

# Oxidation of cyclohexane by transition metal complexes with biomimetic ligands

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## Introduction

The oxidation of cyclohexane is a reaction of great industrial relevance as the main products, cyclohexanol and cyclohexanone, are used as precursors to the synthesis of added value products such Nylon-6 and Nylon-6,6 [1,2,3]. Industrially the reaction is currently performed using a cobalt naphthenate catalyst at 160°C and 15 bar with very low yields and good selectivities [2,3]. Therefore the functionalization of relatively abundant and low cost feedstock such alkanes is still a challenge from a scientific point of view. Catalysis by transition metal complexes has been opening some doors to the functionalization of alkanes under mild conditions [1,2,3]. On the other hand, certain enzymes already perform this reaction efficiently with molecular oxygen under mild conditions constituting the state of the art for alkane oxidation. Hence inspiration on nature, specifically on the active centre of enzymes, could lead to better catalytic systems for the C-H activation.

Several biomimetic ligands have been described as models for the *heme*-containing cytochrome P450 enzyme including metalloporphyrins and metallo*salen*. The later have the advantage of being more stable under strongly oxidizing reaction media and easily synthesized with high yields from readily available and inexpensive precursors [4].

## Experimental

In this work 1<sup>st</sup> row transition metal complexes (Fe, V, Cu, Co) with biomimetic polydentate ligands with N or N,O coordination sphere were synthesized and characterized by FTIR, proton NMR, mass spectrometry (low and high resolution) and/or elemental analysis. They were studied as homogeneous catalysts in the oxidation of cyclohexane at room temperature using environmentally benign reactants: hydrogen peroxide as oxygen source and acetonitrile as solvent. Other oxidants such as H<sub>2</sub>O<sub>2</sub>, urea and iodosylbenzene were tested as well and the effect of different co-catalysts and of the temperature in the reaction was studied. The reactions were followed by gas chromatography (GC) and the products identified against commercially available products or by GC-MS.

## Results/Discussion

Oxygenated products were obtained in the presence of most of the transition metal complexes studied in higher yields than in control experiments where no catalyst was added. Catalytic parameters such as oxygenated product yield, turnover number, turnover frequency and selectivity towards cyclohexanol and cyclohexanone will be discussed.

The best metal catalyst with the polydentate ligand with N,O or O coordination sphere will be also identified. For this best metal catalyst the effect of the temperature on the catalytic parameters (activity and chemoselectivity) will be accessed, as well as the modulation of the catalytic activity by introducing electron withdrawing or electron donating groups in the ligand system and the change to N coordination sphere. The effect of different co-catalysts and oxidants will be also assessed for these catalytic parameters. The oxidation of other cyclic and linear alkanes using hydrogen peroxide as oxidant, under the same experimental conditions, will be also discussed.

*Acknowledgements:* This research was supported by a Marie Curie European Reintegration Grant within the 7th European Community Framework Programme (FP7-PEOPLE-2009-RG-256509). ARS thanks as well the FSE and POPH for a contract under the Ciência 2008 program for PhD contracting for the National Scientific and Technological System. TM thanks FCT for an under-graduate BII fellowship of 2009.

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