Short communication

Epoxidation reactions with hydrogen peroxide activated by a novel heterogeneous metalloporphyrin catalyst

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Abstract

A novel heterogeneous catalyst was developed by immobilization of the robust Mn(TDCPP)Cl on an inorganic support by a strong covalent bond through the β-position of the macrocycle. This new material has demonstrated to be an active, selective and reusable catalyst in clean epoxidation reactions using hydrogen peroxide as oxidant.
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An important challenge for the green chemistry is to find alternatives to the common oxidation synthetic methodologies, based on stoichiometric oxidants, leading to large amounts of non-biodegradable by-products [1]. The use of hydrogen peroxide as a cheap, environmentally clean and easy to handle oxidant [2], in conjugation with robust and easily obtainable metalloporphyrins as catalysts, led to efficient procedures to perform many oxidative reactions [3,4]. In some cases the role of a co-catalyst like ammonium acetate has shown to be essential [4]. However, the potentiality of these systems will only be realized by anchoring the catalyst to a solid support, thus allowing its easy recovery and reuse. Moreover, the local environment of the support can bring higher selectivity and prevent catalyst self-oxidation [5]. The different attempts to create efficient supported metalloporphyrin catalysts use organic [6] or mineral [7] supports; among them silica has been recognized as a very attractive material, due to its stability towards drastic catalytic oxidation conditions [8].

As far as we are aware, an entirely new covalent approach is reported here, consisting of chloro 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinatomanganese(III) [Mn(TDCPP)Cl] covalently bonded to a modified silica at the β-pyrrolic position of the macrocycle (Scheme 1).

The chloro 2-nitro-5,10,15,20-tetrakis(2,6-dichlorophenyl)-porphyrinatomanganese(III) [Mn(βNO₂TDCPP)Cl] was prepared according to described methods [9–11]; 10.0 mg (0.01 mmol) of that complex were taken in 3 mL of xylene. The mixture was refluxed in the presence of 0.5 g of 3-aminopropyl-functionalised silica gel (Aldrich, ∼9% functionalised) for 48 h under a nitrogen atmosphere and magnetic stirring. After cooling, the resulting solid was filtered and exhaustively washed with a mixture of methanol/ethyl acetate (1:9) and subsequently with acetonitrile. Then, the solid was dried at 80 °C for at least 12 h, to afford the new catalyst (**1**) as a dark green powder.

A control experiment was performed in the above described conditions but using Mn(TDCPP)Cl instead of Mn(βNO₂-TDCPP)Cl. In this case, the formation of the covalent bond is not possible due to the absence of the nitro group and the metalloporphyrin can only be adsorbed to silica. In fact, the solid resulting from the control experiment was submitted to the washing procedure described above, but only a pale green solid was obtained. These results confirm that a covalent bond was established only with the nitro derivative at high temperature and they are corroborated by recent observations that β-nitroporphyrins can suffer *ipso* substitution by amine groups [12].

The absorption spectra in the visible region of the homogeneous and immobilized porphyrins are collected in Fig. 1.

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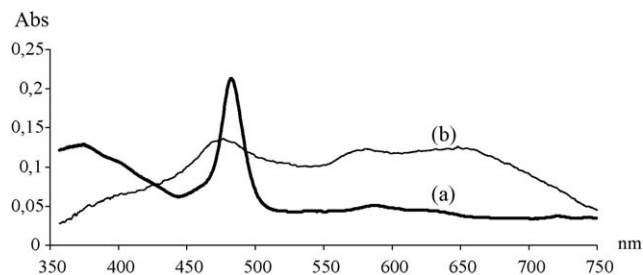jcavaleiro@dq.ua.pt (J.A.S. Cavaleiro).
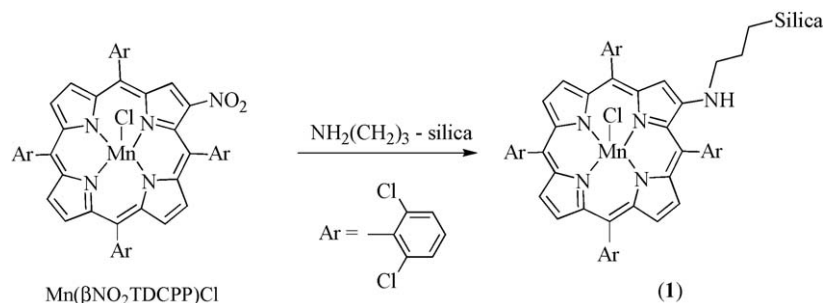
Scheme 1.

Fig. 1. (a) Electronic absorption spectrum of Mn(βNO$_2$TDCPP)Cl in CH$_2$Cl$_2$. (b) Diffuse reflectance spectrum of catalyst (**1**).

Despite the typical peak enlargement observed in the metalloporphyrin bonded to the solid supports, the typical adsorption peaks are retained.

The manganese contents of catalyst (**1**) were determined by ICP-OEP (ion coupled plasma-optical emission spectroscopy) affording 0.90 mg of Mn/g of catalyst (**1**). This result allowed the determination of the amount of metalloporphyrin incorporated into the silica as being 0.02 mmol of metalloporphyrin/g of catalyst (**1**). The reproducibility of the synthetic procedure was also validated, since the analysis of the manganese contents of another sample of (**1**) resulting from a second synthesis did afford 0.86 mg of Mn/g of catalyst (**1**).

The metalloporphyrin loading was also determined by elemental analysis, comparing the carbon content of functionalised silica with and without the metalloporphyrin. The percentage of carbon mass corresponding to the supported metalloporphyrin was 1.33%, corresponding to 0.02 mmol of metalloporphyrin/g of catalyst (**1**), which is in accordance with the result obtained by ICP.

The efficiency of the new immobilized porphyrin (**1**) was tested in the catalytic oxidation of *cis*-cyclooctene as a model substrate and H$_2$O$_2$ as oxidant in acetonitrile, as solvent. The results obtained in different conditions are collected in Table 1. The reactions were stopped when two successive analyses by gas chromatography gave the same percentage of conversion.

The efficiency of the catalytic system was evaluated under several conditions and the best performance was achieved when a low solvent volume (0.5 mL) and a low rate of oxidant addition (0.04 mmol/h) were used (Table 1, entry 2). In this case, 89% of substrate conversion was obtained after 21 h at 20 °C. Higher rates of oxidant addition led to a decrease in the catalytic system performance (entries 3 and 4), probably due to metalloporphyrin bleaching, while higher solvent volumes probably make difficult the substrate approach to the catalyst (entry 1). It was also observed that the temperature increase has no significant effect in the substrate conversion (entry 5). It is remarkable to notice that in all assays the selectivity for cyclooctene oxide was $\geq$99%. In the absence of catalyst, only 0.5% of conversion was registered after 18 h of reaction (entry 6).

Table 1
Epoxidation of *cis*-cyclooctene with H$_2$O$_2$ catalysed by (**1**)[a]

Entry		CH$_3$CN (mL)	Temperature (°C)	H$_2$O$_2$ (mmol/h)	Conversion[b] (%)	Time (h)
1		2.0	20	0.04	72	19
2		0.5	20	0.04	89 $\pm$ 6[c]	21
3		0.5	20	0.15	31	9
4		0.5	20	0.10	52	16
5		2.0[d]	50	0.04	89	21
6	No catalyst	0.5	20	0.04	0.5	18
7	First use[e]	0.5	20	0.04	97	23
8	Second use[f]	0.5	20	0.04	88	23
9	Third use	0.5	20	0.04	51	23

[a] The substrate (0.3 mmol) was dissolved in the desired volume of solvent (CH$_3$CN) and stirred in the presence of catalyst (31 mg) and co-catalyst (NH$_4$AcO, 0.12 mmol) at the chosen temperature. H$_2$O$_2$ (35%, w/w) was diluted in CH$_3$CN and progressively added to the reaction mixture at the specified rate till no progress in substrate conversion was observed.
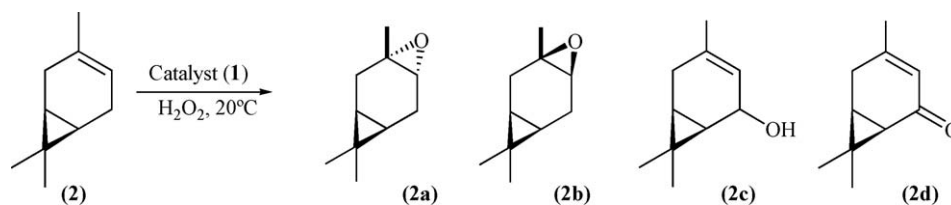
[b] Determined by GC, based on the substrate.

[c] Average of three assays with solid catalysts from different synthesis.

[d] Lower volumes led to complete solvent evaporation.

[e] 125 mg of catalyst (**1**) were used.

[f] The catalyst was filtered, rinsed, dried and used in another reaction under the same catalytic reaction conditions.

Scheme 2.

Table 2
Oxidation of 3-carene with H_2O_2 catalysed by (**1**)[a]

t (h)	Conversion (%)[b]	Selectivity (%)[b]		α/β[c]	Selectivity (%)[b]	
		α-Epoxide (**2a**)	β-Epoxide (**2b**)		5-Alcohol (**2c**)	5-Ketone (**2d**)
12	51	23	7	3.3	39	9
27	65	32	10	3.2	25	17

[a] Reaction conditions: substrate: 0.3 mmol; solvent: CH_3CN: 0.5 mL; co–catalyst (NH_4AcO): 0.12 mmol; at 20 °C.
[b] Determined by GC, based on the substrate.
[c] α/β-Epoxide ratio.

No manganese porphyrin was observed by UV–vis analyses of the reaction supernatant and the recovered silica after reaction of entry 2 presented a Mn content by ICP-OES analysis of 0.70 mg of Mn/g of catalyst, showing that only minor leaching has occurred during the reaction. This recovered catalyst was reused affording only 5% of substrate conversion. However, increasing catalyst amount to a substrate:supported metalloporphyrin ratio of 100 instead of 600 (entries 7–9), for the Second and Third catalyst reuse the experiments afforded 88 and 51% conversion, respectively.

In order to evaluate the potential applicability of this new heterogeneous metalloporphyrin catalyst (**1**) in the oxidation of substrates with potential economical interest, the oxidation of 3-carene (**2**) was performed. After 27 h of reaction time, 65% of substrate conversion and 42% selectivity for the epoxides were obtained (Scheme 2 and Table 2). The α/β-epoxide ratio was 3.2, which did not change during the reaction course. It is worth to notice that in the oxidation of 3-carene with H_2O_2 in the presence of the homogeneous catalyst Mn(TDCPP)Cl the α/β-epoxide ratio was only 1.7 [4]. This increase on the epoxide ratio is indicative of the significant influence of the support environment on the diastereoselectivity of the epoxidation reaction.

To obtain some mechanistic information and diastereoselective systems, similar studies are being carried out in our laboratories with other metalloporphyrins, other supports and different natural chiral substrates.

Acknowledgements

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