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Synthesis of γ-lactones from easily and accessible reactants catalyzed by Cu–MnO$_x$ catalysts

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ABSTRACT

The mechanism of the oxidative [3+2] cycloaddition of alkenes with anhydrides using oxygen as an oxidant to synthesize γ-lactones has been studied using a heterogeneous dual copper-manganese–based catalyst. The cyclization takes place through two coexisting reaction mechanisms, the involvement of different reaction intermediates and a clear synergistic effect between copper and manganese. In fact it appears that CuO clusters dispersed on the surface of a manganese-based oxide increase the redox capability of manganese ions and leads to an increase in the release of oxygen from the surface.

1. Introduction

The direct preparation of γ-lactones from linear substrates (vs carboxylic acids, ketoesters, and so on) has attracted much attention despite the main restrictive limitation of these linear molecules is that they are usually obtained through a multiple-step synthesis [1]. For this reason, the use of simple and easily available substrates is highly desirable. Among such alternative strategies, the carboesterification reaction of alkenes is a useful approach to γ-lactones [2] because of their high potential for application in natural product and drug synthesis [3].

Among the elements that have shown activity in this reaction, the case of manganese and copper must be emphasized. In this regard, manganese has not behaved as a true catalyst, because stoichiometric quantities of this element are needed to complete the reaction [4], whereas copper complexes have shown activity although with the problems of recovery and reuse [5]. In this context, a full mechanistic study has been conducted on different manganese-based oxides to understand the main physicochemical features of these solids that can lead to maximize both the activity and selectivity values during the carboesterification reaction of alkenes.

For achieving this, a variety of different manganese-based oxides have been prepared and some of them have been doped with copper [6], in an attempt to find if these elements were acting separately or jointly through a plausible synergistic mechanism.

Indeed, previous studies reported the use of copper(II) as co-oxidant in transformations of intermediate radicals to carbocations [7] and for improving the ability of manganese to exchange electrons in eventual oxidation/reduction processes [8].

In view of these precedents, here we developed a manganese/copper dual system that uses air as a terminal oxidant so that the carboesterification reaction of alkenes can take place. We have shown that the reaction mechanistic studies not only allow a better understanding of how the reaction occurs but also help to improve the catalyst design for achieving higher activities and selectivities.

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2. Results and discussion

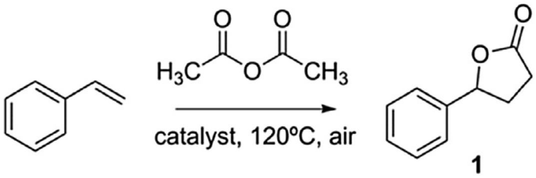
2.1. Screening of copper and manganese-based catalysts for the carboesterification reaction of styrene to obtain γ-lactones

Pioneering mechanistic studies on the synthesis of γ-lactones from olefins in the presence of the Mn(III) salt ($Mn(OAc)_3$) [4] pointed to two possible reaction pathways to explain the formation of these cyclic esters: (1) a radical mechanism and (2) a single-electron transfer mechanism. A more recent study described the MnO_2-promoted carboesterification of alkenes pointing to the intervention of a radical pathway as a plausible reaction mechanism in the presence of additives such as LiBr and NaOAc [9].

In this context, previous studies by Huang et al. showed that a copper(II) salt efficiently catalyzed the [3+2] cycloaddition of alkenes with acetic anhydrides to give γ-lactones [5] with good to excellent yields and a tentative mechanism based on the enolization of the starting anhydride was suggested [10]. A priori, both reaction routes with copper and manganese have in common the use of LiBr (20%) and bases as additives. Nonetheless, the route with copper differs in the participation of ionic intermediates unlike the manganese route.

Taking into account the aforementioned precedents, a series of amorphous (MnO_x) and crystalline manganese-based oxides (Mn_2O_3, molecular sieve cryptomelane OMS-2 and the layered manganese-based oxide birnessite OL-Na) were synthesized via a variety of preparative methods (see Section 3). The resulting materials were properly characterized [6,11]. All these materials were applied as catalysts for the carboesterification reaction of alkenes with anhydrides as a simple approach to γ-lactones, using the styrene carboesterification reaction with acetic anhydride as a model reaction (Scheme 1).

Copper(II) was also incorporated as co-oxidant on these materials to assist in the transformation of hypothetically formed radical intermediates [7] and/or to improve the performance of manganese oxides in eventual redox processes (see Section 3) [8]. We envisaged that copper would influence positively the intermolecular or intramolecular addition to carbon–carbon multiple bonds through any of the hypothetical mechanisms that have been previously pointed out. Then, preliminary investigations focused on the styrene carboesterification reaction with acetic anhydride to give γ-butyrolactone (**1**) as a model reaction using this series of manganese solids in the presence of 20 mol % LiBr and 1 equiv of NaOAc, under air, at 120 °C. Under these reaction conditions, the aforementioned reaction proceeds to afford rather low yields of the cyclic ester **1** (entries 1–6, Table 1).



Scheme 1. Reaction scheme for the [3+2] cycloaddition of styrene with acetic anhydride to afford γ-lactone **1**.

According to the results presented in Table 1, because most manganese-containing materials were active in the reaction (entries 1–6, Table 1), the presence of this element was taken into account along with copper in metal-doped manganese oxides for the interpretation of results (Table 1). Besides, when dealing with mixed valence oxides containing mainly trivalent and tetravalent manganese such as the case of cryptomelane OMS-2 and the laminar material OL-Na, all manganese centers were considered, in principle, as potential active sites [6].

In principle, the fact that similar yields of **1** were achieved with OMS-2 under the aerobic and inert atmosphere evidenced the lack of a regeneration process promoted by molecular oxygen (entries 1–2, Table 1) and reinforced the participation of OMS-2 as a stoichiometric oxidant as it will be shown subsequently. Effectively, we concluded that Mn neither behaved as a true nor as an effective catalyst in the carboesterification of styrene because even stoichiometric amounts of this element were insufficient to complete the conversion of the alkene and afford high yields of **1** (entries 1 and 3, Table 1). Moreover, looking closely at these results included in Table 1, it was observed that increasing amounts of Mn increased significantly the conversion of the vinyl aromatic alkene as well as the selectivity and yield of compound **1** but, in both cases, the mass balances were rather low (entries 1 and 3, Table 1).

Besides, it must be noted that with this series of manganese solids the most relevant secondary products detected by gas chromatography (GC) along with the main product, that is, γ-lactone **1** were (1,2-dibromoethylbenzene) (**2**) and 1-phenylethane-1,2-diyl diacetate (**3**), whereas 2-oxo-2-phenylacetate was detected at the level of traces (entries 1–6, Table 1) (Fig. 1).

At this point, we attempted to make the reaction catalytic by incorporating copper on the solids and reducing the amount of manganese accordingly. The incorporation of copper on the microporous material OMS-2 led to a slight improvement in the conversion and selectivity values, the mass balances notably improved, although the catalytic results were still rather far from optimum (entries 1 and 7, Table 1).

In parallel, a series of differently loaded copper catalysts were prepared using the same manganese oxide OMS-2 as support. All materials gave from low to moderate results as catalysts (entries 8–12, Table 1). Transmission electron microscopy (TEM) analysis of these copper-doped samples showed a rather heterogeneous distribution of CuO particles on the surface of OMS-2 regardless of the copper loading, evidencing the lack of an optimal and adequate dispersion and explaining the poor catalytic results.

From the aforementioned results, it was found that stoichiometric amounts of manganese from mixed valent oxide OMS-2 doped with copper Cu(1.66%)/OMS-2 afforded the best results of activity and selectivity for the synthesis of the lactone **1** (entry 11, Table 1), whereas other combinations with upper or lower copper and manganese loadings gave much poorer results (entries 8–12, Table 1). At this point, we could confirm that the lactonization reaction was taking place on the surface of Cu(1.66%)/OMS-2, and not by dissolved species because the elimination of the

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