Mn(III) porphyrins anchored on *in natura* and chloropropyl-functionalized mesoporous silica HMS as catalyst for oxidation reaction

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keywords: *porphyrin, mesoporous silica, catalyst, oxidation, manganese, functionalization.*

Intoduction

Metalloporphyrins (MP) are widely used as biomimetic catalyst of the cytochrome P450 enzyme family. The immobilization of MP on chemical supports has been an optimal strategy for circumventing problems observed with the use of MP in homogeneous medium, such as oxidative destruction and catalytic deactivation *via* bimolecular interactions[1]. Mesoporous silica are promising supports for catalyst immobilization since it has high specific surface area and regular pore diameter, which may be involved in controlling the access of oxidant and substrate to the catalytic site, yielding a more efficient and selective catalyst. In this work, mesoporous silica HMS was used as support to attach Mn(III) porphyrins (MnPs), yielding two types of heterogenized catalysts (Fig. 1): 1) three isomers of the Mn(III) *N*-pyridylporphyrins covalently immobilized on chloropropyl-functionalized HMS (HMS-Cl) (MnP1(**X**), **X**= **2**, **3**, **4**) to yield HMS-Cl/MnP1(**X**) solids and 2) three isomers of the Mn(III) *N*-methylpyridiniumporphyrins (MnP2(**X**), **X**= **2**, **3**, **4**) immobilized electrostatically on non-modified HMS to yield HMS/MnP2(**X**) solids.

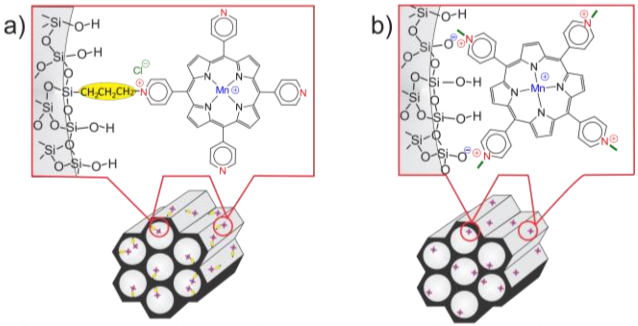

Figure 1. Schematic representation of the two classes of supported catalysts: a) MnP1(**4**) immobilized on HMS-Cl and b) MnP2(**4**) on HMS.

Results and Discussion

MnPs, HMS, and HMS-Cl were prepared as previously described.[2-4] Mesoporous silicas were characterized by FTIR, elemental analysis, TGA/DTA, nitrogen adsorption-desorption, SEM, and TEM. FTIR spectra of HMS and HMS-Cl showed all major silica-related bands: 3400 (νO-H), 1640 (δO-H), 1100 (ν_{as}Si-O-Si), 970 (νSi-OH), 800 (ν_{s}Si-O-Si), and 470 cm^{-1} (δSi-O-Si). HMS-Cl showed also C-H vibrational modes at 2850-2920 cm^{-1}, attributed the chloropropyl moieties. The carbon percentage (2.36%) in HMS-Cl relates to 0.66 mmol of chloropropyl moiety *per* gram of HMS. TGA/DTA curves for the supports exhibited two mass loss events related to the loss of water molecules, followed by silanol groups condensation; for HMS-Cl, the decomposition of the chloropropyl groups was also observed. The specific surface area (1024 m^{2}g^{-1}), pore diameter (3.1 nm), and pore volume (0.39 cm^{3}g^{-1}) of HMS were consistent with literature data.[2] HMS-Cl showed a decrease in both specific surface area (447 m^{2}g^{-1}) and pore volume (0.24 cm^{3}g^{-1}) due to chloropropyl blocking of HMS pores. The SEM and TEM images for HMS and HMS-Cl were identical and showed the formation of spherical aggregates of irregular size distribution. HMS-Cl/MnP1(**X**) and HMS/MnP2(**X**) catalysts were prepared by immobilizing the corresponding MnP on the appropriate support under H$_2$O reflux for 24 h. DR-UV/VIS analyses confirmed MnP immobilization, as the spectra of the materials were similar to those of the corresponding MnP in solution, which indicates that no major structural change (*e.g.*, demetallation) took place. The MnP loadings on the supports were determined by UV/VIS, ranged from 2 to 5 μmolg^{-1}. The HMS-Cl/MnP1(**X**) and HMS/MnP2(**X**) materials are being evaluated as catalysts for cyclohexane hydroxylation by iodosylbenzene (PhIO).

Conclusion

The HMS and HMS-Cl supports were prepared and characterized.[3,4] Two classes of immobilized materials, HMS-Cl/MnP1(**X**) and HMS/MnP2(**X**), of low MnP loadings (0.3% w/w) were prepared by two simple strategies: 1) covalent attachment of neutral MnP1(**X**) onto chloropropyl mesoporous silica HMS-Cl, and 1) electrostatic immobilization of cationic MnP2(**X**) on mesoporous silica HMS.

Acknowledgment

UFPR/UFPB/CNPq/CAPES/Fundação Araucária

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