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Regular Article

Practical, economical, and eco-friendly starch-supported palladium catalyst for Suzuki coupling reactions

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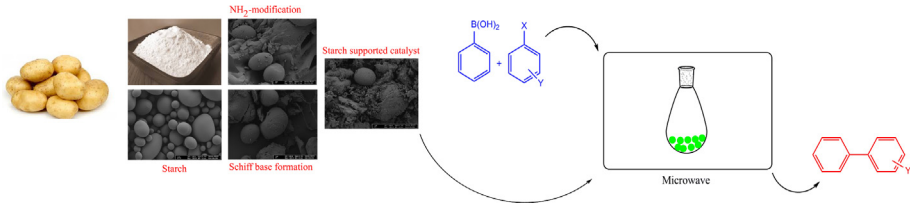
GRAPHICAL ABSTRACT



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ABSTRACT

In catalytic systems, the support materials need to be both eco friendly and low cost as well as having high thermal and chemical stability. In this paper, a novel starch supported palladium catalyst, which had these outstanding properties, was designed and its catalytic activity was evaluated in a Suzuki coupling reaction under microwave heating with solvent-free and mild reaction conditions. The starch supported catalyst gave remarkable reaction yields after only 5 min as a result of the coupling reaction of the phenyl boronic acid with 23 different substrates, which are bearing aril bromide, iodide, and chloride. The longevity of the catalyst was also investigated, and the catalyst could be reused for 10 runs. The starch supported Pd(II) catalyst yielded remarkable TON (up to 25,000) and TOF (up to 312,500) values by using a simple, fast and eco-friendly method. In addition, the catalytic performance of the catalyst was tested against different commercial palladium catalysts, and the green starch supported catalyst had excellent selectivity. The catalytic tests showed that the novel starch based palladium catalyst proved to be an economical and practical catalyst for the synthesis of biaryl compounds.

1. Introduction

Nowadays, eco friendly catalysts are one of the most important areas of research due to their environmental and economic attributes [1,2]. So far, many researchers have focused on the synthesis of a green metal catalyst system, and they have investigated the catalytic performance of the catalyst in the synthesis of biaryl compounds [3–7]. The palladium-catalyzed Suzuki cross coupling reaction ($C(sp^2)$-$C(sp^2)$) is known as an influential method for the synthesis of biaryl compounds, which are used in different areas such as cosmetics, medicine, pharmacology, and materials science [8–11]. Recently, researchers have developed different homogenous palladium catalysts for catalyst systems, but they do not have high reaction yields due to the difficulties in the separation of the catalyst from the reaction media [12,13]. Therefore, solid supported heterogeneous catalysts have gained much attention because they provide long life time (reusability) and easier work-up, and they can be separated from the reaction mixture [14–16].

The support material selection, as a ligand for the metal ions, is a very important parameter of catalyst systems owing to the

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thermal stability and catalytic efficiency of the catalyst. Catalyst support materials are usually preferred to have the following properties: (i) high thermal and chemical durability, (ii) inertness against air and moisture, (iii) low cost, (iv) ease of chemical modification, and (v) environmentally friendliness. Biological macromolecular biopolymers as the support material have gained a great deal of attention due to their unique properties, such as being renewable, chemical stable, and more environmental friendly than commercial materials [17,18]. Especially, polysaccharides, such as chitosan, cellulose, and chitin, are currently being explored intensively as support materials for catalyst systems [19–21]. Among the polysaccharides, starch (ST) is the most significant biocompatible, biodegradable, and non-toxic bio-polymer that is obtained from plants [22]. In addition, the reactive free —OH groups on the starch easily enable chemical modifications. More importantly, this versatile polysaccharide has not been well investigated in the catalytic reactions. There have been few studies in the literature about it as a support material in Suzuki coupling reactions [23]. Therefore, starch should be investigated as a support material for catalyst systems.

In the present study, to eliminate this deficiency in literature, a novel starch supported Pd(II) catalyst was designed as follows: firstly, starch was functionalized with 3-aminopropyltriethoxysilane by reflux in anhydrous toluene. Second, the Schiff base reaction of NH_2-functionalized starch was done with 2,4-dihydroxybenzaldehyde to prepare the support material for the palladium ions, Then, a starch supported Pd(II) catalyst was obtained as a result of the reaction of the scratch Schiff base with Na_2PdCl_4 in water. Finally, the catalytic efficiency of the starch supported palladium(II) catalyst was explored against a Suzuki cross coupling reaction under mild conditions (without any solvent, in microwave heating, for 5 min), and it exhibited excellent activity. The reusability of the heterogeneous starch supported Pd(II) catalyst was tested and demonstrated good reusability performance. In addition, the catalytic activity of the novel starch based catalyst was tested against different commercial palladium catalysts in Suzuki C—C reactions. At the same time, the green microwave procedure, which is used in the synthesis of the biaryls, was also evaluated with regards to a traditional reflux system. In the tests, the novel palladium catalyst showed excellent selectivity, reaction activity, turn over number (TON), and turn over frequency (TOF).

2. Materials and method

2.1. Materials

Starch from potato, 2,4-dihydroxybenzaldehyde, 3-aminopropyltriethoxysilane (APTES), $PdCl_2$, $Pd(CH_3CN)_2Cl_2$, Na_2PdCl_4, phenyl boronic acid, aryl halides, K_2CO_3, NaOH, CS_2CO_3, KOH, $MgSO_4$, toluene, ninhydrin, and ethanol were obtained from Sigma-Aldrich.

2.2. Instrumentation

FT-IR spectra of the samples were analyzed on a Perkin Elmer Spectrum 100 FT-IR spectrophotometer. X-ray diffractograms were recorded on a Rigaku smart lab system (at 40 kV, 30 mA, and 2θ with a scan angle of 10–60°). Thermal and mechanical stability of the samples were performed on an EXSTAR S11 7300 (nitrogen atmosphere; 30–650 °C heating range). The surface images were obtained on a Zeiss Supra 55VP. The analyses of palladium, chloride, and silane ions on the catalyst were determined using an EDAX-Metek. Palladium ion content of the catalyst was performed by using Perkin Elmer Optima 2100 DV Inductively Coupled Plasma (ICP) Optical Emission Spectrometer (OES). Characterization of biaryl compounds were done on GC–MS Agilent GC-7890 A- MS 5975. Magnetic moment analysis of the catalyst was measured using Sherwood magnetic susceptibility balance. A domestic microwave oven was used in the catalytic performance tests.

2.3. Experimental studies

2.3.1. Silylation procedure of starch (ST-NH_2)

NH_2 functionalized starch was prepared by refluxing 1 g of starch and 3-aminopropyltriethoxysilane (4 mL) in a dry toluene (50 mL) at 100 °C for 48 h. Following this time, the NH_2 modified starch (ST-NH_2) was filtered and rinsed with hot ethanol. Then the product was dried at 70 °C.

2.3.2. Schiff base reaction of ST-NH_2 (ST-Sc)

0.5 g of ST-NH_2 and 1 g of 2,4-dihydroxybenzaldehyde were refluxed in ethanol (30 mL) for 72 h. The imine band formation was followed via FTIR analysis. After the Schiff base reaction, a yellow product was filtered out and washed with hot ethanol to remove any unreacted 2,4-dihydroxybenzaldehyde.

2.3.3. Synthesis of starch Schiff base supported catalyst

The design procedure for the catalyst is presented in Scheme 1. Briefly, the starch Schiff base supported catalyst was synthesized by stirring 0.3 g of ST-Sc and Na_2PdCl_4 (0.4 g) in water (25 mL) at room temperature overnight. Once the reaction was completed, the palladium catalyst was filtered and rinsed several times with water and dried at 50 °C.

2.3.4. General synthesis method of Suzuki cross coupling reaction

Typically, 1.12 mmol aril halide, 3.75 mmol potassium carbonate (K_2CO_3), 1.87 mmol phenyl boronic acid, and 4×10^{-3} mol% starch based palladium catalyst were added into a Schlenk tube and irradiated at 50 °C and 400 W for 5 min using a microwave without any organic solvent. After the reaction time, the mixture was extracted with toluene:water (2:1) three times and organic phase containing biaryl compounds was separated. Then, $MgSO_4$ was added into the organic phase to remove the water. Finally, biaryl compounds were obtained by evaporating the anhydrous organic phase, and the compounds were characterized with GC/MS analysis.

3. Results and discussion

3.1. Characterization studies

3.1.1. FT-IR spectra

The FT-IR spectra of the ST, ST-NH_2, ST-Sc, and palladium catalyst are presented in Fig. 1. In the spectrum of the ST, the characteristic peaks were observed at 3288 cm^{-1} (—OH stretching), 2926 cm^{-1} (—C—H stretching), 1635 cm^{-1} (O—H bending), 1456 cm^{-1} (CH_2 bending), and 763–1456 cm^{-1} (C—O stretching) (Fig. 1a) [24]. In the spectrum of ST-NH_2, the bands at 3277, 2925, and 1644 cm^{-1} can be attributed to —OH and —NH_2 vibration, stretching vibration of —C—H, and bending vibration of N—H in APTES, respectively (Fig. 1b) [25] These important changes showed that APTES was attached on the starch polymer chain [25]. In addition, a ninhydrin color test was done to confirm the NH_2-modification of the ST by stirring the ST-NH_2 with APTES in ethanol at 80 °C. The ninhydrin test is used to detect the primer amino groups on the polymer surface [26]. After the ninhydrin color test, the color of the ST-NH_2 turned to a dark purple, as seen in Fig. 2,