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Research Paper

Main-chain diphosphine-Pd polymers: Efficient self-supported heterogeneous catalysts for Suzuki-Miyaura reaction

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ABSTRACT

Two diphosphines 1,4-bis(diphenylphosphino)benzene (M1) and 4,4′-bis(diphenylphosphino)-1,1′-biphenyl (M2) were synthesized by employing Grignard reaction. They were subsequently employed to coordinate with palladium chloride to construct main-chain diphosphine-Pd organometallic polymers P1 and P2, respectively. Both polymers were used as self-supported heterogeneous catalysts for Suzuki-Miyaura coupling reactions of various aryl halides and arylboronic acids at room temperature. A higher catalytic activity for P1 and P2 than their homogeneous counterpart were observed, and the activity of P2 is slightly higher than that of P1. Moreover, polymer P2 can be readily recovered and reused for further transformations at least six times without decrease in catalytic activity, while an obvious decline of activity for P1 was observed after the fourth run.

1. Introduction

Palladium catalyzed Suzuki-Miyaura coupling reaction of aryl halides with arylboronic acids are among the most useful synthetic transformations to construct fine chemicals, pharmaceuticals, and agrochemicals [1]. In general, the coupling reaction can efficiently proceed in the presence of homogeneous palladium complexes. Despite significant progress for Suzuki-Miyaura reaction has been achieved in recent years [2–4], there are some drawbacks of homogeneous palladium catalysis including the difficulty in recovery and reuse of the usually expensive catalysts, as well as product contamination by incomplete separation of metal catalysts [5]. The typical way to solve these problems is anchoring palladium catalysts on suitable support [6–8], such as carbon [9–11], polymers [12–14], silica [15–17], magnetic particals [18–20], biomaterials [21–23], dendrimers [24–26] and porous polymers [27–29]. However, some of these heterogeneos palladium catalysts show lower catalytic activity in comparison with the homogeneous counterparts. Progress for heterogeneous palladium catalysts with enhanced activity are still highly desirable.

In the field of heterogeneous metal catalysis, a self-supporting strategy for catalyst immobilization has been developed based on coordination bonds between active metal centers and organic ligands [30]. The resulting organometallic polymers usually have high stability against hydrolysis and thermal decomposition. The metal-ligand units are equally distributed in the polymer backbone which promote easy access of substrates to catalytic sites, leading to enhanced mass transfer and good reaction efficiency. Due to the metal and ligand diversity, catalytic property of the organometallic polymer could be finely tuned to meet specific requirement. Therefore, a variety of these organic-inorganic hybrid materials have been facilely obtained and successfully used as heterogeneous catalysts [31–37].

Phosphines are a class of versatile ligands owing to their strong σ-donating ability and easy preparation. It's not surprising that they have been widely employed as functional groups in heterogeneous transition metal catalysis [38–41]. Recently, Sijbesma et al. reported a new kind of main-chain phosphine-based organometallic polymers which were prepared through reaction of diphosphine compounds with Pd(II), Pt(II) salts [42–44]. The good solublility which results from long alkyl chain in the diphosphine unit, as well as the potential reversible coordination of phosphines make these polymers cannot be directly used in heterogeneous metal catalysis. However, this type of self-assemblies have the typical features of organometallic polymers. If properly designed, the diphosphine-metal polymer should have the ability to act as efficient heterogeneous catalyst.

In this study, two diphosphines M1 and M2 were synthesized and subsequently used as palladium ligands to construct organometallic polymers. These two polymers were employed as

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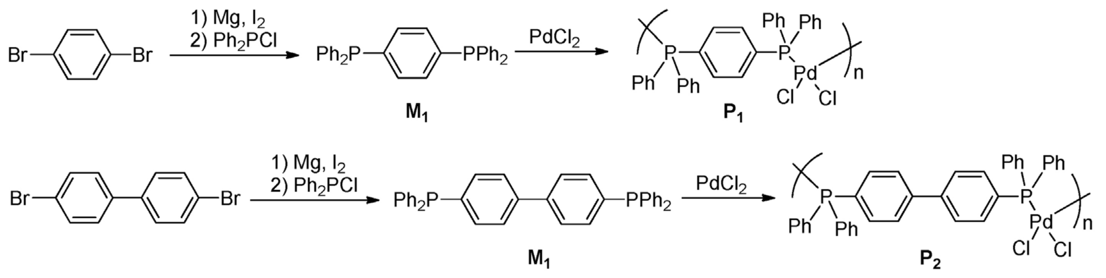

Scheme 1. The synthetic route towards diphosphines and self-supported polymers.

heterogeneous palladium catalyst for the Suzuki-Miyaura coupling of a variety of aryl halides and arylboronic acids. Their catalytic efficiency and recyclability were presented. To the best of our knowledge, this is the first time to report the study of heterogeneous catalysis with diphosphine-Pd polymer.

2. Experimental

2.1. Materials and methods

1,4-Dibromobenzene, 4,4′-dibromo-1,1′-biphenyl, chlorodiphenylphosphine and iodine were purchased from Adamas. Tetrahydrofuran (THF) was refluxed with sodium prior to use. Magnesium turnings was pretreated in dilute hydrochloric acid. NMR spectra were recorded on Varian Unity Inova 600 spectrometer (^{1}H at 600 MHz, ^{13}C at 150 MHz and ^{31}P at 240 MHz). Solid-state ^{13}C and ^{31}P cross-polarization magic-angle spinning (CP/MAS) NMR spectroscopy were recorded on Varian Infinity-plus 300 spectrometer. Thermogravimetric analyses (TGA) were carried out in a N_2 atmosphere with a heating rate of 20 °C/min on a Diamond TG/DTA thermal analyzer (Perkin Elmer). Scanning electron microscopy (SEM) images were conducted on a JEOL JSM-6510 electron microscope. ICP-AES analysis was performed on a Perkin Elmer Optima 8000 instrument. Elemental analyses (EA) was performed on a Vario Micro cube Elemental Analyzer (Elementar, Germany).

2.2. Synthesis

(a) Synthesis of diphosphines. M1 was synthesized by modified procedure of previous report [45]. A three-necked flask charged with Mg turnings (2.88 g, 120 mmol) and a grain of I_2 (about 35 mg) was degassed and purged with N_2, and then 60 mL of THF was added. After slowly adding a solution of 1,4-dibromobenzene (4.68 g, 20 mmol) in THF (30 mL), the reaction mixture was stirred at 60 °C for 10 h. Next, Ph_2PCl (8.80 g, 40 mmol) was slowly added to the resulting solution at room temperature followed by stirring at the same temperature for 8 h. The reaction was quenched with aqueous NH_4Cl solution and the mixture was extracted with ethyl acetate. The organic layer was washed with water, dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum) to obtain 1,4-bis(diphenylphosphanyl)benzene. Yield: 6.19 g, white powder, 69%; M.p. 166–167 °C; ^{1}H NMR (600 MHz, $CDCl_3$, ppm): $\delta = 7.22–7.24$ (m, 4H), 7.31–7.33 (m, 20H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): $\delta = 128.5$, 128.8, 133.3, 133.8, 136.7, 137.9; ^{31}P NMR (240 MHz, $CDCl_3$, ppm): $\delta = -6.6$.

M2 was synthesized under the same conditions except that the dibromo compound used was 4,4′-dibromo-1,1′-biphenyl instead of 1,4-dibromobenzene. Yield: 6.41 g, white powder, 61%; M.p. 193–194 °C; ^{1}H NMR (600 MHz, $CDCl_3$, ppm): $\delta = 7.34–7.38$ (m, 24H), 7.55–7.57 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): $\delta = 127.3$, 128.8, 129.0, 134.0, 134.4, 136.7 137.2, 140.9; ^{31}P NMR (240 MHz, $CDCl_3$, ppm): $\delta = -7.0$.

(b) Synthesis of diphosphine-Pd polymers. Both polymers were prepared by modified procedure for the synthesis of bis(triphenylphosphine)palladium chloride [46]. Palladium chloride (0.45 g, 2.5 mmol) was dissolved in 4 mL of acidified ethanol (concentrated HCl-EtOH, v:v = 1:2) and this mixture was added dropwise to a solution of diphosphine (2.5 mmol) in a 1:4 mixture of 1,2-dichloroethane/ethanol (100 mL). The reaction mixture was stirred at 60 °C for 2 days and filtered. The resulting solid catalyst was washed successively with ethanol, toluene and dichloromethane, and finally dried under reduced pressure at 60 °C for 12 h to give the diphosphine-Pd polymer.

Polymer catalyst P1. Yield: 1.40 g, yellow powder, 89%; Polymer catalyst P2. Yield: 1.49 g, brown powder, 85%;

Elemental analysis for P1 $(C_{30}H_{24}P_2PdCl_2)_n$ and P2 $(C_{36}H_{28}P_2PdCl_2)_n$:

C: P1, 0.61%; calcd 57.78, found 58.39. P2, 0.63%; calcd 61.80, found 61.17.

H: P1, 0.07%; calcd 3.85, found 3.92. P2, 0.17%; calcd 4.00, found 3.83.

P: P1, 0.12%; calcd 9.95, found 9.83. P2, 0.23%; calcd 8.87, found 8.64.

2.3. Catalytical testing

A mixture of aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (277 mg, 2.0 mmol) and polymer catalyst (0.3 mol%) in EtOH-H_2O (3 mL, v:v = 1:1) was stirred in a Schlenk tube at room temperature in air. After completion of the reaction, the mixture was extracted with dichloromethane. The organic phase was dried, evaporated and purified by silica gel column chromatography to afford the coupling product. The aqueous phase was filtered and the solid was washed with dichloromethane and reused in further reactions as the recovered catalyst.

3. Results and discussion

As shown in Scheme 1, two diphosphines were prepared through Grignard reaction. The reaction of diphosphine with stoichiometric amount of Palladium chloride at 60 °C gave rise to organometallic polymers P1 and P2 in high yield. Both polymers were almost insoluble in water or any common organic solvent. The Pd contents in P1 and P2 were 16.80 wt% and 14.36 wt%, respectively, as determined by an ICP-AES analysis. Elemental analysis showed that the contents of carbon, hydrogen, phosphorus matched well with the calculated values for the polymers with proposed structures, which were further confirmed by solid-state NMR spectra (Fig. 1). The peaks in ^{13}C NMR spectra at about 138 ppm was attributed to the P-C_{Ar} sites for the two polymers [47]. The signals at around 127–135 ppm can be assigned to the other phenyl carbon atoms. In the solid-state ^{31}P NMR spectra for polymer P1, the signal at 23.8 and 17.2 ppm can be ascribed to the Pd-P site,