



Mn porphyrins immobilized on non-modified and chloropropyl-functionalized mesoporous silica SBA-15 as catalysts for cyclohexane oxidation

Victor Hugo Araújo Pinto^{a,b}, Júlio Santos Rebouças^b, Geani Maria Ucoski^a, Emerson Henrique de Faria^c, Breno Freitas Ferreira^c, Rosane Aguiar Silva San Gil^d, Shirley Nakagaki^{a,*}

^a Universidade Federal do Paraná, Departamento de Química, Laboratório de Bioinorgânica e Catálise, 81531-990, Curitiba, PR, Brazil

^b Universidade Federal da Paraíba, Departamento de Química, 58051-900, João Pessoa, PB, Brazil

^c Universidade de Franca, Departamento de Química, 14404-600, Franca, SP, Brazil

^d Universidade Federal do Rio de Janeiro, Instituto de Química, 21941-909, Rio de Janeiro, RJ, Brazil

ARTICLE INFO

Article history:

Received 6 May 2016

Received in revised form 4 July 2016

Accepted 19 July 2016

Available online 20 July 2016

Keywords:

Porphyrin

Mesoporous silica

SBA-15

Heterogeneous catalysis

Cyclohexane oxidation

ABSTRACT

In this work, solid catalysts were prepared by the heterogenization of Mn porphyrins (MnP) on mesoporous silica SBA-15 by two simple strategies: (1) immobilization of the three cationic isomers of Mn(III) *N*-methylpyridiniumporphyrins (MnTM-*X*-PyPCL₅, *X* = 2, 3, 4) on mesoporous silica SBA-15 by electrostatic interaction; and (2) anchoring of the three neutral isomers of Mn(III) *N*-pyridylporphyrins (MnT-*X*-PyPCL, *X* = 2, 3, 4) on chloropropyl-functionalized mesoporous silica SBA-15Cl via covalent bonding. SBA-15 and SBA-15Cl solids were characterized by FTIR, TGA-DTA, elemental analysis, SAXS, textural analysis, SEM, TEM, and ¹³C CP-MAS NMR (for SBA-15Cl only). The resulting MnP-supported materials with MnP loadings of 0.3% w/w were characterized by diffuse reflectance UV/VIS spectroscopy and explored as catalysts for hydroxylation of cyclohexane using iodobenzene as oxygen donor. Changes on SBA-15Cl silanol and C–Cl bands on FTIR spectra, and UV/VIS analyses confirm the porphyrin immobilization. The heterogenized catalysts were more efficient and selective toward alcohol than the corresponding homogeneous systems. The covalently immobilized catalysts SBA-15Cl/MnT-*X*-PyPCL (*X* = 2, 3, 4) showed total oxidation yields and selectivities slightly higher than those of SBA-15/MnTM-*X*-PyPCL₅. In both solid systems, the efficiency and selectivity remained essentially unaffected by the immobilized MnP isomer. The strong interaction between MnP and the mesoporous silica, in both SBA-15 and SBA-15Cl systems, was verified by the low-leaching of MnP from the materials even after exhaustive washings. The solid catalysts were recovered and reused in recycling studies showing high resistance against oxidative destruction with no significant changes in catalytic efficiency upon recycling.

© 2016 Elsevier B.V. All rights reserved.

Abbreviations: MnP, Mn(III)porphyrin or Mn(III)porphyrins; CPTS, (3-chloropropyl)trimethoxysilane; SBA-15Cl, mesoporous silica SBA-15 modified with CPTS; MnT-2-PyPCL, Mn(III) *meso*-tetrakis(2-pyridyl)porphyrin chloride; MnT-3-PyPCL, Mn(III) *meso*-tetrakis(3-pyridyl)porphyrin chloride; MnT-4-PyPCL, Mn(III) *meso*-tetrakis(4-pyridyl)porphyrin chloride; MnTM-2-PyPCL₅, Mn(III) *meso*-tetrakis(*N*-methylpyridinium-2-yl)porphyrin chloride; MnTM-3-PyPCL₅, Mn(III) *meso*-tetrakis(*N*-methylpyridinium-3-yl)porphyrin chloride; MnTM-4-PyPCL₅, Mn(III) *meso*-tetrakis(*N*-methylpyridinium-4-yl)porphyrin chloride.

* Corresponding author at: Departamento de Química, Laboratório de Bioinorgânica e Catálise, Universidade Federal do Paraná Curitiba, PR, 81531-990, Brazil.

E-mail addresses: shirleyn@ufpr.br, shirleynb17@gmail.com (S. Nakagaki).

1. Introduction

Synthetic metalloporphyrins have been successfully applied as cytochrome P-450 biomimetic model catalysts since the pioneering works of Groves and co-workers in 1979 [1,2]. This recognized catalytic activity of MnP in homogeneous system has been combined with various chemical matrices in an attempt to obtain catalysts more stable against oxidative destruction, more efficient and of easier recovery for reuse [3–5].

In the last years, a broad variety of inorganic and organic matrices has been used to immobilize metalloporphyrins as oxidation catalysts. Inorganic supports stand out, in general, by their resistant to oxidative destruction, rigidity, thermal stability, and organic

solvent resistance [3,5,6]. Among the most studied inorganic surfaces as supports are amorphous silica gel [3,5,7,8], functionalized amorphous silica gel [3,5,8,9], non-modified and modified ordered mesoporous silica [10–12], zeolites [3,6,13], alumina [14], clay minerals [3,6,15–17], silica-coated magnetic particles [18–20], organic resin [3,9], and nanoparticles [21].

Discovered in 1992 by Mobil Corporation researchers, nanostructured mesoporous silica comprises a promising class of catalyst support with singular properties, such as high surface area (from 700 to 1000 m² g⁻¹), pore size uniformity, thermal stability, and synthetic reproducibility [22,23]. In addition, the material versatility can be improved by functionalization with alkoxysilane groups bearing amine, imidazole, thiol, carboxyl, or halogen moieties [24–27].

The chemical functionalization of the mesoporous silica changes the surface reactivity and material properties, such as hydrophobicity and acidity, which allow the development of hybrids materials with application in catalysis, sensors, optical materials, magnetic solids, chemical adsorption, drug controlled release, electronic and biotechnology [24–26,28–30].

In this work, two mesoporous silica materials, *i.e.*, the non-functionalized mesoporous silica SBA-15 and the chloropropyl-functionalized counterpart, SBA-15Cl, were employed as supports for the immobilization of Mn porphyrins (MnP) using two different immobilization strategies. SBA-15 was obtained by hydrolytic sol-gel process [31] and, then, modified with (3-chloropropyl)trimethoxysilane (CPTS) by the post-synthesis route to yield the chloropropyl SBA-15Cl material. The preparation of two classes of heterogenized solid catalysts were carried out by: a) electrostatic immobilization of each of the three cationic isomers of Mn(III) *N*-methylpyridiniumporphyrin (MnTM-X-PyPCL₅, X=2, 3, 4) (Fig. 1) on SBA-15, and b) covalent anchorage of each of the three neutral isomers of Mn(III) *N*-pyridylporphyrin (MnT-X-PyPCL, X=2, 3, 4) (Fig. 1) on SBA-15Cl via pyridyl quaternization reactions.

The catalytic efficiency and selectivity of the resulting solids (SBA-15/MnTM-X-PyPCL₅ and SBA-15Cl/MnT-X-PyPCL) were investigated using cyclohexane oxidation as a model reaction and iodosylbenzene as oxygen donor. In these oxidation reactions, the following aspects were evaluated: (1) the support effect (by comparison with the corresponding homogeneous medium catalysts), (2) the recycling feasibility (recovery and reuse of the supported catalysts), and (3) the catalyst oxidative stability (by increasing the PhIO/MnP molar ratio from 10 to 100).

2. Experimental

2.1. Reagents

CHCl₃ (≥99%, Aldrich), CH₃CN (99.8%, Carlo Erba), and cyclohexane (Sigma-Aldrich, 99.5%) were used as provided. Iodosylbenzene (PhIO) of 95% purity, as determined by iodometric titration, was obtained by hydrolysis of (diacetoxyiodo)benzene (Aldrich, 98%) [32].

2.2. Synthesis of porphyrins and MnP

2.2.1. Neutral porphyrins synthesis

Ortho (meso-tetrakis(2-pyridyl)porphyrin, H₂T-2-PyP) and *meta* (meso-tetrakis(3-pyridyl)porphyrin, H₂T-3-PyP) isomers of the free-base *N*-pyridylporphyrins were bought from Frontier Scientific Inc. (Logan, UT, EUA). The *para* isomer (meso-tetrakis(4-pyridyl)porphyrin, H₂T-4-PyP) was prepared as described by Hambright and collaborators [33].

Mn(III) meso-tetrakis(2-pyridyl)porphyrin chloride (MnT-2-PyPCL), Mn(III) meso-tetrakis(3-pyridyl)porphyrin chloride (MnT-

3-PyPCL), and meso-tetrakis(4-pyridyl)porphyrin chloride (MnT-4-PyPCL) were obtained by Mn metallation of the corresponding free-base H₂T-X-PyP (X=2, 3, 4) [34].

2.2.2. Cationic porphyrin synthesis

The three isomers of the complexes Mn(III) *N*-methylpyridiniumporphyrins (MnTM-X-PyPCL₅, X=2, 3, 4) were prepared by methylation of the corresponding Mn(III) *N*-pyridylporphyrin (MnT-X-PyPCL) [35,36].

2.3. Preparation of the mesoporous silica SBA-15

The synthesis of the ordered mesoporous silica SBA-15 was carried out according to a hydrolytic sol-gel process [31]. 25.0 g of pluronic P123 and 815 mL of HCl solution (2 mol L⁻¹) were magnetically stirring at 35 °C for 24 h. Then, 57 mL of TEOS were added and the system was maintained under same conditions for an additional 24 h period. Afterward, the suspension was left in an oven at 80 °C for 24 h and then filtrated. The solid was washed with deionized water until the filtrate reached neutral pH. The solid was collected and dried at 80 °C for 24 h, then, calcined at 550 °C for 6 h with a heating rate of 1 °C min⁻¹ for slow removal of the organic template. 15.41 g of mesoporous silica SBA-15, 54% of calcined matter, was obtained at the end of the process. SBA-15 was characterized by elemental analysis, FTIR, textural analysis, thermogravimetry (TGA-DTA), small-angle X-ray scattering (SAXS), scattering and transmission electronic microscopy (SEM and TEM).

2.4. Functionalization of the SBA-15 with (3-chloropropyl)trimethoxysilane

Chemically modified mesoporous silica SBA-15 was prepared by post-synthesis route [24,37]. 4.0 g of SBA-15 and 2.0 mL (10.9 mmol) of (3-chloropropyl)trimethoxysilane were suspended in 200 mL of dry toluene (Fig. 2, route a). The system was maintained at 80 °C for 24 h under argon atmosphere. The resulting chloropropyl-functionalized SBA-15 (SBA-15Cl) was filtrated and washed with toluene, ethanol, and deionized water. The resulting solid was dried at 80 °C for 24 h. SBA-15Cl was characterized by elemental analysis, FTIR, ¹³C CPMAS NMR, textural analysis, thermogravimetry (TGA-DTA), small-angle X-ray scattering (SAXS), scattering and transmission electronic microscopy (SEM and TEM).

2.5. Anchoring of the cationic MnP isomers on mesoporous silica SBA-15

The immobilization of the three cationic MnP (MnTM-X-PyPCL₅, X=2, 3, 4) on silica SBA-15 by electrostatic interaction was carried out by the following method: 12 μmol of MnP (as 10⁻³ mol L⁻¹ aqueous solution) and 1.00 g of SBA-15 were placed under magnetic stirring at 25 °C (Fig. 2, route b). After 6 h, the suspension was filtrated and the supernatant was transfer to a 10 mL volumetric flask. An UV/VIS spectrum of the immobilization reaction supernatant was recorded in order to quantify spectrophotometrically the amount of non-immobilized, unreacted MnP. The recovered solids (SBA-15/MnTM-X-PyPCL₅, X=2, 3, 4) were exhaustively washed at room temperature, with deionized water, methanol, ethanol, and chloroform (in this order) until the absence of MnP in the washings as determined by UV/VIS spectroscopy. The quantification of the amount of MnP on the support (*i.e.*, the MnP loading) was determined indirectly by the difference between the initial amount of MnP used and the amount of MnP recovered in the various supernatants and washings. The concentration of MnP in these solutions was determined by UV/VIS spectroscopy using the molar absorptivity of the MnP Soret band [35]. Finally, the solid materials were dried at 80 °C for 24 h. SBA-15/MnTM-2-PyPCL₅ and

Download English Version:

<https://daneshyari.com/en/article/4755906>

Download Persian Version:

<https://daneshyari.com/article/4755906>

[Daneshyari.com](https://daneshyari.com)