enabled a comparison of the catalytic performances associated to the two systems with different pore size diameters. Together, the studies with hydrocarbons provided better understanding of the nature of the microenvironment created by the solvent and support around the MnP and its influence on the resulting catalytic profile.

2. Experimental

2.1. Chemicals

The TPF₅PP porphyrin (5,10,15,20-*tetrakis*(pentafluorophenyl) porphyrin) acquired from Aldrich, was metalated with manganese(III) ions according to a literature procedure [35], to afford the metalloporphyrin [Mn^III(TPF₅PP)Cl], designated MnP hereafter. The surfactants cetyltrimethylammonium bromide (CTAB) and poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(-ethylene glycol) (Pluronic P123) were purchased from Aldrich and used without further purification. Sodium acetate (NaOAc, Merck), iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, Aldrich), tetraethoxysilane (TEOS, Acros), mesitylene (MES, Aldrich), and 3-aminopropyltriethoxysilane (APTES, Aldrich) were also used as received, as well as concentrated aqueous ammonia (NH₃(conc) 28% m/m, Synth), ethanol (EtOH, Fmaia) and ethylene glycol (EG, Aldrich). The solvents *N,N*-dimethylformamide (DMF, Acros), toluene (Fmaia), 1,2-dichloroethane (DCE, Acros) and dichloromethane (DCM) were previously distilled and dried over 3 Å molecular sieves. HPLC grade cyclohexane (Aldrich) and (Z)-cyclooctene (Acros) were used as substrates; both of them were purified by column liquid chromatography on basic alumina (Merck 70—230 mesh) prior to use; their purities were checked by gas chromatography (GC) analysis. The oxidant iodosylbenzene (PhIO) was prepared and purified according to a literature procedure [36,37]. Bromobenzene (Acros) was used as internal standard during GC tests.

2.2. Synthesis of the catalysts

2.2.1. Preparation of the magnetite nanoparticles (Fe_3O_4)

The Fe_3O_4 nanoparticles were obtained according to the microwave-assisted solvothermal method proposed by Zhang et al. [38]. Briefly P123 (0.80 g) was dissolved in ethylene glycol (40.0 mL), and then $FeCl_3 \cdot 6H_2O$ (1.0 g) and NaOAc (3.6 g) were added to the resulting solution. The mixture was stirred vigorously to obtain a homogeneous suspension and transferred to a Teflon digestion vessel (80.0 mL capacity), which was later deaerated by applying an argon flux for 10 min. The resulting solution was treated under microwave irradiation (2.54 GHz) for 30 min in a Milestone StarSynth equipment. The irradiation power (600 W at maximum) was regulated through the software apparatus in order to follow a heating program comprising an initial ramp from ambient temperature to 210 °C in 10 min, and maintenance of the temperature at 210 °C for 20 min under autogenous pressure. A black precipitate (Fe_3O_4 nanoparticles) emerged; it was removed from the solution by application of an external magnetic field. The Fe_3O_4 nanoparticles were washed with ethanol and water (five times each) and then dried under vacuum for three days.