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Journal of Molecular Catalysis A: Chemical 280 (2008) 20–23
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Polymethyl methacrylate micro-spheres supported palladium: A new catalyst for Heck and Suzuki reactions

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Received 7 August 2007; received in revised form 12 October 2007; accepted 17 October 2007
Available online 23 October 2007

Abstract

Polymethyl methacrylate (PMMA) micro-spheres, a kind of commercially available polymeric material was treated with $PdCl_2$ and formaldehyde giving a reagent with a palladium loading of 0.79 (wt.%). The Pd-PMMA catalyzed the highly efficient Heck and Suzuki reactions. The reactions can be performed under ligand-free conditions in an air atmosphere. The palladium catalyst is easily separated and can be reusable with negligible leaching of palladium.

Keywords: PMMA; Palladium catalyst; Heck reaction; Suzuki reaction

1. Introduction

Heck and Suzuki reactions are powerful methods for C–C bond formation [1–5]. They can be used in the synthesis of a variety of compounds, including heterocycles, several natural products and pharmaceuticals [1–5]. Traditionally, palladium-catalyzed Heck and Suzuki reactions often require relatively large amounts of catalysts, which have to be removed from the reaction product. In recent years, various homogeneous palladium catalysts have been developed for the efficient Heck and Suzuki cross-coupling reactions. However, homogeneous palladium has several shortcomings such as limited reusability, which impacts cost and palladium contamination in the product [6]. Therefore, removal of residual palladium is a challenging task for chemists and a topic of enormous importance in the pharmaceutical industry that involves palladium-catalyzed process [7]. Many methods have been introduced to address the palladium contamination issue, which include palladium-containing perovskites [8], palladium supported on various materials such as carbon [9], zeolites [10], silica [11,12], sepiolites [13,14], polyionic gels [15] and hydrotalcite [16]. Although the palladium level in the product was lower in these systems when compared to homogeneous, the systems exhibit generally lower activity and the activity of the catalysts decreases gradually in the recycled systems because the palladium leaches away from their supports [17].

Polymer-supported organotransition metal catalysts offer several significant advantages in synthetic and industrial chemistry; among these, the ease of separation of catalyst from the desired reaction products and the ease of recover and reuse of the catalyst are most important. Various polymer-supported palladium catalysts for the Heck and Suzuki cross-coupling reaction have been reported [6,18–36]. However, most of them are related to the Pd(II) complexes in combination with triarylphosphines, sterically demanding trialkylphosphines, statically demanding *N*-heterocyclic carbenes or ligands, and in many cases residual palladium in the product was still under the level that satisfies specifications required by regulators. To our knowledge, the use of polymer-supported Pd(0) catalysts for efficient C–C couplings has not been exploited well until recently [17,37,38]. When compared with the most frequently used expensive palladium catalysts (e.g., $Pd(PPh_3)_4$, $(PPh_3)_2PdCl_2$, $Pd(OAc)_2/PPh_3$, etc.), polymer-supported Pd(0) catalysts have an economic advantage and hence remain attractive in large or industrial scale applications.

Polymethyl methacrylate (PMMA) is a kind of commercially available polymeric material. PMMA micro-spheres with

Abbreviations: SEM, scanning electron microscope; ICP, inductively coupled plasma; TLC, thin layer chromatography; PMMA, polymethyl methacrylate; DMF, dimethyl formamide; NEt_3, triethylamine; EtOAc, ethyl acetate.

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doi:10.1016/j.molcata.2007.10.017

narrow size distribution can be obtained by dispersion polymerization [39,40]. There are functional groups on the surface of PMMA, which can adsorb noble metal hydronium. Homogeneous size of micrometer is favorable to recycle of the catalyzer [39,40]. As a part of our studies to explore palladium-catalyzed cross-coupling reactions, we decided to use the palladium adsorbed on micrometer PMMA micro-spheres as a catalyst in Heck and Suzuki cross-coupling reactions.

2. Experimental

2.1. General remarks

^{1}H NMR spectra were characterized with a Bruker Advance RX300 spectrometer. Mass and GC analyse were performed on a Saturn 2000GC/MS instrument. Field-emission scanning electron microscope (SEM) photograph were recorded with a LEO1530VP instrument. Inductively coupled plasma (ICP) spectra were measured on an Ultima2C apparatus. Micrometer PMMA micro-spheres was commercially obtained from Zongyan Chemical Co. of Suzhou. Commercially available reagents were used without further purification. Pd contents were measured by ICP analysis method after the reaction mixture was filtered, then diluted with water, extracted with ether, dried, and concentrated to dryness.

2.2. Preparation of Pd-PMMA

$PdCl_2$ (0.27 g, 1.5 mmol) was dissolved in 20% hydrochloric acid (40 ml). Then PMMA micro-spheres (15 g) were added. After vigorous stirring at 90 °C for 2 h, 35% formaldehyde (5 ml) was added. Then, the mixture was stirring at 90 °C for 1 h. The mixture was cooled to 15 °C and the pH was adjusted to 6 by using 30% sodium hydroxide solution. After stirring at 15 °C for 30 min, the mixture was allowed to stand for *ca*. 2 h without stirring. Then the deposite was separated and washed with water (20 ml × 3) and toluene (20 ml × 2). The isolated solids was dried at 120 °C for 24 h in vacuum to give a gray solid (15.13 g). The solid contained 0.79% Pd by weight based on the ICP analysis.

2.3. Typical procedure for Heck reaction with Pd-PMMA

Styrene (6 mmol) was added to a mixture of Pd-PMMA (1.29 g, 1% Pd) and DMF (5 ml) in a glass flask under vigorous stirring. After 5 min, iodobenzene (5 mmol) and NEt_3 (7.5 mmol) were introduced into the flask. After stirring at 100 °C for 2 h, the mixture was cooled and the catalyst was filtered. The filtrate was diluted with water (5 ml) and extracted with ether (10 ml × 2). The combined organic extracts were dried over Na_2SO_4 and evaporated under vacuum to give a crude product (examined for Pd). The crude product was subjected to column chromatography on silica gel with hexane and EtOAc (9:1, v/v) as eluent to give *trans*-stilbene product (0.87 g, 95%). The product was characterized by GC/MS and ^{1}H NMR.

2.4. Typical procedure for Suzuki reaction with Pd-PMMA

Bromobenzene (5 mmol) was added to a mixture of Pd-PMMA (1 g, 1% Pd) and DMF (5 ml) in a glass flask under vigorous stirring. After 10 min, phenylboronic acid (7.5 mmol) and a solution of K_3PO_4 (2.66 g, 10 mmol) in water (5 ml) were introduced into the flask. After stirring at 95 °C for 2.5 h, the mixture was cooled and the catalyst was filtered. The filtrate was diluted with an aqueous KOH (10 ml, 10%) and extracted with ether (10 ml × 2). The combined organic extracts were dried over Na_2SO_4 and evaporated under vacuum to give a crude product (examined for Pd). The crude product was subjected to column chromatography on silica gel with petroleum ether and EtOAc (25:1, v/v) as eluent to give biphenyl product (0.67 g, 87%). The product was characterized by GC/MS and ^{1}H NMR.

2.5. Typical procedure for catalyst recycling

After the reaction as described above, the mixture was allowed to stand for *ca*. 30 min without stirring at room temperature, and then filtered. The solids were washed with water (5 ml × 3) and toluene (5 ml × 3). The catalyst isolated was dried at 120 °C for 24 h in vacuum. The resulting catalyst was ready for further runs in Heck reaction and Suzuki reactions.

3. Results and discussion

Palladium can be easily loaded onto PMMA by stirring a solution of $PdCl_2$ and PMMA micro-spheres and then reduction with formaldehyde at elevated temperature. After filtration and washing, the catalyst was dried and the content of palladium confirmed by weight and analysis. The SEM photograph of the catalyst was shown in Fig. 1. From the figure, we can clearly see that palladium was absorbed onto the PMMA micro-spheres.

We first examined the palladium-catalyzed Heck coupling of aryl halides with various Heck acceptors, such as styrene, alkyl acrylate and propenyl cyanide. In a typical experiment, a base (1.5 equiv.) was added and the mixture was heated at 100 °C

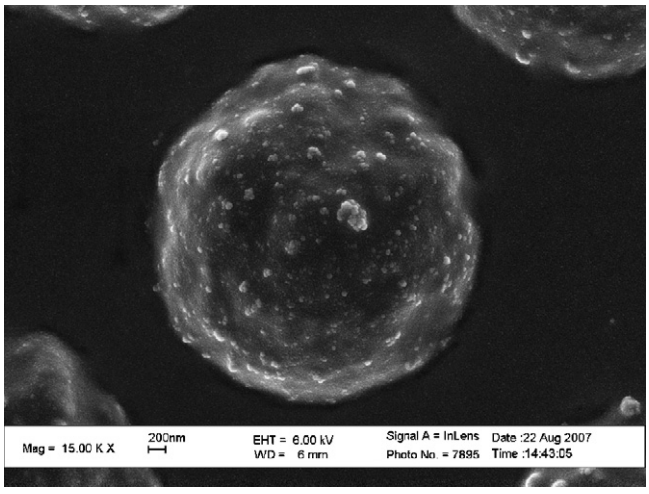

Fig. 1. The SEM photograph of Pd-PMMA catalyst.