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A highly efficient, green and recoverable catalytic system for the epoxidation of fatty esters and biodiesel with H_2O_2

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ABSTRACT

A highly efficient and green strategy for the epoxidation of fatty esters, combining a green oxidant (aqueous hydrogen peroxide) and a recyclable catalyst (a seleninic acid derivative) is presented. The possibility of integrating renewable solvents derived from glycerol in the productive cycle of biodiesel commodities is also explored. Fluorinated solvents (both commercial and glycerol-derived) play a double key role on this methodology: on the one hand, they strongly accelerate epoxidation reaction with respect to common non-fluorinated solvents and, on the other hand, some of them allow catalyst recycling. Mono- and polyunsaturated fatty esters, as well as soy biodiesel have been epoxidized with excellent yields and selectivities towards epoxide under the optimal conditions and with minimum catalyst loads.

1. Introduction

In the last decade great interest has been focused in the development of new efficient processes for the functionalization of fatty acids through oxidation reactions [1]. This interest has been prompted by the need of reaching renewable chemicals in order to satisfy society demands for a greener chemistry. In this way, epoxidation of fatty acids derivatives is one of the most promising reactions to achieve the synthesis of a large variety of interesting products such as hydroxyethers, hydroxyesters, diols, *etc.* To this aim, the use of hydrogen peroxide (H_2O_2) for selective epoxidations is highly desirable because it is cheap, it has a high content in active oxygen, and it is clean, since the only byproduct formed is water [2]. The use of H_2O_2 as oxidant often requires an efficient catalytic process in order to achieve high conversions and selectivities, because of the poorer reactivity of H_2O_2 compared to other classic epoxidizing reagents such as organic peracids, peroxyesters or persulfates. Many catalytic systems based on different metals have been reported for the epoxidation of a wide range of alkenes using hydrogen peroxide [3].

With respect to fatty acid derivatives epoxidation, several examples using the classical conditions based on peroxy acids generated *in situ* from carboxylic acids (typically formic or acetic acids) as active oxygen carriers, H_2O_2 as oxygen donor and strong mineral acids (H_2SO_4, HNO_3, H_3PO_3) as catalysts have been reported [4]. Inorganic and organometallic catalysts based on tungsten [5], rhenium and manganese [6] have also been used. The heterogeneous version of the epoxidation reaction with H_2O_2 on fatty derivatives has also been explored using amorphous SiO_2/Ti [7] and methyltrioxorhenium on niobia catalysts [8], ion exchange resins [9], and sol–gel aluminas [10]. In the past years, the enzimatically promoted epoxidation of vegetable oils and fatty acids is gaining increasing interest [11].

Aryl diselenides [12] and their oxidized counterparts, *i.e.* aryl seleninic [13] and peroxyseleninic acids [14] have been described as highly efficient oxygen transfer catalysts for different processes, principally the epoxidation of olefins. Heterogenized versions of these catalysts have been also described [15]. On the other hand, the so-called "booster effect" of fluorinated alcohols, which has been beautifully described by the groups of Neumann and co-workers

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