

Immobilization of iron porphyrins into porous vycor glass: characterization and study of catalytic activity

Shirley Nakagaki*, André Ricardo Ramos, Flávio Luiz Benedito,
Patricio Guillermo Peralta-Zamora, Aldo José Gorgatti Zarbin

Departamento de Química, Universidade Federal do Paraná (UFPR), Caixa Postal 19081, CEP-81531990, Curitiba, Paraná, Brazil

Received 14 May 2001; accepted 12 January 2002

Abstract

In this paper we report the immobilization and characterization of neutral and pentacationic iron porphyrins into the nanometric pores of an inorganic matrix (porous vycor glass, PVG) and the use of these materials as catalyst in mimetic–enzymatic processes. The concentration of iron porphyrin in the large glass pores depends on the conditions present during the incorporation process. The materials obtained were used as catalyst in the oxidation reaction of cyclohexane and cyclohexene by iodosylbenzene. The catalytic results were promising, evidencing adequate characteristics of PVG for immobilization of iron porphyrin and strong potential of these nanocomposites for heterogeneous catalytic procedures. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Porphyrin; Porous glass; Oxidation; Cytochrome P-450; Catalysis

1. Introduction

Inorganic compounds such as silica gel, clays and zeolites have been extensively investigated as matrices for the immobilization of metalloporphyrins. These materials present high stability to oxidative degradation reactions, a fact that allows their use in oxidation processes that mimetize the catalytic cycle of cytochrome P-450 and peroxidase enzymes (e.g. horseradish or lignin peroxidases) [1]. Moreover, the matrix structure can provide a better selectivity for the approach of the substrate into the active sites of the immobilized metallocomplex, where the selective catalytic oxidation takes place [1]. Porous vycor glass (PVG) is an inorganic host matrix that can be

used to produce several nanocomposites with a great variety of materials, like semiconductors, oxides and polymers [2–4]. It is a transparent porous material obtained by acid leaching of a phase-separated alkaline borosilicate glass [5]. The soluble borate phase is dissolved, leaving an open porous structure of essentially pure silica with interconnecting pores of narrow size distribution (between 20 and 200 Å), and a pore volume of nearly 28%. The pore surface contains slightly acidic silanol groups [5]. Chemically, PVG resembles silica gel as they both have hydroxylated surfaces. However, because of the method by which it is manufactured, PVG also possesses B₂O₃ Lewis acid sites [6], although the influence of these sites on the surface chemistry of this material has not yet been described in the literature.

Immobilization of porphyrins in porous glasses has been reported in the literature especially in sol–gel derived materials. These hybrid materials are used as

* Corresponding author. Tel.: +55-41-361-3180;
fax: +55-41-361-3186.
E-mail address: shirley@quimica.ufpr.br (S. Nakagaki).

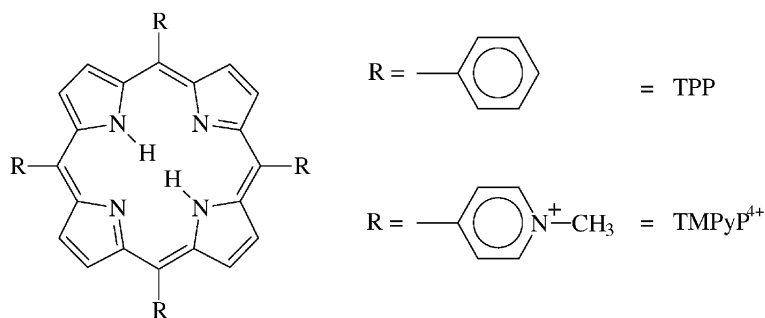


Fig. 1. Structure of porphyrins.

catalysts, non-linear optics materials and sensors [7–9]. In this paper we report the immobilization of traditional metalloporphyrins (Fig. 1) into the nanometric pores of an inorganic matrix (PVG) and the use of these materials as catalyst in mimetic–enzymatic processes [10].

2. Experimental

2.1. Treatment of PVG

Code 7930 PVG was obtained from Corning Glass. Plates of PVG with dimensions of $10 \times 10 \times 1 \text{ mm}^3$ in size were dipped first in a 2 mol l^{-1} HCl solution for 30 min and then in acetone for the same period of time. The glass plates were then heated at 550°C for 72 h, cooled to room temperature and stored in a desiccator prior to use.

2.2. Immobilization of iron porphyrins in PVG

Commercially available porphyrins (TPPH₂: 99% pure, TMPyPH₂ tosylate salt: 97% pure; Fig. 1) were purchased from Aldrich. Iron insertion into the free base porphyrins was carried out by an adaptation of the method described by Adler et al. [11] and purified by chromatographic column [26].

The iron porphyrins (FePor) FeTPPCl (5,10,15,20-tetraphenylporphyrin iron(III) chloride and FeTMPyP-PCl₅ (5,10,15,20-tetrakis(4-*N*-methylpyridyl)porphyrin iron(III) pentachloride) were either incorporated into the PVG plate or into PVG previously powdered to particle sizes below 50 mesh (Table 1). The general procedure used to immobilize iron porphyrins into PVG was the following: (i) The PVG plate previously dried at 80°C in vacuum during 2 h was added to a flask containing 10 ml of a $3.0 \times 10^{-4} \text{ mol l}^{-1}$ solution of iron porphyrin in water (FeTMPyP-PCl₅) or CH₂Cl₂ (FeTPPCl), at controlled temperature. The flask was

Table 1
Iron porphyrin immobilized into the PVG (reaction conditions and obtained products)

FePor	PVG	Sample code	Temperature	Reaction time	PVG/FePor (mol g^{-1})
FeTMPyP-PCl ₅	Plate	PVG/FeTMPyP-1	Room	8 days	7.0×10^{-7}
	Plate	PVG/FeTMPyP-2	Room	17 days	2.0×10^{-6}
	Powder	PVG/FeTMPyP-3	50°C	2.5 h ^a	1.4×10^{-5}
FeTPPCl	Plate	PVG/FeTPP-1	0°C	2.5 h	3.0×10^{-8}
	Plate	PVG/FeTPP-2	0°C	5 days	4.0×10^{-7}
	Powder	PVG/FeTPP-3	40°C	1.0 h ^a	2.8×10^{-6}

^a After the immobilization time of the PVG powder with the iron porphyrin solution under magnetic stirring and appropriated temperature, the suspension was maintained under rest at room temperature during 24 h for PVG/FeTMPyP and 7 days for PVG/FeTPP.

maintained closed during a controlled time. After this, the green-reddish plate was removed from the solution, washed several times with solvent to remove unbound and weakly bound iron porphyrins, and dried for 4 h at 80 °C. The supernatant and the solvents used in this washing process were analyzed to control the concentration of the removed iron porphyrins. (ii) Two hundred milligrams of ground PVG were added to a flask containing an iron porphyrin solution with the same concentration described above at room temperature or at 60 °C during controlled times in a closed flask under magnetic stirring. After this the solid was isolated by centrifugation, washed and dried in a manner similar to the one described for the plate samples.

Different amounts of iron porphyrins in the PVG were obtained as a function of the immersion time, the temperature of the process and the form of PVG used (powder or plate). The immobilization was monitored by UV–Vis spectroscopy. The solids obtained and the respective amount of porphyrin were labeled as illustrated in Table 1.

2.3. Characterization

The PVG/iron porphyrin solids were characterized by UV–Vis, IR and electron paramagnetic resonance (EPR) spectroscopy. UV–Vis spectra were recorded in an HP 8452A Diode Array Spectrophotometer in the 200–800 nm range. Spectra of the powder samples were recorded in a 0.1 cm path length quartz cell (Hellma) using a suspension of the supported catalyst in CCl₄. Spectra of the plate samples were obtained by placing the samples directly in the beam, using air as reference.

Diffuse reflectance infrared spectra (DRIFT) were obtained using a Bomem B-100 spectrophotometer. The samples were powdered and mixed with dried KBr, and the spectra were collected using a Gemini 0008-3XX accessory, over the 4000–400 cm⁻¹ region, with 64 scans and a resolution of 4 cm⁻¹.

EPR measurements of the powder materials were performed with a Bruker ESP 300E spectrometer at X-band (ca. 9.5 GHz) at 293 K.

2.4. Oxidation reactions

Oxidation reactions of cyclohexane and cyclohexene with iodosylbenzene (PhIO) were carried

out in a 2 ml vial with an open top screw cap containing a silicone–Teflon-faced septum. The catalysts (PVG/FeTMPyP-**3** or PVG/FeTPP-**3**) and PhIO (1:5–1:200 FePor:PhIO ratio) were mixed under argon atmosphere at room temperature and then 350 μl of solvent (dichloromethane–DCM, acetonitrile–ACN or DCM–ACN mixture, DCM:ACN 1:1 (v/v)) and 150 μl of substrate (cyclohexane or cyclohexene) were added. The mixture was stirred at room temperature during 1 h in the absence of light. The products were extracted and transferred to a 2 ml flask. The solid was washed with small amounts of solvent followed by stirring and centrifugation. The extraction solvent was transferred to the same 2 ml flask and the washing procedure was repeated until the 2 ml flask was filled. The products were analyzed by gas-chromatography using *n*-octanol as the internal standard. The yields were based on PhIO.

PhIO was obtained through the hydrolysis of iodosylbenzenediacetate [12] and stored in a freezer. The purity was checked by iodometric assay.

3. Results and discussion

3.1. Characterization of materials

The different samples obtained in this study and the amount of porphyrin impregnated in each of them is shown in Table 1. As expected, charged porphyrin FeTMPyP-**3** showed better immobilization into PVG than FeTPP-**3**. The positive charges distributed along the porphyrin ring contributed to the efficient immobilization process. When the contact time of the PVG plate with the iron porphyrin solution was higher, a better immobilization was obtained (compare PVG/FeTMPyP-**1** and **2**). An increase in the amount of immobilized porphyrin was obtained using a mild temperature of 30–50 °C during the process, and powdered PVG rather than PVG plates (PVG/FeTMPyP-**3** and PVG/FeTPP-**3**). However for the FeTPP-**3**, the immobilization process did not proceed after 5 days (PVG/FeTPP-**2**).

Fig. 2 shows the UV–Vis spectra of FeTMPyP-**3** in aqueous solution and after its immobilization in PVG. In Fig. 2a, the aqueous solution of the FeTMPyP porphyrin presents an envelope Soret band at 398 nm (shoulder at 416 nm) and the three

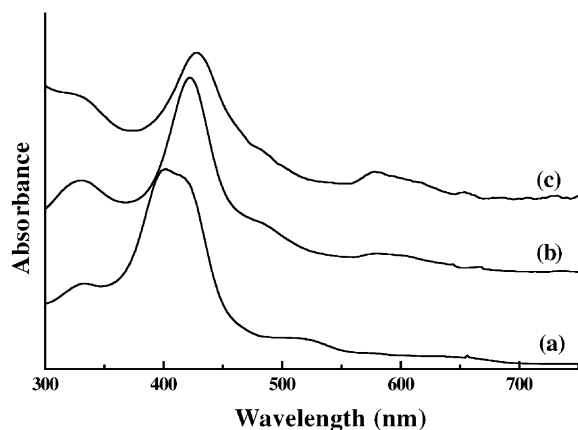


Fig. 2. UV-Vis spectra at room temperature of: (a) aqueous solution of FeTMPyP₅ (qualitative spectrum); (b) plate containing FeTMPyP₅ (PVG/FeTMPyP-2); (c) powder of PVG containing FeTMPyP₅ (PVG/FeTMPyP-3).

typical bands attributed to high spin Fe(III) porphyrin species (500–700 nm) [13]. After the immobilization in PVG a redshift of the Soret band was observed (422–430 nm) together with two new bands at 478 and 580 nm (Fig. 2b and c). A similar redshift was previously reported for Co(II) and Mn(II) porphyrins and other aromatic molecules intercalated in the interlayer space of montmorillonite clay, and for Cu(II) and Fe(III) porphyrins immobilized in the zeolite NaY [14–17]. These observations have been interpreted as the result of the π -interaction between the aromatic ring and the oxygen groups of the aluminosilicates.

The PVG porous surface presents Si–O–H groups, which makes this material a proton-exchanger. This way, cationic species (such as the FeTMPyP⁵⁺ molecules) can be adsorbed into the porous glass without co-adsorption of the anions, by displacement of the slightly acidic silanol protons [5]. Hence, the immobilization of this charged iron porphyrin occurs by the establishment of electrostatic interactions with the Si–O[−] groups present on the surface of PVG. The differences observed in PVG immobilized spectra of the porphyrin, when compared to the aqueous solution spectrum, indicated that the immobilization is accompanied by changes in the coordination of this porphyrin. Kobayashi et al. [18] attributed the band at 580 nm found in the spectrum of the FeTMPOH solution to the iron axial coordination of the oxygen. This

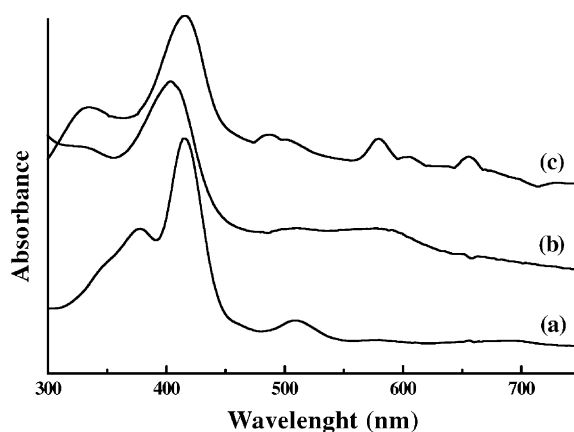


Fig. 3. UV-Vis spectra at room temperature of: (a) DCM solution of FeTPP (qualitative spectrum); (b) plate containing FeTPP (PVG/FeTPP-2); (c) powder of PVG containing FeTPP (PVG/FeTPP-3).

observation was confirmed by Balch and coworkers [19] for the FeTPPOCH₃, Kuwana and Forshey [20] and Nakagaki et al. [21] for FeTMPyPClO₄ in alkaline aqueous solution. Therefore, the presence of the 580 nm band in the spectra of PVG/FeTMPyP suggests the occurrence of axial interactions between the iron porphyrin and the Si–O[−] of PVG pore surfaces.

The UV-Vis spectra of FeTPP in solution and after immobilization are shown in Fig. 3. As can be seen, no significant changes were observed in the UV-Vis spectra of the FeTPP after immobilization (Fig. 3b and c) when compared to the spectrum in DCM solution (Fig. 3a). In contrast with FeTMPyP, the band at 580 nm was not observed after immobilization, which can be interpreted as absence of strong chemical interactions between the immobilized porphyrin and the PVG pore surface. The similarity observed between the electronic spectra of this species adsorbed onto PVG and the corresponding solution spectrum indicates that this porphyrin physisorbs onto the PVG with no changes in its coordination. Similar results have been clearly observed for several other neutral molecules physisorbed onto PVG [2,22].

The occurrence of strong chemical interactions between PVG and FeTMPyP, and the absence of these interactions between PVG and FeTPP, were confirmed by FT-IR spectroscopy. Because of the low concentration of the incorporated porphyrin, the IR

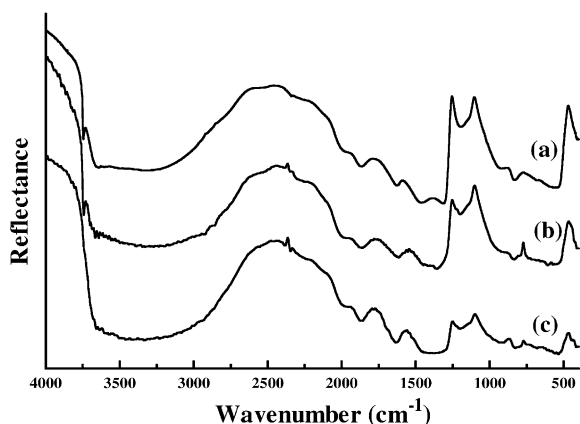


Fig. 4. DRIFT spectra of: (a) PVG; (b) PVG/FeTPP-3; (c) PVG/FeTMPyP-3.

spectra of the samples in KBr disks or Nujol dispersions are strongly dominated by the spectrum of the pure glass. This effect is also observed when the spectra are obtained in the diffuse reflectance mode (DRIFT). However, spectra obtained by this latter mode showed indirect information about the interactions between the PVG and the incorporated porphyrins, which corroborated the data obtained by UV–Vis spectroscopy. Fig. 4 shows the DRIFT spectra of pure PVG (Fig. 4a), PVG/FeTPP-3 (Fig. 4b) and PVG/FeTMPyP-3 (Fig. 4c). The PVG spectrum presents a sharp band at 3745 cm^{-1} attributed to the free O–H stretching of surface silanol groups [4]. When the charged FeTMPyP⁵⁺ was impregnated onto PVG, this band disappears (Fig. 4c) indicating the occurrence of chemical interactions between this porphyrin and the silanol groups of the PVG surface. This effect was not observed in the PVG/FeTPP spectrum (Fig. 4b) confirming that the FeTPP was incorporated into PVG pores without strong chemical interactions.

The EPR spectra of PVG, PVG/FeTPP-3 and PVG/FeTMPyP-3 are shown in Fig. 5. EPR spectra were recorded at room temperature aiming at assigning the iron ion oxidation and the spin states in each case. In examining the EPR spectrum of the pure PVG no signal was observed in the EPR region of $g = 6.0$ (0.0–0.2 T) as can be seen in Fig. 5a. Recently, we observed that EPR spectra of the frozen solution of both iron porphyrins presents the typical signals in the $g_{\parallel} = 6.0$, which is characteristic of

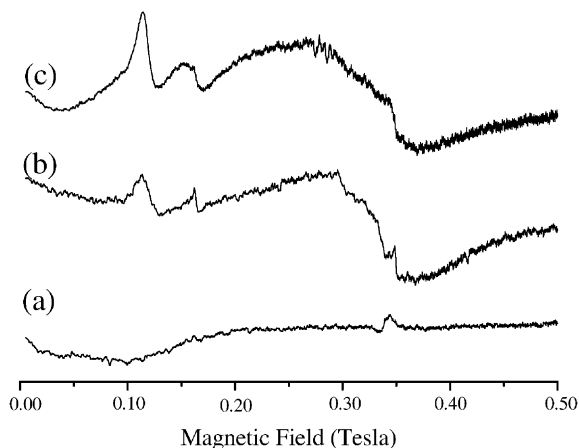


Fig. 5. EPR spectra in X-band at room temperature (298 K) of the solid compounds recorded at microwave frequency = 9.7656 GHz: (a) PVG; (b) PVG/FeTPP-3; (c) PVG/FeTMPyP-3.

high spin iron(III) porphyrins in axial symmetry [23]. After PVG immobilization, the spectra of FeTPP-3 (Fig. 5b) and FeTMPyP-3 (Fig. 5c) showed an extra signal at $g = 4.3$ (beyond the signal at $g = 6.0$). These EPR parameters supported the hypothesis that the iron(III) porphyrins were incorporated into PVG and modified during the encapsulation process probably through the formation of new species with a high rhombicity distortion [14].

3.2. Oxidation reactions of cyclohexane and cyclohexene

Cyclohexane and cyclohexene were used as substrates for the iron porphyrin catalyzed oxidation by PhIO [24]. Therefore, oxidation of these substrates by PhIO was used as a test reaction to compare the catalytic properties of the different PVG supported iron porphyrins obtained in this study. Reaction yields expressed as turnovers and recovery of catalytic products (based on PhIO) are shown in Tables 2 and 3.

It has been observed in the literature that in the presence of iron porphyrins the main products of cyclohexane oxidation are cyclohexanol (C–ol) and cyclohexanone (C–one) and, to the cyclohexene oxidation, a mixture of 2-cyclohexen-oxide (C=oxi), 2-cyclohexen-one (C=one) and 2-cyclohexen-1-ol (C=ol) [24,25].

Table 2

Products from the oxidation reaction of cyclohexane by PhIO using PVG/iron porphyrin catalysis^a

FeP	Sample code	Solvent	C-ol + C-one yield (%) ^b	C-ol/C-one ratio	Turnover ^c
FeTMPyP-3	PVG/FeTMPyP-3	ACN ^d	27	5.7	15
	PVG/FeTMPyP-3	DCM	88	10	24
FeTPP-3	PVG/FeTPP-3	ACN	21	0.3	5
	PVG/FeTPP-3	DCM	29	0.45	5

^a Reactions were carried out under argon, in the dark and yields were based on PhIO, ultrasound stirring for 1 h. [PhIO]/[FeP] = 20. DCM: dichloromethane and ACN: acetonitrile. Yields based on starting PhIO after 1 h reaction at room temperature.

^b C-ol: cyclohexanol and C-one: cyclohexanone.

^c Turnover: (C-ol + C-one)/[catalyst].

^d First cycle of reaction–recovery–reuse in the same reaction condition produced C-ol + C-one yield = 28% with C-ol/C-one ratio = 6 and turnover = 14.

The catalytic activity of the PVG/iron porphyrin materials was investigated only for the compounds named PVG/FeTMPyP-3 and PVG/FeTPP-3 because their higher iron porphyrin concentrations facilitated the formation of reaction intermediate active species. Cyclohexane oxidation reactions performed in ratios of FeP/PhIO greater than 1:100 showed a decrease in alcohol production with the best results obtained under ratios of 1:20. As a result, 1:20 FeP/PhIO ratio was chosen for all oxidation reactions discussed in this work. Reactions were always performed in 1 h because the high porosity of PVG greatly facilitates the diffusion of both reagents through the matrix. We are currently investigating further increases in reaction time in order to determine whether this would have any considerable effect on the catalyst performance. On the other hand, reactions were always carried out at 0 °C in order to have better temperature control since stirring may promote local heating. Magnetic stirring also helped to promote a better contact between the PVG powder and PhIO since the oxidant is poorly soluble in the solvents used herein.

The efficiency of the system, as well as the distribution of the main reaction products, depended primarily on the solvent properties, at least under the standard conditions adopted for this work (Tables 2 and 3) [14].

The use of FeTMPyP and FeTPP catalysis in the oxidation of cyclohexane by PhIO in homogeneous and heterogeneous systems has been investigated by Nakagaki et al. [26], and Leonard and Lindsay-Smith [27] and poor yields have been obtained in optimized conditions. Even for ACN, the best solvent for FeTMPyP, only 20% of cyclohexanol was obtained with an alcohol/ketone ratio of 5. Lower results have been also observed for the FeTPP system [25]. These poor catalytic results and the low solubility of the components used in the reaction mixture (catalysts, oxygen donor and substrate) have been attributed to the absence of electron-withdrawing effects and the steric hindrance introduced by porphyrin ring substituents.

Immobilization of these iron porphyrins seems to be a good strategy to avoid problems found in homogeneous catalysis, mainly those caused by bimolecular

Table 3

Products from the oxidation reaction of cyclohexene by PhIO using PVG/iron porphyrin catalysis^a

FeP	Sample code	Solvent	C=oxi yield (%)	C=one yield (%)	C=ol yield (%)	PhI yield (%)
FeTMPyP-3	PVG/FeTMPyP-3	ACN	19	29	11	81
	PVG/FeTMPyP-3	DCM	34	24	40	74
FeTPP-3	PVG/FeTPP-3	ACN	33	126	39	85
	PVG/FeTPP-3	DCM	10	164	9	90

^a Reactions using the PVG without FeP gave lower yields under identical conditions (<1%). Yields based on starting PhIO after 1 h reaction at room temperature.

interactions between porphyrin rings that could lead to auto-oxidative destruction of the catalyst. In fact, FeTMPyP immobilized on silica gel produced 30% of cyclohexanol during the catalytic oxidation of cyclohexane by PhIO in DCM [26]. The use of PVG is our new strategy to promote catalyst stabilization and substrate selectivity in these types of catalytic reactions.

Cyclohexane oxidation catalyzed by FeTMPyP–PVG (PVG/FeTMPyP-3) and FeTPP–PVG (PVG/FeTPP-3) showed the best alcohol production and selectivity when the reaction was performed in DCM rather than in ACN (Table 2). This is indicative that the non-polar solvent favored the access of the substrate to the active catalytic site due to the immiscibility of cyclohexene in ACN. However, cyclohexane oxidation resulted in significant quantities of ketone and for the PVG/FeTPP catalysis, the ketone concentration was even higher than the alcohol concentration. These observations contradicted some preliminary studies in which iron porphyrin used in homogeneous catalysis presented higher alcohol-to-ketone selectivity when cyclohexane was oxidized in ACN [26]. Our results suggest that the alcohol concentration found inside the hydrophilic glass pores could result in a further substrate oxidation, leading to ketone accumulation and therefore contributing to the poor selectivity we have observed.

The difference observed in the catalytic activity between the PVG/FeTMPyP and PVG/FeTPP can be attributed to different factors:

- (i) FeTPP is a poor stable compound in this kind of catalytic reaction and a large destruction of the catalyst is likely to be observed [25]. Immobilization in inorganic supports like silica gel or modified silica gel has improved its stability.
- (ii) The concentration of FeTPP immobilized in PVG is lower than the concentration of FeTMPyP that contributed to former low quantities of catalytic active species.
- (iii) The difference in linkage of FeTMPyP and FeTPP to the support pore, which directly affects the catalytic activity of these porphyrins.

Epoxydation of cyclohexene produced 10–35% of cyclohexen-oxide with concomitant production of iodobenzene (PhI, $\approx 90\%$) and allylic compounds

(Table 3). It is well documented that, with PhIO, epoxides are the main products of cyclohexene oxidation [28,29]. However, this reaction is complicated by the observation of additional amounts of allylic oxidation products (alcohol and ketone) generated by reaction with dioxygen. This fact usually permits the observation of apparent total yields higher than 100% [28,29]. The PVG contains oxygen absorbed inside the pores, which can be simultaneously consumed in the reaction together with substrate. The removal of the oxygen is a hard process and even though the reaction is carried out under argon, the total absence of oxygen cannot be guaranteed.

PhIO was converted to PhI in all cyclohexene oxidation reactions indicating participation of the PhIO. The amount of PhI was always superior to that of cyclohexen-oxide, suggesting the participation of the PhIO in the oxidative conversion of the substrate to the corresponding alcohol and ketone.

Finally, the release of FeTMPyP from PVG was not observed by UV–Vis analysis of the reaction mixture solution in any of the reactions carried out in this study, indicating that the immobilization process is resistant to the harsh oxidation conditions developed during the catalytic reaction. In contrast, a nearly 10% release of FeTPP was observed as a result of the oxidation reaction.

4. Conclusions

The vycor glass appears to be a very promising matrix for the immobilization of charged and uncharged metalloporphyrins. High concentrations of iron porphyrins can be obtained if ideal immobilization reaction conditions are used with respect to concentration, glass particle size and heating.

The PVG/iron porphyrin systems exhibit a remarkable catalytic activity for the oxidation of cyclohexane and cyclohexene by PhIO. For instance, the catalytic efficiency of the PVG/iron porphyrin systems to cyclohexane oxidation was higher than the efficiency observed to the iron porphyrins in solution (homogeneous catalysis). The stability of the supported catalyst in the reaction conditions used in this study was remarkable. No appreciable amounts of iron porphyrins were observed by the UV–Vis analyses in the reaction supernatant.

Acknowledgements

Our thanks to the Professor Antonio S. Mangrich (LABEPR, DQ/UFPR) for the EPR analysis, to Professor Luiz Pereira Ramos for critically reading the manuscript, LACTEC, CNPq (Proc. 00523308/95-7 and 461683/00-8), PIBIC/CNPq, FUNPAR, UFPR and Fundação Araucaria for the financial support received.

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