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Porphyrinosilica and Metalloporphyrinosilica: Hybrid Organic-Inorganic Materials prepared by Sol-Gel Processing

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ABSTRACT

New materials porphyrinosilica and metalloporphyrinosilica template have been obtained by a sol-gel processing where functionalized porphyrins and metalloporphyrins "building blocks" were assembled into a three-dimensional silicate network. The optimized conditions for preparation of these materials are revised. The monomer precursors porphyrinopropylsilyl and metalloporphyrinopropylsilyl preparation reactions and subsequent one pot sol-gel processing with tetraethoxysilane are discussed. In the case of metalloporphyrins the nitrogen base coordinates to the central metal and acts as a template in the molecular imprinting technique. UV-visible absorption spectroscopy, thermogravimetric analysis, electron paramagnetic resonance, nuclear magnetic spectra, infrared spectra, luminescence spectra, surface area and electron spectroscopy imaging of the materials are used to characterize the prepared materials. The catalytic activities of these metalloporphyrinosilica- template are compared.

Key words: metalloporphyrin silica, sol-gel, catalysis, hybrid material.

INTRODUCTION

Developments in the last decades in sol-gel method resulted in new ceramic materials with high purity, unique structures, microstructures and compositions (Brinker & Scherer 1990, Shea *et al.* 1992, Buckley & Greenblatt 1994, Corriu & Leclercq 1996). The explosion of literature in this interdisciplinary field led to the statement of a new area known as "sol-gel science" and the physical and chemical principles of sol-gel processing have been described (Brinker & Scherer 1990). The solid morphology is probably the result of several directing factors. The nature

and the structure of the precursor as well as the experimental conditions (solvent, concentration, temperature, etc), which may influence the kinetics of hydrolysis and the polycondensation steps are probably important parameters (Corriu *et al.* 1992). The great versatility in way of preparations and the various forms of resulting materials as monoliths, thin films, powders and fibers (Livage 1994, Avnir 1995) open many applications in optics, photonics, sensors and coatings (Mark 1995, Dave *et al.* 1994).

Silicate glasses obtained by the mild sol-gel processing may provide a good host matrix for enzymes and others proteins immobilization. The major advantages of encapsulated proteins are close control of the reaction medium and conditions, pre-

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vention of chemical degradation, cost-effective recycling of the protein, and enhanced biomolecular stability (Dave *et al.* 1994, Gill & Ballesteros 1998, Hüsing *et al.* 1999).

New materials have been “engineered” at molecular level assembling molecular sized building blocks into a three-dimensional network (Shea *et al.* 1992). In this approach porphyrins or metalloporphyrins (MP, $M = 2H^+$, Fe^{3+} or Mn^{3+}) can be inserted into silicate network.

Several systems based on Fe^{III} - and Mn^{III} -porphyrins associated with different oxygen atom donors are able to mimic cytochrome P450-dependent monooxygenases (Meunier 1992, Mansuy & Battioni 1994, Groves & Han 1995, Lindsay Smith 1994, Iamamoto *et al.* 1994, Assis & Lindsay Smith 1998, Prado-Manso *et al.* 1999). In order to construct a selective P-450 model, a new class of hybrid organic-inorganic material, the metalloporphyrinosilica (MPS), have been prepared by a sol-gel process, where the MP is part of the matrix (Battioni *et al.* 1996, Ciuffi *et al.* 1999). A convenient system can be created using the hybrid material MPS ($M = Fe^{3+}$ or Mn^{3+}) where the M is coordinated to N-substituted nitrogen bases (Battioni *et al.* 1996, Ciuffi *et al.* 1999). The base can act as a template molecule in the molecular imprinting technique, creating a polymeric substance containing specific binding sites as receptor in enzyme models (MPS-template). Thus, the molecular imprinting technique can lead to the formation of materials containing molecular cavities regularly spaced, generating heterogeneous catalysts with specific microstructural properties, such as porosity and surface area (Bystrom *et al.* 1993).

These new materials, with specific surface area and controlled microstructural properties, can catalyze shape-selective hydroxylation of alkanes (Battioni *et al.* 1996).

SYNTHESES OF PORPHYRINOSILICA AND METALLOPORPHYRINOSILICA

These syntheses were carried out by a one-pot reaction, where monomer precursors porphyrinopropyl-

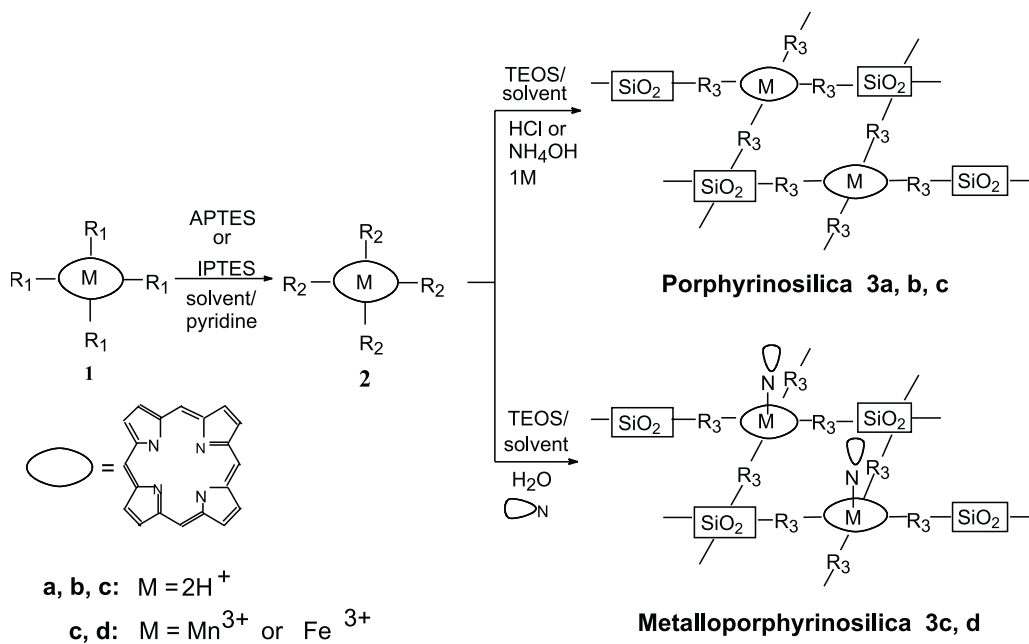
isilyl species (Fig. 1, species 2) are formed and then hydrolysed and condensed with TEOS through a sol-gel processing.

MONOMER PRECURSORS

The reaction between reactive R_1 groups present in the porphyrin ring (Fig. 1, species 1) with 3-aminopropyltriethoxysilane (APTES) or with 3-isocyanatopropyl-triethoxysilane (IPTES) in the case of **1a**, allows the preparation of the monomer precursors porphyrinopropylsilyl (Fig. 1, species 2). During this process, urea, amide, sulfonamide or amine linkages are formed. The solvent and temperature of reactions are determined by the reactivity of R_1 in the porphyrin ring and the kind of linkage formed. For example, $-SO_2Cl$ or $-COCl$ groups are very reactive and do not require high temperatures to form the corresponding sulfonamide or amide bond when the porphyrins react with APTES (**2b**, **2c**) and DCM can be used as solvent, while nucleophilic substitution of the p-F atoms in the aromatic ring (**2d**) requires higher temperatures (Battioni *et al.* 1996) and DMF should be used as solvent. It is important that no APTES group remains unreacted in the mixture to avoid additional isolation and purification step of monomer species **2**. Pyridine is the most effective nitrogen base to catalyze monomer **2** formation (Sacco 1999). The formation of the monomer **2** species can be confirmed through IR spectra, where we can observe the characteristic stretching of urea, amide and sulfonamide groups (Biazzotto *et al.* 1999).

SOL-GEL PROCESSING

The sol-gel polymerization process involves the hydrolysis of monomers **2** and TEOS in the presence of water to the corresponding silanols, which then condense with each other to generate siloxane bonds (Shea *et al.* 1992). In this process, pyridine or N-substituted nitrogen base in excess act as a base catalyst, while HCl acts as an acid catalyst. The mixture becomes viscous and gels within two days when HCl or imidazole are used as catalyst and within fourteen days when pyridine or N-substituted nitrogen base



1	R_1	2	R_2	3	R_3
a		a		a	
b		b		b	
c		c		c	
d		d		d	

Fig. 1 – Synthesis of MPS. Template =

are used as catalyst. The evaporation of the solvent leads to a dry solid MPS ($M = 2H^+$, Fe^{3+} or Mn^{3+}) **3** (xerogel). During the transformation to the xerogel state, most of the liquid in the pores has evaporated (Brinker & Scherer 1990), and the collapse of the pores leads to a considerable shrinkage. The xerogel formed is in general $\approx 10\%$ of both the original volume and weight. The amount of porphyrin that did not polymerize was determined through UV-Vis spectra of the combined washing liquids of xerogels **3**. Porphyrin loading onto **3** varied between 1% and 18% (m/m).

The one-pot procedure used to obtain these MPS involves mild conditions and does not require the monomer isolation. The procedure related in literature to prepare the MPS material (Battioni *et al.* 1996) involves the treatment of the resulting polysilylsesquioxanes with HF in order to isolate the monomer porphyrinotrifluorosilane. We observed that the use of HF in preparations of perhalogenated FeP monomer precursor led to the destruction of porphyrin, while the use of MnP yielded the metal free porphyrin.

PORPHYRINOSILICA PROPERTIES

ABSORPTION AND LUMINESCENCE SPECTROSCOPY

These methods are carried out to verify the properties of the free-base porphyrins after its grafting into the silica. The absorption spectra of the H_2PS **3a-c** are corresponding to those porphyrins, H_2PS **1a-c** in solution, with the Soret bands in the same region. The emission spectra of the H_2PS have bands at 650 nm and 715 nm, also similar to those porphyrins in solution. These results indicate that the porphyrin rings were not modified during the polymer preparation confirming that their properties have been retained and the porphyrin are really present in the silica matrix (Biazzotto *et al.* 1999, Biazzotto *et al.* submitted).

CP MAS ^{29}Si NMR SPECTROSCOPY

This technique was used to examine the degree of network condensation in H_2PS **3a**, prepared with different solvents (EtOH or DMF) and catalysts

(HCl or NH_4OH 1M). Q peaks represents a quaternary oxygen tetrahedron and the superscripts denote the numbers of alkoxide or Si-OH groups that have reacted to form Si-O-Si linkages (Suratwala *et al.* 1998). The chemical shifts of the Q peaks were identified by their relative positions and by assigned peak values from the literature (Engelhardt & Michel 1987). The ^{29}Si NMR spectrum of **3a** synthesized using EtOH/HCl condition shows only peaks Q^3 with chemical shift in -102.6 ppm and Q^4 in -112.7 ppm; also in DMF/ NH_4OH condition shows only Q^3 (-97.2 ppm) and Q^4 (-106.4 ppm). Quantitative analysis of the Q species is elaborate. The raw data from the CP technique reveal that the ratio Q^4/Q^3 is 0.37 for **3a** using DMF/ NH_4OH and 0.54 using EtOH/HCl indicating for this last condition a greater degree of polycondensation and extent of network formation (Biazzotto *et al.* 1999).

METALLOPORPHYRINOSILICA PROPERTIES

The MPS (where $M = Fe^{3+}$ or Mn^{3+}) material exhibits the characteristic pattern of the corresponding metalloporphyrin in solution in their diverse oxidation states, indicating that the structure of MP were preserved in the xerogel matrix.

FEPS(3)-TEMPLATE

UV-Vis spectroscopy of FeP provides information on the spin and oxidation state of the iron atom from the Soret peak (typically near 400 nm) and the less intense α and β bands (between 500 and 700 nm). Although the Soret peaks of FeP present in FePS(**3**)-template were clearly visible, the α and β bands could not be assigned, due the presence of UV-Vis silica bands. The Soret band of FePS(**3c** and **3d**)-pyridine and FePS(**3c** and **3d**)-4-phenylimidazole are similar to that of $Fe^{III}P$ in solution. EPR spectra shows that in the FePS(**3d**)-pyridine, Fe^{III} is in high spin state, with typical g value at ~ 6 (Palmer 1974), while in general, in the FePS(**3**)-N- substituted nitrogen base the Fe^{III} is in the hexacoordinated, low-spin state, with g components at 2.9, 2.3 and 1.8. Template removal of FePS(**3**)-N-substituted nitrogen base can be achieved through Soxhlet extraction

using dichloromethane acidified with HCl (Ciuffi *et al.* 1999). The EPR spectra of the iron(III) porphyrinosilica after template removal is typical of high-spin Fe(III) species, with components at $g = 5.9$ and 2.0 .

UV-Vis spectra of FePS(3d)-imidazole presents Soret band red shifted when compared to that of Fe^{III}P in solution. It is documented that with some ligands as imidazole, the reduction of Fe^{III}P to a low spin hexacoordinated Fe^{II}P can occur (Tsang & Sawyer 1990). This iron (II) complex have a red shifted Soret peak (Cooke *et al.* 1995), as is observed in our FePS(3d)-imidazole sample. Besides that, FePS(3d)-imidazole is EPR silent, as is expected for Fe^{II}P species (Palmer 1974). The reduction of iron in FePS(3d)-imidazole is favored by the electron-withdrawing pentafluorophenyl groups (Cooke *et al.* 1995).

MnPS(3)-TEMPLATE

The presence of Soret band of MnP is clear in the UV-Vis spectra of all MnPS(3)-template. MnPS(3c)-template presents the Soret band similar to that of the parent Mn^{III}P solution in the presence of template, while in MnPS(3d)-template the Soret peak are blue shifted when compared with the corresponding Mn^{III}P solution in the presence of template. The region where the Soret peaks of MnPS(3d)-template appear (between 414 and 426 nm) is very similar to that of Mn^{II}P (Ozette *et al.* 1998). We argue that the MnTFPP in the presence of nitrogen base in excess leads to the formation of Mn^{II}P complex as was observed before for the corresponding FeP complex (Cooke *et al.* 1995).

EPR spectra of MPS(3c)-template, present a sharp signal at $g = 2.006$. This signal has been assigned in the literature to the dangling bonds of the radical sites present in the xerogel. The Si—Si• radical sites are created by breaking weak Si—Si bonds (Dhas *et al.* 1998).

SURFACE AREA

The preparation of MPS by sol-gel process using the molecular imprinting technique allowed us to obtain

hybrid materials with different surface area (Table I). All MPS-template exhibit specific surface area between 19 and 674 m²/g.

ELECTRON SPECTROSCOPY IMAGE (ESI)

The ESI technique gives the elemental distribution imaging (Cardoso *et al.* 1998) and was used to study the solid morphology of MnPS(3c)-4-phenylimidazole (Sacco *et al.* submitted) and FePS(3d)-pyridine (Ciuffi *et al.* submitted). The image of MnPS(3c)-4-phenylimidazole reveals the presence of crystalline particles, while for FePS(3d)-pyridine presents a non crystalline microstructure. In both materials, silicon and manganese are uniformly distributed in the network, as expected for covalently bounded metalloporphyrinosilica.

CATALYTIC ACTIVITY OF MPS-TEMPLATE

The catalytic activity of MnPS-template were compared with that of FePS-template (Table I). All MPS can catalyze the epoxidation of cyclooctene, using PhIO as oxygen donor. The system generates a high-valent metal-oxo porphyrin complex. This metal-oxo porphyrin complex species can mimic the catalytic activity of cytochrome P450, which transfer the oxygen atom to an organic substrate. In general the reactions were completed after 24 hours with high yields. The lower catalytic activity of MnPS(3d)-template is due to the reduction of Mn^{III}P complexes to Mn^{II}P complexes, caused by the presence of a high concentration of nitrogen bases in the xerogel preparation. No leaching of MP from MPS 3c and 3d was observed during the epoxidation reactions, confirmed by the UV-Vis spectrum of the filtered reaction mixture. When the filtrate was used in the second oxidation (without catalyst) further epoxidation was negligible. In the cyclooctene epoxidation no correlation between the surface area or solid morphology of MPS and the catalytic activity was observed.

The catalytic activities of MPS 3c and 3d were compared to the respective MP in solution in the (Z)-cyclooctene epoxidation (Table I). The rate of epoxidation with homogeneous MP is faster than

TABLE I
Catalytic activity of MePS-template in the oxidation of
(Z)-cyclooctene using PhIO as oxygen donor

Catalyst	Porphyrin Loading (m/m)	Surface Area (m ² /g)	Cyclooctene oxide yield (%)	
			1 hour	24 hour
Mn(TDCSO ₂ ClPP)Cl ^a	—	—	70	70
MnPS(3c)-Py ^a	18	66	35	96
MnPS(3c)-4-Phim ^a	5	674	20	69
Mn(TFPP)Cl ^b	—	—	84	84
MnPS(3d)-Py ^b	3	132	0	34
MnPS(3d)-4-Phim ^b	2	159	7	30
FePS(3c)-Py ^a	9	19	97	100
FePS(3c)-4-Phim ^a	9	85	13	100
Fe(TFPP)Cl ^b	—	—	89	89
FePS(3d)-Py ^b	3	142	43	85
FePS(3d)-4-Phim ^b	2	141	14	50

^a(Sacco, 1999) and ^b(Ciuffi et al., submitted). Py. = pyridine. 4-Phim. = 4-phenylimidazole.

that obtained with MPS systems. It was observed before that the epoxidation of (Z)- cyclooctene was ten times faster in FeP homogeneous system than in the modified silica supported system (Lindsay Smith 1994). The difference in reactions rates can be attributed to the presence of the silica matrix, which makes difficult the approach of the substrate to the catalyst active site and may slow down the diffusion of product epoxide into the reaction medium.

CONCLUSIONS

The nature of functionalized MP “building blocks” allowed to construct a new hybrid organic-inorganic materials, where MP are inserted covalently in a silica matrix, obtained by sol-gel processing in one-pot reaction. The molecular imprinting technique is proven to be useful for the synthesis of heterogeneous catalysts with controlled architectures via templating routes.

In general high yields in epoxidation are observed with MPS-template as expected for cytochrome P450 model. Conditions in which the metal centers are reduced to Fe^{II}PS-template or Mn^{II}PS-template decrease the catalytic efficiency.

Up to now, with MPS-template studied was not observed surface area or solid morphology effect on the catalytic activity. The MPS-template show the advantage that no MP leach from matrix. The use of these new materials as catalysts is very promising.

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