

# Mn(III) porphyrins immobilized on mesoporous silica SBA-15 *in natura* and functionalized with chloropropyl groups as catalysts for cyclohexane oxidation

Victor H. A. Pinto<sup>1,2</sup>(PQ)\*, Júlio S. Rebouças<sup>2</sup>(PQ), Shirley Nakagaki<sup>1\*</sup>(PQ). \*victorhugopinto@hotmail.com and shirleyn@ufpr.br

<sup>1</sup> Laboratório de Bioinorgânica e Catálise, Depto. de Química, Universidade Federal do Paraná, Curitiba, PR, Brasil, 81531-970. <sup>2</sup> Depto. de Química, CCEN, Universidade Federal da Paraíba, João Pessoa, PB, Brasil, 58051-900.

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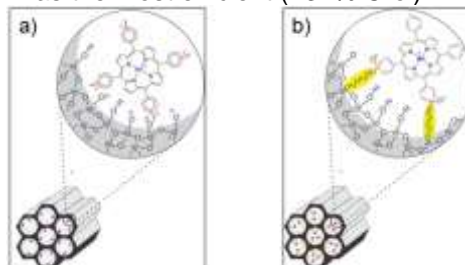
## Introduction

The activity of Mn(III) porphyrins (MP) in homogeneous system have been combined with various chemical matrices in an attempt to obtain catalysts more stable to oxidative destruction, more efficient and of easier recovery for reuse<sup>1</sup>. Thus, there is great interest in chemical supports that are capable of mimicking the performance of the apoprotein in biological system (e.g., cytochromes P-450), controlling the access of both oxidant and substrate to the catalytic site, and preventing catalyst inactivation through bimolecular interactions in solution. Within this context, two mesoporous materials, *i.e.*, *in natura* SBA-15 mesoporous silica (SBA-15) or the chloropropyl functionalized analogue (SBA-15Cl), were used as supports for (MnP) immobilization. The three isomers of a neutral MnP, (MnT-X-PyPCL, X= 2, 3, 4), were covalently supported on chloropropyl-functionalized silica to yield SBA-15Cl/MnP materials. Additionally the three isomers of a cationic MnP (MnTM-X-PyPCL<sub>5</sub>, X= 2, 3, 4) were electrostatically supported on *in natura* mesoporous silica SBA-15 to yield SBA-15/MnP materials. The isolated solids (Fig. 1) were used in hydroxylation reactions of cyclohexane by iodosylbenzene (PhIO). Herein, the following effects were studied: 1) immobilization effect (heterogeneous x homogeneous catalysis), 2) reuse of heterogenized catalysts, 3) oxidative stability toward increased PhIO/MnP molar ratio, 4) support effect (SBA-15 x SBA-15Cl), and 5) influence of the MnP isomers anchored.

## Results and Discussion

The supports (SBA-15 and SBA-15Cl) were obtained according to the literature<sup>2,3</sup> and characterized by FTIR, SEM, TEM, SAXS, <sup>13</sup>C NMR (only for SBA-15Cl) and BET. MnPs were prepared as previously described.<sup>4</sup> The materials SBA-15Cl/MnT-X-PyPCL and SBA-15/MnTM-X-PyPCL<sub>5</sub> (X= 2, 3, 4), with MnP loadings of 3 to 8 μmol/g, were characterized by DR-UV/VIS. These catalysts were more selective toward cyclohexanol (C-ol) than cyclohexanone (C-one), with selectivity for C-ol of ~60%, in the

following reaction conditions: CHCl<sub>3</sub>/CH<sub>3</sub>CN(1:1,v/v) as solvent, magnetic stirring, air atmosphere, 25 °C, total volume of 350 μL, catalyst/PhIO/substrate molar ratio of 1:10:5000. The immobilized systems were both more efficient and more selective than the corresponding homogeneous systems. All materials were recovered and reused for at least two cycles of reactions. The increase of PhIO/MnP molar excess from 10 to 100 promoted some destruction of the catalysts SBA-15Cl/MnP and SBA/MnP but the supports avoided extensive catalyst destruction. MnP leaching from the supports was not observed during the reactions, nor in the catalyst recovery process. Within the SBA-15Cl/MnP systems the *para* isomer was more efficient (~45% C-ol) than the others, whereas for SBA-15/MnP materials the *orto* isomer was the most efficient (~32% C-ol).



**Figure 1.** Representation of immobilized *para* isomers: a) cationic MnP, MnTM-4-PyP<sup>5+</sup> anchored into SBA-15 and b) neutral MnP, MnT-4-PyP<sup>+</sup> into SBA-15Cl.

## Conclusions

Two classes of solid catalysts (SBA-15/MnTM-X-PyPCL<sub>5</sub> and SBA-15Cl/MnT-X-PyPCL) were prepared and found to be catalytically active for efficient and selective oxidation of inert C-H bond of cyclohexane. The SBA-15Cl/MnP solids were more efficient than the corresponding SBA-15/MnP materials (~40% vs ~30 % C-ol, respectively). Conversely, SBA-15/MnP catalysts were more resistant to oxidative destruction for reuse reactions.

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<sup>1</sup> Nakagaki, S. et al. *J. Curr. Org. Synth.*, **2014**, 11, 67. <sup>2</sup> Zhao, D. et al. *Science*, **1998**, 279, 548. <sup>3</sup> Oliveira, F.J.V.E. et al. *Materials Research Bulletin*, **2013**, 48, 1045. <sup>4</sup> Pinto, V. H. A. et al. em Anais da 36<sup>a</sup> Reunião Anual da Sociedade Brasileira de Química, Águas de Lindóia, **2013**.