



# An immobilized imidazolyl manganese porphyrin for the oxidation of olefins



Rodrigo De Paula<sup>1</sup>, Isabel C.M.S. Santos, Mário M.Q. Simões, M. Graça P.M.S. Neves\*, José A.S. Cavaleiro\*\*

QOPNA, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

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## ABSTRACT

A new catalytic system based on an immobilized imidazolyl manganese porphyrin for the oxidation of olefins is presented. Merrifield resin (MR) and functionalized silica gel (SG) were chosen as supports. The results indicate that the MR system shows high reaction rates, high efficiency with hydrogen peroxide as oxidant and good recyclability up to four times, without a dramatic loss in the catalytic efficiency. The catalytic behavior seems to be strongly influenced by the immobilization reaction conditions. The oxidation reactions performed for *cis*-cyclooctene, styrene, cyclohexene and geraniol give the corresponding epoxides, with very high selectivity, when the MR system is used. Some considerations concerning the high efficiency of the MR system are put forward.

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## 1. Introduction

Metalloporphyrins are widely used as catalysts in oxidation reactions [1–3], mimicking the natural functions performed by cytochrome P450 monooxygenase enzymes [4–7]. The natural system is constituted by an iron porphyrin surrounded by proteins which is capable of selectively catalyze the oxidation and, in particular, the epoxidation of a wide range of substrates [8–10]. Iron is the “workhorse” in many biological processes and, concerning the *monooxygenases*, iron drives the oxidation of many substrates by mechanistic routes involving a hypervalent oxo-species [9,11–18]. Like iron, manganese also forms a high-valent oxo intermediate that can promote the oxidation of many substrates [19–21], and manganese complexes are often preferred for biomimetic *in vitro* catalysis, due to their higher activity [9,10].

There are a lot of reports concerning metalloporphyrins catalyzed oxidation under homogeneous conditions [9,10,21–34]. However, the synthesis of metalloporphyrins is a challenging task

and usually a low yielding process. Also the known instability of these catalysts towards oxidative degradation and the difficulty in their recovery can limit the putative practical applications of metalloporphyrins as catalysts in both laboratory synthetic chemistry and industrial processes. On the other hand, immobilization of metalloporphyrin complexes on solid supports can provide catalysts easier to handle, that may exhibit improved selectivity and activity due to the support environment [35–40]. To date, different approaches have been developed for the design of heterogeneous metalloporphyrin catalysts, including: (i) electrostatic binding of charged porphyrins to counter-charged supports; (ii) intercalation or entrapment of porphyrins between the layers of clays or within the pores or matrices of solids; (iii) axial anchoring to surface-bound ligands; and (iv) covalent binding to appropriate supports. Recently, our group was able to develop two immobilized systems, one using a manganese complex of 5,10,15,20-tetrakis(2,6-dichlorophenyl) porphyrin [41] and the other based on the corresponding chlorin [42].

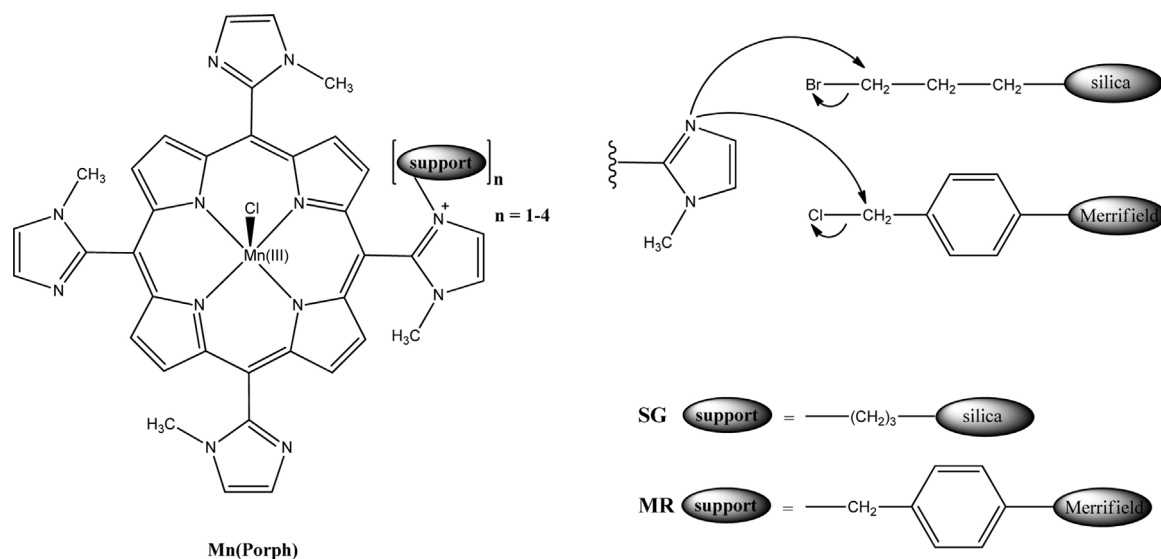
Differently from the well-studied *meso*-phenyl substituted porphyrins, we have recently published the use of an imidazolium-based tetracationic manganese porphyrin as catalyst under homogeneous conditions [12,24]. The neutral parent of that catalyst, the manganese complex of 5,10,15,20-tetrakis(1-methylimidazol-2-yl)-21*H*,23*H*-porphyrin [Mn(Porph)] did not exhibit a great catalytic activity in homogeneous media; however, when linked to a solid support, a great improvement is observed. This paper

\* Corresponding author. Tel.: +351 234 370 710; fax: +351 234 370 084.

\*\* Corresponding author. Tel.: +351 234 370 717; fax: +351 234 370 084.

E-mail addresses: [gneves@ua.pt](mailto:gneves@ua.pt) (M.G.P.M.S. Neves), [jcavaleiro@ua.pt](mailto:jcavaleiro@ua.pt) (J.A.S. Cavaleiro).

<sup>1</sup> Present address: Universidade Federal do Recôncavo da Bahia – Centro de Formação de Professores, 45.300-000 Amargosa/BA, Brazil. Tel.: +55 75 3634 3042; fax: +55 75 3634 3703.



**Fig. 1.** Structure of the immobilized manganese porphyrin (Mn(Porph)). The supports are a functionalized silica (3-bromopropylfunctionalized silica gel) and a Merrifield resin (SG and MR, respectively).

deals with the experimental results obtained for the imidazolyl-based manganese porphyrin covalently bound to two distinct solid supports, the 3-bromopropylfunctionalized silica gel and the Merrifield resin (Fig. 1) in the epoxidation of *cis*-cyclooctene. This support selection was based on the fact that the 3-bromopropylsilica and the Merrifield resin allow, by a simple nucleophilic substitution reaction, to covalently anchor the metalloporphyrin, instead of other systems where the immobilization lies on support/metal interactions or through support/macrocycle electrostatic interactions.

The most promising Mn(Porph)-MR heterogeneous catalyst was also tested for styrene, cyclohexene and geraniol oxidation and the results are also presented here.

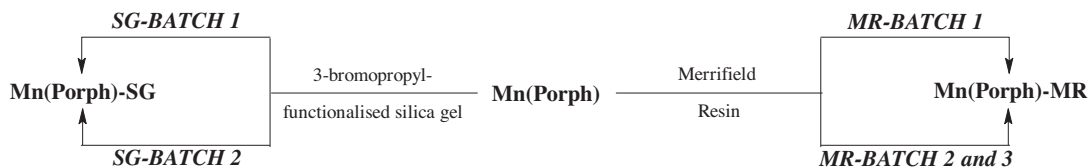
## 2. Results and discussion

### 2.1. Synthesis and characterization

Some previous results showed that the neutral manganese(III) complex of 5,10,15,20-tetrakis(1-methylimidazol-2-yl)-21H,23H-porphyrin has extremely low catalytic activity [11]. However, once positively charged, its activity changes dramatically reaching high conversion and high selectivity to epoxide for many olefins [24]. In this way, we have decided to attach the metalloporphyrin into a solid support, in order to obtain a positively

charged and immobilized material, simultaneously. The different experimental procedures used to immobilize the Mn(Porph) in the two supports selected, the Merrifield resin (MR) and the 3-bromopropylfunctionalized silica gel (SG), are summarized in Scheme 1; these conditions were adapted from a procedure reported by Tangestaninejad and co-workers [36,43].

For the Merrifield resin based heterogeneous catalyst [Mn(Porph)-MR], two different conditions were used being the principal difference the temperature of the immobilization. In the first procedure, designed by MR-Batch 1, the MR was added to a DMF solution of Mn(TMImP)Cl and the reaction was left at 80 °C under strong stirring for 2 days in an inert atmosphere (N<sub>2</sub>), plus 24 h at r.t. before filtration. Under these conditions, the experimental loading obtained was 0.75% far from the maximum expected one, 4.78% (w/w) if all the metalloporphyrin added was incorporated into the solid. In the second procedure (MR-Batch 2), aiming to improve the load of catalyst, the ratio catalyst/MR was slightly increased to 6.6% (w/w) and the immobilization was performed at 150 °C. After 4 h under N<sub>2</sub>, a control showed that almost no free porphyrin was present, and the reaction was terminated as in the previous procedure. Under these conditions the porphyrin loading was really improved to 4.8%. MR-Batch 3 with the same loading of 4.8% was obtained under similar conditions of MR-Batch-2 which confirmed the reproducibility of the immobilization conditions.



**BATCH 1:** 16.5 mg ( $2.29 \times 10^{-5}$  mol) of Mn(Porph), 295.5 mg of SG, 153 °C, DMF, N<sub>2(g)</sub>, 4 hours.

**BATCH 2:** 15.1 mg ( $2.10 \times 10^{-5}$  mol) of Mn(Porph), 405.5 mg of SG, 153 °C, DMF, N<sub>2(g)</sub>, 4 hours.

**BATCH 1:** (1) 25.2 mg ( $3.50 \times 10^{-5}$  mol) of Mn(Porph), 502.6 mg of MR, 80 °C, DMF, N<sub>2(g)</sub>, 48 hours; (2) 24 hours under stirring.

**BATCH 2:** 39.7 mg ( $5.52 \times 10^{-5}$  mol) of Mn(Porph), 563.1 mg of MR 150 °C, DMF, N<sub>2(g)</sub>, 4 hours. (BATCH 2)

**BATCH 3:** 16.3 mg ( $2.27 \times 10^{-5}$  mol) of Mn(Porph), 227.8 mg of MR 150 °C, DMF, N<sub>2(g)</sub>, 4 hours. (BATCH 3)

**Scheme 1.** Routes for the preparation of the heterogeneous catalysts; 3-bromopropylfunctionalized silica gel (SG); Merrifield resin (MR).

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