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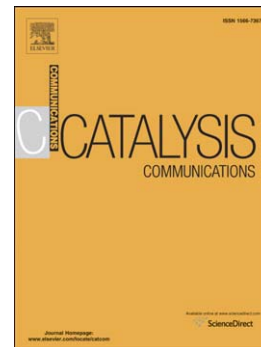
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# Selective Oxidation of Glycerol to Formic Acid Catalyzed by Iron Salts

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## Abstract

Glycerol is oxidized by hydrogen peroxide to formic acid with excellent selectivity in the presence of iron salts. The oxidation takes place at room temperature in water; at the end of the reaction the catalytic system is still active and available to restart the oxidation.

## Keywords

Iron catalysts; Glycerol valorization; Selective oxidation; Hydrogen peroxide; Formic acid.

## 1. Introduction

In recent years the blooming business of biodiesel fuels has led to an increasing surplus of glycerol as the main by-product of transesterification of biomass-derived triglycerides with methanol. As a consequence, studies regarding the development of feasible and convenient ways to transform glycerol in higher value products have proportionally increased in number. Such valorization would make the biofuels production significantly cheaper and therefore affordable in comparison to traditional fossil fuels.

From several points of view glycerol is a versatile molecule, however its high number of functional groups - which is a valuable characteristic for its use as chemical building block - causes at the same time the hardest difficulties in the set up of selective reactions. Among the possible glycerol valorization routes oxidation is one of the most studied, since the potentially obtainable products are all commercially relevant (Scheme 1) [1,2]. However, some of the most appealing products obtainable by glycerol oxidation, *e.g.* dihydroxyacetone (DHA), are themselves rather reactive compounds: therefore, selective oxidation of glycerol often leads to poor yields due to subsequent decomposition of the oxidation products [3].

The difficulties experienced in developing selective routes for a partial oxidation of glycerol would be overcome by pushing the oxidation process to its end, for example to formic acid (FA) as final product. Few studies report glycerol oxidation to FA in the past literature [4], but their number has been growing in very recent years [5-8]. Most of the reported systems are based on heterogeneous catalysts and the oxidant agent can be hydrogen peroxide as well as molecular oxygen.

The rising interest in efficient FA production lies in its use as hydrogen carrier. With its 4.4% hydrogen content and several well known systems able to decompose it in mild conditions to hydrogen and carbon dioxide [9-12], FA might provide a supply for the hydrogen fuel cells [13], as well as for the hydrogenation process of biomasses [14] and even directly as automotive alternative fuel [15] which would perfectly fit with the biofuel production above cited. On the other hand, FA is also a convenient source of C1 raw material for the chemical industry, as it can be easily transformed into carbon monoxide [16].

The pushing requirements of the twelve Green Chemistry principles [17] urge to shift towards more sustainable reactions and the use of iron catalysts in place of rarer and more expensive transition metals [18] meets such expectations, as demonstrated by the growing interest in their applications [19]. Iron compounds have been known to promote alcohols and diols oxidation by hydrogen peroxide since nineteenth century and even glycerol oxidation was briefly described in 1899 [20], but also in the last years both iron salts [21-24] and iron complexes [25-28] were reported to catalyze alcohol oxidation by either molecular oxygen or hydrogen peroxide.

Our group has recently described glycerol oxidation by hydrogen peroxide catalyzed by iron complexes with the tridentate ligand bis(2-pyridinylmethyl)amine (BPA) [29]; these studies have shown that by careful tuning of the experimental setup a remarkably selective formation of DHA can be obtained: on the other hand, in some cases we also detected a significative amount of FA as by-product.

Here we present our results in the oxidation of glycerol by hydrogen peroxide catalyzed by iron salts to give FA with high selectivities and in very mild conditions.

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