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Polymer supported palladium nanocrystals as efficient and recyclable catalyst for the reduction of nitroarenes to anilines under mild conditions in water

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ABSTRACT

Polymer supported palladium nanoparticles, generated *in situ* by Pd(II) reduction under reaction conditions, catalyzed the hydrogenation of nitroarenes to anilines with high efficiency in water at room temperature in the presence of $NaBH_4$. The protocol proved to be highly selective and generally favored the formation of the desired aniline as single product in high yields with short reaction times. TEM analyses revealed that the size distribution of the formed Pd nanocrystals was regulated by the reductant agent. In details, when 1 atm H_2 was used as the nitroarene reductant, the *in situ* generated polymer supported palladium nanoparticles were crystallites with diameters ranging from 6 to 10 nm. On the contrary, when the reaction was carried out in the presence of $NaBH_4$ in water under N_2 or air, the formation of Pd nanocrystallites was observed as well, but this time they were smaller (mean size diameter *ca.* 3 nm) and catalytically more active compared to the palladium nanoparticles formed under 1 atm H_2 in the absence of $NaBH_4$.

The catalyst displayed excellent recyclability over twelve cycles and no leaching of metal into solution occurred, which made the overall system eco-friendly and economic.

1. Introduction

Aromatic amines are highly valuable chemical intermediates widely used in the manufacture of pharmaceuticals, polymers, pesticides, explosives, fibers, dyes and cosmetics [1]. Current industrial production of aniline involves the catalytic hydrogenation of nitrobenzene with copper, palladium or palladium-platinum supported on carbon or inorganic oxides, with the use of high pressure (up to 3 MPa) and high temperature (up to 300 °C). On the other hand, the traditional Béchamp reduction treats the nitroarene with stoichiometric amounts of Fe metal under acidic conditions, thus generating large amounts of waste. Another challenge that persists in these reactions is the unavoidable formation of harmful azo- and azoxyderivatives, which lower the yield into the desirable anilines. In order to overcome all these disadvantages, great efforts have been made by the scientific community with the aim to develop greener and cheaper hydrogenation catalytic systems with higher yields. Numerous protocols for the reduction of aromatic nitro compounds have been reported in the literature [2–7]. They include: 1) hydrogenation under H_2 at various pressures promoted by various catalysts [8], such as Pt/C [9], Rh_3Ni_1 [10], Pd/C [11–13], Pd [14,15] and Rh [16] nanoparticles; 2) catalytic reduction in the presence of CO and H_2O [17] and photocatalytic hydrogenation [18]; 3) catalytic transfer hydrogenation promoted, for example, by Cu [19], Pd [20], palladium/graphene [21], Au [22], Ru [23] or Fe_3O_4-Ni [24] nanoparticles with reducing agents other than molecular hydrogen [25,26], including hydrazine [27–32], silanes [33,34] and sodium borohydride [35–41]. In this last case, large use of Au based catalysts has been explored [42].

However, the major problems remains unsolved and the development of more effective, less toxic, and handle-convenient catalysts for this transformation is still highly desirable.

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

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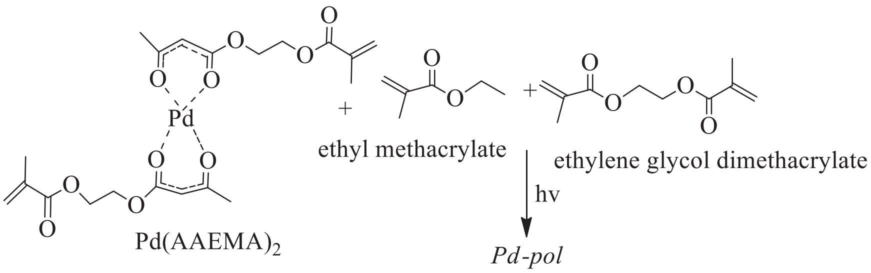

Scheme 1. Synthesis of *Pd-pol*.

evaluate the catalytic activity of a polymer supported palladium catalyst (in the following *Pd-pol*) for the hydrogenation of nitroarenes in water. In order to obtain a material with a uniform distribution of the catalytically active sites, the catalyst was not synthetized by classical immobilization of palladium centers onto a pre-fabricated support, but it was prepared by co-polymerization of the metal-containing monomer [43] Pd(AAEMA)$_2$ [AAEMA$^-$ = deprotonated form of 2-(acetoacetoxy)ethyl methacrylate] with suitable co-monomer (ethyl methacrylate) and cross-linker (ethylene glycol dimethacrylate) [44,45] (Scheme 1).

Pd-pol was already found active and recyclable in several palladium promoted reactions [46–51]. As reported for nanoclustered palladium supported on methacrylate based resins [52], 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 [53], for the aerobic selective oxidation of benzyl alcohols in water [54], for the selective hydrogenation of quinolines in aqueous medium under mild conditions [55], and for the reductive amination reaction under 1 atm of H_2 [50]. Furthermore, its good swellability in water renders *Pd-pol* an ideal potential catalyst for reactions carried out in aqueous solvent, since the migration of the reagents to the active sites would be not hampered by the solid support.

Herein, we report on the high activity and recyclability of *Pd-pol* in promoting the nitrobenzenes hydrogenation into anilines in water in the presence of sodium borohydride, a well-known reducing agent with wide applications in organic synthesis for its ready availability, ease of handling, and low cost [56]. In addition, in this paper we demonstrate how the way in which the hydrogen is added to the reaction mixture (by reaction between $NaBH_4$ and water or by external balloon) influences the nanostructure and consequently the activity of the *in situ* formed Pd nanoparticles.

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* was synthesized according to literature procedure [45]. Palladium content in *Pd-pol* was assessed after sample mineralization by atomic absorption spectrometry using a Perkin–Elmer 3110 instrument. The experimental error on the palladium percentage was ±0.3.

Mineralization of *Pd-pol* prior to Pd analyses was carried by microwave irradiation with an ETHOS E-TOUCH Milestone applicator, after addition of HCl/HNO_3 (3:1, v/v) solution (12 mL) to each weighted sample.

Microwave irradiation up to 1000 W was used, the temperature being ramped from rt to 220 °C in 10 min and the sample being held at this temperature for 10 min. After cooling to room temperature the digested *Pd-pol* was diluted to 1000 mL before submitting to Graphite Furnace Atomic Absorption Spectrometric palladium determination.

GC-MS data (EI, 70 eV) were acquired on a HP 6890 instrument using a HP-5MS cross-linked 5% PH ME siloxane ($30.0\,m \times 0.25\,mm \times 0.25\,\mu m$) 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 ($60.0\,m \times 0.25\,mm \times 1.0\,\mu m$). Conversions and yields were calculated by GLC analysis by using biphenyl as internal standard, or by column chromatography using silica gel and *n*-hexane/ethyl acetate as the eluent.

The microstructure of the polymeric matrix embedded Pd nanoparticles was determined by TEM observations at acceleration voltage of 200 kV (Model JEM 2010, Jeol, Akishima Tokyo, Japan), equipped with X-ray energy dispersive spectroscopy (EDS). The samples were prepared by dispersing the powders in distilled water using an ultrasonic stirrer and then placing a drop of suspension on a copper grid covered with a transparent polymer film, followed by drying and carbon coating. The particle size distributions were obtained by TEM image analysis using the ImageJ software (freeware software: http://rsb.info.nih.gov/ij/). Each morphology observation was accompanied by EDS confirmation for the presence of Pd.

2.2. General experimental procedure for the reduction of nitroarenes catalyzed by Pd-pol using NaBH$_4$ as reducing agent

1.0 mmol of nitroarene, 37.2 mg of *Pd-pol* ($Pd\%_w = 5.0$, 0.0175 mmol of Pd) and 10.0 mmol of sodium borohydride were stirred under nitrogen at room temperature in 5 mL of double deionized water for the appropriate amount of time, using a three-necked flask equipped by a gas bubbler in order to discharge the hydrogen excess produced during reaction. The progress of the reaction was monitored by GLC. After completion of the reaction, the reaction mixture was centrifuged to separate the catalyst. The solid residue was first washed with deionized water and then with acetone and diethyl ether to remove any traces of organic material. The filtrate containing the reaction mixture was extracted with ethyl acetate (3× 5 mL) and then dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to yield the crude product, which was then purified by column chromatography using silica gel and *n*-hexane/ethyl acetate as an eluent to afford the pure product. The products were characterized by GC–MS by comparison with authentic samples. For the assessment of