

## Highly chemoselective metal-free oxidations with diluted H<sub>2</sub>O<sub>2</sub> in continuous flow reactors

C. Giancarlo Piscopo,<sup>\* 1,2</sup> Raimondo Maggi,<sup>1</sup> Soheila Chitsaz,<sup>2</sup> Stefan Loebbecke,<sup>2</sup> Giovanni Sartori<sup>1</sup> and Maud Schwarzer<sup>2</sup>

<sup>1</sup> "Clean Synthetic Methodology Group", Dipartimento di Chimica Organica e Industriale dell'Università, Parma, Italy.

<sup>2</sup> Fraunhofer Institute for Chemical Technology ICT, Pfinztal, Germany.

\* calogero.giancarlo.piscopo@nemo.unipr.it

### Introduction

One of the major challenges of green chemistry is, undoubtedly, the achievement of more environmentally friendly processes in organic synthesis. An important goal in this field is the development of cleaner and safer metal-free synthetic routes for oxidation reactions [1].

Hence, in the last decades many studies have been devoted to replace common oxidants with aqueous hydrogen peroxide [2], which is a cheap, mild and environmentally benign reagent since water is formed as the only by-product. Furthermore continuous processing of catalytic reactions offers significant improvements compared to conventional batch processes due to a precise control of residence time, heat and mass transport [3].

### Experimental

A glass column packed with Amberlite IR 120 H, dipped in a water bath, was utilized as reactor. Two pulsation-free syringe pumps were connected to the reactor allowing a precise control of the flow rate of the two reagent solutions (Figure 1). The eluates, collected and diluted in MeOH, were analyzed by HPLC.

Here, are reported two examples of highly chemoselective oxidation reactions performed with diluted hydrogen peroxide, namely the oxidation of thioanisole to the corresponding methylphenylsulfoxide and the oxidation of methylhydroquinone to the corresponding methylbenzoquinone.

### Results/Discussion

Concerning the thioanisole oxidation, initially the best result was achieved by performing the reaction at 22 °C with a stoichiometric amount of 30% aqueous H<sub>2</sub>O<sub>2</sub> and a residence time of

25 minutes. Methylphenylsulfoxide has been obtained in 94% yield and 99% selectivity. The oxidation of thioanisole has been also performed with the more diluted and safer hydrogen peroxide. When a 3% aqueous H<sub>2</sub>O<sub>2</sub> solution has been employed, only a small lowering in sulfoxide yield was found, being still very high at 90%. Moreover, as the sulfoxide was the only product, the selectivity was 100%. The catalyst may be used for at least 2,000 minutes without any loss of activity.

A similar system was successfully developed for the oxidation of methylhydroquinone to the corresponding methylbenzoquinone with 30% aqueous H<sub>2</sub>O<sub>2</sub>. Thus a mixture of methylhydroquinone and hydrogen peroxide in methanol was passed through the reactor with a residence time of 10 minutes, obtaining the product in 59% yield and 95% selectivity, for at least 360 minutes.

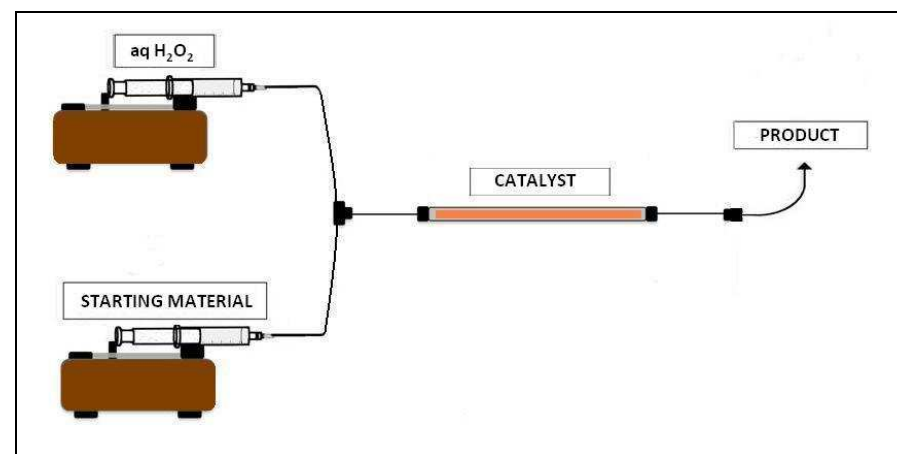


Figure 1. Schematic diagram of the reactor setup for the continuous flow oxidation reactions with hydrogen peroxide.

### References.

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