CHINESE JOURNAL OF CATALYSIS
Volume 32, Issue 11, 2011
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Chin. J. Catal., 2011, 32: 1667–1676.

RESEARCH PAPER

Suzuki Reaction of Aryl Bromides Using a Phosphine-Free Magnetic Nanoparticle-Supported Palladium Catalyst

Nghia T. BUI, Trung B. DANG, Ha V. LE, Nam T. S. PHAN*

Department of Chemical Engineering, HCMC University of Technology, VNU-HCM, 268 Ly Thuong Kiet, District 10, Ho Chi Minh City, Viet Nam

Abstract: A palladium catalyst immobilized on superparaganetic nanoparticles was prepared with a palladium loading of 0.30 mmol/g. The catalyst was characterized using X-ray diffraction, scanning electron microscopy, transmission electron microscopy, vibrating sample magnetometry, thermogravimetric analysis, Fourier transform infrared, atomic absorption spectrophotometry, and nitrogen adsorption. The immobilized palladium catalyst was an efficient catalyst without added phosphine ligands for the Suzuki cross-coupling reaction of several aryl bromides with phenylboronic acid. The recovery of catalyst was simply by magnetic decantation in the presence of a magnet. The immobilized palladium catalyst can be reused many times without significant degradation in catalytic activity. No leaching of active palladium species into the reaction solution was detected.

Key words: superparamagnetic nanoparticle; Suzuki reaction; palladium; aryl bromide

Biaryl units as molecular components in biologically active molecules and functional polymers have attracted enormous interest [1,2]. The Suzuki cross-coupling reaction is an increasingly popular approach for the construction of unsymmetrical biaryl compounds since the organoboranes used are environmentally safer than other organometallic reagents [3]. Toxic and expensive homogeneous palladium phosphine complexes, which are rarely recoverable [4], are used as the catalysts for the Suzuki reaction [5–7]. The phosphines can be more costly than even the palladium in some cases [8]. From economic and environmental considerations, it is desirable to use a solid catalyst that does not have the hazardous phosphine additives as a green alternative to the conventional homogeneous processes for the Suzuki reaction [8,9]. Several phosphine-free solid palladium catalysts have been investigated for the Suzuki reaction, e.g., palladium species immobilized on polymer [10–13], silica [14–21], zeolite [22–24], hybrid organic-inorganic material [25,26], and palladium nanoparticle-based catalysts [27–31].

Nanoparticles have attracted significant interest as efficient supports for homogeneous catalyst immobilization [32,33]. When the size of the support is decreased to the nanometer scale, the activity of the supported catalyst can be dramatically improved compared to homogeneous catalysts immobilized on conventional supports under conditions where internal pore diffusion is rate limiting [32,34]. However, the facile separation and recycling of the nanoparticle materials from the reaction media still remains a challenge [34]. The problem can be solved by employing magnetic supports that allow the catalyst to be easily separated from the liquid reaction media by a magnet [35,36]. Magnetic nanoparticles have been utilized as catalyst supports for several organic transformations [36,37] such as olefin hydroformylation [38], alcohol hydrogenation [39], olefin hydrogenation [40], asymmetric hydrogenation [41,42], aldol reaction [43], Suzuki and Heck reactions [44–48], Sonogashira and Carbonylative Sonogashira reactions [44,49,50], Knoevenagel condensation [34], dehalogenation [51], oxidation [52–54], ring-opening polymerization of ε-caprolactone [55], ring-closing metathesis [56], cycloaddition reaction [57], and as supports for biocatalysts [58–61]. In this paper, we report the Suzuki cross-coupling reaction of aryl bromides with phenylboronic acid by a palladium catalyst

---

Received 30 May 2011. Accepted 20 July 2011.

*Corresponding author. Tel: +84-8-917416018; Fax: +84-8-38637504; E-mail: ptsnam@hcmut.edu.vn

This work was supported by the Ho Chi Minh City Department of Science and Technology, Viet Nam.

DOI: 10.1016/S1872-2067(10)60270-7

without added phosphine ligands immobilized on superparamagnetic nanoparticles. The magnetic catalyst can be isolated from the reaction mixture by simple magnetic decantation, and can be reused without significant degradation in activity.

1 Experimental

1.1 Materials and instrumentation

Chemicals were purchased from Sigma-Aldrich, Fisher, and Merck and used as received without further purification unless otherwise noted. Distilled water was purged with nitrogen for 2 h prior to use. A Fischer Scientific FS60H ultrasonic bath was used to sonicate samples. Fourier transform infrared (FT-IR) spectra were obtained on a Bruker TENSOR37 instrument. The samples were dispersed on potassium bromide pallets. Magnetic properties were measured with a PPMS 6000 vibrating sample magnetometer (VSM) at 32 °C. Samples were sonicated in dimethylformamide for 30 min before measurements were taken. Scanning electron microscopy (SEM) studies were conducted on a JSM 740 scanning electron microscope. Transmission electron microscopy (TEM) studies were performed using a JEOL JEM 1400 transmission electron microscope at 100 kV. The samples were dispersed on holey carbon grids for TEM observation. Nitrogen physisorption measurements were conducted using a Quantachrome 2200e system. Samples were pretreated by heating under vacuum at 150 °C for 3 h. Elemental analysis with atomic absorption spectroscopy (AAS) was performed on an AA-6800 Shimadzu instrument. X-ray diffraction (XRD) patterns were recorded using a Cu K_α radiation source on a D8 Advance Bruker powder diffractometer.

A Netzsch Thermoanalyzer STA 409 was used for thermogravimetric analysis (TGA) with a heating rate of 10 °C/min in air. Gas chromatographic (GC) analyses were performed using a Shimadzu GC 17-A chromatograph equipped with a flame ionization detector (FID) and an DB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The temperature program for the GC analysis was from 60 to 140 °C at 10 °C/min, held at 140 °C for 1 min, heated from 140 to 300 °C at 50 °C/min and held at 300 °C for 3 min. The inlet and detector temperatures were set at 300 °C. *n*-Hexadecane was used as an internal standard to calculate reaction conversions. GC-MS analyses were performed using a Hewlett Packard GC-MS 5972 instrument with a RTX-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0. 5 μm). The temperature program for GC-MS analysis was from 60 to 280 °C at 10 °C/min and held at 280 °C for 2 min. The inlet temperature was set at 280 °C. MS spectra were compared with the spectra in the NIST library.

1.2 Synthesis of amino-functionalized magnetic nanoparticles

The superparamagnetic nanoparticles were synthesized and functionalized with *N*-[3-(trimethoxysilyl)propyl]ethylenediamine by a slight modification of a reported procedure [34,62]. The nanoparticles (2.5 g) were dispersed in a mixture of ethanol and water (400 ml, 1:1 by volume). Ammonium hydroxide (40 ml, 25% v/v aqueous solution) was added, and the mixture was stirred vigorously at 60 °C for 24 h under argon. The nanoparticles were washed with copious amounts of deionized water, ethanol, and *n*-hexane by magnetic decantation. The resulting product was redispersed in a mixture of ethanol and water (400 ml, 1:1 by volume), and sonicated for 30 min at room temperature. *N*-[3-(trimethoxysilyl)propyl]ethylenediamine (2.8 g) was then added, and the solution was heated at 60 °C with vigorous stirring for 36 h under argon. The final product was washed with copious amounts of deionized water, ethanol, and *n*-hexane by magnetic decantation, and dried under vacuum at room temperature overnight to yield diamino-functionalized magnetic nanoparticles (1.98 g).

1.3 Synthesis of palladium catalyst immobilized on superparamagnetic nanoparticles

The diamino-functionalized magnetic nanoparticles (1.82 g) were added to a round-bottom flask containing ethanol (99.5 %, 270 ml) and 2-acetyl pyridine (18 ml, 150 mmol) [63,64]. The resulting mixture was sonicated for 30 min, and then heated under reflux with rapid stirring for 36 h under argon. After that, the reaction mixture was cooled to room temperature and the solid was separated by magnetic decantation. The magnetic solid was then redispersed in ethanol and hexane and sonicated for 30 min at room temperature. The product was then separated by magnetic decantation and dried under vacuum at room temperature to yield the immobilized Schiff base (1.80 g). The immobilized Schiff base (1.60 g) was added to the round-bottom flask containing a solution of palladium acetate (0.1815 g, 0.80 mmol) in acetone (280 ml). The mixture was then stirred vigorously at room temperature for 36 h under argon. The solid was separated by magnetic decantation, redispersed in acetone, sonicated for 30 min at room temperature, and then separated by magnetic decantation. The magnetic catalyst was washed with copious amounts of acetone and dried under vacuum at room temperature to yield the immobilized palladium catalyst (1.50 g).

1.4 Catalytic studies

Unless otherwise stated, a mixture of 4'-bromoacetophenone (0.2149 g, 1.08 mmol), phenylboronic acid (0.1975 g, 1.62 mmol), K_3PO_4 (0.8628 g, 3.24 mmol), and *n*-hexadecane (0.12 ml) as the internal standard in dimethylformamide (5 ml) were added to a round-bottom flask containing the required amount of the immobilized palladium catalyst. The flask was heated at the required temperature with magnetic stirring. Reaction