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Highly efficient Suzuki cross-coupling reaction of biomaterial supported catalyst derived from glyoxal and chitosan

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ABSTRACT

In this study a new chitosan based water soluble Schiff base was produced through carboxymethylation of chitosan and its Pd(II) complex were synthesized and characterized by FTIR, ^{1}H NMR, ^{13}C CP-MAS NMR, TG/DTG, SEM/EDAX, XRD, ICP-OES, UV–Vis, magnetic moment measurements, molar conductivity measurements. The catalytic activity of the complex was tested in Suzuki coupling reactions for synthesis of biaryls containing various substrates. The identifications of the biarlys were performed by ^{1}H NMR and GC–MS. The catalytic activity tests revealed that high selectivity was achieved with a small addition of the catalyst. Moreover by-product formation was not observed in the spectra of ^{1}H NMR and GC–MS. Mercury poisoning and leaching test confirmed that the catalyst has heterogeneous character. The reusability tests showed that the catalyst did not lose its activity after six runs.

1. Introduction

Chitosan, a biodegradable, biocompatible, nontoxic and eco-friendly biopolymer, is a derivative of chitin produced by deacetylation treatment of chitin polymer [1–4]. Chitosan has many applications [4–6] but its non-solubility in water restricts its wider applications [7]. Therefore chitosan is subject to different modifications to make it soluble in aqueous media. Many water soluble carboxymethyl chitosan derivatives have been synthesized [8]. O-carboxymethyl chitosan (OCMCS) is one of the water soluble derivatives. Free amino groups of OCMCS allow doing modifications via pendant $-NH_2$ groups such as Schiff bases.

Due to their high selectivity, the ease of separation from the media and no by-product formation, heterogeneous palladium catalysts have been extensively used in Suzuki coupling reactions [9,10]. However the high cost of the ligands used in Suzuki coupling reactions a problem. So, various low-cost materials such as silica, zeolite, carbon, cellulose and chitosan have been used as alternative support materials [11–13]. Among them chitosan has been preferred because of its unique properties: it is low-cost (1), abundant (2), environmentally friendly (3), and renewable (4), also it has reactive $-NH_2$ and $-OH$ groups capable of undergoing different modifications (5) [14,15].

This study aimed to produce a new water soluble O-carboxymethyl chitosan Schiff base and its palladium complex and to test the catalytic activity of the complex in C–C coupling reactions. In the presence of this heterogeneous catalyst high conversion of different biaryls was achieved in Suzuki reactions. High reusability of the catalyst was observed in the tests. TG/DTG analysis revealed that the catalyst had high decomposition temperature, indicating its suitability for C–C coupling reactions.

2. Experimental

2.1. Material

All chemicals provided from Sigma–Aldrich.

2.2. Physical measurements

The FT-IR spectra of the products were investigated on a Perkin Elmer Spectrum 100 FTIR spectrophotometer. The ^{1}H NMR and spectrum of the compound was recorded on a Varian Mercury 400 MHz spectrometer using Acetone-d_6 solvents. The ^{13}C CP-MAS NMR spectrum of OCMCS-2a was measured using a Bruker Superconducting FT.NMR Spectrometer Advance TM 300 MHz WB. TG/

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DTG curves of all compound and metal complex were obtained with an EXSTAR S11 7300 at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. XRD spectra of the Pd(II) complex was observed with a Rigaku D max 2000 system at 40 kV, 30 mA and 2θ with a scan angle from 5° to 50°. GC/MS spectrums of biarlys were obtained Agilent GC-7890 A- MS 5975 Surface images were investigated using a QUANTA-FEG 250 ESEM. The EDAX spectra of the metal complex were obtained by an EDAX-Metek. The metal content of the complex was studied with a PerkinElmer Optima 2100 DV Inductively Coupled Plasma (ICP) Optical Emission Spectrometer (OES). UV–Vis spectra of the Pd(II) complex was obtained with a Genesys 10S UV-VIS spectrophotometer. A magnetic susceptibility of the catalyst was measured with a Sherwood magnetic susceptibility balance at 25 °C. The molar conductivities of the metal complexes were determined using a tabletop-digital conductivity-meter CD-2005 at 25 °C.

2.3. The synthesis of (E)-4-(2-oxoethylideneamino) benzoic acid

4-Amino benzoic acid (1.0 g, 7.29 mmol) and glyoxal (0.83 mL 7.29 mmol) were mixed in methanol under reflux for 72 h. Reaction was monitored by TLC and FTIR spectroscopy. Then the mixture was poured into ice-water, the yellow precipitate was removed from the media. The yellow product (2a) was rinsed with methanol, ethanol and diethyl ether sequentially (Yield: % 75). FTIR (ATR, cm^{-1}): 1599 υ(C=N), 1569, 1516 υ(C=C), 1421 υ(C–N). (DMSO-d_6), ^{13}C NMR (DMSO-d_6), δ (ppm): 191.1 C(1), 167.7 (C2), 143.3 (C3), 113.7 C(4), 131.5 C(5), 121.2 C(6), 171.3 C(7).

2.4. Synthesis of [OCMCS-2a]

0.5 g chitosan was dissolved in 2% acetic acid solution (25 mL; v:v). Then, methanol was added into the chitosan solution and the mixture was stirred for 1 h. Subsequently, 2a in methanol was added into the mixture. This reaction media was refluxed for 7 h (CS-2a). Following the reflux, 2.5 g of monochloroacetic acid in 10 mL of methanol was added into the reaction media and was stirred at 60 °C for 7 days. Finally the brown precipitate formed in the reaction media was filtered out and rinsed with hot methanol for removed of unreacted 2a compound (Yield: 75%).

2.5. Synthesis of Pd(II) complexes

0.2 g of OCMSC-2a was dissolved in 10 mL of water. Then aqueous solution of 0.35 g Na_2PdCl_4 was added into the solution and stirred at 50 °C for 5 h. The yellowish-green precipitate was separated from the media by filtration. The filtrate was washed with water and dried in an oven at 50 °C (Yield: 72%) (Scheme 1).

2.6. Determination of the optimum conditions

The efficiency of Suzuki coupling reaction is highly dependent on the catalyst amount, reaction temperature, reaction time and base system. The optimum condition were tested and determined by using a model coupling reaction of 4-bromoanisole with phenyl boronic acid.

2.7. The amount of catalyst

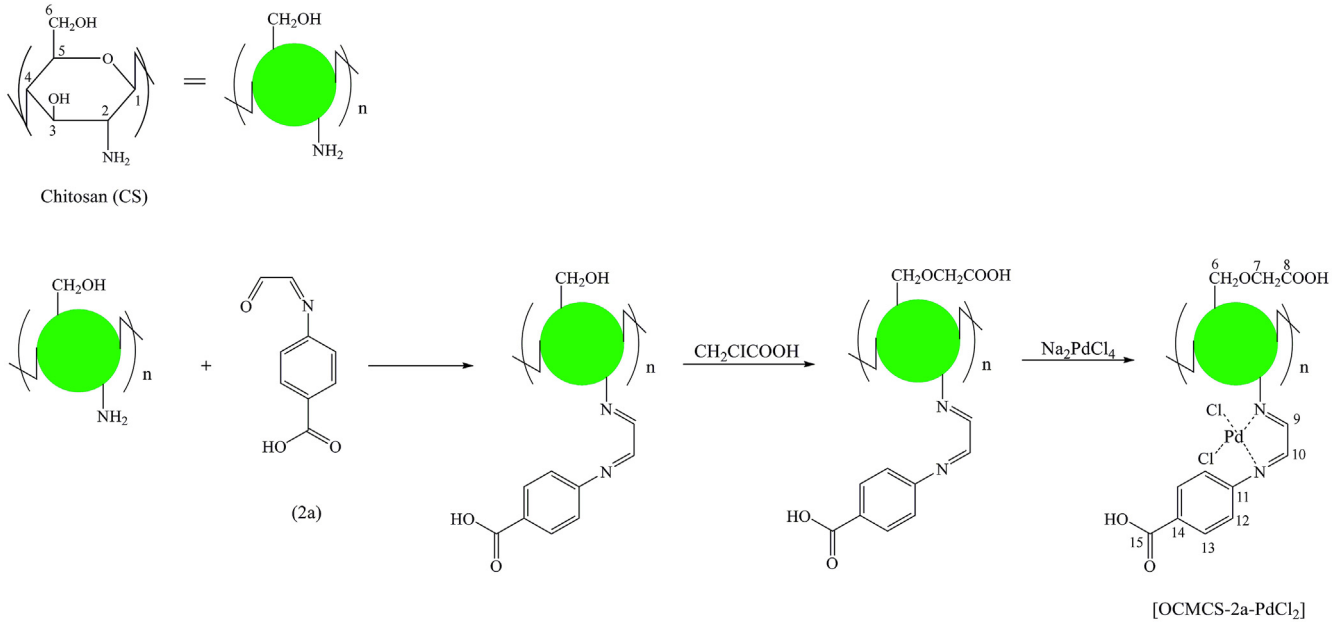
The amount of the catalyst is an important parameter governing the efficiency of Suzuki coupling reactions. Preliminary experiments were conducted with different amount of catalyst to determine optimum amount of the catalyst. These experiments revealed that the optimum amount of [OCMCS-2a-$PdCl_2$] was 0.02 mol % (Fig. 1).

2.8. Reaction temperature

Preliminary studies demonstrated that the optimum reaction temperature was 100 °C (Fig. 2).

2.9. Reaction time

Experiments were conducted in different reactions time. The highest conversion was achieved after 12 h (Fig. 3).



Scheme 1. The synthesis of O-carboxymethyl chitosan Schiff bases and its Pd(II) complex.