

The catalytic activity of immobilized on modified silica metalloporphyrins bearing antioxidative 2,6-di-*tert*-butylphenol pendants

Elena R. Milaeva^{a,*}, Olga A. Gerasimova^a, Anton L. Maximov^a, Ekaterina A. Ivanova^a, Eduard A. Karachanov^a, Nick Hadjiliadis^b, Maria Louloudi^{b,*}

^a Department of Organic Chemistry, Moscow State Lomonosov University, Moscow 119992, Russia

^b Department of Chemistry, University of Ioannina, Panepistimioupoli Douroutis, Ioannina 45-110, Greece

Received 7 February 2007; received in revised form 4 April 2007; accepted 5 April 2007

Available online 30 April 2007

Abstract

A comparative study of the catalytic activity of supported manganese(III) and iron(III) chlorides of *meso*-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrin (R_4PMnCl , R_4PFeCl) and *meso*-tetraphenylporphyrin ($TPPMnCl$, $TPPFeCl$) is reported. The metalloporphyrins have been immobilized via coordination bond on the surface of two series of imidazole modified silica, imidazole propyl silica (IPS) and imidazole 3-(glycidyoxypropyl) silica (IGOPS). The heterogenised catalysts have been evaluated for hydrocarbon oxidation by sodium periodate. The critical role of 2,6-di-*tert*-butylphenol groups on the periphery of porphyrin ring in their catalytic activity has been evaluated and pertinent structural and mechanistic aspects are discussed.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Supported metalloporphyrins; 2,6-di-*tert*-butylphenol; Biomimetic oxidation

1. Introduction

Porphyrins exhibiting a wide range of redox properties have been used successfully in various applications, such as catalysts [1–8], antioxidants [9–11], or pro-oxidants [12].

Synthetic metalloporphyrins have been often used as cytochrome P450 models catalyzing the transfer of an oxygen atom from a great variety of oxidizing agents into hydrocarbon molecules [2,3]. However, the homogeneous catalysts have some drawbacks: (a) they can easily be decomposed during the catalytic reaction and (b) it is not easy to recover them at the end of reaction for re-use [13–16].

The stability of metalloporphyrin catalysts may be improved by grafting them onto solid surfaces. The immobilization can provide additional benefits arising from steric and electronic effects of the support which are in some respects analogous to the influence of the polypeptide chain in hemoproteins [15,17,18]. Silica is an attractive support for metalloporphyrins, since it is inert even under drastic experimental conditions [13]. Among heterogenisation procedures, anchoring of metalloporphyrins via axial ligation of the metal center presents an interesting alternative approach [19–26].

The goal of this work is to study the catalytic activity of several novel supported manganese(III) and iron(III) chlorides of *meso*-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrin (R_4PMnCl , R_4PFeCl) and *meso*-tetraphenylporphyrin (Ph_4PMnCl , Ph_4PFeCl) in hydrocarbons oxidation with sodium periodate. 2,6-di-*tert*-butylphenol which has been used as substituent on the porphyrin ring, offers an interesting perspective in catalytic oxidations.

* Corresponding authors. Tel.: +7 495 9393864; fax: +7 495 9395546 (E.R. Milaeva), Tel.: +30 26510 98418; fax: +30 26510 44831 (M. Louloudi).

E-mail addresses: milaeva@org.chem.msu.ru (E.R. Milaeva), mlouloud@uoi.gr (M. Louloudi).

Due to the antioxidative properties of such compounds, the metal complexes based on 2,6-di-*tert*-butylphenol can show a multifunctional activity in catalytic reactions [27]. Silica was modified as a coordinative support by converting its surface silanol groups into silypropyl imidazole derivatives providing two series of imidazole modified silica, imidazole propyl silica (IPS) and imidazole 3-(glycidyoxypropyl) silica (IGOPS).

2. Experimental

2.1. Materials

All solvents and reagents were of commercial grade unless otherwise stated and were purchased from Merck and Aldrich. Infrared spectra were collected on a Perkin Elmer "Spectrum One" spectrophotometer and on a Spectrum GX Perkin Elmer FT-IR System in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} and 64 scans by a DRIFT setup. UV–vis spectra were recorded using a UV/VIS/NIR JASCO and a Varian 100S spectrophotometer. Diffuse reflectance UV–vis spectra were recorded at room temperature on a Shimadzu UV-2401PC with a BaSO_4 coated integration sphere. GC analysis was performed using a Shimadzu GC-17A gas chromatograph coupled with a GCMS-QP5000 mass spectrometer. A SPB™-5 capillary column (30 m, 0.25 mm i.d.) was used with the following temperature program: initial temperature, 80 °C (5 min); heating rate, 10 °C/min; final temperature, 150 °C (final time 5 min); injector temperature, 230 °C; detector temperature, 230 °C. Elemental analyses were obtained using a Carlo Erba 1108 elemental analyzer. Thermogravimetric analyses were carried out on a Shimadzu DTG-60 analyser at a heating rate of 10 °C/min under static air atmosphere from 20 to 700 °C.

2.2. Metalloporphyrins

The porphyrins **1**, **4**, **1a**, **4a** were synthesized as described previously by the known procedures [28,29] and purified by silica gel column chromatography using CHCl_3 , 80% CHCl_3 and 20% hexane as the eluting solvents.

Modified silicas IPS and IGOPS. The modified silica IPS was obtained using the procedure described previously [30]: (3-chloropropyl)-trimethoxysilane (3 mmol; 0.552 ml) was added to a stirred solution of imidazole (3 mmol; 0.204 g) in 50 ml of toluene. The resulting mixture was then heated at 80 °C for 24 h, and after drying commercial SiO_2 (1.5 g) and EtOH (5 ml) were added. The reaction mixture was stirred at 80 °C for 24 h. The obtained functionalized silica IPS was collected by filtration in vacuo and washed with EtOH and diethyl ether. IPS was then dried for 12 h. The loading achieved is 8.5% determined by thermogravimetric and elemental analysis.

The modified silica IGOPS was obtained by adding 3-(glycidyoxypropyl)-trimethoxysilane (3 mmol; 0.663 ml) to a stirred solution of imidazole (3 mmol; 0.204 g) in

50 ml of toluene [31]. The subsequent treatment used is analogous as previously described for IPS. The IGOPS loading achieved is 20% determined by thermogravimetric and elemental analysis.

2.3. Supported metalloporphyrins ($R_4\text{PM}(\text{IPS})$, $\text{Ph}_4\text{PM}(\text{IPS})$, $R_4\text{PM}(\text{IGOPS})$, $\text{Ph}_4\text{PM}(\text{IGOPS})$)

The metalloporphyrin ligation to IPS and IGOPS was achieved by stirring a CH_2Cl_2 solution of a known amount of metalloporphyrin into a suspension of the support for 24 h. The resulting supported catalyst was washed with CH_2Cl_2 to remove unbound catalyst and weakly bound porphyrin and dried for 3 h at 60 °C. The loadings were quantified by measuring the amount of unloaded metalloporphyrin in the combined reaction solvent and washings by UV–vis spectroscopy. The loading achieved for $R_4\text{PM}(\text{IPS})$ and $\text{Ph}_4\text{PM}(\text{IPS})$ is 11.5% while for $R_4\text{PM}(\text{IGOPS})$ and $\text{Ph}_4\text{PM}(\text{IGOPS})$ is 27%. These values were comparable with those obtained by thermogravimetric analysis.

2.4. Catalytic reactions

Sodium periodate was added to a solution of alkene and cocatalyst (imidazole), in a $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (540/270 μl) solvent mixture at room temperature. As an internal standard, acetophenone was used. Catalytic reactions were started by adding 1 μmol of the corresponding catalyst. The ratio of catalyst:oxidant:cocatalyst:substrate was equal to 1:46:10:23.

The progress of the reaction was monitored by GC–MS, in small sample volumes removed from the reaction mixture. Heterogeneous catalyzed reactions were usually completed within 24 h. To establish the identity of the products unequivocally, the retention times and MS-spectral data were compared to those of commercially available compounds. Blank experiments showed that no reaction occurred in the absence of the catalysts in reactions performed under identical conditions.

3. Results and discussion

Two modified silicas, IPS and IGOPS, with *N*-imidazolyl functional groups were synthesized. IPS bears an $-(\text{CH}_2)_3-$ spacer bridging the imidazolyl-moiety and the inorganic support, while the corresponding spacer of IGOPS is the longer $-\text{C}(\text{OH})\text{CH}_2\text{O}(\text{CH}_2)_3-$ group.

Two series of metalloporphyrins bearing the antioxidative 2,6-di-*tert*-butylphenol groups ($R_4\text{PM}$) ($R_4\text{PFeCl}$ – **1** and $R_4\text{PMnCl}$ – **4**) and phenyl groups (Ph_4PM) (Ph_4PFeCl – **1a** and Ph_4PMnCl – **4a**) were synthesized. Immobilization of these metalloporphyrins on the functionalized silicas was carried out by axial coordination of metal center to N_1 nitrogen atom of the imidazolyl groups (Fig. 1). The obtained solids, $R_4\text{PFeCl}(\text{IGOPS})$ – **2**, $R_4\text{PFeCl}(\text{IPS})$ – **3**, $R_4\text{PMnCl}(\text{IGOPS})$ – **5**, $R_4\text{PMnCl}(\text{IPS})$ – **6**, Ph_4PFeCl –

Download English Version:

<https://daneshyari.com/en/article/52484>

Download Persian Version:

<https://daneshyari.com/article/52484>

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