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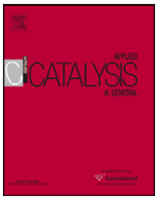

Room temperature aerobic Suzuki cross-coupling reactions in DMF/water mixture using zeolite confined palladium(0) nanoclusters as efficient and recyclable catalyst

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ABSTRACT

Herein we report the use of zeolite confined palladium(0) nanoclusters as efficient and recyclable catalyst for Suzuki cross-coupling reactions of aryl bromides with phenylboronic acid. Zeolite confined palladium(0) nanoclusters are highly active catalyst for the Suzuki cross-coupling reactions under mild conditions (room temperature, in air) in DMF/water (1:9) mixture. A variety of aryl bromides undergo Suzuki cross-coupling with phenylboronic acid with quantitative GC yields of biaryl derivatives. Recycling experiments showed that zeolite confined palladium(0) nanoclusters can be used as recyclable catalyst in the Suzuki cross-coupling reactions.

1. Introduction

The palladium-catalyzed Suzuki cross-coupling reaction of arylboronic acids with aryl halides is one of the most powerful and versatile methods for the selective construction of carbon–carbon bonds and has been widely used in the synthesis of pharmaceuticals, herbicides, natural products, and advanced materials [1–5]. Traditionally, these coupling reactions involve the use of various palladium complexes, including phosphine-based as well as phosphine-free palladium, as catalyst in organic solvents [6–8]. However, the fact that phosphine ligands are toxic, expensive, air- and moisture-sensitive make the ‘ligand-free’ palladium catalysts attractive due to both economical and environmental concerns [9].

Recently, different types of colloidal palladium nanoparticles have been prepared and used as catalyst for the Suzuki-coupling reactions [10–13]. The large surface-to-volume ratio of metallic nanoparticles makes them very attractive as catalysts in chemical reactions over the other bulk catalytic materials [14]. However, the liquid suspensions of metal nanoparticles are usually not reusable because of difficulties in recovery of the catalyst and separation of the products; the products are commonly contaminated by residual palladium [15,16]. These problems have to be overcome in the application of homogeneous Pd-catalyzed coupling reactions in industry and are still a challenge [17]. For this purpose, heterogeneous or heterogenized palladium catalysts have been developed [18–24]. Palladium has been supported on materials such as activated carbon [25–27], zeolites and molecular sieves [28–34], metal oxides [35–37] (mainly silica or alumina but also MgO, ZnO, TiO_2, and ZrO_2), clays [38,39], alkali and alkaline earth salts ($CaCO_3$, $BaSO_4$, $BaCO_3$, and $SrCO_3$), porous glass [40], organic polymers [28], or polymers embedded in porous glass [41], mesoporous silica [42,43], capsules [44], and basic metal phosphates (apatites) [45]. Among them, zeolites with confined void spaces appear to be a promising inorganic support providing an efficient way of solving the problems of separation and reusability of catalyst, as well as preventing the aggregation of nanoclusters [46–48]. In this regard, zeolite-Y has been considered as a suitable host providing highly ordered large cavities (supercages) with a diameter of 1.3 nm to encapsulate metal species [49–51]. Moreover, metal nanoclusters encapsulated within the cavities of zeolites may provide kinetic control for the catalytic reactions [52].

Indeed, our recent study [53] has shown that zeolite confined palladium(0) nanoclusters can be used as highly active catalyst in the hydrolysis of ammonia–borane. This has stimulated us to use the zeolite confined palladium(0) nanoclusters as catalyst in the Suzuki cross-coupling reactions too. Zeolite confined palladium(0) nanoclusters have been prepared by following a two step procedure (ion-exchange and reduction) and characterized by using a

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combination of advanced analytical techniques as described elsewhere [53]. Zeolite confined palladium(0) nanoclusters were found to be highly active catalyst in the Suzuki reaction, as well. In what follows we will discuss the activity and recyclability of the zeolite confined palladium(0) nanoclusters catalyst in the Suzuki cross-coupling reaction of aryl bromides with phenylboronic acid.

2. Experimental

2.1. Materials

Palladium(II) nitrate (98+%), sodium borohydride (99%), and sodium zeolite-Y were purchased from Aldrich and used without further purification. Deionized water was distilled by water purification system (Milli-Q System). All glassware and Teflon coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with distilled water before drying in an oven at 150 °C.

2.2. Preparation and characterization of zeolite confined palladium(0) nanoclusters

Zeolite confined palladium(0) nanoclusters were prepared by following the procedure as described in a previous article [53]. For this purpose, the sodium form of zeolite-Y (1.0 g) was added to a solution of palladium(II) nitrate in 100 mL H_2O in a 250 mL round bottom flask. This slurry was stirred at room temperature for three days until the supernatant solution became colorless. The Pd^{2+}-exchanged zeolite-Y samples were filtered by using Whatman-1 filter paper, washed with 20 mL deionized water three times, and dried in the oven at 80 °C. Then, the Pd^{2+}-exchanged zeolite-Y samples were added into 50 mL of 150 mM (284 mg) of aqueous sodium borohydride solution at room temperature. Palladium(II) ions were reduced forming the palladium(0) nanoclusters within the cavities of zeolite-Y. The zeolite confined palladium(0) nanoclusters samples were filtered again, washed thoroughly with deionized water, and dried in the oven at 80 °C.

The palladium content of the samples was determined by ICP-OES (Leeman-Direct Reading Echelle). For this purpose, the samples were dissolved in a mixture of nitric acid and hydrochloric acid. High Resolution Transmission Electron Microscopy (HRTEM) analysis was carried out with the expert assistance of Dr. Joan Hudson at Clemson University using a Hitachi H7600T operating at 120 kV and with a 2.0 Å point-to-point resolution. Samples were examined at magnification between 100 and 400 K. One drop of dilute suspension of sample in pentane was deposited on the TEM grids and the solvent was then evaporated. The nitrogen adsorption/desorption experiments were carried out at 77 K using a NOVA 3000 series instrument. The sample was outgassed under vacuum at 573 K for 3 h before the adsorption of nitrogen.

2.3. GC analysis

GC analyses were performed on a HP 6890N instrument equipped with a capillary column (5% biphenyl, 95% dimethylsiloxane) (30 m × 0.32 mm i.d. × 0.25 μm film thickness). The GC parameters were as follows: initial temperature, 50 °C; initial time, 1 min; solvent delay, 3.70 min; temperature ramp 1, 10 °C/min; final temperature, 150 °C; temperature ramp 2, 15 °C/min; final temperature, 250 °C; final time, 20.67 min; injector port temperature, 250 °C; detector temperature, 250 °C; and injection volume, 2.0 μL.

2.4. General procedure for the Suzuki cross-coupling reactions

Suzuki cross-coupling reactions were conducted as follows: to a mixture of arylbromide (1.0 mmol), phenylboronic acid (1.5 mmol), base (2.0 mmol), zeolite confined palladium(0) nanoclusters (0.01 mmol) and 10 mL of solvent (DMF/water (1:9)) was placed in a Schlenk tube (25 mL), and the mixture was vigorously stirred under air atmosphere. Then, the progress of the reaction was monitored by GC. Upon completion, the mixture was cooled to room temperature and then the products formed were extracted with acetone (2× 10 mL), filtered through a pad of silica gel with copious washing, concentrated and purified by flash chromatography on silica gel. The purity of the compounds was checked by ^1H NMR and GC, and yields are based on arylbromide.

2.5. Catalyst recycling in Suzuki cross-coupling reaction

The same reaction mixture solution was used for recycling after the addition of fresh amounts of the reactants. For recycling, an assumption was made that all of the *p*-bromoacetophenone was used up because it is the limiting reactant. After the first cycle, 1 mmol *p*-bromoacetophenone and 1.5 mmol phenylboronic acid were added to start the second cycle of the Suzuki cross-coupling reaction and the mixture was stirred for another 30 min to complete the second cycle. Similar procedure was followed for the following cycles of coupling reaction.

3. Results and discussion

3.1. Preparation and characterization of zeolite confined palladium(0) nanoclusters

Zeolite confined palladium(0) nanoclusters were prepared at room temperature following a two step procedure: ion-exchange of Pd^{2+} ions with the extra framework Na^+ ions in zeolite-Y, followed by the reduction of Pd^{2+} ions in the cages of zeolite-Y with sodium borohydride in aqueous solution. Zeolite-Y is first added to the aqueous solution of palladium(II) nitrate and the suspension is stirred for three days at room temperature. After filtering, copious washing with water, and drying in the oven at 80 °C, Pd^{2+}-exchanged zeolite-Y samples were obtained. Then, upon addition of sodium borohydride, palladium(II) ions were reduced forming the palladium(0) nanoclusters within the supercages of zeolite-Y [53].

The morphology of the zeolite confined palladium(0) nanoclusters was investigated by high resolution transmission electron microscopy (HRTEM). The high resolution TEM micrograph of the sample given in Fig. 1 shows the encapsulation of palladium in the highly ordered cages of zeolite-Y. Nitrogen adsorption–desorption isotherms of both zeolite-Y and zeolite confined palladium(0) nanoclusters samples (figure not shown) showed the type I isotherm, which is typical for microporous materials. The micropore volume and area for the zeolite-Y and zeolite confined palladium(0) nanoclusters were calculated by *t*-plot method. On passing from zeolite-Y to zeolite confined palladium(0) nanoclusters, both micropore volume (from 0.332 to 0.275 $cm^3 g^{-1}$) and the micropore area (from 823 to 682 $m^2 g^{-1}$) were noticeably reduced. The decrease in both micropore area and micropore volume can also be attributed to the encapsulation of palladium(0) nanoclusters in the cavities of zeolite-Y [53].

3.2. Catalytic activity of zeolite confined palladium(0) nanoclusters in the Suzuki cross-coupling reactions

Palladium(II) ion-exchanged zeolite-Y has already been tested in Suzuki cross-coupling reactions of aryl halides with arylboronic acid and found to show activity only in DMF/water mixture with 1:1 ratio [54]. In a control experiment starting with palladium(II) ion-exchanged zeolite-Y with a loading of 1.66 wt.% Pd, coupling reaction of p-bromoacetophenone with phenylboronic acid in the