

Preparation of catalytic solids based on manganese(III) porphyrins immobilized on mesoporous silica at magnetic particles

Geani M. Ucoski^{1*} (PQ), Victor H. A. Pinto^{1,2} (PQ), Júlio S. Rebouças² (PQ), Fábio S. Nunes¹ (PQ), Shirley Nakagaki^{1*} (PQ)

¹Universidade Federal do Paraná, Departamento de Química - Laboratório de Bioinorgânica e Catálise CP 19081, fax: +55-41-33613186, CEP 81531-990, Curitiba, PR, Brazil, ²Departamento de Química, CCEN, Universidade Federal da Paraíba, Caixa Postal 5093, João Pessoa 58051-970, PB, Brazil. *geanigmu@gmail.com and shirleyn@ufpr.br

Keywords: porphyrin, magnetite, mesoporous silica, catalysis, oxidation

Introduction

The heterogenization of metalloporphyrins (MP) in different solid supports has been extensively investigated mainly for promote the recovery and reuse of these solids in heterogeneous catalysis¹. In this sense, magnetic mesoporous silica has been investigated as support since leads to catalysts of heterogeneous phase with higher surface area and homogeneous porosity, which tend to improve the catalytic performance. These solids are suitable for the immobilization of complexes with catalytic activity,

including MP. In this work it is reported the immobilization of cationic MP (Figure 1) on magnetic HMS

mesoporous silica. It is expected that the magnetic behavior facilitates the catalyst recovery and reuse.

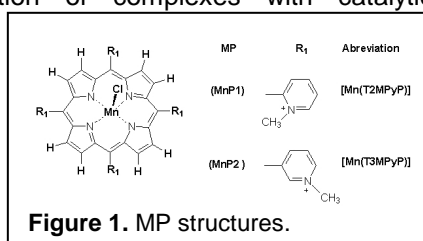


Figure 1. MP structures.

presents a porous structure with peak centered in about 1.5 nm. The BET surface area of Mag-HMS was calculated to be 725.59 m²/g lower than only HMS⁴. The prepared solids were used as catalysts in the cyclooctene and cyclohexane oxidation (1 h, room temperature, under magnetic stirring, using dichloromethane:acetonitrile (1:1) as solvent).

Tabela 1. Catalytic results¹.

Run	Catalyst (MP-HMS-Mag)	Catalytic Yield results (%) heterogeneous (homogeneous)	
		Epoxid	Alcohol
1	MP = MnP1	81 (87)	22 (22)
2	MP = MnP2	70 (74)	13 (5)
3	Mag-HMS	12	-

¹1:50:5000 (catalyst:PhIO:substrate molar ratio).

The solids MP-HMS-Mag showed catalytic results similar or higher than homogeneous catalysis when cyclooctene and cychohexane were used as substrate. Catalysts MP-HMS-Mag were easily separated from the reaction by use of the magnet and maintained the catalytic activity after at least three recycling.

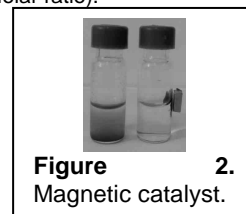


Figure 2. Magnetic catalyst.

Results and Discussion

The magnetite (**Mag**) were obtained by co-precipitation method³ and coated by mesoporous silica (hexagonal mesoporous silica) using dodecylamine like template according to the methodology described by Pinnavaia⁴ (**Mag-HMS**). The MP were immobilized on this solid under reflux for 5 h and washed with CH₃OH and dried at 70 °C. The loading (L) of each MP in the support was determined by UVVIS analysis of the washing extracts (L (mol of MP/g solid): **MP-HMS-Mag**: **MnP1** = 3.66 x 10⁻⁶ and **MnP2** = 2.92 x 10⁻⁶). The UVVIS spectra confirm the presence of each MP on the solids (MP-HMS-Mag) by the observation of the typical MP Soret band at 450-460 nm. The low-angle XRD patterns of the samples present the peak 100 at around 3.0° (2θ), which suggest the ordered mesopore symmetry. The samples TEM images are well defined, like strands of interconnected spheres and showed that the magnetite was completely covered by the silica and porous structure. The N₂ adsorption-desorption analyses for Mag-HMS exhibit IV-type isotherm. The pore size distribution curve

Conclusion

The new catalysts based on MP immobilized on magnetic mesoporous at silica exhibited promising results for oxidation catalysis of cyclooctene and cyclohexane and were easily recovered and reused, showing similar results to the first use.

Acknowledgments

CNPq, CAPES, Centro de microscopia eletrônica.

¹Ucoski, G. M.; Nakagaki, S., et al. *Applied Catalysis A: General*, **2013**, 459, 121.

²Pal, N.; Bhaumic, A., *Advances in Colloid and Interface Science*, **2013**, 180-190, 21.

³Philipse, A. P.; Vanbruggen, M. P. B. and Pathmamanoharan, C. *Langmuir*, **1994**, 10, 92.

⁴Tanev, P. T. and Pinnavia, T. J. *Science*, **1995**, 267, 865.