Biomimetic epoxidation by supported manganese-porphyrin: an approach to CYP450

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Introduction

Metalloporphyrins are widely used as catalysts in oxidation reactions, mimicking the natural functions performed by cytochrome P450 monooxygenase enzymes¹. Like iron, manganese also forms a highvalent oxo intermediate that can promote the oxidation of many substrates, and manganese complexes are often preferred for biomimetic in vitro catalysis, due to their higher activity. 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. To date, different approaches have been developed for the design of heterogeneous metalloporphyrin catalysts. This work shows the results obtained in olefin epoxidation reactions using H_2O_2 as oxygen donor² and an immobilized imidazolium metalloporphyrin [Mn(Porph)] on Merrifield Resin (MR) as heterogeneous support through covalent bond.

Results and discussion

The immobilization gives a material constituted by a cationic Mn(Porph), which showed great catalytic activity. Fig. 1 shows the solid catalyst and some physical characterizations.

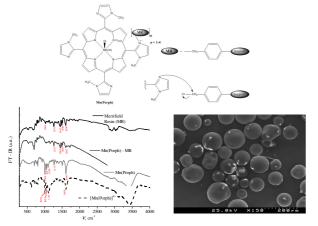


Fig. 1. Top: Studied supported catalyst and reaction conditions. Bottom: Left- FTIR spectrum of metalloporphyrin, support and immobilized material; Right - SEM image.

The first studies (Fig. 2) involved an olefin epoxidation. Worthnote that the efficiency of the heterogeneous material are not greatly affected even after 3 cycles.

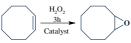


Fig. 2. cis-Cyclooctene studied epoxidation.

Table 1. Experimental results for *cis*-cyclooctenereaction.

Cycle	Epoxide yield, %	Time, min.
1	100	150
2	100	180
3	85.8	180

The analysis was stopped when the same result was observed after two consecutive injections on GC/MS. The observed catalyst performance can be attributed to the covalent bond between Mn(Porph) and MR, which avoid catalyst bleaching and its destruction. In this material, the Mn(Porph) is charged (by bonding to MR). This reinforce the efficiency, according the homogeneous studies showed².

Conclusions

The heterogeneous material is able to selectively oxidize olefins in high yields as well as it can be recycled for, at least, three times with reasonable efficiency. Similar studies are being carried out for the oxidation of several organic substrates.

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