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Production of novel palladium nanocatalyst stabilized with sustainable chitosan/cellulose composite and its catalytic performance in Suzuki-Miyaura coupling reactions

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ABSTRACT

In this study, we designed a new palladium nanocatalyst on chitosan/cellulose composite for the first time to increase the use of sustainable polysaccharides, which are cheap, non-toxic, environmental friendly, abundant in nature, and can be used as support materials for metallic nanoparticles. Physicochemical characterization of fabricated palladium nanocatalyst was illuminated with FT-IR, TG/DTG, SEM/EDAX, XRD, and ICP-OES analyses. Pd nanoparticles were found to be almost spherically structured, and the average particle size was 26–30 nm. Then catalytic performance of the designed nanocatalyst was investigated in the synthesis of a series of biphenyl compounds via the Suzuki-Miyaura reaction by using the green method which is conducted in a very short-time, under low temperature, and without the presence of any toxic chemical solvents (e.g., 5 min treatment in microwave oven at 400W at 50 °C). As a result of the tests, palladium nanocatalyst showed excellent catalytic performance with high conversion yields for a wide range of substrates and with a very low catalyst loading for the Suzuki reactions. Sustainability performance of palladium nanocatalyst was also studied, and it is found that the catalyst was able to be recycled for eight successive runs.

1. Introduction

Recently, immobilization of the metallic nanoparticles on solid materials has received growing interest because of their potential use in various fields such as microelectronics, therapeutics, sensors, and antimicrobials (Darder, Colilla, & Ruiz-Hitzky, 2005; Nair & Laurencin, 2007; Rai, Yadav, & Gade, 2009). One of the most important application areas of metal nanoparticles is their use as catalysts in catalytic systems because they present several benefits such as ease of removal from reaction media, low level waste, and low cost (Fakhri, Jaleh, & Nasrollahzadeh, 2014; Nasrollahzadeh, Sajadi, & Maham, 2015). In recent years, different solid supports such as silica, magnetic materials, and carbon nanotube have been designed to stabilize metallic nanoparticles, and their potential use in catalytic systems has been investigated (Bernini et al., 2010; Karimi, Zamani, Abedi, & Clark, 2009; Polshettiwar & Molnár, 2007). Among these support materials, polysaccharides have received more attention than their synthetic counterparts because they are nontoxic, biodegradable, inexpensive, and environmentally friendly (Yi, Lee, Sin, & Lee, 2007). Khazaei, Rahmati, and Saednia (2013) reported that new palladium nanoparticles stabilized on pectin were designed, and their catalytic activity were investigated in Sonogashira reactions. Firouzabadi, Iranpoor, and Ghaderi (2011) prepared palladium nanoparticles immobilized on gelatin. Then catalytic performance of the palladium nanoparticles was studied in Mizoroki–Heck reactions. In an another study, Khazaei, Khazaei, and Rahmati (2015) fabricated stabilized palladium nanoparticles by using gelatin/pectin mixture, and the synthesized palladium nanoparticles were evaluated in Mizoroki–Heck reactions. Despite the fact that polysaccharides have unique properties, are abundant in nature, and have low cost, composites which are derived from polysaccharides have been ignored by researchers in terms of stabilizing palladium nanoparticles. Therefore, there is a large gap in literature in both syntheses and characterizations of polysaccharide composites about their ability to stabilize palladium nanoparticles and their applications in catalytic systems.

Palladium catalyzed catalytic reactions such as Suzuki–Miyaura, Stille, Mizoroki–Heck, and Sonogashira–Hagihara reactions are effective processes to form the carbon–carbon bond in organic syntheses (Baran, 2017; Milstein & Stille, 1978; Sonogashira, Tohda, & Hagihara, 1975; You et al., 2016). Among the coupling reactions, Suzuki is the most important reaction of organo-boronic acids with aryl halides for synthesis of biaryls compounds which are utilized in different areas

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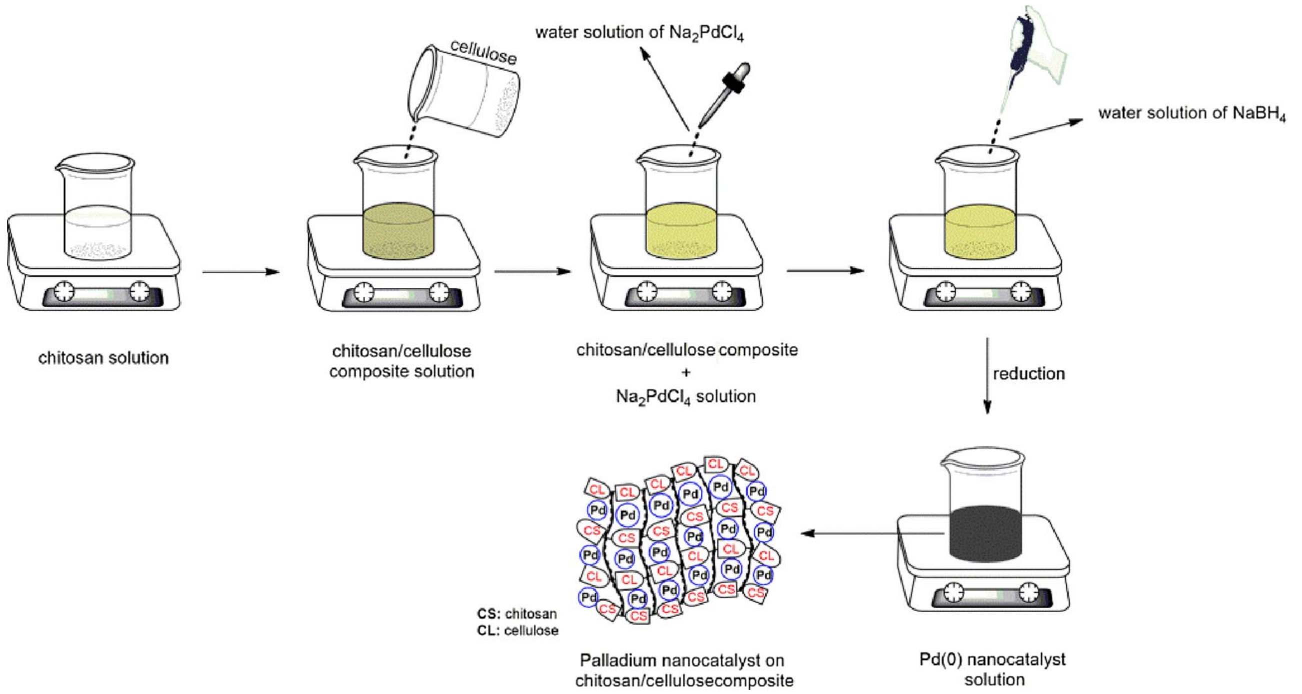

Scheme 1. Preparation of Pd nanocatalyst.

such as medicine, pharmacology, advanced materials, cosmetics, and herbicides (Cotugno et al., 2014; Makhubela, Jardine, & Smith, 2011). In addition, Suzuki C—C reactions have a special place compared to other coupling reactions due to their tolerance to both a broad range of functional groups on the substrate and many different transition metals. However, coupling reactions have serious drawbacks such as long reaction time, high reaction temperature, and high cost (Alonso & Nájera, 2010). In order to overcome the problems of long reaction time and high reaction temperature, microwave irradiation technique is widely utilized for Suzuki C—C reactions because it provides fast and clean syntheses under benign reaction conditions (Baran, Sargin, Kaya, & Menteş, 2016a). To eliminate the cost problem in the coupling reactions, researchers turn towards low cost sustainable bio-polymers as metal support (Baran et al., 2016a). Additionally, these bio-based polymers have high metal-support interaction capacity and durability which are the unique properties making them ideal candidates for catalytic reactions.

In the present study, palladium nanoparticles stabilized on chitosan/cellulose composites have been designed and characterized with different analytic tools to increase their use as sustainable carbohydrate-composites and a support for metallic nanoparticles. Then catalytic performance of the prepared palladium nanoparticle was explored for the first time in the coupling reactions of various aryl halides with phenyl boronic acid under mild conditions employing environmentally friendly microwave heating technique. The chitosan/cellulose composite, which were supported with palladium nanocatalyst, indicated excellent catalytic activity in Suzuki cross coupling reactions. Additionally, the sustainability of palladium nanoparticles was investigated, and it was found that it retained its activity even after 8 recovery and recycle times.

2. Materials and method

2.1. Materials

Chitosan, cellulose, Na_2PdCl_4, KOH, $NaHCO_3$, NaOH, Na_2CO_3, Cs_2CO_3, K_2CO_3, $MgSO_4$, $NaBH_4$, phenyl boronic acid, aryl halides toluene, ethanol, and acetic acid were purchased from Sigma-Aldrich.

2.2. Instrumentation

FT-IR spectra of the chitosan/cellulose composite and Pd nanocatalyst were obtained on a Perkin Elmer Spectrum 100 FT-IR spectrophotometer. X-ray diagrams were recorded on a Rigaku smart lab system (at 40 kV, 30 mA, and 2θ with a scan angle of 10 − 70°). Thermal and mechanical durabilities of chitosan/cellulose composite and Pd nanocatalyst were studied on EXSTAR S11 7300 (nitrogen atmosphere; 30–650 °C heating range). The surface properties of the products were obtained on QUANTA-FEG 250 ESEM by coating with platinum. The analysis of Pd ion on the chitosan/cellulose composite was determined using EDAX-Metek. Palladium ion content of Pd nanocatalyst was determined by using Perkin Elmer Optima 2100 DV Inductively Coupled Plasma (ICP) Optical Emission Spectrometer (OES). The characterizations of biaryl compounds were done on GC–MS Agilent GC-7890 A- MS 5975. A domestic microwave oven was used in the catalytic tests.

2.3. Experimental studies

2.3.1. Synthesis of chitosan/cellulose composites stabilized with palladium nanoparticles

Chitosan (1 g) was dissolved in a solution of 2% acetic acid (100 mL). Then cellulose (1 g) was added into chitosan solution and stirred for overnight at room temperature (RT) to obtain chitosan/cellulose composite. After the reaction was completed, Na_2PdCl_4 solution (0.2 g in 10 mL water) was added into the reaction mixture and stirred for 3 h. Subsequently, a freshly prepared $NaBH_4$ solution (0.8 *M*, 10 mL in water) was added to the reaction media to reduce Pd (II) to Pd (0), and it was observed that the light yellow colour of the reaction solution turned immediately into dark gray. This mixture was also stirred for 30 min to ensure the complete conversion of Pd(II) to Pd(0). Then the reaction solution was adjusted to neutral pH with a NaOH solution. Finally, the obtained dark gray palladium nanoparticles were filtered out, rinsed with distilled water, and dried at RT (Scheme 1).

2.3.2. General procedure for suzuki coupling reactions in the presence of Pd nanocatalyst

In a typical experiment, the aryl halides, phenyl boronic acid