Mild Oxidative Functionalization of Alkanes Catalyzed by Self-Assembled Multicopper(II) Cores and Metal-Organic Networks

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Keywords: Bioinspired Catalysts, C–H Functionalization, Oxidation Catalysis, Coordination Polymers, MOFs, Design and Synthesis.

Abstract

The present contribution will discuss our recent research studies on the self-assembly, synthesis, full characterisation, structural and topological features, and catalytic use (in mild oxidative functionalization of alkanes) of a wide diversity of mixed-ligand aminoalcoholate copper(II) complexes and metal-organic networks.

Introduction

Different copper compounds constitute a vast variety of catalytic systems and are widely applied in the areas of both heterogeneous and homogeneous catalysis. The use of copper containing catalysts is primarily governed by the versatile redox properties of this metal, its natural abundance and relatively low cost, low toxicity, and rich inorganic and coordination chemistry. Besides, copper ions are present in the active sites of diverse oxidation enzymes, thus justifying an extensive research in the fields of copper bioinorganic chemistry and related areas of biomimetic and/or bioinspired catalysis. Among the Cu-based enzymes, particulate methane monooxygenase (pMMO) represents an especially interesting case given its multicopper active site with an *N,O*-environment that is capable of catalyzing the hydroxylation of such inert substrates as alkanes (main components of natural gas and oil).

Thus, the main objective of this study consisted of the search for new efficient protocols and rather simple bioinspired Cu-based catalytic systems for the mild oxidative functionalization of alkanes.[1–3]

Results and Discussion

The current contribution will discuss our recent research results on the application of aqueous-medium self-assembly synthetic methods toward the design and generation of a wide diversity of the mixed-ligand copper(II) compounds with an *N,O*-environment, which range from 0D multinuclear complexes to 1D or 2D coordination polymers, and 3D metal-organic frameworks. These compounds have been constructed from different aminoalcohols as main building blocks and various carboxylic acids as typical spacers or ancillary ligands. The presentation will focus on the following main topics.

(A) Aqueous medium self-assembly generation, characterization, selected properties, and structural and topological features of the copper(II) containing metal-organic or supramolecular networks driven by aminoalcohol building blocks (e.g., triethanolamine, *N*-alkyl-diethanolamines, or biological buffers with an aminoalcohol functionality).

(B) Application of the obtained copper(II) compounds and related derivatives as highly efficient bioinspired (pre)catalysts for (i) the mild oxidation of alkanes (typically cyclohexane as a model substrate with industrial relevance) by hydrogen peroxide into alcohols and ketones, and (ii) the hydrocarboxylation of gaseous and liquid C_n alkanes, by carbon monoxide, water and potassium peroxodisulfate, into the corresponding C_{n+1} carboxylic acids.

(C) Investigation of the influence of various reaction parameters on the catalytic activity, namely including the amount and type of (pre)catalyst and acid promoter, solvent composition, substrate scope, and different selectivity features.

Conclusions

New series of copper(II) coordination compounds of diverse nuclearity and dimensionality have been prepared, fully characterized, and applied as efficient (pre)catalysts for the mild oxidative functionalization of alkanes.

Acknowledgements

This work was supported by the FCT (IF/01395/2013/CP1163/CT005, PTDC/QUIQUI/121526/2010, UID/QUI/00100/2013, and SFRH/BSAB/114190/2016), Portugal. AK is very grateful to Prof. Dalmo Mandelli (UFABC) and FAPESP for a visiting researcher fellowship, (2015/21051-8, CAPES A017_2013).

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