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A Pd-metalated porous organic polymer as a highly efficient heterogeneous catalyst for C–C couplings

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ABSTRACT

An efficient catalyst system based on a Pd-metalated porous organic polymer bearing phenanthroline ligands was designed and synthesized. This catalyst was applied to various C–C bond-forming reactions, including the Suzuki, Heck and Sonogashira couplings, and afforded the corresponding products while exhibiting excellent activities and selectivities. More importantly, this catalyst can be readily recycled. These features show that such catalysts have significant potential applications in the future.

1. Introduction

Carbon–carbon bond forming reactions catalyzed by Pd species, such as the Suzuki, Heck and Sonogashira couplings, have been extremely important in the synthesis of pharmaceuticals and functionalized materials for some time now [1–8]. To promote these couplings, a wide range of homogeneous catalytic systems have been developed, some of which have achieved widespread acceptance due to their superior selectivity and activity, such that several have found industrial applications. Despite these achievements, the common usage of such coupling reactions in industrial processes has often been hindered by the complicated nature of the synthetic processes and the difficultly in recycling the catalyst [9,10]. To overcome these issues, a series of Pd-based heterogeneous catalysts have been developed, using a variety of insoluble supports, such as those based on carbon and silica [11,12]. However, carbon supports are relatively difficult to modify owing to their inert structures [13,14] and silica supports readily dissolve in alkaline media [15–17]. Therefore, it would be greatly beneficial to design highly stable, easily modified supports for the heterogenization of homogeneous catalysts.

Recently, porous organic polymers (POPs) exhibiting relatively good stability and capable of unique functionalization have emerged as an interesting class of materials with significant potential in the fields of gas storage, separation and catalysis [18–21]. In particular, POPs may act as highly tunable platforms, through the introduction of specific active species, for the development of extremely efficient heterogeneous catalysts with applications to various organic transformations [22–25].

More recently, we have shown that the stable, porous POP polydivinylbenzene (PDVB) can function as a powerful, insoluble support for the functionalization of catalytically active spe-

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cies as heterogeneous catalysts [26]. In the present work, the rational synthesis of a POP containing phenanthroline ligands was attempted, through the copolymerization of divinylbenzene and vinyl-functionalized phenanthroline monomers under solvothermal conditions. The phenanthroline ligand was selected owing to its strong metal coordination ability and relatively high chemical stability [27–31]. After metalation with $Pd(OAc)_2$, the resulting heterogeneous catalyst exhibited excellent activity and recyclability during the Suzuki, Heck and Sonogashira coupling reactions.

2. Experimental

2.1. Sample synthesis

Solvents were purified according to standard laboratory methods; THF was distilled over sodium/benzophenone, DMF was distilled over calcium hydride, and $CHCl_3$ was distilled over anhydrous $CaCl_2$. Divinylbenzene (DVB), azobisisobutyronitrile (AIBN) and ethylbenzene were obtained from Tianjin Guangfu Chemical Reagents, whereas 1,10-phenanthroline monohydrate, $Pd(OAc)_2$, bromobenzene, phenylboronic acid, phenylacetylene and ethyl acrylate were purchased from the Aladdin Company, Ltd.

As shown in Scheme 1, a POP containing phenanthroline ligands (POP-Phen) was synthesized by the copolymerization of DVB with vinyl-functionalized phenanthroline monomers. In a typical reaction, 2.0 g DVB and 0.5 g vinyl-functionalized 1,10-phenanthroline (V-Phen) were dissolved in 20 mL DMF, followed by the addition of 0.05 g AIBN. The mixture was subsequently transferred to an autoclave and held for 24 h at 100 °C. After washing with ethanol, a solid orange product was obtained, denoted as POP-Phen herein [32].

The Pd-metalated POP (Pd/POP-Phen) catalyst was prepared by treating the POP-Phen with $Pd(OAc)_2$ in toluene. The mixture was initially stirred overnight at room temperature, followed by filtration of the solid product and washing with a significant quantity of toluene. After drying under vacuum at room temperature, the brown Pd-supported catalyst was obtained. Inductively coupled plasma optical emission spectroscopy (ICP-OES) determined that the Pd loading in the polymer was approximately 5.0% by weight.

2.2. Characterization

Nitrogen sorption isotherms at −196 °C were acquired using Micromeritics ASAP 2020M and Tristar systems. The samples were outgassed for 10 h at 100 °C prior to these measurements. Scanning electron microscopy (SEM) was performed using a Hitachi SU1510 and SU4800 and transmission electron microscopy (TEM) was carried out with a Hitachi HT-7700. X-ray photoelectron spectroscopy (XPS) spectra were acquired on a Thermo ESCALAB 250 with Al K irradiation at $\theta = 90°$ and the binding energies were calibrated using the C1*s* peak at 284.9 eV. ICP-OES analysis was performed with a PerkinElmer plasma 40 emission spectrometer and ^1H NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer, with chemical shifts expressed in ppm downfield from TMS at $\delta = 0$ ppm. ^{13}C (100.5 MHz) magic angle spinning (MAS) NMR spectra were recorded on a Varian infinity plus 400 spectrometer equipped with a magic angle spin probe and a 4-mm ZrO_2 rotor.

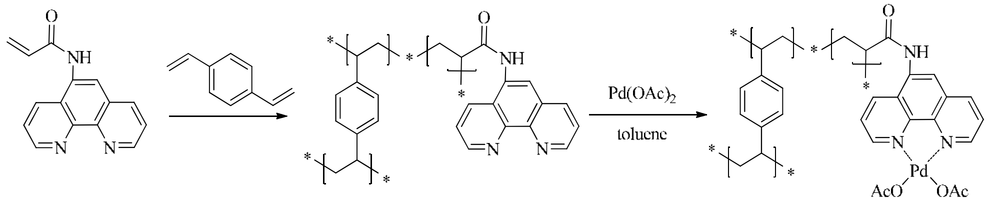
2.3. Catalytic tests

In a typical Suzuki coupling, 1 mmol halide, 1.2 mmol phenylboronic acid, 1.5 mmol $K_3PO_4·3H_2O$, 0.01 g catalyst, 3 mL water and 2 mL ethanol were reacted at 80–120 °C with constant stirring. A typical Heck coupling used 1 mmol halide, 1.2 mmol vinylic substrate, 1.5 mmol $K_3PO_4·3H_2O$, 0.01 g catalyst and 5 mL NMP (1-methy-2-pyrrolidinone) at 130–140 °C. In a typical Sonogashira coupling, 1 mmol halide, 1.2 mmol benzyne, 1.5 mmol $K_3PO_4·3H_2O$, 0.01 g catalyst and 5 mL solvent were used at 120–140 °C. After each reaction, the catalyst was removed by centrifugation and analyzed by gas chromatography (GC-1690, Kexiao Co.) using a flame ionization detector and a DB-1 capillary column.

3. Results and discussion

3.1. Characterization

Figure 1 shows the ^{13}C MAS NMR and IR spectra of the PDVB and POP-Phen samples. In the ^{13}C MAS NMR spectra of the POP-Phen, two peaks are seen at 163 and 175 ppm, both of which are associated with C=O and C=N bonds in the V-Phen component [33–36]. The IR spectrum of POP-Phen displays a strong band at 1698 cm^{-1} that is assigned to the V-Phen C=O bond [32]. These results indicate successful incorporation of the 1,10-phenanthroline ligand into the sample. Furthermore, TG analysis found that the mass loss of the POP-Phen occured above 360 °C, associated with decomposition of the polymer skeleton, indicating its superior thermal stability. N_2 sorption isotherms revealed that both POP-Phen and Pd/POP-Phen (Fig. 2(a)) generated a hysteresis loop over the relative pressure range of 0.45 to 0.95, demonstrating the presence of mesopores in the samples. The sample pore sizes were primarily distrib-



Scheme 1. Structure and synthetic procedures for the preparation of Pd/PCP-Phen.