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Catalytic oxidation of cyclohexane and cyclooctene over a new metalloporphyrin supported on $VOPO_4$ catalyst

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In this work, we report the use of oxovanadium phosphate as support of the 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin iron (III) chloride (Fe(TDCPP)Cl) and of the 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin manganese (III) chloride (Mn(TDCPP)Cl) catalysts for cyclohexane and cyclooctene oxidations by iodosylbenzene. The catalytic results have shown that oxovanadium phosphate support is suitable for metalloporphyrin catalysts leading to an efficient system for the cyclooctene epoxidation and very selective for cyclohexane hydroxylation.

KEY WORDS: oxovanadium phosphate; metalloporphyrin; epoxidation; cyclooctene.

1. Introduction

Since the pioneering work of Groves *et al.* [1] in which it was demonstrated that a system constituted of synthetic metalloporphyrin and chemical oxidant mimics several oxidation reactions of cytochrome P-450 monooxygenases (P-450), interests in this field have mushroomed. As a consequence, studies involving catalytic oxidation mediated by metalloporphyrins have been increased in many areas such as in the conversion of both saturated and unsaturated hydrocarbons to valuable fine chemicals and oxidation of drugs and pollutants [2–4]. In addition, most of these studies have been carried out in homogeneous catalytic medium involving several variants such as metal ion, porphyrin, substrate and solvent. However, homogeneous catalysts are inclined to an easy deactivation and are difficult to be recovered from the reaction mixtures, leading to many restrictions in large-scale process. Besides, transition metal complexes such as metalloporphyrins are often expensive to purchase, synthesize and/or manipulate. As a result, heterogeneous catalysis has been focused as a strategy to overcome these problems [5–8]. Nevertheless, catalyst leaching during the course of a reaction, lack of accessibility of the active sites and mass transport limitations are examples of disadvantages that must be further investigated. Thus, much work has been devoted to development of solid supports to immobilization of metalloporphyrins such as silica networks, cross-linked polymers, clays and layered materials [5–8]. In this context, herein we report for the first time the utilization of oxovanadium phosphate as support for metalloporphyrins with the aim to get more selective and reusable catalytic systems for hydrocarbon oxidations. The tetraarylmetalloporphyrins, especially iron and manganese complexes with chloro substituents, were chosen because they are commercially available and have been extensively investigated as catalysts in oxidation reactions.

2. Experimental

All compounds used in this study were commercially available from Aldrich, Mallinckrodt or Merck of analytical grade purity or HPLC unless otherwise stated. The free base 5,10,15,20-tetrakis(2,6-dichlorophenyl) porphyrin was purchased from MidCentury and used as received. The Z-cyclooctene was purified immediately before use through chromatography using activated alumina column (Merck). Iodosylbenzene (97%) was prepared as described previously [9]. Water was purified using a Millipore Milli-Q System.

UV/Vis spectra were obtained with a Hewlett-Packard 8452 diode array spectrometer. The spectra were recorded in 10-mm path length quartz cells (Hellma). GC analysis was performed on a Varian 3400 CX chromatograph with a hydrogen flame ionization detector using a DB-wax (1 μm thickness) megabore column (30 m $\times$ 0.538 mm). Nitrogen was used as the carrier gas. The results were recorded and processed on a Varian workstation. Fourier-transform infrared spectra (FTIR) were recorded from 4000 cm^{-1} to 400 cm^{-1} on a Bomem MB 100 spectrometer and the samples were dispersed in KBr and pressed into pellets.

The matrix $VOPO_4 \cdot 1.2H_2O$ was prepared in accordance with literature [10], through the reaction of V_2O_5 with concentrated H_3PO_4 in purified water. The green crystalline solid obtained from this reaction was isolated by filtration, washed with acetone and vacuum dried.

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The solid was characterized by infrared spectroscopy and powder X-ray diffraction. The metalloporphyrins Fe(TDCPP)Cl and Mn(TDCPP)Cl were obtained by metallation of the free ligand H_2(TDCPP) following the method described in the literature [11,12].

The 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin iron (III) chloride, (Fe(TDCPP)Cl) and 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin manganese (III) chloride, (Mn(TDCPP)Cl) were immobilized by refluxing the metalloporphyrin (3.34×10^{-7} mol) in dichloromethane with oxovanadium phosphate matrix (20 mg) during 24 h. The resulting green solid was filtered and vacuum dried given a 1.64×10^{-5} mol of catalyst/g of support.

In a typical oxidation reaction, the immobilized metallophorphyrin (2.0×10^{-7} mol, 12 mg of solid) was stirred with the substrate (5.0×10^{-4} mol) in dichloroethane (1.5 cm^3) and the reaction was initiated by the addition of iodosylbenzene (3.0×10^{-5} mol) (the molar ratio was: 1:120:2000 of catalyst:oxidant:substrate). For reactions with homogeneous Mn(TDCPP)Cl, imidazole was added as co-catalyst (the molar ratio was 1:30:120:2000 of catalyst:cocatalyst:oxidant:substrate). After 24 h, the internal standard (bromobenzene) was added and the products were analyzed by GC analysis. All the reactions were carried out at room temperature with magnetic stirring. Control reactions were carried out in the same conditions with the matrix without metalloporphyrin. The supernatant of reaction was isolated and analyzed by UV/Vis in order to verify the leaching of the metalloporphyrin during reaction.

3. Results and discussion

The Fe(TDCPP)Cl and Mn(TDCPP)Cl metalloporphyrins were successfully supported on the $VOPO_4$ matrix as shown by the UV/Vis spectra of a suspension of the material in chloroform. The spectra present the characteristic Soret bands of these metalloporphyrins at 416 and 478 nm, respectively, as shown in figure 1 [13]. The presence of the unchanged Soret bands indicates that the complexes were immobilized on the structure of the support without any distortion of the porphyrin ring as is usual when metalloporphyrin are immobilized on solid supports [14–17]. The bands at 581 and 660 nm are normally present in spectra of all supported metalloporphyins [14,15,17] and can be attributed to the solid effects. In addition, the spectra of the filtrates isolated from the reaction mixtures did not show any band related to metalloporphyrin indicating no leaching of the complex from the support during reaction.

The FTIR spectra of the catalysts are dominated by the support's vibrational bands [18,19] shown in table 1. One can observe shifts of some bands of the supported catalysts in relation to the free support, suggesting that although the overall framework is preserved after the immobilization, there is an electrostatic interaction between the support and metalloporphyrin, involving a negative superficial density charge of the support and the positive complex. In addition, it should be noted that two bands around 3400 and 1600 cm^{-1} can be ascribed to vibrational modes related to water molecules.

To investigate the catalytic activities of hybrid inorganic-organic metalloporphyrin immobilized on oxovanadium phosphate, preliminary experiments involving oxidation of Z-cyclooctene and cyclohexane using PhIO as oxygen transfer agent were performed. The results are shown in table 2, including the homogeneous catalysts for comparison. The oxidation of cyclooctene by PhIO using Fe(TDCPP)Cl as catalyst in homogeneous medium led to a yield of 83% of epoxide, whereas under identical conditions FeP–$VOPO_4$ led to a yield of 94% (table 2). These results evidence the efficiency of this supported catalyst when compared with analog systems reported in literature [14–18]. For the cyclohexane, which is less reactive, the efficiency of the

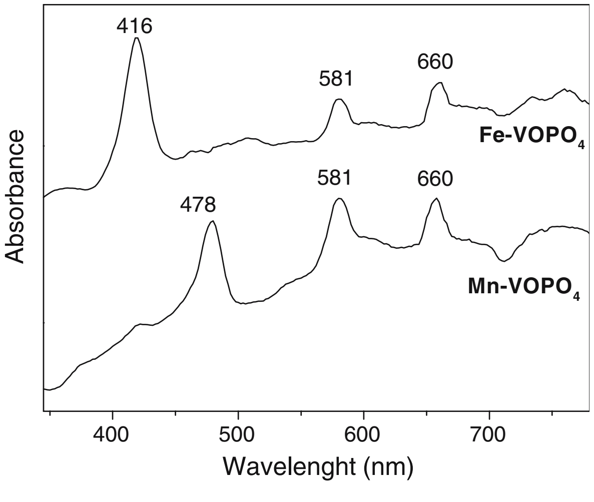

Figure 1. UV/Vis spectra of a chloroform suspension of the metalloporphyrins immobilized to $VOPO_4$ matrix.

Table 1
Main vibration modes of the solid catalysts and $VOPO_4$ matrix

Vibrational modes	$VOPO_4$	Fe–$VOPO_4$	Mn–$VOPO_4$
ν (V=O)	994(s)	980(s)	979(s)
ν (V-OH)	946	950	951
ν (P–O)	1090	1088	1086
δ (V–O–P)	678	678	678
δ (O–P–O)	571	571	571
ν (H–O)	3403	3428	3412
δ (H–O)	1623	1626	1626

(s): shoulder.

Table 2
Product yields from the oxidation of cyclooctene and cyclohexane by PhIO catalyzed by homogeneous and supported metalloporphyrins, in dichloroethane solution

Catalyst	Product yields (%)[a]		
	Cyclooctenoxide	Cyclohexanol	Cyclohexanona
Fe(TDCPP)Cl	83	32	7
FeP–$VOPO_4$	94	12	nd
Mn(TDCPP)Cl	75	37	6
MnP–$VOPO_4$	47	10	nd
$VOPO_4$	13	nd	nd

[a] Based on PhIO after 24 h; nd, not detected.

supported ironporphyrin is lower than that of the homogeneous catalyst (table 2). This is probably due to the polar effect of the support, which disfavors the interaction of the catalyst with more non-polar substrate. In addition, the low activity of the cyclohexane reaction may be due to the difficulty to access the active sites on the supported catalyst. Moreover, this difference in reactivity might also be related to the slow diffusion of oxidant and substrate to and from the catalyst on the support surface [17]. However, the FeP–$VOPO_4$ was selective to hydroxylation of cyclohexane. This observed selectivity indicates the same classical mechanism as in homogeneous system, involving the high-valent oxo-iron(IV) porphyrin π-cation radical, ($Fe^{IV}(O)P^{\cdot +}$), as catalytic species [3].

Preliminary experiments using MnP–$VOPO_4$ catalyst for the oxidation of cyclooctene and cyclohexane by PhIO led to good yields of the cyclooctane epoxide (47%) and cyclohexanol (10%) under the same conditions as mentioned above. The yields obtained with MnP-$VOPO_4$ are lower than those from homogeneous catalysis (table 2). Probably these low yields can be attributed to the stabilization of the intermediate oxo-manganese(IV) porphyrin, (P)Mn^{IV}(O), on the support, which is not efficient to transfer the oxygen atom to epoxide.

The hybrid inorganic-organic catalyst appeared to be stable under experimental conditions and could be easily recovered by simple filtration from reactional medium. In addition, the leaching of the metalloporphyrin during the reaction was not verified, evidencing a strong interaction between $VOPO_4$ and the metalloporphyrins. Moreover, it should be noted that the inorganic matrix has poor reactivity (yields ~13% for epoxidation and non-reactive for hydroxylation). Therefore, it appears that a synergic effect occurs between the two component resulting in good yield and selectivity.

4. Conclusions

This report describes a new catalyst based on immobilization of a metalloporphyrin on an oxophosphate vanadyl solid support, which is stable and easy to prepare. The catalytic results showed that supported metalloporphyrins are efficient in the cyclooctene epoxidation and very selective for cyclohexane hydroxylation, mainly the ironporphyrin. In addition, the reaction is faster when compared with other analog systems. The nature of interactions between the solid support and metallic complexes and the mechanism of the reactions is not understood and further experiments are necessary in order to investigate the catalytic species and to explore the catalytic potentiality of these systems.

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