



Probing the support effect at the molecular level in the polyaniline-supported palladium nanoparticle-catalyzed Ullmann reaction of aryl iodides



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ABSTRACT

A series of polyaniline (PANI)-supported palladium nanoparticles (Pd@PANIs) were fabricated from electron-deficient and -enriched substituted anilines and palladium chloride. PANIs' support effect in the Pd@PANIs-catalyzed Ullmann reaction of aryl iodides for generation of biaryls was then studied. The results revealed that, though having similar Pd content and morphology, these Pd@PANI catalysts behaved quite differently in catalytic activities in the Ullmann reaction of aryl iodides, with the electron-enriched PANI supports having obviously enhanced activities for the reaction. Mechanistic studies revealed this is due to the stronger coordination of the nitrogen ligands on the electron-enriched PANI support with the Pd centers, higher adsorption rates of the reactant on the electron-enriched Pd@PANI catalysts, especially those promoted by the Pd loading, and easier generation and higher ratio of the Pd(0) species in the catalyst, which is the active catalysts in the Ullmann reaction responsible for the products' yields and the TONs of the reactions. In contrast, the specific surface area of the Pd@PANI catalyst is found to have little influence on the catalytic activity and adsorption capacity of the catalysts, and thus its influence may be omitted in the present Pd@PANIs-catalyzed Ullmann reaction of aryl iodides. Therefore, a simple fine tuning of the PANI support's electronic property by introducing electron-donating groups can be an effective protocol for enhancing the catalyst's activity. This work may be the first example of a support effect study in PANI-supported metal nanoparticle-catalyzed reactions.

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1. Introduction

Polyaniline-supported metal nanoparticles (M@PANIs) have drawn much attention in recent years for the ready availability of the aniline monomers, the low cost and low toxicity of the PANI supports [1,2], and their easy preparation through the absorption of metals onto PANI supports [3]. Since the metals in M@PANIs can be tightly anchored by the nitrogen atoms in the PANI supports, they are difficult to release into the reaction solvents, as the metal residues in the products can be detected to be as low as 0.04 ppm [4,5]. M@PANIs are also very stable materials that can be stored for more than one year without obvious deactivation and are usually recyclable and reusable for many runs of the reaction [3–6]. Therefore, M@PANIs have been employed extensively as

catalysts in many types of reactions, such as cross-coupling, hydrogenation, hydroxylation, and oxidation reactions [3–21].

Owing to the advantages listed above, M@PANIs are potential alternatives to the expensive and unrecyclable homogeneous transition metal complex catalysts, especially in pharmaceutical synthesis, which requires extremely low metal contaminants in the products. To enhance the catalytic activity of M@PANIs, in the past, much attention was paid in a long period of time to improving the materials' morphology [7–10,16–21]. Methods of controlling the size of the nanoparticles or preparing supports with very high specific surface area have also been investigated [7–10,16–21]. However, special reaction conditions, tedious fabrication steps, or complex additives are always required in the existing methods. Therefore, other easily accessible protocols that can effectively enhance the catalytic activities of M@PANIs are still highly desirable. Here, we report that a simple fine tuning of the support's substituents by introducing electron-donating groups (EDGs) into the polyaniline support can be an effective protocol for enhancing the catalytic activity of Pd@PANIs. Consequently, the electron-enriched

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Pd@PANIs are found to be more active catalysts than electron-deficient ones in the Ullmann reaction of aryl iodides.

2. Experimental

2.1. General considerations

Chemicals were purchased from reagent merchants with purities more than 98% and were used as received. Solvents were analytical pure (AR) and used without any special treatment. Infrared (IR) spectra were determined on an ENSOR-27 Fourier infrared spectrometer (KBr). Scanning electron microscope (SEM) images were obtained with a Zeiss-Supra55 field emission scanning electron microscope. Transmission electron microscope (TEM) images were obtained from a Tecnai G2 F30 S-TWIN field emission transmission electron microscope. X-ray photoelectron spectroscopy (XPS) spectra were determined with an ESCALAB 250Xi X photoelectron spectroscopy apparatus. Inductively coupled plasma mass spectrometry (ICP-MS) analysis was performed on an Optima 7300 DV inductively coupled plasma spectrometer. Melting points were measured using a XRC-1 micro melting point apparatus. ^1H NMR spectra were recorded on a Bruker Avance 600 instrument (600 MHz). Chemical shifts for ^1H NMR were referred to internal Me_4Si (0 ppm) and J -values were shown in Hz. The UV–vis analysis of PhI absorption onto the PANI supports or the Pd@PANI catalysts was conducted on an Agilent Cary 5000 UV–vis–NIR spectrometer. The specific surface areas of the PANI supports and the Pd@PANI catalysts were determined by a Beishide3H-2000PS2 surface area analyzer.

2.2. Preparation of the Pd@PANI catalysts

A solution of 0.25 mmol of PdCl_2 in 100 mL of aqueous HCl (1 mol/L) was added into a solution of 10 mmol of anilines in 100 mL of aqueous HCl (1 mol/L). The mixture was stirred for 2 min and let stand for 24 h. The solution was then neutralized by 1 mol/L aqueous NaOH to pH 7.0, which led to yellow flocculent precipitations, which were isolated by centrifugation, washed with deionized water, and baked at 100 °C for 6 h. The obtained yellow powders were employed as catalysts for the Ullmann reaction.

2.3. Details of sample treatment for ICP analysis of the Pd content in Pd@PANIs

A quantity of 2.0 mg of Pd@PANIs was dissolved in 40 mL of aqua regia. The solvents were diluted by deionized water to 100 mL and sent to ICP analysis.

2.4. Experimental details for the studies on the rates of PhI adsorption on the PANI supports or the Pd@PANI catalysts

To a 2 mL PhI solution in ethanol (50 $\mu\text{mol/L}$) was added 10 mg of a PANI support or a Pd@PANI catalyst. The mixture was then stirred in the dark for a given time (see Section 3.4) and separated by centrifugation. The supernatant solution was analyzed using an Agilent Cary 5000 UV–vis–NIR spectrometer. The characteristic adsorption peak of PhI was detected to be at 227 nm.

2.5. Detailed procedure for the Pd@PANI-catalyzed Ullmann reaction

To a 15 mL reaction tube, 0.6 mg of Pd@PANIs, 1 mmol of ArI, 1 mmol of hydrazine hydrate (58.9 mg, 85 wt% aqueous solution), 1 mmol (*i*-Pr) $_2$ NEt (129.2 mg), and 0.5 mL of *N*-methylketone were added. The tube was charged with N_2 and sealed with a tetrafluoroethylene screw plug. After being heating at 140 °C for 24 h, the

mixture was cooled to room temperature and separated by preparative TLC (eluent: petroleum ether) to provide the related coupling products.

2.6. Detailed procedure for catalyst recycling and reuse

To a 15 mL reaction tube, 20 mg of Pd@PANI-(OMe) $_2$, 10 mmol of PhI (2.04 g), 10 mmol of hydrazine hydrate (0.59 g, 85 wt% aqueous solution), 10 mmol of (*i*-Pr) $_2$ NEt (1.29 g), and 5 mL of *N*-methyl ketone (NMP) were added. The tube was charged with N_2 and sealed with a tetrafluoroethylene screw plug. After being heated at 140 °C for 24 h, the tube was cooled to room temperature and 5 mL saturated NaCl solution was added. The mixture was then extracted with EtOAc (5 mL \times 3) and solvent in the combined organic layers was removed by evaporation with a rotary evaporator. The residue was subjected to flash column chromatography to give the desired product 3a. The suspended catalyst in the aqueous layer was directly recycled and reused in the next reactions.

2.7. Characterization of the Pd@PANI catalysts and products

Pd@PANI-H: IR (KBr) ν : 3473, 3414 (N–H stretching vibration), 3285, 3200, 3120, 3043 (=C–H stretching vibration), 1578 (quinoid ring stretching vibration), 1491 (benzenoid ring stretching vibration), 1214 (C–N stretching vibration), 1119 (vibration band of dopant anion), 824, 756 cm^{-1} .

Pd@PANI-CF $_3$: IR (KBr) ν : 3474, 3420 (N–H stretching vibration), 3240, 3200, 3123 (=C–H stretching vibration), 1591 (quinoid ring stretching vibration), 1520, 1432 (benzenoid ring stretching vibration), 1326 (C–F stretching vibration), 1126 (vibration band of dopant anion), 835, 756 cm^{-1} .

Pd@PANI-OMe: IR (KBr) ν : 3476, 3415 (N–H stretching vibration), 3281, 3202, 3122, 3013 (=C–H stretching vibration), 2948 (C–H asymmetrical stretching vibration), 2833 (C–H symmetrical stretching vibration), 1595 (quinoid ring stretching vibration), 1509, 1453 (benzenoid ring stretching vibration), 1302 (C–N stretching vibration), 1249 (C–O stretching vibration), 1173 (=C–O–C asymmetrical stretching vibration), 1121 (vibration band of dopant anion), 1029 (=C–O–C symmetrical stretching vibration), 822, 741 cm^{-1} .

Pd@PANI-(OMe) $_2$: IR (KBr) ν : 3449 (N–H stretching vibration), 3230, 3123, 3010 (=C–H stretching vibration), 2950 (C–H asymmetrical stretching vibration), 2837 (C–H symmetrical stretching vibration), 1603 (quinoid ring stretching vibration), 1493 (benzenoid ring stretching vibration), 1352 (C–H twisting vibration), 1307 (C–N stretching vibration), 1208 (C–O stretching vibration), 1149 (vibration band of dopant anion), 1058 (=C–O–C symmetrical stretching vibration), 821 cm^{-1} .

1,1'-Biphenyl 3a: 58.1 mg, solid, m.p. 69–70 °C (lit. 69–71 °C); ^1H NMR (600 MHz, CDCl_3 , TMS, ppm): δ 7.60 (d, J = 7.2 Hz, 4H), 7.43 (t, J = 7.8 Hz, 4H), 7.34 (t, J = 7.2 Hz, 2H); known compound [22].

4,4'-Dimethyl-1,1'-biphenyl 3b: 58.0 mg, solid, m.p. 121–122 °C (lit. 122–123 °C); ^1H NMR (600 MHz, CDCl_3 , TMS, ppm): δ 7.48 (d, J = 6.6 Hz, 4H), 7.23 (d, J = 7.8 Hz, 4H), 2.38 (s, 6H); known compound [22].

4,4'-Dimethoxy-1,1'-biphenyl 3c: 53.8 mg, solid, m.p. 175–176 °C (lit. 178–180 °C); ^1H NMR (600 MHz, CDCl_3 , TMS, ppm): δ 7.48 (d, J = 9.0 Hz, 4H), 6.96 (d, J = 9.0 Hz, 4H), 3.83 (s, 6H); known compound [22].

4,4'-Difluoro-1,1'-biphenyl 3d: 72.4 mg, solid, m.p. 86–87 °C (lit. 87–88 °C); ^1H NMR (600 MHz, CDCl_3 , TMS, ppm): δ 7.49–7.46 (m, 4H), 7.13–7.09 (m, 4H); known compound [23].

3,3'-Difluoro-1,1'-biphenyl 3e: 72.8 mg, oil; ^1H NMR (600 MHz, CDCl_3 , TMS, ppm): δ 7.41–7.37 (m, 2H), 7.34 (d, J = 7.8 Hz, 2H), 7.26–7.24 (m, 2H), 7.07–7.04 (m, 2H); known compound [24].

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