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An environmental catalyst derived from biological waste materials for green synthesis of biaryls via Suzuki coupling reactions

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ABSTRACT

Synthesis of bio-macromolecular supported catalysts has gained much recent attention due to their greener nature. Among the biopolymers, chitosan is widely used as a support material due to its high affinity for metal ions. In this study, chitosan-*Ulva* sp. (green alga) composite microbeads were prepared as a support material for palladium catalyst. *Ulva* sp. particles were incorporated into chitosan matrix to enhance the interaction with palladium ions. The catalytic performance of chitosan-*Ulva* supported Pd(II) catalyst was investigated in the synthesis of biaryls via the Suzuki coupling reaction. All the experiments were conducted without using any solvent under the microwave irradiation, which is also considered as a green technique. This green catalyst exhibited high selectivity and efficiency in the reactions of phenyl boronic acid with different aryl halides in only 4 min at low temperature (50 °C). Excellent TON and TOF values were achieved for the catalyst; 4950 and 75000. In addition, the catalyst did not lose its activity even after 8 cycles. It showed high thermal stability (216.8 °C) and durability in presence of oxygen. This green catalyst has a potential to be used in pharmacology, medicine and cosmetics.

1. Introduction

Biaryl compounds have been utilized in various areas such as pharmacology, medicine, cosmetics due to their unique biological properties [1,2]. Synthesis of biaryl compounds has gained much recent attention and the palladium-catalyzed Suzuki coupling reaction has been efficiently used as a general method in the production of biaryls [2–4]. However, the Suzuki coupling reaction has serious disadvantages; (1) high reaction temperatures and long reaction times, (2) non-environmental nature because of the use of toxic organic solvents (3) labour-intensive nature and (4) high operational costs [5]. To overcome these problems, microwave irradiation technique has emerged as an efficient method in the last decade [6]. This technique does not require harsh conditions and enables high product yields in very short reaction times. The most striking aspect of this technique is the elimination of organic solvents by making it a more green-friendly method in the synthesis of biaryl compounds. Due to their cleaner, biodegradable and renewable properties, biopolymers have been widely used as catalyst support material in Suzuki coupling reactions [7,8].

Chitosan is widely considered as an eco-friendly biopolymer due to its biodegradable, non-toxic and renewable nature. It is cheaply and abundantly produced by deacetylation of chitinous waste of seafood industry processing shrimp, krill, crab and crayfish [9]. This versatile biopolymer can be easily functionalised via pendant reactive hydroxyl and amine groups on its backbone. Additionally, these groups facilitate the binding of metal ions and therefore chitosan is acknowledged as a supramolecular bio-ligand for the Suzuki coupling reaction. To further enhance its metal binding capacity; (1) chitosan is generally cross-linked with agents like glyoxal, glutaraldehyde and epichlorohydrin and also (2) chitosan composites are produced by incorporation of bio-based materials (e.g., cellulose, oil palm ash, cotton and alginate) exhibiting affinity for metal ions [10].

Ulva sp. is a ubiquitous fast growing macroalga [11]. Due to functional moieties (e.g., thiol, hydroxyl, carboxyl, amino and imidazole groups) on the cell surface, biomass from *Ulva* sp. has been applied in uptake of metal ions [12]. Especially, a recent study demonstrated that it has high affinity for platinum group elements (i.e., rhodium, palladium and platinum) [13].

Palladium ions can coordinate with imine groups of glutaraldehyde cross-linked chitosan Schiff base. In coordination of palladium ions with imine groups nitrogen atoms can function as donor atoms. As mentioned, chitosan-*Ulva* sp. composite can bind palladium ions efficiently and therefore they can exhibit desired catalytic activity

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in C-C coupling reactions. This study aimed (1) to synthesize a new green palladium catalyst for the Suzuki coupling reaction, (2) to characterise the chitosan-*Ulva* supported Pd(II) catalyst via analytical tools (e.g., FT-IR, TGA, SEM-EDAX, XRD and ICP-OES), (3) to investigate the performance of the catalyst in synthesis of biaryls under mild conditions by microwave irradiation technique without using any solvents and (4) to determine the reusability of the synthesized green catalyst.

2. Experimental

2.1. Materials

Medium molecular weight Chitosan (448877-250G, deacetylation: 75–85%), glutaraldehyde (40%), CH_3COOH, Na_2PdCl_4, $PdCl_2$, phenyl boronic acid, aryl halides, NaOH, KOH, K_2CO_3, $MgSO_4$, toluene and methanol were purchased from Sigma-Aldrich and used as supplied. In experiments double distilled water was used.

2.2. Preparation of the catalyst support

In preparation of chitosan-*Ulva* beads, commercial medium molecular weight chitosan (Sigma–Aldrich 448877-250G) was used. *Ulva* biomass was collected in the banks of Uluırmak River (Aksaray, Turkey, August 2015). After extensively washing with water, *Ulva* samples were allowed to dry at room temperature. Dried *Ulva* samples were ground and sieved with a 100 μ sieve and then treated in NaOCl (2%) solution for 10 min at 40 °C.

Ulva powder (0.5 g) was added into 75 mL of chitosan solution (2% w:w, dissolved in 2% acetic acid solution) and stirred for 3 h. Chitosan-*Ulva* mixture was then dropped into alkaline water-methanol coagulation solution (water:methanol:NaOH; 100 mL:150 mL: 30 g) [14]. The beads were incubated in the coagulation solution for 16 h. Subsequently, the beads were removed by filtration and washed with water. In the cross-linking procedure, the beads were transferred into crosslinking solution (45 mL methanol and 0.4 mL of glutaraldehyde solution of 25%) and heated under reflux in a fume hood to arrest any glutaraldehyde vapour. Finally, glutaraldehyde cross-linked beads were rinsed with water and dried at room temperature.

2.3. Synthesis of chitosan-Ulva supported Pd(II) catalyst

Chitosan-*Ulva* composite bead (0.2 g) and Na_2PdCl_4 (0.35 g) were added into 20 mL of water and stirred for 6 h at room temperature. Then, yellow-brownish beads were recovered by filtration and washed with water to remove any uncomplexed ions. Finally, the chitosan-*Ulva* supported Pd(II) catalyst was oven-dried at 50 °C.

2.4. Instrumentation

FT-IR spectra of chitosan-*Ulva* composite bead and chitosan-*Ulva* supported Pd(II) catalyst were recorded on a Perkin Elmer Spectrum 100 FTIR spectrophotometer. Thermal stability of the beads was investigated on an EXSTAR S11 7300 under nitrogen atmosphere in a range of 30–650 °C. Examination of the surface morphology of the beads was carried out on QUANTA-FEG 250 ESEM. The presence of Pd ions on the catalyst was detected using EDAX-Metek. The XRD patterns of the beads were obtained on a Rigaku D max 2000 system at 40 kV, 30 mA and 2θ with a scan angle from 5° to 50° using $Cuk_{\alpha 1}$ radiation (λ = 1.54059 Å). Palladium ion content of the catalyst was determined by using PerkinElmer Optima 2100 DV Inductively Coupled Plasma (ICP) Optical Emission Spectrometer (OES).

Table 1
Optimization of base for Suzuki reaction.

Base	Reaction yield (%)
NaOH	33
KOH	67
K_2CO_3	99

Reaction conditions: 1.12 mmol 4-bromoanisole, 1.87 mmol phenyl boronic acid, 3.75 mmol base, 0.02 mol% chitosan-*Ulva* supported Pd(II) catalyst, 50 °C, 4 min under microwave irradiation.

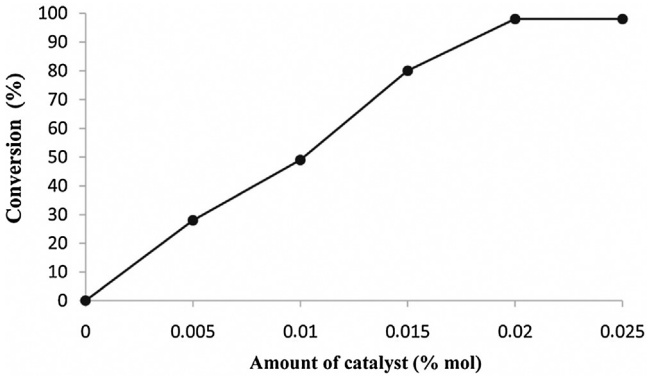

Fig. 1. The effect of catalyst loading on Suzuki coupling reaction.

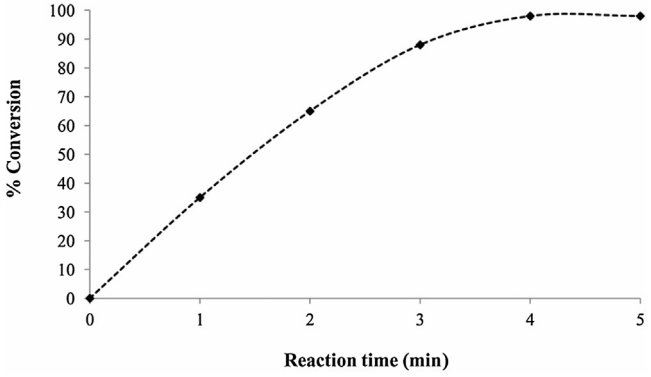

Fig. 2. The effect of reaction time on Suzuki coupling reaction.

3. Results and discussions

3.1. Catalytic performance of chitosan-Ulva supported Pd(II) catalyst

3.1.1. Determination of optimum conditions

To determine the optimum experimental parameters, the C-C coupling reaction of 4-bromoanisole with phenyl boronic acid was carried out on a model reaction. All the parameters i.e., base system (K_2CO_3, NaOH and KOH), catalyst amount (0.005–0.025% mol), and reaction time (1–5 min) were studied under microwave irradiation.

In C-C coupling reactions, base system plays a key role during the transmetallation. Therefore, as presented in Table 1 three different base systems were tested and K_2CO_3 gave the highest yield.

Achieving high product yield with minimum amount of catalyst is desired for catalyst systems. Fig. 1 displays the relationship between the amount of the catalyst and the rate of product conversion.

The test experiments with the model reaction demonstrated that optimum reaction time was 4 min (Fig. 2).