

# Alkene epoxidation by Mn(III)porphyrin and Jacobsen catalysts immobilized on nanostructured carbon CMK-3

H. Gaspar<sup>1</sup>, M. Andrade<sup>2</sup>, S. L. H. Rebelo<sup>1\*</sup>, J. Pires<sup>2</sup>, A. P. Carvalho<sup>2</sup>, C. Freire<sup>1</sup>

<sup>1</sup> REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal.

<sup>2</sup> Departamento de Química e Bioquímica, Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Ed. C8 Campo Grande, 1749-016 Lisboa, Portugal.

\*susana.rebelo@fc.up.pt

## Introduction

The Mn(III) complexes of porphyrins and salen ligands are found among the most versatile catalysts for selective oxidation reactions.[1,2] However, the use of heterogeneous catalysts would be preferable, due to advantages associated with its separation, recovery and re-use. In the present work the heterogenization of Mn(III) catalysts (Figure 1) was performed on mesoporous carbon materials [3] with characteristic high hydrophobicity, surface area and pore sizes.

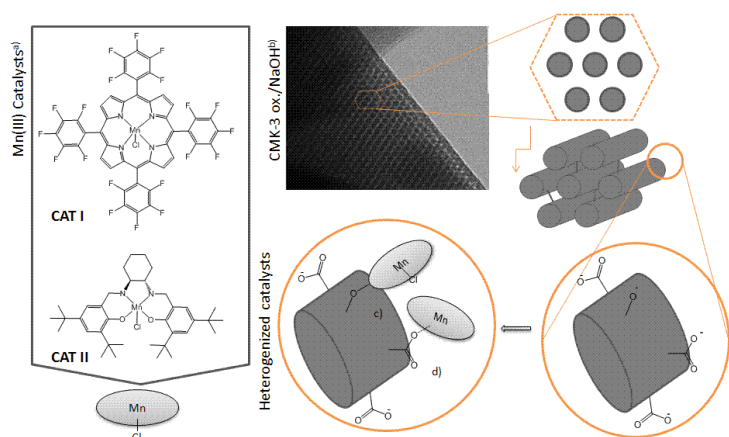


Figure 1. Heterogenization of homogeneous catalysts: a) metalloporphyrin [Mn(TPFPP)Cl] and Jacobsen catalysts; b) TEM of CMK-3 material, that was oxidized and treated with NaOH; c) immobilization through nucleophilic substitution of the pentafluorophenyl rings; d) immobilization through axial coordination.

## Experimental

**Catalyst preparation:** The CMK-3 material was oxidized with HNO<sub>3</sub> and subsequently treated with NaOH [2]. The material was suspended in solutions of the metal complexes (25% w/w) and the mixtures were refluxed under microwave heating (30 min.) or conventional heating (24h). After refluxing in clean solvent, the materials were dried and analyzed by XPS and FTIR.

**Catalysis:** The catalysts were suspended in a solution of the olefin (*cis*-cyclooctene or 6-cianodimethylchromene) and the oxidant (hydrogen peroxide or *m*-CPBA at 0°C) were progressively added. The reactions were followed by GC and at the end of reaction the catalyst was filtered washed and re-used.

## Results/Discussion

The Mn(III) complexes were efficiently immobilized onto CMK-3 (Table 1). Material CMK-3ox.[CAT I] showed to be efficient in the oxidation of *cis*-cyclooctene with a green oxidant such as hydrogen peroxide at room temperature in acetonitrile, whereas CMK-3ox.[CAT II] catalyzed the oxidation of 6-cianodimethylchromene, at 0°C in dichloromethane, using *m*-CPBA/NMO system. Both catalysts kept their activity for 3 runs.

Table 1. Surface characterization and catalytic performance of the materials

Material	Atomic percentages by XPS (%)						Catalytic run		
	C	O	N	Si	F	Mn	1st	2nd	3th
CMK-3ox.	80.3	17.9	0.8	1.0	-	-	-	-	-
CMK-3ox.[CAT I]	81.2	15.6	2.2	-	2.1	0.6	40% <sup>a</sup>	41% <sup>a</sup>	30% <sup>a</sup>
CMK-3ox.[CAT II]	78.5	20.5	1.0	-	-	1.7	49% <sup>b</sup>	45% <sup>b</sup>	34% <sup>b</sup>

<sup>a</sup>Epoxide yield after 30h of reaction time; <sup>b</sup>Cromene conversion after 26h of reaction time.

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## References.

- S.L.H. Rebelo, M.M.Q. Simões, M.G.P.M.S. Neves, A.M.S. Silva, J.A.S Cavaleiro, *Chem. Commun.*, 608 (2004)
- A.R. Silva, C. Freire, B. de Castro, *Carbon*, **42**, 3003 (2004)
- V.K. Saini, M. Andrade, M.L. Pinto, A.P. Carvalho, J. Pires, *Sep. Purif. Technol.*, **75**, 366 (2010).