



# Oxidation of benzyl alcohols to aldehydes and ketones under air in water using a polymer supported palladium catalyst



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## ARTICLE INFO

### Article history:

Received 8 November 2013

Received in revised form 27 January 2014

Accepted 1 February 2014

Available online 11 February 2014

### Keywords:

Polymer-supported palladium nanoparticles  
Alcohol aerobic oxidation  
Green chemistry  
Recyclable catalyst  
Water solvent.

## ABSTRACT

This work deals with the catalytic conversion of benzyl alcohols to aldehydes or ketones using a polymer supported palladium catalyst which formed metal nanoparticles under reaction condition. The oxidation reaction was carried out on a series of substituted benzylic alcohols under air in water. The obtained results showed high selectivity also for the oxidation of primary alcohols to aldehydes without over-oxidation products. In addition, the catalyst was recycled several times with negligible metal leaching into solution.

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## 1. Introduction

The oxidation of alcohols to aldehydes and ketones is very important from the academic and industrial point of view because compounds containing carbonyl groups are intermediates of several valuable fine chemicals such as fragrances, perfumes, flame retardants, pharmaceuticals [1]. Commonly, this reaction is obtained by adding stoichiometric amounts of inorganic oxidants ( $\text{KMnO}_4$  or  $\text{CrO}_3$ ) to the alcohol [2]. However, this procedure has the drawback to give pollutant and toxic by-products. With the aim to develop greener processes, the use of molecular oxygen as the oxidant has received growing attention in the past years [3,4], being water the only by-product of the reaction. In this regard, several methods that use molecular oxygen for the oxidation of alcohols under homogeneous and heterogeneous conditions have been exploited [5], using metal promoters such as: ruthenium [6,7], platinum [8,9], rhodium [10,11], copper [12], chromium [13], bimetallic gold–palladium [14] and gold [15–18] catalysts. During the past years there have been significant advances in palladium catalyzed oxidation reactions [19–21], and when the palladium catalyst was soluble, the use of particular ligands was crucial because it led to

high selectivity and turnover numbers [22–24]. The alcohol aerobic oxidation reaction is also promoted by a variety of recyclable palladium catalysts supported onto insoluble matrices, such as SBA-15 [25], nanocrystalline starch [26], mesocellular foam [27], DNA-montmorillonite [28], poly(ethylene-glycol) [29], ionic liquid based organosilica framework [30] and graphene [31]. In these cases, the active species were found to be mostly palladium nanoparticles [26–31]. Although noticeable improvements in terms of selectivity and performance have been achieved, there is still need to develop new recoverable palladium catalysts able to work in “greener” reaction media, since generally the solvents employed in the aforementioned heterogeneous catalytic systems are: toluene [25,26], *p*-xylene [27], supercritical carbon dioxide [29] and  $\alpha,\alpha,\alpha$ -trifluorotoluene [30]. Actually, water was used for the recyclable palladium catalyzed oxidation of several alcohols into carboxylic acids [28] and really interesting results were obtained in the aerobic oxidation of alcohols into aldehydes or ketones in water by employing: an amphiphilic resin dispersion of palladium nanoparticles [32], an aluminum hydroxide-supported palladium catalyst [33], hydroxyapatite-supported palladium nanoclusters [34]. However, in the latter cases, except for the Uozumi amphiphilic resin [32], the use of water as the solvent was limited to a marginal portion of the studies, being the activity and recyclability of the catalysts tested mostly in toluene or trifluorotoluene. The use of water as reaction media for the aerobic alcohol oxidation would be preferable and it

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has several benefits, since it is cheap, nontoxic, nonflammable and allows an easy recovery of the products due to the insolubility in water of the majority of the organic compounds. Furthermore, the solubility of molecular oxygen in water is higher than in common organic solvents. With this scenario in mind, we decided to evaluate the catalytic activity of a polymer supported palladium catalyst (in the following *Pd-pol*) for the aerobic alcohol oxidation in water. The catalyst was obtained by co-polymerization of the metal-containing monomer [35] Pd(AAEMA)<sub>2</sub> [AAEMA<sup>-</sup> = deprotonated form of 2-(acetoacetoxy)ethyl methacrylate] with suitable comonomer (ethyl methacrylate) and cross-linker (ethylene glycol dimethacrylate) [36,37] and it was already found active and recyclable in many palladium promoted reactions [38–43], even under air in water [44]. The reticular and macro porous polymeric support of *Pd-pol* is able to immobilize and stabilize palladium nanoparticles (formed under reaction conditions by reduction of the pristine Pd(II) anchored complex), suitable for the Suzuki cross coupling of arylhalides with arylboronic acids in water [44] and for the reductive amination reaction under 1 atm of H<sub>2</sub> [42]. Furthermore, the good swellability in water renders *Pd-pol* an ideal potential catalyst for reactions carried out in water, since the migration of the reagents to the active sites would not be hampered by the solid support.

Herein we report on the ability of *Pd-pol* in efficiently catalyzing the selective oxidation of a wide variety of alcohols into aldehydes and ketones under air as the oxidant and water as solvent.

## 2. Experimental

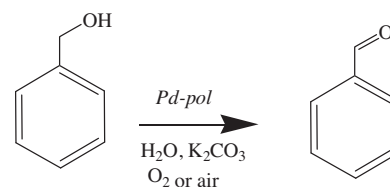
### 2.1. Materials

Tap water was de-ionized by ionic exchange resins (Millipore) before use. All other chemicals were purchased from commercial sources and used as received. *Pd-pol* was synthesized according to literature procedure [37]. Palladium content in *Pd-pol* was assessed after sample mineralization by atomic absorption spectrometry using a Perkin–Elmer 3110 instrument. Catalyst mineralization prior to Pd analyses was carried by microwave irradiation with an ETHOS E-TOUCH Milestone applicator, after addition of 12 mL HCl/HNO<sub>3</sub> (3:1, v/v) solution to each weighted sample.

GC-MS data (EI, 70 eV) were acquired on a HP 7890 instrument using a HP-5MS cross-linked 5% PH ME siloxane (30.0 m × 0.25 mm × 0.25 μm) capillary column coupled with a mass spectrometer HP 5973. The products were identified by comparison of their GC-MS features with those of authentic samples. Reactions were monitored by GLC or by GC-MS analyses. GLC analysis of the products was performed using a HP 6890 instrument equipped with a FID detector and a Supelcowax-10 capillary column (30.0 m × 0.25 mm × 0.25 μm). Conversions and yields were calculated by GLC analysis as moles of oxygenated product per mole of starting alcohol by using biphenyl as internal standard.

### 2.2. Typical oxidation of alcohols

Into a reaction vessel with a reflux condenser were placed *Pd-pol* (23.1 mg, Pd<sub>w</sub> = 2.3), benzyl alcohol (108.1 mg, 1.0 mmol), K<sub>2</sub>CO<sub>3</sub> (138.2 mg, 1.0 mmol) and water (5 mL). The resulting mixture was stirred at 100 °C under 1 atm of air. After 6 h, the mixture was cooled down to room temperature and the organic product was extracted with ethyl acetate (3 mL). The water phase was washed with ethyl acetate (2 × 5 mL) and the organic layers were collected. GLC analysis of the ethyl acetate solution using biphenyl as an internal standard gave a 98% yield of benzyl aldehyde with >99% selectivity.



**Scheme 1.** Aerobic oxidation of benzyl alcohol under aerobic conditions in the presence of *Pd-pol*.

### 2.3. Recycling experiments

A two necked round flask was charged in air with *Pd-pol* (0.5 mol% Pd), benzyl alcohol (108.1 mg, 1.0 mmol), K<sub>2</sub>CO<sub>3</sub> (138.2 mg, 1.0 mmol) and water (5 mL) and the whole system was put in a thermostated bath at 100 °C under vigorous magnetic stirring at reflux. After the minimum time needed to reach reaction completion, the mixture was cooled down to room temperature. The catalyst was recovered by filtration, washed with water, acetone, and diethyl ether and dried under high vacuum. The recovered catalyst was weighed and reused employing appropriate amounts of organic substrate and base, assuming that the palladium content remained unchanged with the recycles. Iteration of this procedure was continued for six reuses of the catalyst.

## 3. Results and discussion

The aerobic oxidation of benzyl alcohol was used as the model reaction in the presence of *Pd-pol* as the catalyst (Scheme 1).

The reaction was significantly affected by different parameters, such as reaction temperature and presence of the base. After the explorative experiments summarized in Table 1, the best conditions were found to be those employed in entry 5, that is: benzyl alcohol (1.0 mmol), *Pd-pol* (0.5 mol% of Pd), K<sub>2</sub>CO<sub>3</sub> (1.0 mmol), air (1 atm) in water (5 mL) at 100 °C for 6 h.

The reported results revealed that in the absence of base at room temperature the conversion into benzyl aldehyde was poor both under air and under 1 atm pressure of O<sub>2</sub> (entries 1 and 2), while at 100 °C it increased under air up to 57% in 16 h (entry 3) with a 77% selectivity in benzyl aldehyde, being benzoic acid and its benzyl ester the over oxidation side-products. The reaction performed at 100 °C under dioxygen in the absence of base gave better results (entry 4) giving a 75% conversion into benzyl aldehyde in 6 h, and the presence of the base at 100 °C (entry 5) increased the catalytic activity of the system avoiding the use of 1 atm pressure of O<sub>2</sub>.

The best conditions reported in entry 5 of Table 1 were applied in the same oxidation reaction carried out in the absence of the palladium catalyst (entry 6). No oxidation of the model substrate occurred at all, even after 12 h stirring.

Using the optimized reaction conditions, the activity and the scope of the catalyst was explored in the aerobic oxidation of a variety of different primary and secondary alcohols (Table 2).

Table 2 summarizes the most significant results. Both electron rich (entries 1–3) and electron deficient (entries 4 and 5) derivatives of benzyl alcohol showed excellent reactivity and afforded the corresponding aldehydes in quantitative yields. As expected, secondary alcohols were more difficult to oxidize. In fact, 1-phenylethanol (entry 6) and 1-phenylpropanol (entry 7) furnished excellent yields of corresponding ketones under optimized reaction conditions, though it was necessary to increase the reaction times to 16 h to ensure complete conversion. It is also noteworthy that, under the same conditions, the aerobic oxidation of benzyl alcohol promoted by a palladium(II) soluble catalyst extensively used in these kind of reactions, [24] such as palladium acetate (entry 8) gave only 40% conversion of the substrate into benzylaldehyde

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