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Preparation, structural characterization, and catalytic performance of Pd(II) and Pt(II) complexes derived from cellulose Schiff base

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ABSTRACT

In this study, we reported production, characterization, and catalytic behavior of two novel heterogeneous palladium(II) and platinum(II) catalysts derived from cellulose biopolymer. In order to eliminate the use of toxic organic or inorganic solvents and to reduce the use of excess energy in the coupling reactions, we have developed a very simple, rapid, and eco-friendly microwave irradiation protocol. The developed microwave-assisted method of Suzuki cross coupling reactions produced excellent reaction yields in the presence of cellulose supported palladium and platinum (II) catalysts. Moreover, the catalysts easily regenerated after simple filtration, and they gave good reusability. This study revealed that the designed catalysts and method provide clean, simple, rapid, and impressive catalytic performance for Suzuki coupling reactions.

1. Introduction

Transition metal catalyzed cross coupling reactions (Suzuki, Negishi, Sonogashira and Heck etc) play an essential role in the production of significant and versatile biphenyl molecules, which are used in medicine, cosmetics, and synthesis of biologically active molecules, therefore these reactions have been extensively utilized in both academia and industry [1–4]. Suzuki reaction is one of the most important coupling reactions used for formation of carbon–carbon bond (Csp^2-Csp^2) which is obtained after the reaction of aryl halides with aril boronic acids [5]. Since the discovery of this reaction, researchers have developed various ligands such as phosphines [6], salen [7], and hydrazone [8] for Suzuki reactions. However, the coupling reaction suffers from two main drawbacks: (1) the requirement of high energy and (2) the usual use of toxic organic or inorganic solvents. To resolve these issues, researchers have turned to the use of non-conventional methods such as ultrasound irradiations, grinding, and photo-activated processes in catalytic reactions [9]. Among these methods, microwave irradiation technique (MW) is the most significant in terms of Green Chemistry approach. Especially solvent-free microwave-assisted organic reactions have recently been receiving increasing attention as they enable (i) high reaction yields with minimum by-products, (ii) use of less energy, and (iii) the reduction of toxic solvent wastes [10,11]. On the other, another important problem in catalytic reaction is that most of the used ligands are high-cost and sensitive to air and moisture oxidation. Therefore, there is a need for ligands which are thermally stable, low-cost, and unaffected by air and moisture because ligands play a critical role by immobilizing the active metal ion in Suzuki reactions.

Bio-polymers have superior properties as support materials for catalytic systems due to their biodegradable and eco-friendly nature, low cost, and insensitivity to air and moisture oxidation [12,13]. These properties provide (1) easy recovery of catalyst, (2) reuse of catalyst, and (3) easy separation of catalyst and product [11]. Because of these unique advantages, transition metal-supported biopolymer catalyst designs play a great role in catalytic systems. One of the most important polymers in nature is cellulose which has inexpensiveness, considerable thermal stability, high metal interaction capacity, high tolerance to most solvents, active surface, and easy functionalization [14]. These unique properties of cellulose show that it has a great potential for catalytic reactions as a support material.

In this study, we produced a highly active, thermally stable, resistant to air and moisture oxidation, and easily re-collectable, and environmentally-friendly palladium(II) and platinum(II) heterogeneous catalysts for Suzuki coupling reactions to remove

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aforementioned problems. Subsequently, catalytic activities of catalysts were investigated using a simple and efficient MW protocol which is solvent-free and includes low reaction time. Recyclability performances of green catalysts were studied as well. The obtained results show that palladium(II) and platinum(II) catalysts have superior catalytic properties such as high selectivity, easy work up, and multiple recovery and reuse.

2. Materials and methods

2.1. Materials

Cellulose (CL), 3-Aminopropyltriethoxysilane (APTES), ninhydrin, glyoxal solution (40% in H_2O), $PdCl_2$, $PtCl_2$, NaCl, K_2CO_3, NaOH, KOH, Cs_2CO_3, $MgSO_4$, phenyl boronic acid, aryl halides, toluene, and ethanol were purchased from Sigma-Aldrich.

2.2. Instrumentation

FT-IR spectra of produced samples were recorded on a Perkin Elmer Spectrum 100 F T-IR spectrophotometer. UV–vis spectrum was measured on Genesys 10 S UV-VIS Spectrophotometer. Thermal behaviors of products were explored with EXSTAR S11 7300 (nitrogen atmosphere; heating range: 30–650 °C). Powder X-Ray diffractograms were recorded on a Rigaku D max 2000 system (at 40 kV, 30 mA, and 2θ with a scan angle: 5–70°). SEM images of products were taken on a Zeiss Supra 55 V P. Palladium and platinum content of catalysts were determined by using Perkin Elmer Optima 2100 DV Inductively Coupled Plasma (ICP) Optical Emission Spectrometer (OES). GC/MS spectra were recorded on Agilent GC-7890 A- MS 5975. A domestic microwave oven was used in the catalytic activity tests.

2.3. Synthesis of support materials for Pd and Pt metal ions (CL-Gly)

2.0 g of CL and 5 mL of APTES were refluxed in toluene (50 mL) at 100° for 48 h, and amino functionalisation of cellulose was achieved (CL-NH_2). Then, Schiff base modification of cellulose was carried out by stirring CL-NH_2 (1 g) and glyoxal (6 mL) in ethanol (40 mL) at 70 °C for 72 h. Imine bond formation was followed by FT-IR. After the reaction was completed, the acquired yellow product (CL-Gly) was filtered and rinsed with hot ethanol and dried in an oven at 60 °C.

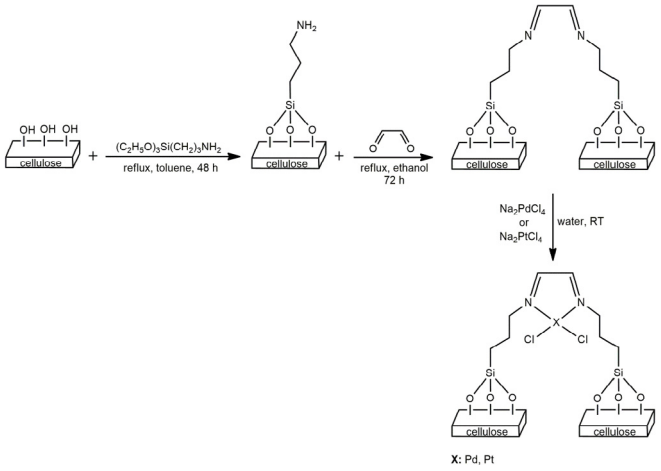
2.4. Fabrication of Pd (II) and Pt(II) catalysts (CL-Gly-Pd and CL-Gly-Pt)

Na_2PdCl_4 and Na_2PtCl_4, which are water soluble forms of $PdCl_2$ and $PtCl_2$, respectively, were prepared according to our previous study [15]: Briefly, $PdCl_2$ or $PtCl_2$ (5.63 mmol) and NaCl (11.28 mmol) was dissolved in water (100 mL), and the mixture was stirred at room temperature (RT) overnight. After the reaction completed, the water in the reaction medium was evaporated, and then the product was collected and dried.

0.5 g of CL-Gly was dispersed in water (25 mL). Then 0.6 g of Na_2PdCl_4 or Na_2PtCl_4 solution in water (15 mL) was dropped into the reaction mixture. The mixture was stirred at RT for 6 h. At the end of this period, brownish cellulose Schiff base supported Pd(II) and Pt(II) catalysts were filtered, washed with hot water, and dried at 50 °C. Scheme 1

2.5. General procedure for Suzuki reactions

Schlenk tube was charged with aryl halides (1.2 mmol), phenyl boronic acid (1.8 mmol), K_2CO_3 (2.00 mmol), and CL-Gly-Pd or CL-Gly-Pt catalysts (2×10^{-3} mol %), and the mixture was irradiated in a microwave oven at 50 °C, 400 W for 7 min. After cooling to RT, the reaction mixture was diluted with water and extracted with toluene. Then organic phase was dried on $MgSO_4$ and was sent for GC/MS analysis.



Scheme 1. Preparation of CL-Gly-Pd and CL-Gly-Pt catalysts.

3. Results and discussion

3.1. Characterization studies

Chemical characterizations of the fabricated products were performed using FT-IR, ninhydrin test, TG/DTG, powder XRD, SEM, and EDAX. FT-IR analysis is widely used in characterization studies because it enables the acquisition of easy and rapid information during various chemical modifications. Fig. 1 shows FT-IR spectra of CL, CL-NH_2, CL-Gly, CL-Gly-Pd, and CL-Gly-Pt. The following significant peaks were observed in FT-IR spectrum of CL: stretching of intra-molecular hydrogen bonding at 3337 cm^{-1}, symmetric CH_2 stretching band at 2895 cm^{-1}, stretching of C–O–C band at 1160 cm^{-1}; C–O bond stretching at 1108 cm^{-1} [16,17]. After the immobilization of NH_2 groups on cellulose, intra-molecular hydrogen bonding of cellulose decreased and shifted to lower wavenumber. However, Si–O–Si bands of CL-NH_2 could not be precisely exhibited due to the intensive C–O–C band of cellulose. So, we performed ninhydrin test to confirm NH_2 modification of CL. On the other hand, a new sharp vibration band appeared at 1646 cm^{-1}, which belongs to the imine band, following the condensation reaction of CL-NH_2 with glyoxal. This peak confirmed that Schiff base formation was successfully achieved [18]. This band shifted to lower wavelength in the spectrum of CL-Gly-Pd (1640 cm^{-1}) and CL-Gly-Pt (1638 cm^{-1}) catalysts because of the complexation through electron donation of the imine groups (Fig. 1) [15].

Ninhydrin test is performed to detect primary amines groups on the material surface, and it has been widely used for characterization studies [19]. The test depends on the formation of purple color which gives strong absorption at ~570 nm [20]. To confirm the presence of amino groups on cellulose after the treatment of APTES with CL, we carried out the ninhydrin test according to our previous study [21]. The test showed that the immobilization of primary amino group on cellulose surface was achieved (Fig. 2).

Fig. 3 displays TG/DTG curves of CL, CL-NH_2, CL-Gly, CL-Gly-Pd, and CL-Gly-Pt. TG/DTG curve of CL shows that it was durable up to 360 °C. Thermal durabilities of CL-NH_2 and CL-Gly were