

## Article

# In Situ Decorated Palladium Nanoparticles on Chitosan Beads as a Catalyst for Coupling Reactions

Khaoula Oudghiri <sup>1</sup>, Lahoucine Bahsis <sup>2,\*</sup> , Said Eddarir <sup>1</sup>, Hafid Anane <sup>2</sup>  and Moha Taourirte <sup>1</sup>

<sup>1</sup> Laboratoire de Recherche en Développement Durable et Santé, Faculté des Sciences et Techniques de Marrakech, Université Cadi Ayyad, Marrakech 40000, Morocco; khaoulaoudghiri08@gmail.com (K.O.); eddarir@fstg-marrakech.ac.ma (S.E.); m.taourirte@uca.ma (M.T.)

<sup>2</sup> Laboratoire de Chimie Analytique et Moléculaire, LCAM, Faculté Polydisciplinaire de Safi, Université Cadi Ayyad, Safi 46030, Morocco; ananehafid@gmail.com

\* Correspondence: bahsis.lahoucine@gmail.com

**Abstract:** A green protocol for the in situ synthesis of Pd nanoparticles on chitosan beads (Pd NPs-CS) is reported without the need to use any toxic reducing agents. The preparation of the Pd nanoparticles catalyst was performed using a simple coordination reaction between the prepared chitosan beads and palladium ions (Pd NPs-CS). The obtained catalyst was characterized by different techniques, including SEM, EDX, DRX, and FTIR analyses. The Pd NPs-CS catalyst was investigated in the *Suzuki–Miyaura* cross-coupling reaction and *Heck* reaction under greener conditions, and the results show high catalytic activity and selectivity. The bead form of the Pd NPs-CS catalyst was easily separated from the reaction mixture to obtain the desired products, as confirmed by spectroscopic methods. This sustainable catalyst has the advantages of having sustainable organic reactions such as biopolymer support and recovery without significant loss of catalytic activity or selectivity.

**Keywords:** chitosan; *Suzuki–Miyaura*; *Heck* reaction; sustainable catalysis; coupling reaction



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## 1. Introduction

In view of the growing concerns about the effects on the environment, considerable efforts have been made to develop new processes that minimize pollution during chemical synthesis. For this and other reasons (catalyst disposal, recovery, and recycling), heterogeneous catalysis is clearly on the rise, including in industry [1]. Recent developments for cleaner and sustainable chemistry are driven by the shift from petrochemical-based feedstocks to biological materials [2,3]. There is considerable interest in exploiting the natural macrostructures of polymers, and in particular, those of polysaccharides, to create efficient and environmentally friendly catalysts [4]. Indeed, polysaccharides have many advantages that could stimulate their use as polymeric supports for catalysis [5]. Interestingly, although there has been a worldwide awareness that naturally derived polysaccharides can provide raw materials for the production of many industrial consumer goods, their use as catalyst carriers is still in its infancy [6,7]. Chitosan is a particularly attractive polysaccharide for catalytic applications due to the presence of easily functionalized amino groups and its insolubility in organic solvents [8–10]. The applications of chitosan are varied, and the new studies to develop it do not cease multiplying thanks to its physicochemical and biological properties [11]. It is, among other things, non-fermentable, biocompatible, biodegradable, and non-toxic [12,13]. Moreover, its manufacturing costs are low. It is therefore of great interest in pharmaceuticals, the food industry, and cosmetics because of its viscoelastic properties [14,15], which can vary significantly even for small quantities of polymer. It can therefore be used as a texture modifier and stabilizer, etc. [16–19]. Homogeneous catalysts are reported by high catalytic activity and selectivity but are limited by their separation from the reaction mixture, leading to a significant waste of catalyst and the contamination

of the desired product. For these reasons, non-homogeneous catalysts can be the best solution to these catalytic limitations [20,21].

Recently, coupling reactions through the aromatic carbon–carbon bond have been reported as an excellent methodology that conducts the preparation of important pharmaceutical compounds [22,23]. The *Heck* and *Suzuki–Miyaura* reactions are fascinating couplings reactions that can be catalyzed using palladium ions or nanoparticle forms using simpler reactions, and catalyst designs which are active for many reactive substrates are required [24].

The purpose of this work is to elaborate heterogeneous catalysts based on biopolymers, more precisely chitosans, thanks to their structure and due to the presence of primary amine functions, their various sources, and their potential and current applications. In this work, we report the elaboration of a new catalyst using palladium supported by chitosan beads (Pd NPs-CS). The catalytic activity and the reusability of this catalyst in *Suzuki–Miyaura* couplings and *Heck* reactions were investigated under greener reaction conditions.

## 2. Materials and Methods

### 2.1. Materials

All reagents used in this study were obtained from Sigma-Aldrich, Merck, and Fluka and the chitosan polymer was obtained from Thermo Scientific (Mw = 100,000–300,000 g/mol).

### 2.2. Preparation of Chitosan Hydrogel Beads (CS)

Chitosan beads are prepared by solubilizing 3 g of chitosan powder in 100 mL of an acetic acid solution (2%) and allowing the solution to stand for 24 h until the solution is completely homogenized. The mixture is then added dropwise into a NaOH solution (500 mL; 0.5 M) under slow stirring. The beads are left to settle in the solution overnight. The prepared chitosan beads are then filtered and washed several times with distilled water until the pH of the obtained filtrate is neutral (pH  $\approx$  7). Finally, the CS beads are stored in cold distilled water.

### 2.3. Palladium-Supported Chitosan Beads (Pd NPs-CS)

Chitosan beads (144 mg), palladium (II) acetate Pd(OAc)<sub>2</sub> (35 mg), and 10 mL of water (H<sub>2</sub>O) are introduced and stirred into a flask under nitrogen atmosphere (N<sub>2</sub>). The reaction mixture is left at 60 °C for 4 h. The color of the nanoparticles changes from white to black. Finally, the PdNPs-CS beads are recovered after simple filtration.

### 2.4. Characterization

FTIR analysis was carried out using the Bruker VERTEX 70 instrument to reveal the surface functional groups of the prepared materials. SEM using the TESCAN-VEGA3 SEM with an accelerating voltage of 20 kV analyzed surface morphology. In addition, an energy dispersive X-ray (EDAX) was performed to establish the elemental composition of the material surface. NMR analyses were performed using Bruker Corporation's AV II 300 MHz spectrometer, located in Billerica, MA, USA.

### 2.5. General Experimental Procedure for the Catalyzed Suzuki–Miyaura Cross-Coupling Reaction

Additionally, 1-iodo-2,6-dimethylphenyl acetate (0.65 mmol) and phenylboronic acid (0.78 mmol), base K<sub>2</sub>CO<sub>3</sub> (1.95 mmol), and 2 mol% of Pd NPs-CS beads were placed in a reaction tube, and 8 mL water/ethanol (1:1) was added. The reaction tube was placed on a magnetic stirring plate at 40 °C and under a nitrogen atmosphere (N<sub>2</sub>). After completion, as determined by TLC, the obtained product is extracted with dichloromethane (5 mL). The organic phase was evaporated under vacuum, and the obtained product was purified by silica column chromatography (Eluent: hexane/ethyl acetate (97/3)). All obtained products are characterised by NMR analyses, see Supplementary Materials Figures S1–S6. Remarkably, the catalyst demonstrated its durability by being reused at least three times.

To ensure its optimal performance, the recovered catalyst was thoroughly dried before subsequent use.

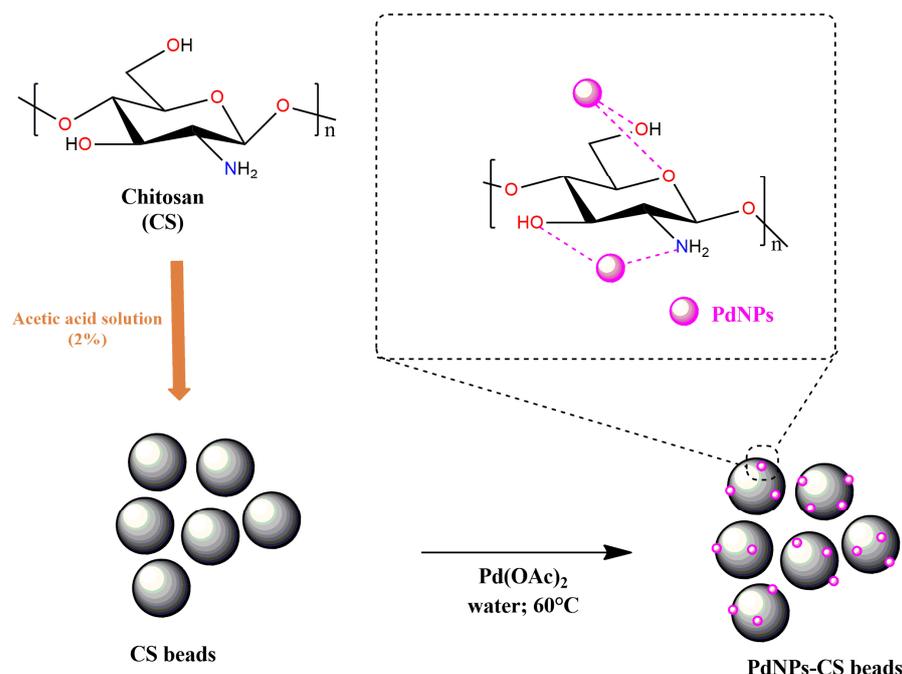
### 2.6. General Experimental Procedure for the Catalyzed Heck Coupling Reaction

In a flask purged with nitrogen ( $N_2$ ), the following components were added: 4-Iodoanisole (0.65 mmol), Styrene (0.78 mmol); 3 mL of  $Et_3N$ , and 3 mol% of Pd NPs-CS beads dissolved in 2 mL of a water/ethanol mixture (1:1). The reaction mixture was heated under reflux at 60 °C for 7 h. After the completion of the reaction, the organic phase containing the product was extracted using 5 mL of dichloromethane. Subsequently, the organic phase was evaporated under vacuum, and the resulting product was purified through silica column chromatography using a hexane/ethyl acetate eluent ratio of 80:20. All obtained products are characterised by NMR analyses, see Supplementary Materials Figures S7–S9. It is noteworthy that the catalyst displayed impressive durability, being successfully reused for a minimum of five cycles. To ensure its optimal performance, the recovered catalyst was meticulously dried before subsequent utilization.

## 3. Results and Discussion

### 3.1. Synthesis and Characterizations of Pd NPs-CS Catalyst

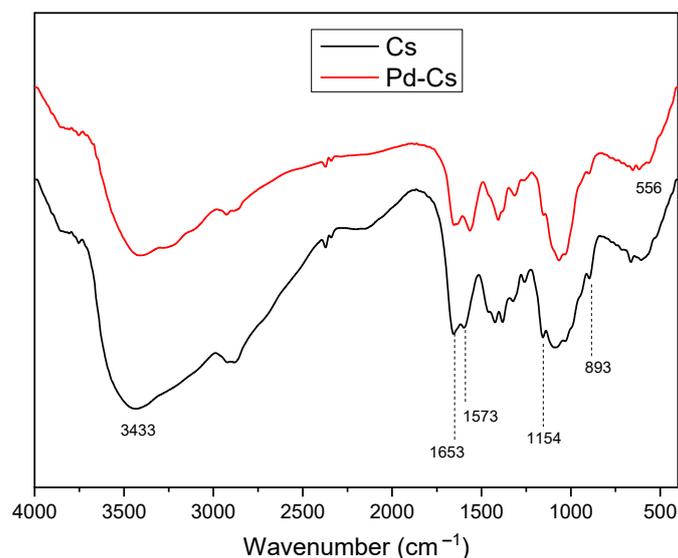
This work aims to synthesize palladium-based catalysts supported by chitosan beads and their application in the coupling of organic reactions. The chitosan powder was used to form the chitosan beads (CS). This biopolymer was formed by the  $\beta$ -(1  $\rightarrow$  4)-linked *d*-glucosamine (deacetylated unit) and the *N*-acetyl-*d*-glucosamine (acetylated unit), confirming the presence of important functional groups such as hydroxy, acetylamino and amino groups) which conducts the easy complexation of metal cations and makes this biopolymer an attractive support for heterogeneous catalysts [25–27]. Interestingly, the coordination reaction between the chitosan beads and the palladium (II) ion conducts the formation of palladium nanoparticles (Pd NPs-CS) using water as a solvent at 60 °C. The characterization and structural features of the obtained heterogeneous catalyst were performed by different techniques such as FTIR, SEM, EDX, and DRX analysis (Scheme 1).



**Scheme 1.** Synthesis of Pd NPs-CS catalyst.

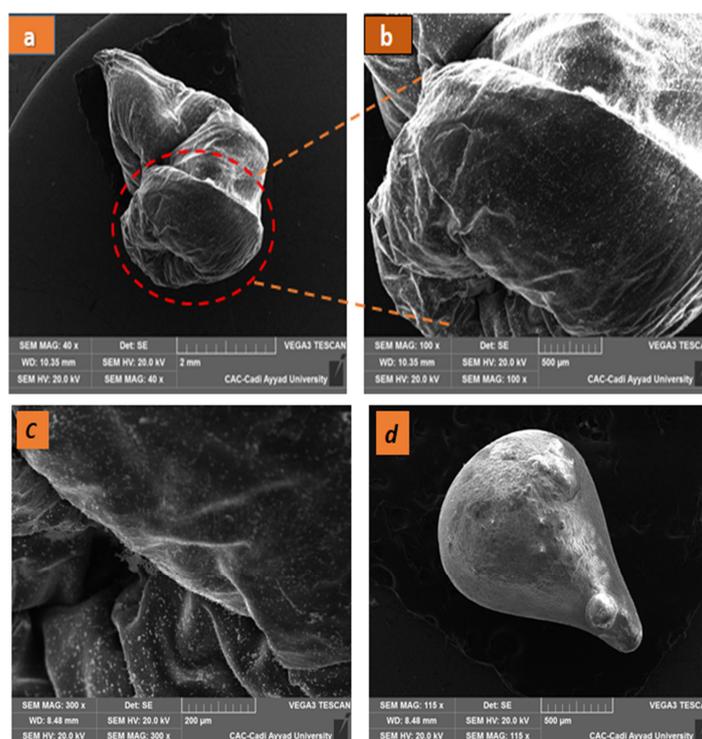
FTIR analysis of chitosan revealed several characteristic peaks. At  $3433\text{ cm}^{-1}$ , a large peak was observed, corresponding to the N–H stretch band of the chitosan (see Figure 1). The

peak at  $1653\text{ cm}^{-1}$  is attributed to the bending vibration of the  $\text{NH}_2$  group. The presence of the  $\text{NH}_3^+$  group is indicated by a band at  $1573\text{ cm}^{-1}$ . The transmission peak at  $1413\text{ cm}^{-1}$  can be attributed to C–H flexion modes and  $1363\text{ cm}^{-1}$  to C–N stretching modes.  $\text{NH}_2$  torsion vibration produced a peak at  $1051\text{ cm}^{-1}$ , and C–O–C stretching vibration was observed at  $1154\text{ cm}^{-1}$ . The peak at  $893\text{ cm}^{-1}$  represents the off-plane C–H vibration. The presence of a palladium load in chitosan was indicated by peaks at  $556\text{ cm}^{-1}$  and  $507\text{ cm}^{-1}$  (Figure 1).



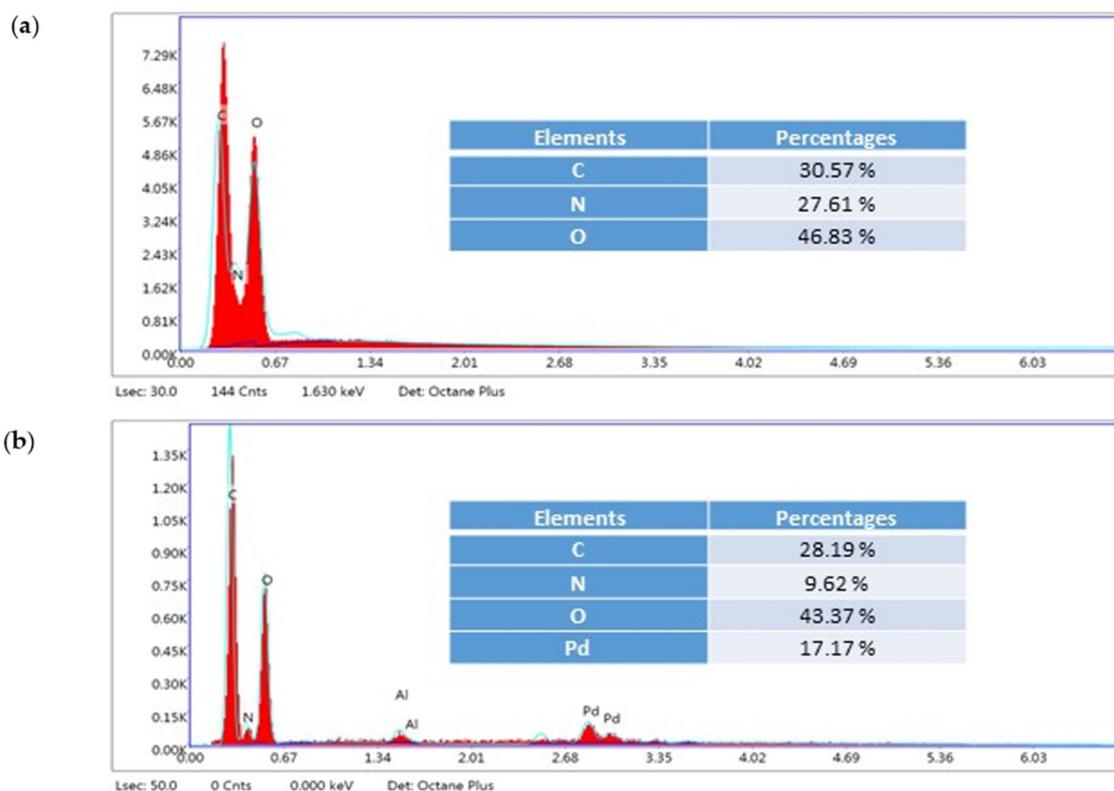
**Figure 1.** FTIR analysis of chitosan (CS) and Pd NPs-CS.

The surface appearance of chitosan and palladium catalysts supported on chitosan powder was examined by SEM analysis (Figure 2). The analyses show that chitosan beads have a smooth folded surface (Figure 2a), while palladium-supported chitosan beads (Pd NPs-CS) have a heterogeneous smooth surface, roughened with agglomerates (Figure 2b).



**Figure 2.** SEM image of chitosan beads (a,b) and Pd NPs-CS beads (c,d).

By conducting energy dispersive X-ray spectroscopy (EDX) analysis, we were able to determine the elemental composition of the surface of the chitosan beads before and after the immobilization of palladium nanoparticles, the results are presented in Figure 3. It can be seen that the chitosan used contains major elements such as 27.61% of nitrogen and 46.83% of oxygen atoms (Figure 3a), which led to the immobilization of an important quantity (17.17%) of palladium atoms compared to Pd NPs-CS catalyst (Figure 3b).



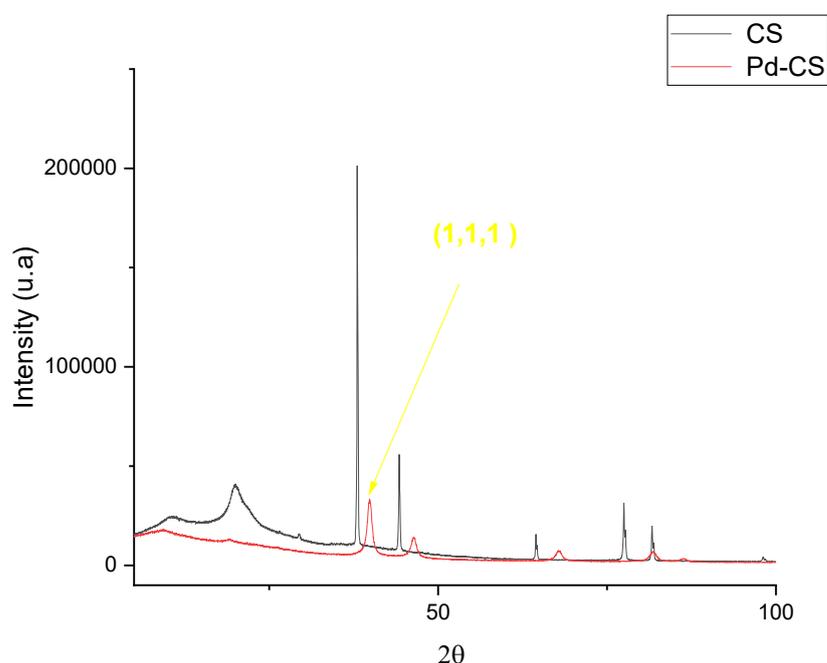
**Figure 3.** EDX analyses of (a) chitosan and (b) Pd NPs-CS.

Figure 4 illustrates the XRD patterns of both chitosan and Pd NP-CS beads. The XRD analysis confirms the presence of peaks corresponding to chitosan nanostructures. Specifically, the peaks observed at  $\sim 10.32^\circ$  and  $20.8^\circ$  suggest the semi-crystalline nature of chitosan (Figure 4). Additionally, the peak at  $40.4^\circ$  is indexed to the (111) reflection of the face-centered cubic structure of the Pd surface observed in the Pd NPs-CS catalyst. The results depicted in Figure 4 confirm the successful immobilization of palladium nanoparticles on the surface of the chitosan beads (Figure 4). Notably, a reduction in peak intensity is observed after the complexation with Pd nanoparticles, indicating a decrease in crystallinity. These decreases in crystallinity and several peaks can be attributed to the deformation of the hydrogen bonds of chitosan following the chemical modifications.

### 3.2. Suzuki–Miyaura Coupling Reaction

The catalytic investigations of the prepared Pd NPs-CS beads were performed in the Suzuki–Miyaura coupling reaction. The coupling reaction between 4-nitro iodobenzene (**1a**) and 3-nitrophenyl boronic acid (**2a**) to prepare 3,4-dinitro-biphenyl (**3a**) was chosen as a model catalytic reaction. The first step of this investigation is the optimization of the Suzuki–Miyaura coupling reaction catalyzed by Pd NPs-CS beads using various reaction conditions, including the quantity of catalyst, solvent effects, reaction time and temperature, and the user base. The obtained results are presented in Table 1. The controlled experiments confirm that the desired product (**3a**) cannot be obtained in the absence of the palladium atoms (entries 1–3). The results show the significant influence of the catalyst type on

*Suzuki–Miyaura* coupling reactions. Comparing the heterogeneous catalysis of Pd NPs-CS beads with the homogeneous catalysis using PdCl<sub>2</sub> with PPh<sub>3</sub> as a ligand for palladium atoms, it was found that Pd NPs-CS beads gave better results in terms of reactivity and yields. In addition, higher yields were obtained when both bases, 1 eq of K<sub>2</sub>CO<sub>3</sub> and 2 eq of KF, were used, whereas lower yields were obtained when only KF or K<sub>2</sub>CO<sub>3</sub> was used. These results confirm that the presence of K<sub>2</sub>CO<sub>3</sub> increases the reaction rate but favors the formation of by-products. Conversely, when KF was used, we noted the absence of by-products, although the reaction rate was slower. Moreover, increasing the reaction temperature to 110 °C has no significant effect on the yield and the reaction time of this coupling reaction (Table 1, Entry 9). Based on the findings, it was determined that the most favorable conditions for the reaction involved 4-nitro iodobenzene (**1a**) and 3-nitrophenyl boronic acid (**2a**), and 2 mol% of prepared catalyst using a solvent mixture consisting of 8 mL water and ethanol in a 1:1 ratio, at a temperature of 40 °C (Scheme 2).

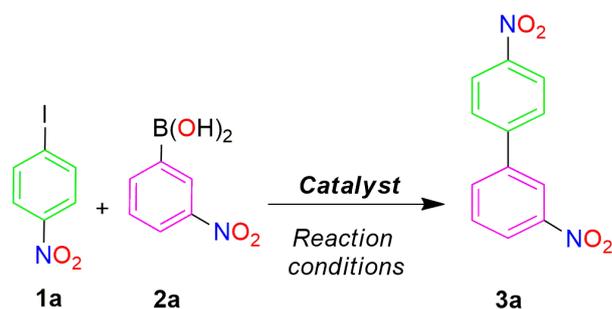


**Figure 4.** XRD analyses of chitosan powder (CS) and Pd NPs-CS beads.

**Table 1.** Optimization of the *Suzuki–Miyaura* coupling reaction catalyzed by Pd NPs-CS beads <sup>a</sup>.

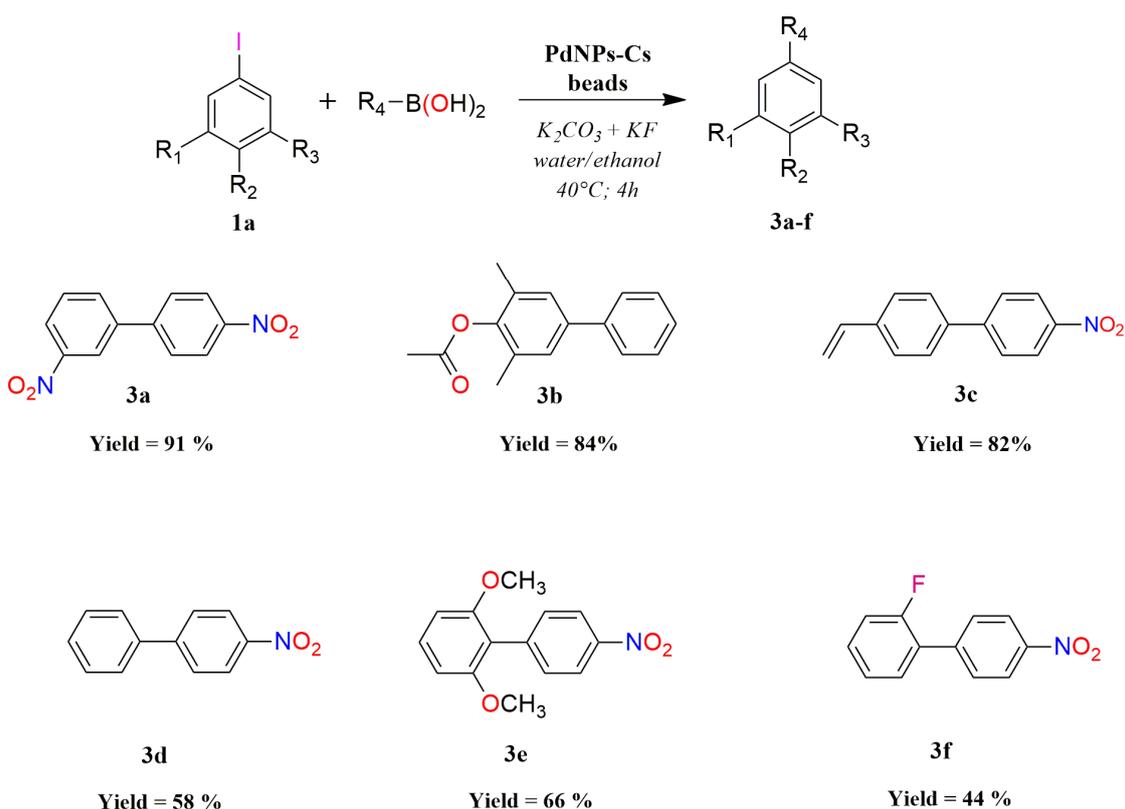
Entry	Catalyst	Base	Time (h)	Yield <sup>b</sup> (%)
1	Neat	K <sub>2</sub> CO <sub>3</sub> (1 eq) + KF (2 eq)	4	0
2	Chitosan	K <sub>2</sub> CO <sub>3</sub> (1 eq) + KF (2 eq)	4	0
3	Cs beads	K <sub>2</sub> CO <sub>3</sub> (1 eq) + KF (2 eq)	4	0
4	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub> (3 eq)	4	28
5	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	KF (3 eq)	6	26
6	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub> (1 eq) + KF (2 eq)	4	34
7	Pd NPs-CS	KF (3 eq)	6	66
8	Pd NPs-CS	K <sub>2</sub> CO <sub>3</sub> (1 eq) + KF (2 eq)	4	82
9	Pd NPs-CS	K <sub>2</sub> CO <sub>3</sub> (1 eq) + KF (2 eq)	4	91

<sup>a</sup> Reaction conditions: 4-nitro-iodobenzene (1 eq); 3-nitrophenylboronic acid (1.2 eq); base; Solvent: 8 mL water/ethanol (1:1), T = 40 °C. <sup>b</sup> Isolated yields.



**Scheme 2.** The *Suzuki–Miyaura* coupling reaction catalyzed by Pd NPs-CS beads.

Once the optimal reaction condition for the *Suzuki–Miyaura* coupling reaction was established, our focus shifted to investigating the catalytic effect of the Pd NPs-CS beads with a range of boronic acids of various structures. The results of these experiments are summarized below, in Figure 5. In all cases, the substrates with the substituents (either electron-rich, electron-withdrawing, or heterocycles) led to the expected products with good to high yields. The substitution in the ortho position has an important effect on the yield of the corresponding products which can be explained by the steric effect between these substitutions and the iodide atom in 4-iodonitrobenzene (**1a**). Moreover, all corresponding products were obtained with high purity and did not require any further purification via conventional methods.

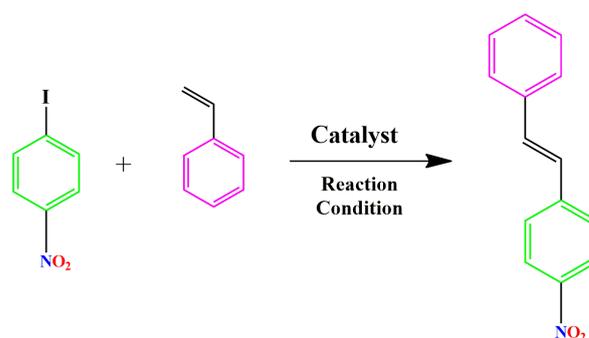


**Figure 5.** Pd NPs-CS catalyzed *Suzuki–Miyaura* coupling reactions of halobenzenes and aryl boronic acids.

### 3.3. Catalytic Heck Reaction

The catalytic properties of the synthesized Pd NPs-CS beads were examined in the context of the *Heck* coupling reaction. The coupling reaction between 4-iodoanisole (**1a**) and styrene (**4**) to prepare 1-Methoxy-2,5-bis-styrylbenzene (**5**) was chosen as a model catalytic reaction (Scheme 3). The first step of this investigation is the optimization of the *Heck* reaction catalyzed by Pd NPs-CS beads using various reaction conditions, including the

quantity of catalyst, solvent effects, and reaction time. The obtained results are presented in Table 2. The controlled experiments confirm that the desired product **3a** is not obtained in the absence of the palladium atoms (entries 1–3). The results show the significant influence of the catalyst type on *Heck* reactions. Comparing the heterogeneous catalysis of Pd NPs-CS beads with the homogeneous catalysis using PdCl<sub>2</sub> with PPh<sub>3</sub> as a ligand for palladium atoms, it was found that Pd NPs-CS beads gave better results in terms of reactivity and yields. Additionally, employing triethanolamine as the exclusive solvent resulted in lower yields. By incorporating two solvents, namely water and ethanol, a significant enhancement was achieved, leading to a notable increase in the reaction yield up to 82%. The investigation concluded that the optimal reaction conditions included the utilization of 4-iodoanisole (**1a**) and styrene (**2a**) as the substrates, along with a catalyst loading of 3 mol%. These conditions were further enhanced by employing a solvent mixture comprising 2 mL of water and ethanol in a ratio of 1:1. The reaction was conducted at a temperature of 60 °C.



**Scheme 3.** The *Heck* reaction catalyzed by Pd NPs-CS beads.

**Table 2.** Optimization of the *Heck* reaction catalyzed by Pd NPs-CS beads <sup>a</sup>.

Entry	Catalyst	Solvent	Yield <sup>b</sup> (%)
1	Neat	Ethanol/Water	0
2	Chitosan (CS)	Ethanol/Water	0
3	CS beads	Ethanol/Water	0
4	Pd NPs-CS	Ethanol/Water	82
5	Pd NPs-CS	Et <sub>3</sub> N	27

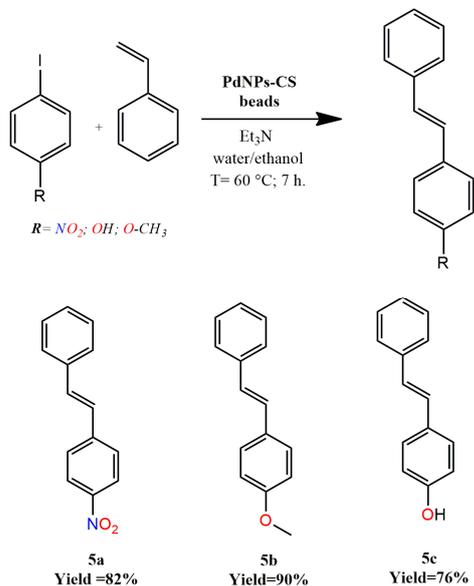
<sup>a</sup> Reaction conditions: 4-iodoanisole (1 eq); styrene (2 eq); Et<sub>3</sub>N; solvent: 2 mL water/ethanol (1:1) T = 60 °C for 7 h. <sup>b</sup> Isolated yields.

With the obtained optimal reaction condition for the *Heck* reaction, our focus was shifted to investigating the catalytic effect of the prepared Pd NPs-CS beads with a range of halobenzenes and styrene, and the results are summarized in Figure 6. In all cases, the coupling reaction between vinyl halides and olefins was reported with an excellent yield, confirming its high applicability in the prepared catalyst for *Heck* reaction under mild reaction conditions.

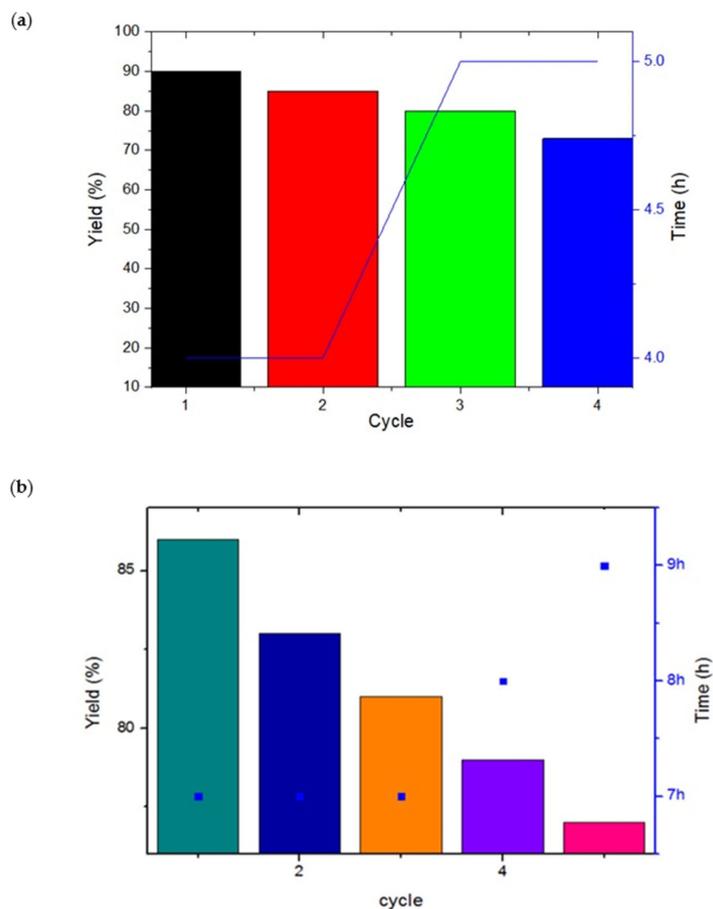
### 3.4. Reusability of Pd NPs-CS Catalyst

To evaluate the reusability of Pd NPs-CS beads in the coupling of organic reactions [28], a model reaction involving 4-nitro iodobenzene (**1a**) and phenylboronic acid (**2a**) was selected using a solvent mixture of ethanol and water at room temperature (Figure 7a). The results show that the prepared catalyst offers an excellent yield (70%), even after four cycles. In particular, the catalytic activity and selectivity of this catalyst did not decrease significantly. To assess the potential reusability of Pd NPs-CS beads for facilitating the construction of a carbon–carbon bond through the *Heck* reaction, a specific model reaction was chosen involving 4-iodoanisole (**1a**) and styrene (**4**). The reaction took place at 60 °C, employing a solvent mixture of ethanol and water (as depicted in Figure 7b). The findings indicate that the catalyst produced displayed remarkable efficacy, yielding a

high percentage (78%) of the desired product, even after undergoing five cycles. Notably, the catalytic performance and selectivity of this catalyst exhibited no significant decline throughout the multiple cycles.

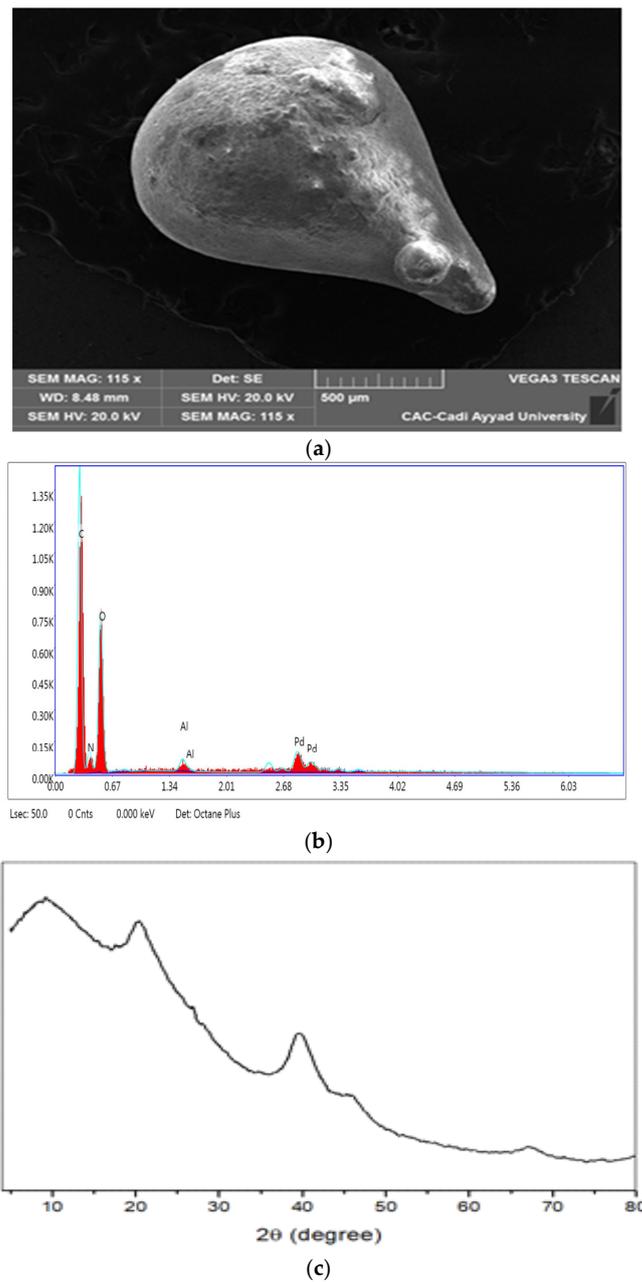


**Figure 6.** Pd NPs-CS catalyzed Heck coupling reactions of halobenzenes and styrene.

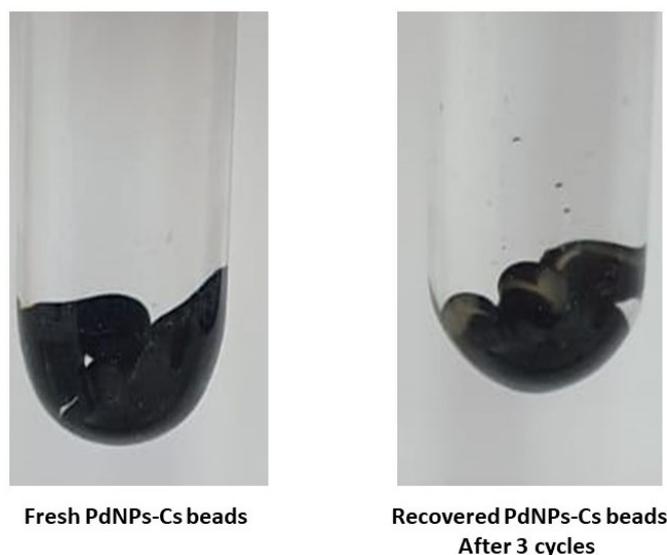


**Figure 7.** Recycling of the Pd NPs-CS catalyst for (a) Suzuki–Miyaura and (b) Heck reactions.

The recovered Pd NPs-CS beads were subjected to analysis and characterization using SEM, EDX, and XRD spectroscopies, as depicted in Figure 8. SEM analysis revealed a smooth and non-porous surface for the recovered material. EDX analysis indicated that the atomic percentage remained nearly unchanged before and after the catalyst, suggesting the stability of the catalyst composition. XRD analysis confirmed the presence of a peak at  $40.4^\circ$ , verifying the presence of palladium nanoparticles on the surface of the retrieved chitosan beads. Furthermore, the stability of the prepared catalyst was observed, explaining the slight decrease in catalytic activity after three cycles (Figure 9). This stability, combined with high catalytic activity, biodegradability, and ease of separation and recycling, positions palladium-based catalysts supported by chitosan as an environmentally benign alternative.



**Figure 8.** (a) SEM, (b) EDX, and (c) XRD for recovered Pd NPs-CS catalyst.



**Figure 9.** Pictures of the fresh Pd NPs-CS beads and the recovered Pd NPs-CS beads.

### 3.5. Comparison of the Catalytic Activity of Pd NPs-CS Beads

To evaluate the efficiency of the Pd NPs-CS beads we have prepared against other reported protocols using chitosan as a biological support for the coupling reactions, an in-depth study was carried out (see Table 3). Comparative analysis reveals that the PdNPs-CS catalyst shows some similarities to the reported catalytic protocol using a combination of pectine, chitosan, and kaolinite as support for palladium nanoparticles in terms of reactivity and reaction time. Similar trends in terms of longer reaction times and reactivity were also observed when comparing our results with those obtained with the Pd@PPh<sub>3</sub>-CS and Pd NPs@CS/Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-NH<sub>2</sub> catalysts. Both catalysts, Fe<sub>3</sub>O<sub>4</sub>@CS@MS@Pd and Pd@CS/ZIF-8@COF, require an extended reaction time and a high reaction temperature (~80 °C). In the case of Pd@chitosan/starch and Pd@chitosan/cellulose, the catalytic *Suzuki–Miyaura* coupling reaction was carried out in a solvent-free environment using microwave irradiation. A similar result is found in the case of the *Heck* coupling reaction. The prepared catalyst shows excellent catalytic activity in mild reaction conditions compared to other reported catalytic systems, see Table 3. Notably, our catalytic systems stand out as they enable coupling reactions without the need for elevated reaction temperatures to initiate the reaction. Additionally, the catalyst can be easily separated from the reaction mixture through simple filtration. These attributes validate the efficacy of Pd NPs-CS beads as an excellent catalyst for *Suzuki–Miyaura* and *Heck* coupling reaction derivatives.

**Table 3.** Comparative results of catalytic efficiency for coupling reactions.

	Catalyst	Conditions	Time (h)	Yields (%)	Ref.
Suzuki–Miyaura coupling reaction	Pd@chitosan/starch	Microwave irradiation (400 W); Neat; 50 °C	0.1	35–99	[29]
	Pd@CS-SB @Fe <sub>3</sub> O <sub>4</sub>	PEG-200:H <sub>2</sub> O (1:1); 50 °C	0.5	72–99	[30]
	Pd@CS-Pectine@Kaolin	H <sub>2</sub> O/EtOH (1:1); 40 °C	0.1–3	50–98	[31]
	Pd@chitosan/cellulose	Microwave irradiation; Neat; 50 °C	0.08	55–100	[32]
	Pd NPs@CS/Fe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> -NH <sub>2</sub>	H <sub>2</sub> O/EtOH (1:1); 40 °C	0.25–12	50–98	[33]
	Fe <sub>3</sub> O <sub>4</sub> @CS@MS@Pd	H <sub>2</sub> O/EtOH(4:1); 80 °C	8	25–98	[34]
	Pd@PPh <sub>3</sub> -CS	H <sub>2</sub> O/EtOH(3:1); 50 °C	4	83–99	[35]
	Pd@CS/ZIF-8@COF	H <sub>2</sub> O/EtOH (1:1); 80 °C	4	39–99	[36]
	PdNPs-CS beads	H <sub>2</sub> O/EtOH (1:1); 40 °C	4	44–91	This work

Table 3. Cont.

	Catalyst	Conditions	Time (h)	Yields (%)	Ref.
Heck coupling reaction	Pd@MMT/CS	DMSO/ethylene glycol (30:2); 110 °C	4	47–96	[37]
	Pd@CS-SB @Fe <sub>3</sub> O <sub>4</sub>	PEG-200:H <sub>2</sub> O (1:1); 110 °C	0.67	62–98	[25]
	Pd/MAAC	DMF (3 mL)/glycol (0.2 g); 110 °C	3–12	67–99	[26]
	Pd@CPS	DMAc (3.0 g); 110 °C	24	0–90	[28]
	PdNPs-CS beads	Et <sub>3</sub> N; H <sub>2</sub> O/EtOH (1:1); 70 °C	7	76–90	This work

CS = Chitosan; SB = Schiff Base; MS = Methyl Salicylate; COF = Covalent organic frameworks; ZIF-8 = Zeolitic Imidazolate Framework-8.

#### 4. Conclusions

In summary, we present an environmentally friendly approach for the in situ synthesis of Pd nanoparticles on chitosan beads, eliminating the need for toxic reducing agents. The prepared catalyst underwent comprehensive characterization using FTIR, SEM, EDX, and XRD spectroscopies. Remarkably, Pd NPs-CS beads show remarkable catalytic activity for the *Suzuki–Miyaura* coupling and *Heck* reactions under mild conditions. It is noteworthy that this catalyst is composed of a biocompatible and biodegradable material, which effectively stabilizes the palladium nanoparticles and enhances their catalytic performance. Moreover, the utilization of chitosan biopolymer instead of hazardous chemicals during the synthesis process further contributes to the environmentally friendly nature of this support material. Overall, Pd NPs-CS beads have important catalytic potential in various organic coupling responses.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/coatings13081367/s1>, NMR analysis of prepared compound 3a–3f; NMR analysis of prepared compound 5a–5c.

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