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Short communication

Highly efficient palladium catalysts supported on nitrogen contained polymers for Suzuki-Miyaura reaction

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ABSTRACT

Through Pd catalyzed C—N coupling reaction, Pd nanoparticles and diadamantylphosphine ligand were immobilized in situ into the formed N contained polymers as heterogeneous Pd catalysts for Suzuki-Miyaura reaction. The Pd@NPad$_2$-1.0 catalyst was found to be highly efficient and only 4 ppm of Pd (Pd@NPad$_2$-1.0) was required for the coupling of aryl bromides with phenylboronic acid, and the corresponding products were obtained in good to excellent yields with high TON and TOF as 250,000 and 41,666 h^{-1} respectively. Moreover, the coupling of various aryl chlorides with phenylboronic acids gave the corresponding products in high yields also. And the Pd@NPad$_2$-1.0 catalyst is reusable at least 5 times with only slight deactivation.

1. Introduction

Pd catalyzed Suzuki-Miyaura reaction had received more and more attention over the past few decades [1], as it was used widely in the synthesis of agrochemicals, pharmaceuticals, natural products and other materials [2–10]. Traditionally, homogeneous catalysts were developed rapidly, and lots of efficient ligands were designed and applied for Suzuki-Miyaura reaction [11–13]. But separation of homogeneous Pd catalysts from the reaction mixtures is difficult in industrial applications. It is highly desirable to develop efficient heterogeneous Pd catalysts for Suzuki-Miyaura reaction. Some heterogeneous Pd catalysts had been developed by immobilizing Pd particles on supports, such as on oxides [14], polymers [15–21], carbon nanotubes [22], magnetic nanomaterials [23], and silica [24]. Unfortunately, heterogeneous Pd catalysts are generally less active than homogeneous Pd catalysts for Suzuki-Miyaura reaction.

In order to combine high activity with good reusability, some highly active heterogeneous Pd catalysts were developed for Suzuki-Miyaura reaction of aryl bromides with phenylboronic acids [25–26]. But the activation of aryl chlorides is much more difficult than that of aryl bromides, so the development of heterogeneous Pd catalysts that can activate aryl chlorides with high efficiency is highly desirable.

We have reported the C—O coupling and C–CN coupling of aryl chlorides and bromides with heterogeneous or homogeneous catalyst systems recently [27–29]. Moreover, we have developed a highly active heterogeneous Pd catalyst for Suzuki-Miyaura reaction of aryl halides with phenylboronic acid [30]. Pd nanoparticles were formed and immobilized in situ in the ionic polymers, and only 10 ppm Pd catalyst was needed for the Suzuki-Miyaura reaction of aryl bromides with phenylboronic acid [30]. Additionally, Pd nanoparticles trapped by Pd catalyzed Suzuki-Miyaura reaction were also reported as highly heterogeneous Pd catalysts, and the Pd catalysts were found to be highly active, recyclable and clean for Suzuki-Miyaura reaction [31]. We are still interested in the development of highly active Pd catalysts through Pd catalyzed cross-coupling reactions. Based on homogeneous Pd catalyst systems, good ligands for cross-coupling reactions combine both electronic and steric properties. On one hand, electron-rich ligands can help the oxidative addition into the Pd center to activate aryl halides. On the other hand, sterically demanding ligands can improve the reductive elimination from the Pd center to form products. Here, using Pd catalyzed C—N coupling reaction, Pd nanoparticles were immobilized in situ in the N contained polymers as highly efficient heterogeneous Pd catalysts for Suzuki-Miyaura reaction (see Scheme 1). Along with Pd nanoparticles, the electron rich and bulky P ligands were immobilized in situ into the N contained polymers. The heterogeneous Pd@NPad$_2$ catalysts were found to be highly efficient for Suzuki-Miyaura reaction of the aryl bromides and chlorides with arylboronic acids. Only 4 ppm Pd (Pd@NPad$_2$-1.0) was required for Suzuki-Miyaura reaction of 4-bromoanisole with phenylboronic acid. And the TON and TOF are as high as 250,000 and 41,666 h^{-1} respectively.

2. Experimental

Reagents were purchased from Sigma-Aldrich Company, Alfa-Aesar Company and Aladdin Reagent Company and used without further

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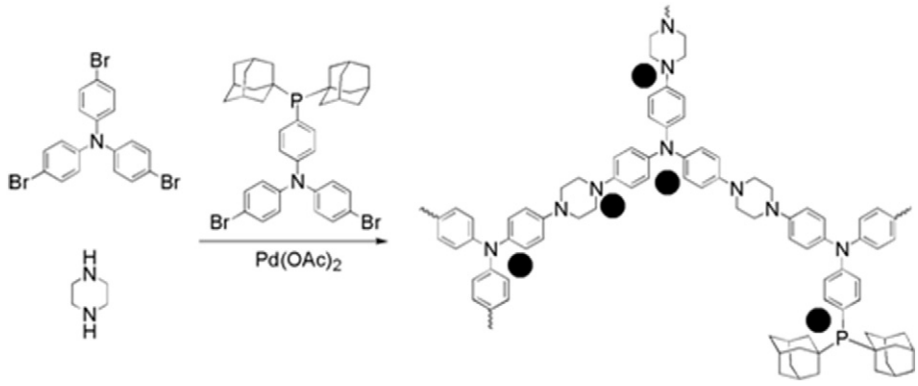

Scheme 1. The preparation of the Pd@NPad$_2$ catalyst.

purification. Thermal gravimetric(TG) analysis was performed on a STA409 apparatus under dry nitrogen at a heating rate of 20 °C/min. ^{1}H NMR spectra were measured with a Bruker AVANCE 400D spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal reference. The solid-state NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer using a double-bearing standard MAS probe for ^{31}P NMR. TEM images were obtained using a JEOL JEM-2010 (200 kV) TEM apparatus and SEM images were obtained with a HITACHI S-4800 field-emission scanning electron microscope. X-ray photoelectron spectroscopy data (XPS) were gained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlKa radiation. The polymer surface area was measured using a Micromeritics ASAP2010 analyzer before samples degassed at 150 °C for 8 h under vacuum. The FT-IR spectra were recorded in the 4000–400 cm^{-1} region using a Nicolet 360 FT-IR instrument. The amount of palladium was measured using a Jarrell-Ash 1100 ICP-AES spectrometer. The dispersion of Pd nanoparticles was also measured using Catalyst Analyzer BELCAT-B, BEL JAPAN, INC.

3. The preparation of catalysts

3.1. The preparation of Pd@NPad$_2$-1.0

The C—P coupling was synthesized according to reference [32]. Pd(OAc)$_2$ (10.3 mg, 0.046 mmol), 1.1′-bis(diisopropylphosphino)-ferrocene (DIPPF, 3.2 mg, 0.0075 mmol), tris(4-bromophenyl)amine (602.5 mg, 1.25 mmol), di-1-adamantylphosphine (75.6 mg, 0.25 mmol) and NaO*t*Bu (36.0 mg, 0.375 mmol) were added in a Schlenk tube with 2.0 mL of toluene. And then the tube was heated to 105 °C. After stirring for 20 h under argon, the mixture was cooled down to room temperature. Toluene (30 mL), 1,4-diazacyclohexane (150.7 mg, 1.75 mmol) and NaO*t*Bu (672.7 mg, 7.0 mmol) were added into the reaction mixture under argon. The reaction mixture was stirred for another 24 h under 120 °C. After the reaction mixture was cooled down to room temperature, a green solid was obtained via centrifugated and washed with water and ethanol three times respectively. The obtained green solid was dried in a vacuum oven at 40 °C for 24 h and stored in argon atmosphere as Pd@NPad$_2$-1.0 catalyst. The amount of Pd in the Pd@NPad$_2$-1.0 catalyst was found to be 0.79 wt% (determined by ICP).

The Pd@NPad$_2$-0.5 was prepared similarly and less Pd(OAc)$_2$ (5.2 mg, 0.023 mmol) was used. The amount of Pd in the Pd@NPad$_2$-0.5 was found to be 0.38 wt% (determined by ICP).

The Pd@NPad$_2$-2.0 was prepared similarly and more Pd(OAc)$_2$ (20.7 mg,0.092 mmol) was used. The amount of Pd in the Pd@NPad$_2$–2.0 was found to be 1.7 wt% (determined by ICP).

3.2. The Pd@NPad$_2$–1.0 catalyzed Suzuki-Miyaura coupling of aryl chlorides with phenyboronic acid

Typically, an aryl chloride (2.0 mmol), phenylboronic acid (3.0 mmol), Pd@NPad$_2$-1.0 catalyst (5.4 mg, 0.02 mol% Pd), K_2CO_3 (552.8 mg, 4.0 mmol) and 4.0 mL of *i*-PrOH/water (1:1) were added into a 25 mL pressure tube under Ar. The reaction mixture was stirred at 100 °C for 18 h in an oil bath. After the reaction mixture cooled down to room temperature, the product was isolated by column with silica gel and analyzed by ^{1}H NMR. The yield was calculated based on the obtained product against the consumed aryl chloride. Yield = obtained product/theoretical product from the consumed aryl chloride. The TON and TOF were calculated based on Pd added (suppose that all Pd atom are accessible for the reaction). TON = the number of product/the number of Pd added (mol product/mol Pd). TOF = the number of product/the number Pd added in 1 h (mol product/mol Pd $*$ h^{-1}).

3.3. The Pd@NPad$_2$–1.0 catalyzed Suzuki-Miyaura coupling of aryl bromides with phenylboronic acid

In a typical reaction, an aryl bromide (25.0 mmol), phenylboronic acid (37.5 mmol), Pd@NPad$_2$-1.0 catalyst (1.35 mg, 4.0 ppm Pd), K_2CO_3 (6.9105 g, 50.0 mmol) and 20.0 mL of *i*-PrOH-water (1:1) were added into a 50 mL pressure tube under Ar. The reaction was performed at 100 °C for 6 h in an oil bath. After the reaction mixture cooled to room temperature, the organic layer was extracted with ethyl acetate (4 × 10.0 mL). The product was isolated by column with silica gel (hexane/ethyl acetate) and analyzed by ^{1}H NMR. The yeild was calculated based on the obtained product against the comsumed aryl bromide. Yield = obtained product/theoretical product from the consumed aryl bromide. The TON and TOF were calculated based on Pd added (suppose that all Pd atom are accessible for the reaction). TON = the number of product/the number of Pd added (mol product/mol Pd). TOF = the number of product/the number Pd added in 1 h (mol product/mol Pd $*$ h^{-1}).

3.4. The Pd@NPad$_2$–1.0 catalyzed Suzuki-Miyaura coupling of 2-nitrochlorobenzene with 4-chlorophenylboronic acid

2-Nitrochlorobenzene (1.5755 g, 10.0 mmol), 4-chlorophenylboronic acid (1.8764 g, 12.0 mmol), Pd@NPad$_2$-1.0 catalyst (27.0 mg, 0.02 mol% Pd), K_2CO_3 (2.7642 g, 20.0 mmol) and 10.0 mL of *i*-PrOH-water (1:1) were added into a 25 mL pressure tube under Ar. The reaction mixture was stirred for 10 h at 100 °C in an oil bath. After the reaction mixture cooled down to room temperature, the organic layer was extracted with ethyl acetate (10.0 mL). The product was isolated by column with silica gel (hexane/ethyl acetate).