



Research paper

Efficient preparation and application of palladium loaded montmorillonite as a reusable and effective heterogeneous catalyst for Suzuki cross-coupling reaction

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ABSTRACT

The Na⁺ montmorillonite (Mt) was modified with L-cystine, and palladium was loaded via an ion-exchange reaction under microwave irradiation to obtain Pd@Mt. The entire process was conveniently carried out under mild reaction conditions in a matter of hours. The XRD, XPS and ICP-AES results confirmed the successful loading of palladium (0.55 wt%). The so obtained Pd@Mt was subsequently explored as a catalyst for the Suzuki cross-coupling reaction and afforded the corresponding products in good to excellent yields for twenty reactants (in the range of 79–99%, only 3 reactants gave yields below 90%). The catalytic mechanism was investigated and discussed in detail. This supported catalyst could be easily recovered from the reaction mixture by simple filtration or centrifugation. Decreased palladium loss and improved reusability were achieved when the catalyst was recovered by filtration. Notably, this recovery method maintained the observed high yields, showing a >90% yield for the 6th run. Although palladium ions were reduced to Pd (0) in the cross-coupling reaction, only a small amount of aggregation was observed in the TEM images, where the diameters of the palladium particles on Mt were in nano scale.

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1. Introduction

Over the past decades, aromatic carbon-carbon (C–C) bond coupling reaction has attracted considerable attention, as it was a very important method for the preparation of many pharmaceuticals and other complex organic molecules. Among the many commonly used cross-coupling reactions, the palladium catalyzed Suzuki reaction was considered one of the most powerful tools of this synthetic methodology for the efficient fabrication of aryl-aryl bonds, owing to the high stability and functional group tolerance under moderate and non-anhydrous reaction conditions (Muenmart et al., 2014; Sun et al., 2014; He et al., 2016). Typically, these reactions were performed using homogeneous, soluble palladium coupled with certain ligands to form a precatalyst (Tan et al., 2011; Liu et al., 2012a, 2012b). However, homogeneous palladium frequently left residual palladium embedded in the products, which may have a dramatic and deleterious effect on toxicity,

conductivity or other properties. Consequently, tedious post treatment was required to achieve high purity, which impeded wider industrial application. Moreover, both the palladium catalysts and elaborate ligands used in the homogeneous reaction were expensive and poisonous, which could cause serious problems for economy and environment. Hence, environmentally friendly heterogeneous catalytic systems were used as alternative methods to overcome these problems. Until now, much efforts had been dedicated to the improvement of reusable heterogeneous palladium catalysts, which could greatly improved the separation procedure and reduce the cost of the catalyst (Phan et al., 2006). Among the studied heterogeneous catalysts, solid materials such as alumina, silicas, zeolites, metal oxide nanoparticles, ionic liquids and polymers have been used to support palladium and achieve superior catalytic performance (Liu et al., 2012a, 2012b; Reynolds et al., 2014; Kaur and Singh, 2015; Pal and Bhaumik, 2015). Borah et al. (2014) modified montmorillonite (Mt) with H₂SO₄ under controlled conditions to generate nanopores on the surface, which served as a 'Host' for Pd nanoparticles. The obtained supported Pd nanoparticles with particle size below 10 nm exhibited efficient heterogeneous catalytic performance in the Suzuki–Miyaura coupling reactions in high isolated yields and 100% selectivity in water under ligand free conditions. Inspired by metalloenzyme, Yamada et al. (2012) prepared a polymeric imidazole Pd, and found that it could be used to smoothly catalyze the coupling of a wide variety of inactivated aryl bromides and iodides in water. The catalyst showed a catalytic turnover number (TON) as high as

Abbreviations: AES, atomic emission spectrometry; DI water, deionized water; EDS, energy dispersive spectrometer; GC, gas chromatography; ICP, inductively coupled plasma; Mt, montmorillonite; NMR, nuclear magnetic resonance; Pd@Mt, palladium loaded montmorillonite which was modified with L-cystine; Pd@Mt-R, the recovered palladium loaded modified montmorillonite which was ever used as catalyst; Pd NPs, palladium nano particles; TEM, transmission electron microscopy; TMS, tetramethylsilane; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction.

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3,570,000. Gu et al. (2015) developed a microPES membrane as a palladium support to catalyze the Suzuki reaction in a flow-through configuration. It took only 10 s to achieve full conversion in a single filtration, demonstrating the extremely excellent performance of this method. Palladium nanoparticles (Pd NPs) were embedded in a microporous polymer by Ogasawara et al. (Ogasawara and Kato, 2010) and used in the Suzuki cross-coupling reaction. The supported catalyst can be successfully recovered by filtration and reused with only a slight loss of activity (the yield was above 90% even on the 8th run). According to ICP-AES analysis, only 0.27% of the initial amount of Pd was released into solution.

Although these supported heterogeneous palladium catalysts were very efficient, they suffered from lengthy fabrication steps and rigorous preparation requirements. Wang et al. (2015) took 2 days to prepare cellulose-supported triphenylphosphine under nitrogen at 80 °C, and spent another 20 h to load palladium under nitrogen atmosphere to obtain the catalyst. The same difficulty was met when preparing microcrystal DUT-67 MOFs, a support for Pd nanoparticles. Zhuang et al. heated a mixture of ZrCl₄, DMF, NMP, 2,5-thiophenedicarboxylic acid and acetic acid at 120 °C for 2 days under autogenous pressure (Zhuang et al., 2015). Although the preparation of the inorganic support was slightly simpler, the loading process was sometimes quite difficult. For example, to complete the ion exchange process, the [Pd(NH₃)₄]²⁺-exchanged sepiolite (Pd-sepiolite) was prepared in an aqueous solution of [Pd(NH₃)₄]Cl₂ at 298 K for 48 h (Shimizu et al., 2004). Looking to obtaining heterogeneous Pd catalysts in a simpler and more convenient manner, we noticed Mt. behaved in high ion exchange capacity, chemical inertness and large surface area, which was very suitable for supporting ionic catalyst (Carretero, 2002; Dimitris and Dadachov, 2003). In this paper, L-cystine was used to modify Mt, and then, palladium was efficiently loaded on the modified Mt. via an ion-exchange reaction under microwave irradiation to obtain the Suzuki catalyst. The entire preparation was performed under mild conditions and the loading process took only 4 min, which revealed remarkable convenience. The successful loading of palladium was confirmed by ICP-AES and XPS. The so as prepared catalyst showed high efficiency in many Suzuki reactions, as the yields were almost all above 90%. Moreover, the catalyst can be easily recovered by centrifugation or filtration. The yield remained above 90% on the 6th run.

2. Experimental

2.1. Materials

Na⁺-montmorillonite (Mt) K10 (CEC: 97 mmol/100 g, typical chemical composition: SiO₂: 73.0%, Al₂O₃: 12.0%, Fe₂O₃: 2.7%, CaO: 0.2%, MgO: 1.1%, Na₂O: 0.6%, K₂O: 1.9%) was bought from Alladin Company. L-cystine was purchased from Shanghai Ziyi Reagent Company. Palladium chloride (PdCl₂) was purchased from Aldrich Chemical. All the solvents and other chemical reagents (AR grade) were purchased from commercial resources and used directly without any further purification.

2.2. Preparation of Pd@Mt

5 g Mt and 1.9 g of L-cystine was dispersed into 500 mL of deionized (DI) water pre-heated to 60 °C, the pH was maintained at 4.6 with HCl (0.1 mol/L). The mixture was put in vigorous stir for 1 h at 60 °C, the modified Mt was separated and obtained then. The amount of introduced cystine was 4.9×10^{-4} mol/g via the sulfur content.

0.443 g PdCl₂ was solved in 1 mL of concentrated hydrochloric acid, the solution was transferred to 100 mL volumetric flask with deionized water to obtain PdCl₂ solution with the concentration of 0.025 mol/L.

0.5 g modified Mt was mixed with 10 mL of PdCl₂ (0.025 mol/L) and stirred continuously at 60 °C for 30 min. Then the sample was put into a WBFY-201 microwave generator for 5 min at the power of 375 W, and washed with distilled water by centrifugation. The powder was labeled

as Pd@Mt after drying in vacuum at 60 °C for 24 h. According to the ICP result, the mole ratio of L-cystine and Pd was 9.48.

2.3. Suzuki cross-coupling reactions with Pd@Mt as catalyst

Aryl halides (1 mmol), phenylboronic acid (1.2 mmol), Pd@Mt (0.02 g), K₂CO₃ (2 mmol), deionized water 2 mL and EtOH 2 mL were added to a round bottom flask with a magnetic stir stick. After the mixture was heated to 65 °C for 3 h, the product was extracted with ethyl acetate. Afterwards, the product was dried over anhydrous Na₂SO₄ and characterized spectroscopically (¹H NMR and ¹³C NMR). The conversion rate of every reaction was analyzed by gas chromatography (GC), based on the peak area normalization method. All of the characterization results were consistent with those of the previous literatures (Han et al., 2008; Polshettiwar et al., 2008; Mao et al., 2009; So et al., 2010).

2.4. Recovery of the catalyst

To test the reusability of Pd@Mt, Pd@Mt was added in the reaction of phenylboronic acid and 4-bromobenzaldehyde. When the reaction was complete, the catalyst was separated from the reaction mixture via two different methods. For the first method, the whole mixture was centrifuged, the so recovered catalyst was labeled as Pd@Mt-R1. For the second method, the catalyst was separated with filtration using a quantitative analysis filter paper. As it was very difficult to scratch the Pd@Mt from the paper, the paper was burnt and only the catalyst was left, the so recovered catalyst was labeled as Pd@Mt-R2. The recovered Pd@Mt-R was washed with ethyl acetate and used for a second run.

2.5. Measurements and characterizations

2.5.1. Specific surface area measurement

Specific surface area (SSA) was measured with a micromeritics equipment (TriStar II 3020, Micromeritics Instrument). Before the measurement, the samples were dried in a vacuum oven at 110 °C for 4 h. The surface area of sample was calculated from the isotherms of nitrogen via the Brunauer-Emmet-Teller (BET) equation, the p/p₀ range for application of the BET equation was 0.05–0.30, for the isotherm tabular report was 0.01–0.99.

2.5.2. Pd content

The Pd@Mt or Pd@Mt-R was dissolved in the mixture of concentrated HCl and fuming HNO₃ (v/v: 1/1), then the solution was subjected to the determination of the Pd content via the inductively coupled plasma-atomic emission spectroscopy (ICP-AES) method using a 7500CE ICP-AES (Agilent, USA).

2.5.3. Yield of reaction

The yield of reaction was determined via gas chromatography. The analysis was performed on an Agilent GC-6820 chromatograph with a 30 m (column height) × 0.32 mm (column diameter) × 0.5 mm (column coating thickness) OV-17 capillary column with a flame ionization detector.

2.5.4. X-ray photoelectron spectroscopy (XPS)

The ESCALAB 250XI (Thermo Scientific, USA) was used to carry out the X-ray photoelectron spectroscopy (XPS) measurements under a base pressure of about 6.67×10^{-7} Pa. The radiation was Al Kα (1486.6 eV, 15kV, CAE mode). The binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon. The curves were deconvoluted from the obtained XP spectra with the XPS peak fitting software.

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