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Highly selective hydrogenation of quinolines promoted by recyclable polymer supported palladium nanoparticles under mild conditions in aqueous medium

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ABSTRACT

Polymer supported palladium catalyst, obtained by copolymerization of Pd(AAEMA)$_2$ [AAEMA$^-$ = deprotonated form of 2-(acetoacetoxy)ethyl methacrylate] with ethyl methacrylate (co-monomer) and ethylene glycol dimethacrylate (cross-linker), exhibited excellent activity and selectivity for the hydrogenation of quinolines to 1,2,3,4-tetrahydroquinolines under mild temperature (80 °C) and H_2 pressure (10 bar) in aqueous medium. Both the activity and selectivity could be maintained for at least nine reaction runs. No metal leaching into solution occurred during application. TEM analyses carried out on the catalyst showed that the active species were supported palladium nanoparticles having a mean size of 4 nm, which did not aggregate with the recycles.

1. Introduction

1,2,3,4-Tetrahydroquinolines are important intermediates for the synthesis of drugs, agrochemicals, dyes, alkaloids, and many other biological active molecules [1–3]. Although different methods have been developed for their synthesis, such as catalytic cyclization [4,5] and the Beckman rearrangement [6], the direct catalytic hydrogenation of readily available quinolines should be the best approach to access tetrahydroquinolines in terms of atom economy. However, this catalytic hydrogenation is not as trivial as the simple reduction of a C═C or a C═N double bond could be [7]. In fact, quinolines are challenging substrates [8] for the following reasons: (i) the aromatic rings render these molecules reluctant to undergo hydrogenation; (ii) the presence of the *N*-heterocycle often results in strong interaction with the catalyst poisoning it [9,10]; (iii) the formation of strong hydrogen bonds between the substrate (at the *N* position) and the solvent molecules (when these are protic molecules) may impede the interaction of the substrate with the catalyst [11], thus rendering the common hydrogenation catalytic systems, generally designed to work in methanol or ethanol, uneffective [12].

Many soluble metal catalysts based on Os [13], Ir [8,14] Ru [15–17] and Rh [18,19] can reduce the quinoline ring, but they are difficult to be re-used and very often they need the presence of a co-catalyst. Recently, heterogeneous catalytic systems based on noble metals [20], such as Ru [21,22], Rh [23] and Au [24] have been developed. In some cases they are vulnerable to the poisoning effect of strongly adsorbed quinolines and/or their hydrogenated derivatives. Moreover, clear drawbacks of these systems are: (i) their low activity under mild reaction conditions, since almost all quinoline hydrogenation catalysts require high pressures (30/60 bar) and temperatures (100/150 °C), (ii) the need of organic solvents (for example: toluene).

Recently, water has been viewed as an eco-friendly alternative to common organic solvents because it is non-toxic, nonflammable, has a high heat capacity, is cheap and renewable. In some cases, due to its high polarity, its acid–base properties and its hydrogen bonding ability, water may influence the reactivity and the selectivity of certain catalytic systems. However, it is known that the formation of hydrogen bonds between the hydroxyl groups of the water and the quinoline nitrogen may inhibit the absorption of the

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substrate on the surface of the catalyst, thus lowering its activity [25]. For this reason, despite the advantages in using water as the solvent, only a limited number of heterogeneous catalysts have been employed for promoting the hydrogenation reactions of quinolines in water. Among them, Ru nanoparticles intercalated in hectorite were found to be active in water under 30 bar H_2 at 100 °C for the partial reduction of quinoline, but their recyclability was really poor because of separation problems in aqueous media [26]. A water soluble Ir complex anchored onto a solid support has been used as catalyst for the hydrogenation of quinolines in water under 20 bar H_2 at 80 °C, but it suffered from severe metal leaching [27]. Palladium nanoparticles stabilized by black wattle tannin were active and recyclable in the quinoline hydrogenation at 60/80 °C under 20 bar H_2 both in neat water [28] and in a biphasic system made by water and an immiscible organic solvent [29]. On the contrary, Pd nanoparticles grafted onto polymeric mesoporous carbon graphitic nitrides were almost inactive for the quinoline hydrogenation in water, being much more efficient catalyst in acetonitrile or toluene even under 1 atm H_2 [30]. A similar behavior has been observed for Pd/MgO catalyst, active in hexane under 40 atm H_2 at 150 °C [31], and for the catalytic system based on hydroxyapatite supported Pd nanoparticles, for which the best solvent in terms of activity and recyclability under mild conditions was toluene [32].

With the aim to develop innovative catalytic processes that enable chemical transformations to be performed under mild and sustainable conditions with high efficiency, we decided to evaluate the catalytic activity of a polymer supported palladium catalyst (in the following *Pd-pol*) for the partial hydrogenation of quinolines in water. In order to obtain a material with a uniform distribution of the catalytically active sites, the catalyst was not synthesized by classical immobilization of palladium centers onto a pre-fabricated support, but it was prepared by co-polymerization of the metal-containing monomer [33] $Pd(AAEMA)_2$ [$AAEMA^-$ = deprotonated form of 2-(acetoacetoxy)ethyl methacrylate] with suitable co-monomer (ethyl methacrylate) and cross-linker (ethylene glycol dimethacrylate) [34,35] (Scheme 1).

Pd-pol was already found active and recyclable in several palladium promoted reactions, [36–41] even under air and in water solvent [42]. 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 [42] for the aerobic selective oxidation of benzyl alcohols in water [43], and for the reductive amination reaction under 1 atm of H_2 [40]. Furthermore, its 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* to efficiently catalyze the selective reduction of quinolines into tetrahydroquinolines under mild conditions in aqueous medium.

2. Experimental

2.1. General considerations

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* ($Pd\%_w = 2.3$) was synthesized according to literature procedure [41]. 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_3 (3:1, v/v) solution to each weighted sample.

GC–MS data (EI, 70 eV) were acquired on a HP 6890 instrument using a HP-5MS crosslinked 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 HP-1 (Crosslinked Methyl Siloxane) capillary column (60.0 m × 0.25 mm × 1.0 μm). Conversions and yields were calculated by GLC analysis as moles of hydrogenated product per mole of starting substrate by using biphenyl as internal standard.

The microstructure of the polymeric matrix embedded Pd nanoparticles was determined by TEM observations at acceleration voltage of 100 kV (Model HITACHI 7700). The samples were prepared by dispersing the powders in distilled water using an ultrasonic stirrer and then placing a drop of suspension on a pretreated copper grid, which was coated with an amorphous thin carbon film. The particle size distributions were obtained by TEM image analysis using the ImageJ software (freeware software: http://rsb.info.nih.gov/ij/).

2.2. General procedure for catalytic hydrogenation of quinolines

In a typical run, a 50 mL stainless steel autoclave equipped with a transducer for online pressure monitoring was charged, under air, of *Pd-pol* (23.2 mg, Pd: 0.5 mol%), the substrate (1.0 mmol), and water (5.0 mL) or water (4.0 mL) and CH_3OH (1.0 mL). The autoclave was then purged three times with hydrogen, then pressurized with 10 bar H_2, set on a magnetic stirrer and heated to 80 °C. After the minimum time needed to reach reaction completion, the autoclave was let to reach room temperature, the hydrogen was vented and the autoclave opened. The catalyst was recovered by filtration while 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. The yields were assessed by GLC analysis of the ethyl acetate solution with the internal standard (biphenyl) method.

2.3. Recycling experiments

The catalyst recovered by filtration was washed with water, methanol, and diethyl ether and dried under high vacuum. The recovered catalyst was thus weighed and reused for a new cycle employing appropriate amounts of organic substrate and solvent, assuming that the palladium content remained unchanged with the recycles. Iteration of this procedure was continued for nine reuses of the catalyst.

3. Results and discussion

In exploratory experiments, we selected the hydrogenation of 8-methylquinoline to the corresponding 8-methyl-1,2,3,4-tetrahydroquinoline as the model reaction to study the catalytic activity and selectivity of *Pd-pol* (Scheme 2). The relevant results are reported in Table 1.

The reaction was significantly affected by different parameters, such as reaction temperature, hydrogen pressure and solvent. After the experiments summarized in Table 1, the best *sustainable* conditions were found to be those employed in entry 6, that is: 8-methylquinoline (1.0 mmol), *Pd-pol* (0.5 mol% of Pd), hydrogen (10 bar) in water/methanol (4 mL/1 mL) at 80 °C for 9 h.