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Esterification, transesterification and hydrogenation reactions of polyunsaturated compounds catalyzed by a recyclable polymer supported palladium catalyst

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ABSTRACT

Aliphatic and aromatic carboxylic acids were converted into their corresponding esters using a polymer supported palladium(II) β-ketoesterate complex under hydrogen atmosphere in the presence of catalytic bromobenzene in alcohols. This method was also applicable to the transesterification of esters. Good to excellent yields were obtained for different aliphatic or aromatic starting materials. The esterification (or transesterification) was promoted by the *in situ* generation of HBr from bromobenzene, which provided a mild acidic reaction environment. Pd(II) centers were converted into polymer stabilized metal nanoparticles (the true active species) under reaction conditions. The palladium catalyst exhibited a remarkable activity and was reusable for eight consecutive cycles. The present system was also tested for the preparation of partially hydrogenated fatty acid methyl esters, starting from a mixture composed by highly polyunsaturated esters and free carboxylic acids, taken as a model acidic feedstock for biodiesel upgrading.

1. Introduction

Esterification of carboxylic acids and transesterification of esters are important reactions having wide industrial applications for the synthesis of fragrances, flavors, polymers, pharmaceutical and agricultural compounds [1–3]. In this regard, many useful and reliable catalytic systems for the synthesis of esters [4–7] and for transesterification reactions [8–13] have been reported in the literature. In addition, esterification and transesterification reactions are of great interest for the preparation of biodiesel [14], which is commonly produced from either transesterification of natural triglycerides (animal fats or vegetable oils) or from esterification of free fatty acids (FFAs) with methanol to give fatty acid methyl esters (FAMEs) [15]. Another important aspect in biodiesel synthesis is the amount of polyunsaturated compounds in the feedstock. Products that comprise large amounts of highly unsaturated FAMEs are more susceptible to oxidation (rancidity) but, on the other hand, have better cold flow properties than highly saturated products [16], so a useful biodiesel should have a large amount of monounsaturated FAMEs and low quantities of both saturated and polyunsaturated FAMEs. Many efforts have been recently made to design catalytic systems aiming at biodiesel upgrading by partial hydrogenation of FAMEs [17,18], also with palladium based catalysts [19–22].

On the basis of the above considerations, we could argue that a catalytic system able to simultaneously promote esterification, transesterification and partially hydrogenation reactions would be interesting both for fine chemicals synthesis and for biodiesel production.

Recently, it has been reported that the esterification of carboxylic acids and the transesterification of esters could be smoothly achieved using Pd/C under hydrogenation conditions (1–4 bars H_2) in the presence of small amount of bromobenzene in alcohols [23]. However, the reported Pd/C catalytic system could be improved (Pd/C is even pyrophoric) mainly from a recyclability point of view, being the catalyst re-usable only up to three times [23].

Aiming at developing a more active system, we decided to evaluate the catalytic activity of a polymer supported palladium catalyst (in the following *Pd-pol*) for the esterification of carboxylic

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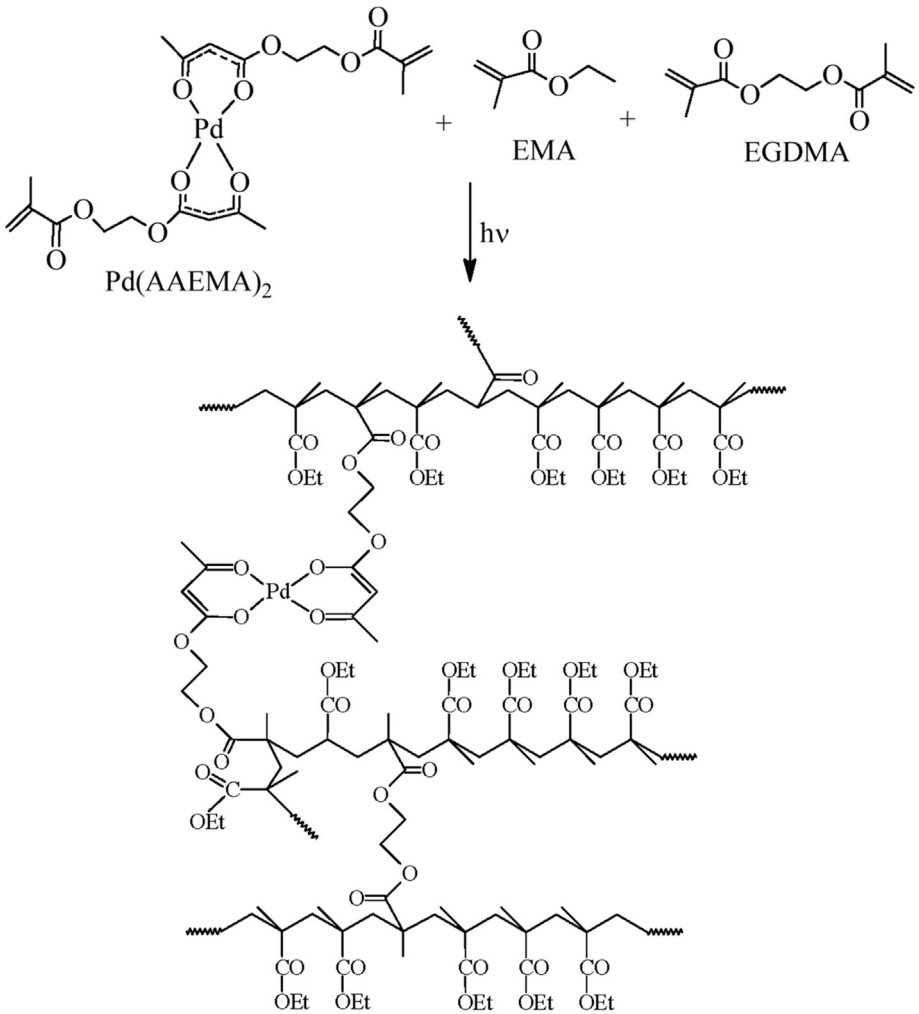
acids and transesterification of esters. In order to obtain a material with a uniform distribution of the active sites, the pre-catalyst was synthesized in an unusual procedure [24], i.e., by co-polymerization of the β-ketoesterate metal-containing monomer $Pd(AAEMA)_2$ [$AAEMA^-$ = deprotonated form of 2-(acetoacetoxy)ethyl methacrylate] with suitable co-monomer (ethyl methacrylate, EMA) and cross-linker (ethylene glycol dimethacrylate, EGDMA) [25] (Scheme 1).

Pd-pol pre-catalyst was successfully employed in several palladium promoted reactions [26–35]. In all cases, the pristine Pd(II) supported complex was reduced *in situ* under reaction conditions to Pd(0), forming palladium nanoparticles (NPs) (the real active species) immobilized onto the insoluble support (*Pd-pol*, Scheme 1) and stabilized by the macro-porous and reticulated polymer matrix [36]. These NPs showed a size distribution centered around 4 nm (when formed under 1 atm H_2 in methanol as the solvent), retaining their morphology and roughly their dimension even after several catalytic runs in hydrogenation reactions [30].

Herein, we report on the catalytic activity and recyclability of *Pd-pol* system in the esterification (and transesterification) reaction by a simple condensation of a carboxylic acid with an alcohol under mild hydrogenation conditions in the presence of catalytic amount of bromobenzene. Since the present system was incidentally able to catalyze also the C=C double bond hydrogenation, we tested the developed protocol in the simultaneous esterification, transesterification and partially hydrogenation of a mixture of free acids and polyunsaturated fatty esters, taken as a model acidic feedstock for biodiesel upgrading.



Scheme 1. Synthesis of *Pd-pol*.