



ELSEVIER

Contents lists available at ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com



Full paper/Mémoire

Immobilization of palladium nanoparticles as a recyclable heterogeneous catalyst for the Suzuki–Miyaura coupling reaction

Ramin Ghorbani-Vaghei*, Narges Sarmast, Farid Rahmatpour

Department of Organic Chemistry, Faculty of Chemistry, Bu-Ali Sina University, 65174 Hamedan, Iran

ARTICLE INFO

Article history:

Received 9 January 2018

Accepted 15 March 2018

Available online xxxx

Keywords:

LDH

Suzuki–Miyaura reaction

Palladium

Biaryl

Tris

ABSTRACT

This work describes the synthesis of Pd nanoparticles that are stabilized on CaAl-layered double hydroxide functionalized with Tris (tris(hydroxymethyl)aminomethane). The synthesized catalyst is characterized by several different analyses and has been successfully applied to the Suzuki–Miyaura reaction.

© 2018 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

1. Introduction

One of the most valuable synthetic methods to prepare symmetric and nonsymmetrical biaryls is a palladium-catalyzed Suzuki coupling reaction of aryl halides with arylboronic acids. So many efforts in the catalysis research have been allocated to extend efficient, safe, and reusable palladium catalysts [1]. Nowadays, the immobilization of palladium active sites onto supports to produce heterogeneous and reusable catalysts has attracted much attention [2,3]. Different inorganic, organic, and hybrid porous systems, such as zeolites [4], metal–organic frameworks (MOFs) [5], and polymers [6], have been applied for supported palladium catalysts. Catalyst-based layered double hydroxides (LDHs) have gained considerable attention because, in addition to their readily dispersed characteristic in a reaction solution with an intrinsically high surface area rendering, they are heterogeneous and can be easily recovered from the reaction mixture. Thus, a lot of LDH-supported catalysts with

high catalytic activities have been extended and used in different organic synthesis, including transesterification reactions [7], hydrogenation and oxidation reactions [8], polymerization of alkene oxide [9], aldol condensation [10], and synthesis of heterocyclic compounds [11].

In this study, in continuation of our research on the stabilization of palladium nanoparticles (NPs) on the novel supports [12–14], we present LDH/Tris/Pd using LDH as a support and Tris as a coupling linker. Tris with three hydroxyl groups in a molecule can chelate to palladium, producing a novel and efficient catalyst.

2. Experimental setup

2.1. Chemicals and instruments

All commercial materials were purchased from Merck companies and used without further purifications. Fourier transform infrared (FT-IR) spectra were recorded using a Shimadzu 435-U-04 FT spectrophotometer (KBr pellets). Scanning electron microscopy (SEM) was performed using field emission SEM instrument (SIGMA, Germany).

* Corresponding author.

E-mail address: rgvaghei@yahoo.com (R. Ghorbani-Vaghei).

Transmission electron microscopy (TEM) was performed in an inert atmosphere (N_2) in the temperature range 0–1000 °C at a heating rate of 10 °C min^{-1} using Zeiss-EM10C-100 kV. The qualitative analysis of LDH/Tris/Pd was performed using energy-dispersive X-ray (EDX) spectroscopy. EDX analysis of the prepared catalyst was performed on an FESEM instrument (SIGMA). TGA was performed on a TA instruments (model 951 DUPONT) apparatus. Ultrasonication was done in a 2200 ETH-SONICA ultrasound cleaner with a frequency of 45 KHz.

2.2. Preparation of LDHs

CaAl LDH material was provided by the coprecipitation method in a one-pot reaction [15]. An aqueous solution containing a molar ratio of 2:1 from mixed metal solutions, calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) and aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) dissolved in deionized (DI) water, was prepared. Then, under vigorous stirring, at 65 °C, the mixed metal solution was slowly added to a 2 M sodium hydroxide solution to maintain a constant pH of approximately 10 or 11. After completion of the addition, the LDH was aged for 18 h at 65 °C. In the next step, the obtained white powder was separated by centrifugation, washed three times with DI water, and dried overnight at 100 °C.

2.3. Preparation of LDH coated with (3-chloropropyl)triethoxysilane (LDH/(CH₂)₃-Cl)

LDH/(CH₂)₃-Cl was synthesized *via* surface reaction of LDH by using 3-chloropropyltrimethoxysilane. LDH (1.0 g) and toluene (50.0 mL) were mixed into a 250 mL round-bottom flask. Then 2.0 mL of 3-chloropropyltrimethoxysilane was added and the mixture was refluxed at 110 °C with continuous stirring for 12 h. The resulting LDH/(CH₂)₃-Cl was collected and washed with toluene and EtOH several times and dried at 70 °C until complete dryness.

2.4. Anchoring of Tris onto LDH/(CH₂)₃-Cl surface (LDH/Tris)

A mixture of 3.0 g of Tris and 50 mL of EtOH was stirred at 80 °C. Then, 1.0 g of LDH/(CH₂)₃-Cl was added to the flask. The reaction was conducted for 48 h. The crude product was filtered off and washed with ethanol three times to remove all unreacted Tris. The final product (white solid) was dried under vacuum overnight.

2.5. Synthesis of LDH/Tris-supported palladium NPs (LDH/Tris/Pd(0))

LDH/Tris (0.5 g) was added to a flask containing a solution of PdCl₂ (2 mmol, 0.34 g) in CH₃CN (10 mL) and stirred for 24 h at 50 °C. After cooling, the resulting product was collected on a filter, washed four times with acetone (8 mL), and dried in an oven at 70 °C. Moreover, with the use of NaBH₄, as a reducing agent, Pd(II) reduced to Pd(0): the obtained catalyst was dispersed in 20 mL CH₃CN, aqueous solution of NaBH₄ (0.2 g in 20 mL) was added to a round-bottom flask, and the mixture was stirred at room temperature for 5 h. Then, with the use of centrifuge, black

solid catalyst was collected, washed with DI water (3 × 4 mL) and CH₃CN (4 mL), and finally dried under vacuum for 18 h. The concentration of palladium in LDH/Tris/Pd(0), which was 13.52 wt %, was determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

2.6. General procedure for the Suzuki–Miyaura coupling reaction using LDH/Tris/Pd

A mixture of ArX (1 mmol), PhB(OH)₂ (1.1 mmol), K₂CO₃ (2 mmol), catalyst (0.05 mol % Pd), and H₂O/EtOH (1:1, 5 mL) were placed in a 25 mL Schlenk tube and the mixture was stirred at room temperature. After the completion of the reaction monitored by thin-layer chromatography (*n*-hexane/acetone 10:4), the catalyst was separated by centrifugation, and then the reaction mixture was washed three times with ethyl acetate. The combined organic layer was dried over magnesium sulfate and evaporated in a rotary evaporator under reduced pressure to obtain the biaryl product.

3. Results and discussion

The catalyst was prepared using a simple and efficient method and characterized by FT-IR, X-ray diffraction (XRD), SEM, EDX, TEM, and X-ray photoelectron spectroscopy (XPS).

In this study, we used NaBH₄ as a reducing agent and reduced Pd(II) to Pd(0) to prepare LDHs/Tris/Pd. After the addition of NaBH₄, the yellow color of the Pd(II) solution immediately changed into black, which indicated the formation of Pd NPs (Scheme 1).

Conversion of Pd(II) to Pd(0) in the resulted Pd-supported NPs was confirmed by the UV–vis spectrum. The disappearance of the peak at 420 nm, which belongs to Pd(II) species, ascertains the formation of the Pd(0) catalysts (Fig. 1).

3.1. Characterization of the prepared LDH/Tris/Pd

The FT-IR spectra of the LDH, LDH/(CH₂)₃-Cl, LDH/Tris, and LDH/Tris/Pd are shown in Fig. 2, peak assignments appeared as “X value”. The broad observed peaks, in all samples, shown at 3400–3650 and 535–580 cm^{-1} were attributed to the Al–OH/H₂O stretching and metal–oxygen vibrations, respectively. The appearance of the strong peak at 1385 cm^{-1} imputed to the interlayer NO₃[−] anion is the other notable finding for these figures. In Fig. 2b observed peaks at 1057 and 1138 cm^{-1} attributed to Si–O–M and Si–O–Si confirm that the (3-chloropropyl)triethoxysilane have functionalized the surface of the LDH. The successful reaction of Tris with LDH/(CH₂)₃-Cl was confirmed with observed peaks at 1353, 1385, and 3423 cm^{-1} attributed to stretching vibration of C–N, C–O, and N–H groups (Fig. 2c). The reduction in the intensity of OH groups at 3641 cm^{-1} in Fig. 2d demonstrated the coordination of Pd NPs on the surface of the functionalized LDH.

To check the thermal degradation property of LDH/Tris/Pd, the TGA of the catalyst was performed. Catalyst started to decompose at less than 150 °C attributed to the loss of the trapped H₂O and interlayer anions. The weight loss at a

Download English Version:

<https://daneshyari.com/en/article/6594401>

Download Persian Version:

<https://daneshyari.com/article/6594401>

[Daneshyari.com](https://daneshyari.com)