



Polydopamine supported palladium nanoparticles: Highly efficient catalysts in Suzuki cross-coupling and tandem Suzuki cross-coupling/nitroarene reductions under green reaction conditions



Attila Kunfi^{a,b}, Zoltán May^c, Péter Németh^c, Gábor London^{a,*}

^a Institute of Organic Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Magyar tudósok körútja 2., 1117 Budapest, Hungary

^b Department of Organic Chemistry, University of Szeged, Dóm tér 8, 6720 Szeged, Hungary

^c Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Magyar tudósok körútja 2., 1117 Budapest, Hungary

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ABSTRACT

The application of an easily prepared and highly active polydopamine-supported Pd nanoparticles catalyst in Suzuki cross-couplings and tandem Suzuki cross-coupling/catalytic transfer hydrogenation sequences under green reaction conditions is described. In Suzuki cross-couplings between aryl bromides and arylboronic acids Pd concentrations down to ppm levels could be used, while reactions were completed within minutes. Heteroaryl bromides needed somewhat longer reaction times but could be transformed under otherwise identical conditions. The efficiency of the Suzuki cross-couplings made them compatible with the mechanistically different catalytic nitroarene transfer hydrogenations, yielding valuable biphenyl aniline products in a mild, one-pot tandem fashion. The influence of reaction time, temperature and Pd particle size on the catalyst efficiency and recyclability is also examined.

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1. Introduction

An important class of transformation which is extensively studied and continuously improved regarding its sustainability and compatibility with environmental requirements is the transition metal catalysed carbon-carbon cross coupling reactions [1–5]. Among these, Pd-catalyzed Suzuki cross-coupling [6–8] is arguably the most powerful method for the construction of biaryl compounds with broad applications spanning from the total synthesis of natural products to pharmaceuticals and organic electronics. Pd nanoparticles (PdNPs), either forming from Pd-salts as pre-catalysts or present as stabilized particles, are considered as active catalytic species during this transformation [9,10]. The efficiency of PdNPs in heterogeneous catalysis has attracted a considerable interest recently [11–17].

There is a great variety of methods to prepare PdNPs. In some cases it does not require costly and toxic ligands and complicated synthetic routes [18], however, when PdNPs are stabilized on the surface of tailor made catalyst supports the preparation of the support material might need rather complex and expensive process,

for example in the case of dendrimer synthesis [19,20]. Nevertheless, the nature of the support is usually the key for growing highly active NPs. Sometimes this catalytic activity is so extreme, that only a few ppm concentrations of the Pd species is enough to reach full conversion in C-C coupling reactions (Mizoroki-Heck, Suzuki-Miyaura) within a reasonable time. Growing number of studies appear on such cross-coupling reactions catalysed by ‘homeopathic’ amount of Pd [21–23]. It has been shown, that the size and shape of the NPs play a crucial role [24–27]. The smaller the NP, the more surface atoms are accessible for the substrate, hence the more catalytically active the NP is.

Recently, we have reported [28] a green method to prepare Pd nanoparticles deposited on polydopamine (PDA) in a two-step process (Fig. 1a). In the first step, polydopamine was prepared via the polymerization of dopamine hydrochloride in an aqueous solution in the presence of Tris-buffer (pH = 8.5). PDA is a versatile, bioinspired and biocompatible polymer [29,30] with the ability to reduce Pd(II) to Pd(0) through the oxidation of its catechol moieties to quinones without the addition of any hazardous reducing agent such as N₂H₄ or NaBH₄.

The resulting Pd/PDA catalyst is bench-stable and not sensitive to air or moisture. PdNPs were observed on the surface of the catalyst support with a diameter of 1–3 nm (Fig. 1b) showing

* Corresponding author.

E-mail address: london.gabor@ttk.mta.hu (G. London).

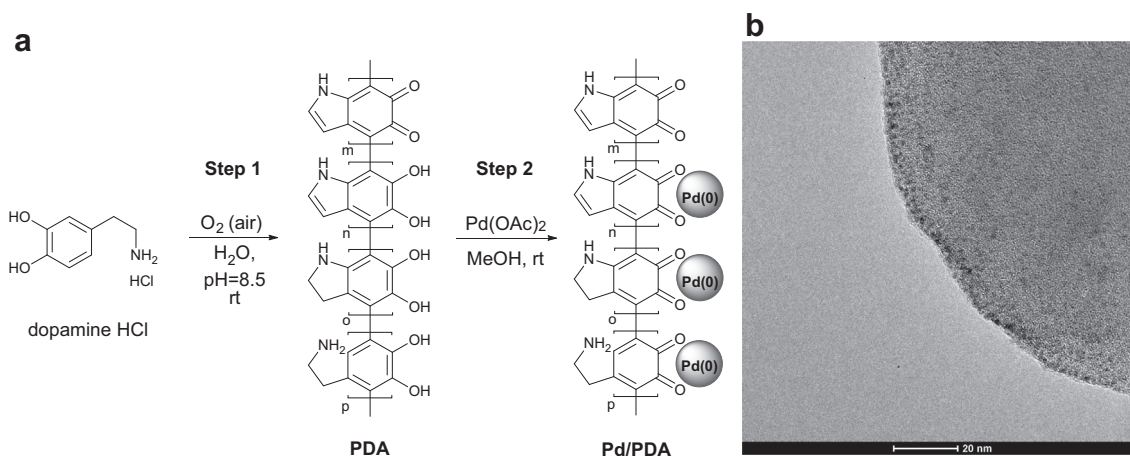


Fig. 1. (a) Preparation of PDA and Pd/PDA from dopamine hydrochloride. (b) TEM image of Pd/PDA.

satisfying activity and recyclability in catalytic transfer hydrogenation (CTH) reactions of nitroaryl compounds [28]. It has to be added, that sugar-based biopolymers are also suitable as support materials of transition-metals for use in catalysis. These systems are mostly cellulose-[31] or chitosan-based [32,33] materials. However, they generally lack the ability to reduce the coordinated metal ions, so either a hydrothermal treatment or external reducing agents (N_2H_4 , $NaBH_4$) are necessary to obtain metal nanoparticles on their surface.

Despite the environmentally benign nature of PDA, there are only a few reports in the literature on C-C coupling reactions catalysed by PDA supported transition metals [34–39] and only a handful of publications are dealing with Suzuki chemistry. Suzuki cross-coupling reactions were performed with Pd/ Fe_3O_4 @PDA catalyst contained PdNPs with a diameter of 10–70 nm [34]. The catalyst was fairly active in the reaction of phenylboronic acid derivatives with iodoarenes delivering the biaryl products after 6 h at 80 °C while the reaction using bromoarenes needed 8–12 h at 100 °C. Using cellulose sponge/PDA composite as a support for PdNPs led to the formation of smaller (1–5 nm) NPs and thus more active catalyst was prepared [37]. In the latter case, the price for the improved activity was a multistep synthesis of the catalyst (including the improvement of the mechanical properties of the cellulose sponge by treatment with γ -glycidoxypropyltrimethoxysilane) and multiple purification steps (including successive Soxhlet extraction with water and acetone). Alternatively, the activity of the larger nanoparticles (10–30 nm) deposited on PDA-CL (CL = carbonized loofah) could be improved by photochemical irradiation in the reaction of haloarenes with phenylboronic acid derivatives at room temperature [36]. (There are other examples where only a single Suzuki-coupling was performed as a model reaction for testing the activity of the prepared catalyst [35].)

In the context of green chemistry [40,41], the development of one-pot multistep transformations is of significant interest in recent organic chemistry [42–44]. These processes have an advantage of reducing waste, energy, cost and time by reducing synthetic steps, saving chemicals and improving atom economy. Regarding one-pot tandem Suzuki-coupling/nitro reduction reaction there are only a moderate number of reports available in the literature [45–52]. Among them the majority is a sequential process, as the reducing agent ($NaBH_4$, $N_2H_4 \cdot H_2O$, H_2) is added after the completion of the Suzuki step [46–49,51,52], and the use of PdNPs in the transformation appears in only a few cases [47,48,51,52].

Here we report that by using Pd/PDA with low Pd concentrations (0.031 – 1.82×10^{-3} mol%) highly efficient Suzuki-coupling under environmentally benign conditions can be achieved without the need of any additional support material or further external

activation (light irradiation). Furthermore, we show that using the same catalyst it is possible to merge the Suzuki coupling with catalytic transfer hydrogenation (CTH) of nitroaryls in a one-pot tandem process yielding valuable biaryl aniline building blocks with high yields in short reaction times in a green process.

2. Experimental section

Commercial reagents, solvents and catalysts (Aldrich, Fluo-rochem, VWR) were purchased as reagent-grade and used without further purification. Solvents for extraction or column chromatography were of technical quality. Organic solutions were concentrated by rotary evaporation at 25–40 °C. Thin layer chromatography was carried out on SiO_2 -layered aluminium plates (60778-25EA, Fluka). Column chromatography was performed using SiO_2 -60 (230–400 mesh ASTM, 0.040–0.063 mm from Merck) at 25 °C or using a Teledyne Isco CombiFlash® Rf + a utomated flash chromatographer with silica gel (25–40 μ m, Zeochem).

NMR spectra were acquired on a Varian 500 NMR spectrometer, running at 500 and 126 MHz for 1H and ^{13}C , respectively. GC-MS analysis was performed on a Shimadzu GCMS-QP2010 Ultra System operated in electron impact ionization (EI) mode. For transmission electron microscopy (TEM) investigation the three types of samples were dispersed in ethanol and deposited onto copper grids covered by carbon supporting films. TEM investigations were performed on a Morgagni 268D electron microscope at 100 kV accelerating voltage. The images and electron diffraction (ED) patterns were recorded with a SIS Megaview 1 K charge couple device camera at 1376×1032 pixel format. The chemical compositions of the catalysts were investigated by simultaneous Spectro Genesis ICP-OES spectrometer.

2.1. Polymerization of dopamine

Tris base (968 mg, 8.0 mmol) was dissolved in deionised water (750 ml) and stirred for 30 min (pH = 8.5). A solution of dopamine hydrochloride (2.0 g, 10.54 mmol) in water (50 ml) was added and the solution was stirred at room temperature for 30 h. The black suspension of polydopamine (PDA) was filtered; the residue was washed with deionised water and dried under air overnight.

2.2. Preparation of Pd/PDA catalyst

PDA (200 mg) was dispersed in a solution of Pd(OAc) $_2$ (21 mg, 0.094 mmol) in MeOH (50 ml) and stirred vigorously at room temperature overnight. The suspension was filtered, washed with

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