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Article

Palladium nanoparticles in cross-linked polyaniline as highly efficient catalysts for Suzuki-Miyaura reactions



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ABSTRACT

Palladium nanoparticles supported on cross-linked polyaniline with bulky phosphorus ligands were developed. These catalysts showed high efficiency in the Suzuki-Miyaura reaction of aryl chlorides and bromides with phenylboronic acids. Aryl chlorides and bromides with functional groups, such as CN, MeO, CHO, MeCO and NO₂, were converted to the corresponding biphenyls in high yields with catalyst loading. Additionally, the catalysts combined high activity with good reusability; they could be used at least five times for the Suzuki-Miyaura coupling reaction.

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1. Introduction

The palladium (Pd)-catalysed Suzuki-Miyaura reaction is one of the most powerful protocols used in the synthesis of agrochemicals, pharmaceuticals, natural products and other materials, and has been studied extensively in the past few decades [1–10]. Recently, numerous homogeneous catalysts have been developed, and lots of efficient ligands for the Suzuki-Miyaura reaction have been designed. However, ligands for Pd homogeneous catalysts are usually expensive and complicated to synthesise [11–15]. The recovery of active Pd/ligand catalyst systems is valuable not only for economic reasons but also to avoid product contamination. Thus, much effort has been devoted to designing heterogeneous Pd catalysts, such as Pd supported on metal-organic frameworks, carbon, mesoporous zeolites, metal oxides and polymers, for use in Suzuki-Miyaura coupling reactions [16–24].

However, heterogeneous Pd catalysts are usually not as active as homogeneous Pd/ligand systems. Although some remarkably active heterogeneous Pd catalysts for the Suzuki-Miyaura cross coupling of aryl bromides with arylboronic acids have been reported, it is still desirable to develop highly active heterogeneous Pd catalysts for the Suzuki-Miyaura reaction of aryl chlorides [25–28]. Because the C–Cl bond is stronger than the C–Br bond, aryl chlorides are difficult to activate. Despite this, aryl chlorides are attractive substrates in Suzuki-Miyaura reactions because they are inexpensive and widely commercially available, so more active Pd catalysts are required. Few heterogeneous Pd catalysts able to activate aryl chlorides for Suzuki-Miyaura reaction have been reported (for example, turnover number (TON) > 1000 with chloroanisole) [29–34].

Recently, we have developed the C–O and C–CN coupling re-

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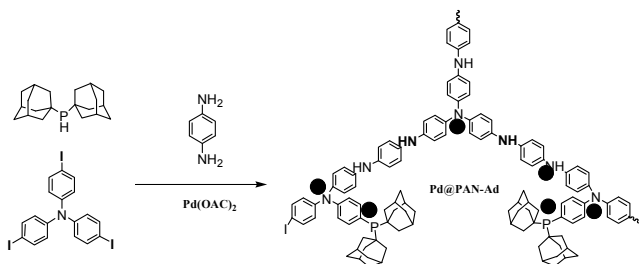
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actions of aryl chlorides and bromides with phenols and $K_4Fe(CN)_6$ using heterogeneous and homogeneous catalyst systems [35–37]. Moreover, Pd nanoparticles formed in situ in ionic solid polymers have been reported as highly active heterogeneous catalysts for the Suzuki-Miyaura reaction; only 10^{-7} Pd catalysts were required for the Suzuki-Miyaura reaction of aryl bromides [38]. In addition, heterogeneous catalysts with highly active Pd nanoparticles immobilised in situ have been designed and used in Suzuki-Miyaura reactions; these catalysts can be reused several times without evident deactivation [39]. It was found that electron-rich and bulky phosphorus (P) ligands enhanced the activity of these Pd catalysts. Besides, Pd nanoparticles immobilised in N-containing polymers by Pd-catalysed C-N coupling of tris(4-bromophenyl)amine with piperazine have been applied as catalysts, achieving a TON and turnover frequency (TOF) as high as 250000 and 41666 h^{-1} , respectively, in Suzuki-Miyaura reactions [40]. We are still interested in the development of highly active Pd catalysts for Pd-catalysed cross-coupling reactions.

In homogeneous Pd catalyst systems, good ligands for cross-coupling reactions combine both favourable electronic and steric properties. On the one hand, electron-rich ligands can aid oxidative addition to the Pd center to activate aryl halides. On the other hand, bulky ligands can improve the reductive elimination from the Pd center to form products. Moreover, Pd nanoparticles supported on polyaniline (PAN) have been reported as highly active and reusable catalysts for Suzuki-Miyaura reactions, but the recycling process was not easy [41–44]. Inspired by these advances, have we attempted to combine a PAN support and bulky ligands with Pd nanoparticles to form highly active, reusable Pd catalysts. Pd nanoparticles are encapsulated in situ in cross-linked PAN by Pd-catalysed C-N coupling of tris(4-iodophenyl)amine with *p*-phenylenediamine as highly active catalysts for Suzuki-Miyaura reactions (see Scheme 1). The resulting Pd catalysts exhibit high efficiency for the Suzuki-Miyaura coupling of aryl bromides and chlorides with aryl boronic acids. No Pd leaching is detected in the reaction solution after filtration of the Pd catalysts, revealing that we attained active, clean Pd catalysts for Suzuki-Miyaura reactions.

2. Experimental

2.1. General methods and reagents



Scheme 1. Synthesis of the palladium nanoparticle/polyaniline/di-1-adamantylphosphine (Pd@PAN-Ad) catalysts.

All chemicals used in this work were purchased from Alfa Aesar, Aladdin Reagent Company and Sigma-Aldrich and used without further purification. 1H NMR spectra were measured with a Bruker AVANCE 400D spectrometer in $CDCl_3$ using tetramethylsilane as an internal reference. Thermogravimetric analysis (TGA) was performed with a STA409 instrument under dry nitrogen at a heating rate of 20 $^{\circ}C/min$. Gas sorption/desorption analysis was performed on a Micromeritics ASAP2010 analyser at -196 $^{\circ}C$ with liquid nitrogen. Samples were pretreated at 140 $^{\circ}C$ under vacuum before analysis. The amount of Pd was measured with a Jarrell-Ash 1100 inductively coupled plasma-atomic emission spectrometer (ICP-AES). Transmission electron microscope (TEM) images were captured using a JEOL JEM-2010 (200 kV) TEM and scanning electron microscope (SEM) images were obtained using a Hitachi S-4800 field-emission SEM. Fourier transform infrared (FT-IR) spectra were recorded in the 500–4000 cm^{-1} region using a Nicolet 360 FT-IR spectrometer with a scan rate of 0.4747 cm/s . X-ray photoelectron spectroscopy (XPS) was conducted with an ESCALab 220i-XL electron spectrometer from VG Scientific using 300-W Al K_{α} radiation. Binding energies were calibrated using the C1s peak at 284.6 eV. X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance powder diffractometer using a Ni-filtered Cu K_{α} radiation source at 40 kV and 20 mA from 5 $^{\circ}$ to 80 $^{\circ}$ with a scan rate of 0.5 $^{\circ}/min$.

2.2. Preparation of heterogeneous Pd catalysts

Synthesis of Pd@PAN-Ad-0.5 catalyst: The C-P coupling reaction was conducted according to a reported method with modification [45]. Di-1-adamantylphosphine (HPad₂, 77.2 mg, 0.25 mmol), tris(4-iodophenyl)amine (1.25 mmol, 778.8 mg), Pd(OAc)₂ (32.7 mg, 0.145 mmol), 1,1'-bis(diisopropylphosphino)ferrocene (dippf, 6.4 mg, 0.015 mmol) and NaOtBu (36 mg, 0.37 mmol) were added into a 100-mL Schlenk tube containing toluene (15 mL) under argon. After the Schlenk tube was heated at 100 $^{\circ}C$ with stirring for 22 h, the reaction mixture was cooled to room temperature. Then, *p*-phenylenediamine (189.3 mg, 1.75 mmol), NaOtBu (673.0 mg, 7 mmol) and toluene (20 mL) were added to the tube under argon. After heating at 100 $^{\circ}C$ with stirring for another 24 h under argon, the reaction mixture was again cooled to room temperature. The dark blue solid catalyst was obtained via centrifugation, and then washed with water and ethanol three times. The Pd@PAN-Ad-0.5 catalyst was obtained after drying under vacuum for 24 h at room temperature. The Pd content of the Pd@PAN-Ad-0.5 catalyst measured by ICP-AES was 0.58 wt%. A Pd@PAN-Cy-0.5 catalyst was prepared similarly using dicyclohexylphosphine instead of di-1-adamantylphosphine. The amount of Pd in the Pd@PAN-Cy-0.5 catalyst was 0.53 wt%.

The catalyst Pd@PAN-Ad-0.2 was prepared similarly to the Pd@PAN-Ad-0.5 catalyst, but 16.3 mg of Pd(OAc)₂ was added instead of 32.7 mg. The Pd content in the Pd@PAN-Ad-0.2 catalyst measured by ICP-AES was 0.25 wt%.

2.3. Typical procedure for Suzuki-Miyaura coupling of aryl

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