

Supported palladium metal as heterogeneous catalyst precursor for the methoxycarbonylation of cyclohexene

Andrea Vavasori^{a,*}, Sara Bravo^a, Francesco Pasinato^a, Nurbolat Kudaibergenov^b, Luca Pietrobon^a, Lucio Ronchin^a

^a Department of Molecular Science and Nanosystems, Ca' Foscari University Venice, Scientific Campus, via Torino 155, 30172 Venezia, Italy

^b Department of Chemistry and Chemical Technology, Al-Farabi Kazakh National University, al-Farabi 71, 050038 Almaty, Kazakhstan

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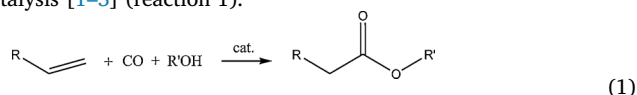
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ABSTRACT

The methoxycarbonylation of cyclohexene has been carried out by using Pd metal deposited on a support as heterogeneous precursors instead of the homogeneous Pd(II) complexes usually proposed in literature. The two catalytic systems (homogeneous and heterogeneous) have been compared in methanol in the presence of free triphenylphosphine and p-toluenesulfonic acid as promoter. The precursor Pd on Amberlyst IRC 50 led to the best catalytic activity which is comparable to the activity obtained by using the homogeneous Pd(II)-catalyst. The leaching of the metal was negligible and the system has been efficiently recycled at least for three times. A reaction mechanism has been also proposed and discussed.

1. Introduction

The alkoxy carbonylation of alkenes, catalyzed by transition-metals, is among the most important processes in the area of homogeneous catalysis [1–3] (reaction 1).



Such reaction is widely used in industry to produce a variety of esters which found application mainly as fragrant components in perfumes, cosmetics, and food essences [4,5], moreover it is also used in many organic syntheses as valuable intermediate products [1–3,6].

As compared to other syntheses of esters, the alkoxy carbonylation of olefins has such important advantages as one-step process, mild reaction conditions, and the use of accessible reagents [1–3]. Furthermore, it is highly atom-efficient which is important for chemical industries interested to the sustainability of the process [7]. Undoubtedly, the Pd(II)-phosphines catalysts appear as the most promising because afford to high activity and selectivity under relatively mild conditions [1–3,8–19]. For instance, in the first step of the Lucite Alpha-process for the production of methyl methacrylate, a very active Pd-diphosphine catalyst is used to catalyze the production of methylpropionate via methoxycarbonylation of ethene [20–25].

With the aim to improve the catalytic activity several authors have studied the influence of the process parameters, the nature of the acid

promoter, the structure of the ligands, the nature of the olefins carbonylated, together with the kinetic and mechanistic aspects of the reaction [26–33]. However, one of the major drawbacks from an industrial point of view of such homogeneous process is the need to recover the catalyst from the reaction mixture [34,35]. An obvious solution to this separation problem could be the use of heterogeneous catalysts, which can be readily recovered by a simple filtration step [36–40]. Among the several approaches proposed, some interesting results have been obtained by immobilizing the homogeneous Pd(II)-catalysts on an insoluble support (e.g., silica, alumina [41–44], or polymers [45–57]). However, the synthetic methods usually utilized are complicated leading to partly unknown structures of the Pd(II) species, which are therefore less active but also more unstable (reduction to inactive Pd(0) or Pd metal species).

In the present paper the authors propose to carry out the methoxycarbonylation of cyclohexene by using Pd metal deposited on a support as heterogeneous catalyst precursor. Such new starting precursor has been compared with an homogeneous ones (for instance with the [Pd(TsO)₂(PPh₃)₂] complex previously studied by the authors [30]) in methanol as solvent and in the presence of phosphines (e.g. triphenylphosphine, PPh₃) and a Bronsted acid (e.g. p-toluenesulfonic acid, TsOH) as a promoter [30,31]. Different heterogeneous pre-catalysts have been readily prepared and tested. Among these the Pd on Amberlyst IRC 50 led to the best catalytic activity, comparable to the homogeneous system [Pd(TsO)₂(PPh₃)₂] [30,31]. The leaching of the

* Corresponding author.

E-mail address: vavasori@unive.it (A. Vavasori).

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