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Microwave assisted synthesis of biarlys by C–C coupling reactions with a new chitosan supported Pd(II) catalyst

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ABSTRACT

In this study a new type chitosan-based support has been produced for Pd(II) catalyst and its catalytic performance in Suzuki C–C reactions has been studied under microwave irradiation without using any solvent. The chemical identification of the catalyst was performed using TG/DTG, FTIR, UV–Vis ICP-OES, SEM/EDAX, ^{13}C NMR, molar conductivity, XRD and magnetic moment techniques. The performance of this new Pd(II) catalyst was studied in Suzuki C–C reactions. The Pd(II) catalyst exhibited a good catalytic performance in very short time (4 min) by giving high TONs and TOFs with low amount of the catalyst (0.015 mol%). The catalyst also had reusability and did not lose its activity until six runs.

1. Introduction

Chitosan is one of the abundant biopolymer in nature and it has excellent properties such as non-toxicity, biodegradability, renewability, and biocompatibility [1,2]. Mechanical strength, chemical stability can be improved by producing its derivatives can through free amino and hydroxyl groups [3,4]. Chitosan modifications, such as carboxymethyl, Schiff base, phosphorylation, and sulfation, result in its enhanced solubility and functionality [5–7]. Especially, reaction of $-NH_2$ groups present on chitosan with reactive ketones or aldehydes gives Schiff base and this modification has been used in many applications in the literature due to its chemical and biological properties [8,9].

Palladium catalysts play a vital role in Suzuki C–C coupling reactions of biaryl compounds [10]. Different homogenous or heterogeneous palladium catalyst systems were developed for coupling reactions in the past decades [11,12]. Particularly, the microwave irradiation system has been extensively used in C–C coupling reactions due to its easier workup, short reaction time, and higher reaction yield [13]. There is a great demand for new biopolymer (cellulose, chitosan, zeolite, and silica) supported heterogeneous catalysts in C–C coupling reactions due to their having high metal adsorpsiyon capacity, cheapness, and being renewable natural polymers [14].

This study reports prepare of a new biopolymer supported Pd(II) catalyst. The chemical structure of the Pd(II) catalyst was illuminated using TG/DTG, ^{13}C NMR, XRD, FTIR, SEM-EDAX, magnetic susceptibility, UV–Vis and conductivity measurements. In addition, the performance of the catalyst was explored in cross-coupling reactions by using microwave heating. The results of the catalytic tests revealed that the catalyst possessed high catalytic activity. In addition, the Pd(II) catalyst yielded higher TON, TOF and reaction yields in synthesis of biaryl compounds by using a fast and clean technique.

2. Experimental

2.1. Instrumentation

FT-IR spectra of chitosan, SL, CCSL and the catalyst were performed on a Perkin Elmer Spectrum 100 FTIR spectrophotometer. Thermal stability of the products was studied on an EXSTAR S11 7300 (nitrogen atmosphere; heating range: 30–650 °C). The surface morphology of the products was examined on a QUANTA-FEG 250 ESEM. The analyses of palladium and chloride ions on the catalyst were done using an EDAX-Metek. X-ray diffractions chitosan, CSSL and Pd(II) catalyst were recorded on a Rigaku D max 2000 system (at 40 kV, 30 mA and 2θ with a scan angle:5–50°). Palladium ion content of the catalyst was analyzed by using Perkin Elmer Optima 2100 DV Inductively Coupled Plasma (ICP) Optical

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Emission Spectrometer (OES). Synthesis of biaryl compounds was conducted using a domestic microwave oven. Identification of the biaryls was done by using GC-MS Agilent GC-7890 A- MS 5975. The ^{13}C NMR spectrum of CSSL was measured by an Agilent 600 MHz spectrometer using D_2O solvent. The magnetic moment of the palladium complex was determined with a Sherwood magnetic susceptibility balance at 25 °C. Electronic spectrum was performed with a Genesys 10S UV–VIS spectrophotometer. The molar conductivity of the catalyst was studied by a digital conductivity-meter (CD-2005) at 25 °C.

2.2. Synthesis of Schiff base (SL)

0.5 g (3.64 mmol) of 3-aminobenzenoic acid was dissolved in 25 mL water. After addition of 0.41 mL glyoxal (3.64 mmol), the reaction media was stirred for 96 h at 75 °C. Then, the reaction mixture was poured out into cold water and compound (SL) was precipitated (Yield: 80%). FTIR (ATR, cm^{-1}): 1688 υ(C=O), 1601 υ(C=N), 1579, 1488 υ(C=C), 1418 υ(C–N). ^{13}C NMR (DMSO-d_6). δ(ppm): 193.15, 168.12, 134.93, 118.84, 129.31, 116.70, 131.72, 113.13, 174.14.

2.3. Synthesis of carboxymethyl Schiff base (CSSL)

Chitosan solution was prepared by dissolving about 0.3 g of chitosan in 25 mL acetic acid (2% v:v). Methanol solution of SL (20 mL) was mixed with the chitosan solution and stirred under reflux for 8 h. Following the addition of 10 mL of methanol solution of monochloroacetic acid (2.5 g), the reaction vessel was stirred for six days at 60 °C. Finally, the CSSL (brown-colored) was recovered by filtration.

2.4. Synthesis of Pd(II) catalyst

CSSL solution in methanol (0.2 g in 20 mL of methanol) was mixed with methanol solution of Na_2PdCl_4 (0.25 g) and agitated at 70 °C for 5 h on a magnetic and stirrer. Then, the Pd(II) catalyst was collected and rinsed with ethanol and water (Scheme 1).

2.5. General procedure of Suzuki coupling reactions

Pd(II) catalyst (0.015% mol), phenyl boronic acid (1.87 mmol), different aryl halides (1.12 mmol) and potassium carbonate (3.75 mmol) were added into a Schlenk tube and microwave irradiated at 50 °C for 4 min at 400 W in a solvent free medium. After cooling to room temperature, reaction medium was extracted with toluene-water mixture (2:1). The organic phase was recovered in a separatory funnel and $MgSO_4$ was added to remove the water content. Dried biarlys compounds were characterized with ^1H NMR and GC/MS.

3. Results and discussion

3.1. FTIR analysis

The infrared spectra of chitosan, CSSL, and Pd(II) catalyst are given in Fig. 1. After the condensation reaction of chitosan with compound SL, the spectrum of CSSL had a new band at 1637 cm^{-1},

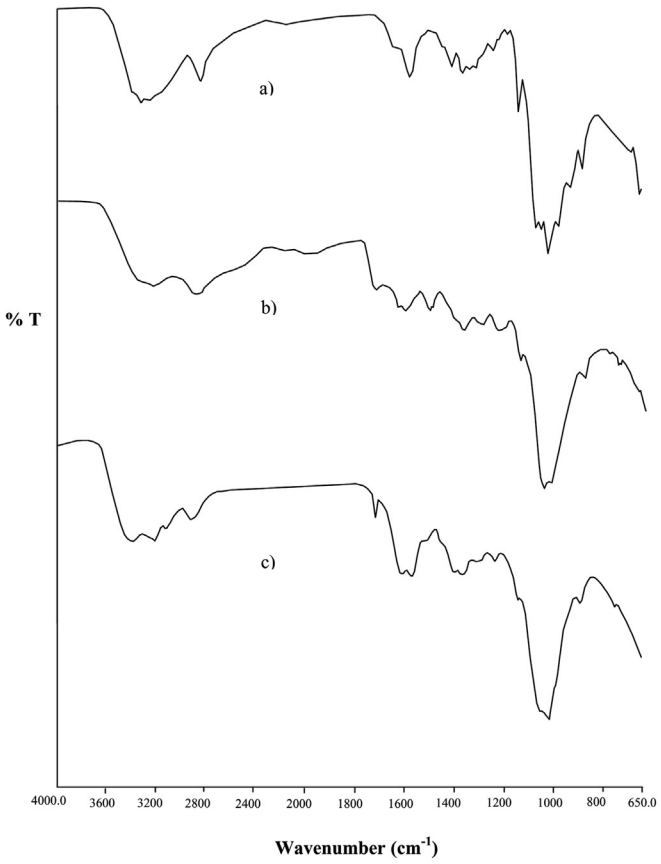
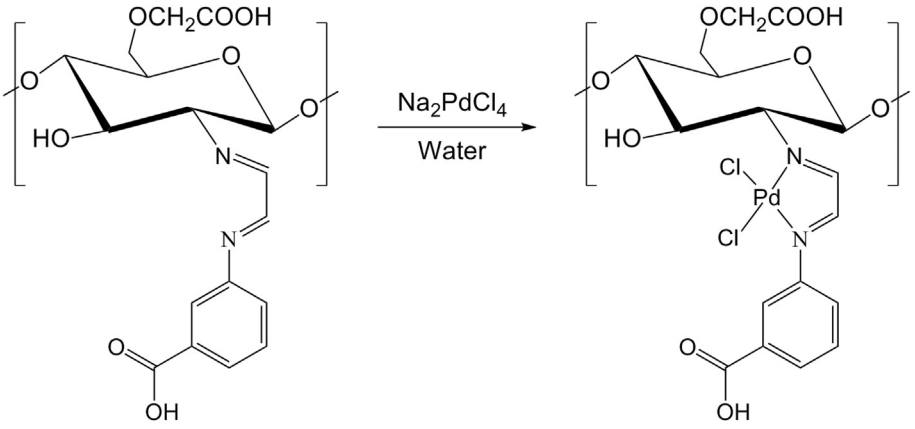


Fig. 1. FTIR spectra of a) chitosan, b) CSSL, c) Pd(II) catalyst.



Scheme 1. Synthesis pathway for Pd(II) catalyst.