

Pd Nanoparticles Entrapped in Chitosan Superfine Fibers as a Highly Active and Stable Catalyst for the Mizoroki-Heck Reaction

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Pd/chitosan/polyacrylate sodium composite fibers (Pd@CS/PAA) with average diameter of (152 ± 30) nm were prepared by electrospinning. The composite fibers were subsequently cross-linked at $160\text{ }^{\circ}\text{C}$ to improve their solvent stability. TEM results showed that entrapment of palladium species into the composite fibers could increase its dispersion. The composite fibers were found to be very active and stable to catalyze the Mizoroki-Heck reaction of iodobenzene with *n*-butyl acrylate. Therefore, a highly active and stable heterogeneous palladium catalyst can be prepared by entrapping the palladium nanoparticles in CS/PAA composite fibers.

1. Introduction

Palladium catalyzed reactions have played an important role in the chemical industry and academic research for the preparation of fine chemicals and pharmaceutically active compounds [1,2]. Homogeneous palladium catalysts are attractive for their high catalytic activity and selectivity, but also suffer problems of separation and recovery of the expensive palladium metal and ligands, which not only increases the cost, but also contaminates the products [3,4]. Immobilization of homogeneous palladium catalyst on/in solid matrices is a suitable method to solve these problems. The heterogeneous palladium catalyst can be easily recovered and reused, which decreases production costs and minimizes waste generation, resulting in a green and sustainable chemical transformation process [5,6].

For most heterogeneous palladium catalysts, palladium species were anchored on the surface of solid matrices through physical adsorption and chemical complexation, such as Pd/C [7]. However, as the interaction between the solid matrices with palladium species would be greatly decreased after the reduction of Pd^{2+} into Pd^0 and the harsh conditions in catalysis would also reduce this interaction, aggregation and leaching of palladium species usually occurs during catalysis, resulting in a decrement of catalytic activity and contamination of the product [8–10]. In order to solve these problems, another type of heterogeneous palladium catalyst has been developed by entrapping the palladium species in a solid matrix [11, 12]. Besides the physical interaction and chemical complexation of solid matrices, the entrapment is another important factor to prevent aggregation and leaching of palladium species. However, it is very important to fabricate the solid matrices into suitable external and internal structures to allow the easy migration of substrates and products in the solid matrices, which increases the contact probability of palladium species with substrates. Nanofibers, prepared by electrospinning, are ideal materials to support palladium species because of their small diameter and large specific area [13, 14]. Moreover, the fiber structure could also facilitate the recovery and reuse of the catalyst.

In this article, well-defined palladium entrapped in chitosan nanofibers was prepared by electrospinning a mixture of PdCl_2 /chitosan/sodium polyacrylate in trifluoroacetic acid/acetic acid aqueous solution, followed by cross-linking at high temperature ($160\text{ }^{\circ}\text{C}$). This novel fiber catalyst exhibited

high catalytic activity and stability towards the Mizoroki-Heck reaction.

2. Experimental

2.1 Materials

Chitosan ($M_n = 2.0 \times 10^5$, pharmaceutical grade, deacetylated degree: 95 %) was bought from Zhejiang Aoxing Biotechnology Co. Ltd (Zhejiang, China). Iodobenzene, *n*-butyl acrylate and sodium polyacrylate (analytic grade) were bought from Aladdin Industrial Co. Ltd (Shanghai, China). PdCl₂ (chemical grade) was bought from Hangzhou Changqing Chemical Industrial Co. Ltd (Zhejiang, China). Deionized water was used in all experiments.

2.2 Preparation of chitosan nanofiber supported palladium catalyst

1.8 g of chitosan and 0.20 g of sodium polyacrylate were dissolved in 40 g of solvent (4.0 g of trifluoroacetic acid, 8 g of H₂O, 28 g of acetic acid). 100 mg of PdCl₂ and 100 mg of NaCl were dissolved in 17 g of H₂O to prepare Na₂[PdCl₄] aqueous solution. After preparation, the Na₂[PdCl₄] aqueous solution was dropped into the chitosan solution slowly and stirred magnetically to achieve a homogeneous solution. The electrospinning was carried out on electrospinning equipment (FM1206, Beijing Future Material Sci-tech Co., Ltd, China). The electrospinning parameters were as follows: needle gauge: 21 G; feed rate: 1.2 mL h⁻¹; applied voltage: 25 kV; work distance: 15 cm. After electrospinning, the nanofiber mat was cross-linked at 160 °C for 2 h and named as Pd@CS/PAA.

For comparison, CS/PAA nanofibers were also prepared by the same method but without the addition of PdCl₂. Palladium was then immobilized on the surface of the CS/PAA nanofibers by the same method as our previous report [15]. This catalyst was named as Pd-CS/PAA.

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) characterization showed that the palladium contents of the Pd@CS/PAA and Pd-CS/PAA were 2.91 % and 2.86 %, respectively.

2.3 Catalysis procedure for the Mizoroki-Heck reaction

0.7 mmol of iodobenzene, 1.4 mmol of *n*-butyl acrylate, 2.0 mmol of triethylamine (Et₃N), 10 mg of catalyst (Pd content: 2.8 μmol) and 3.0 g of *N,N*-dimethylacetamide (DMAc) were added to a 25 mL tubular reactor equipped with a magnetic stir bar. The mixture was allowed to stir at 110 °C and the reaction progress was monitored by GC/MS. After completion, the reaction mixture was cooled down to room temperature, and quenched with 10 mL of water and extracted three times with ethyl acetate (3 × 20 mL). The combined organic layer was washed with water, saturated brine, and then dried over anhydrous Na₂SO₄. Solvent was removed under a reduced pressure. The residue was purified by silica gel chromatography with a mixture of petroleum ether and ethyl acetate (*v/v*=8 : 1) to afford the cross-product [(*E*)-butyl cinnamate]. The ¹H NMR and MS data of (*E*)-butyl cinnamate were listed as follows: ¹H NMR(400 Hz, CDCl₃, TMS): δ = 7.60 (d, ¹H, *J* = 16.0 Hz), 7.44 (d, ¹H, *J* = 3.6 Hz), 7.42 (d, ¹H, *J* = 2.0 Hz), 7.28 (dd, ³H, *J* = 6.4 Hz and 4.0 Hz), 6.35 (d, ¹H, *J* = 16.0 Hz), 4.12 (dd, ²H, *J* = 13.2 Hz and 6.4 Hz), 1.64–1.57 (m, ²H), 1.35 (dd, ²H, *J* = 15.2 Hz and 7.6 Hz), 0.88 (d, ³H, *J* = 14.8 Hz); MS *m/z* (%) 131 (99.9), 148 (71.5), 147 (59.2), 103 (13.3), 149 (11.7). The fiber catalyst was separated by filtration and then used in the next run directly to examine its stability.

2.4 Characterization

The morphology of Pd@CS/PAA was characterized by a scanning electron microscope (SEM) (JEOL, JSM-6360LV, Japan). Quantitative analysis of the Mizoroki-Heck reaction products was determined by GC/MS (Agilent, GC6890/5975 MSD, USA). Dispersions of palladium nanoparticles in Pd@CS/PAA and Pd@CS/PAA were analyzed by high-resolution transmission electron microscopy (HR-TEM) (JEOL, JEM-2100F, Japan). ¹H NMR spectra were recorded in CDCl₃ (Bruker, AVANCE

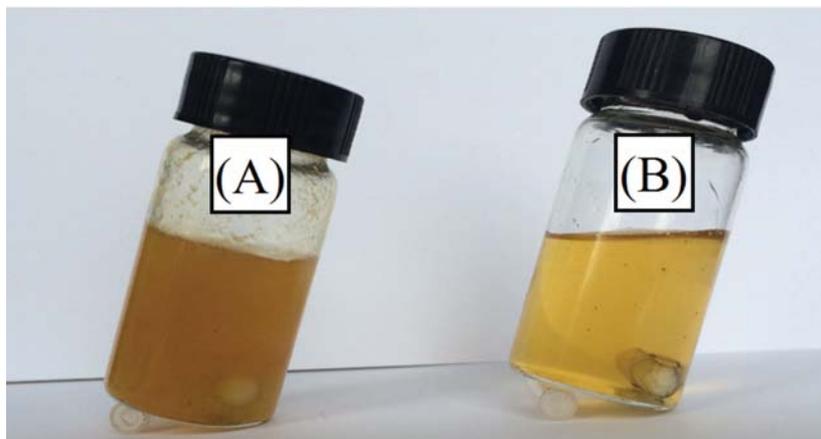


Fig. 1 The $\text{Na}_2[\text{PdCl}_4]$ /chitosan/sodium polyacrylate mixture in acetic acid aqueous solution (A) before and (B) after addition of trifluoroacetic acid.

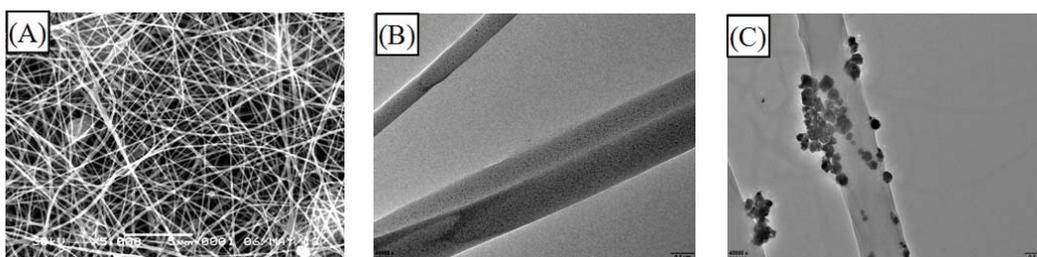


Fig. 2 (A, B) SEM and HR-TEM images of Pd@CS/PAA; (C) HR-TEM image of Pd-CS/PAA.

III 400 MHz, Switzerland) and the proton chemical shifts are reported in ppm relative to TMS as the internal reference.

2.5 Results and discussion

Acetic acid aqueous solution is the most widely used solvent for chitosan. However, addition of $\text{Na}_2[\text{PdCl}_4]$ solution would turn the chitosan solution into a fixed gel due to the strong chelating ability of amine and hydroxyl groups on the chitosan chain (Fig. 1(A)). As shown in Fig. 1(B), the gel could be turned back into homogenous solution after addition of 10 wt% of trifluoroacetic acid (Fig. 1(B)).

Incorporating a water soluble polymer into the chitosan solution is a simple method to prepare chitosan nanofibers by electrospinning [16, 17]. Herein, with sodium polyacrylate as the co-electrospinning agent, palladium entrapped in chitosan fiber with average diameter of (152 ± 30) nm was prepared by electrospinning (Fig. 2(A)). As there were a lot of amine and hydroxyl groups on the chitosan chain and carboxyl groups on sodium polyacrylate, the composite fibers can be cross-linked by simple thermal treatment to improve its solvent stability. HR-TEM images showed that palladium nanoparticles with a diameter of (2.99 ± 1.15) nm are dispersed very homogeneously in the Pd@CS/PAA fiber while the palladium particles in the Pd-CS/PAA had an obviously larger diameter of (41.31 ± 10.18) nm and were seriously aggregated (Fig. 2(B) and 2(C)). This result clearly demonstrated that entrapment of palladium species into the composite fibers could increase its dispersion.

The Mizoroki-Heck reaction is a powerful method for the construction of sp^2 - sp^2 carbon-carbon

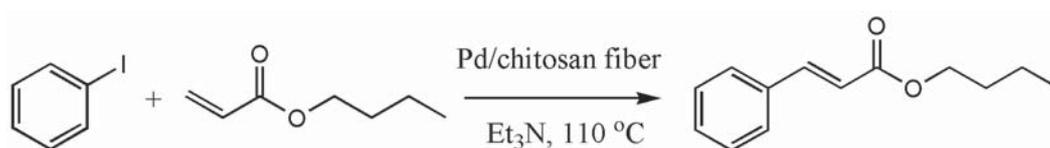


Fig. 3 Mizoroki-Heck reaction of iodobenzene with *n*-butyl acrylate.

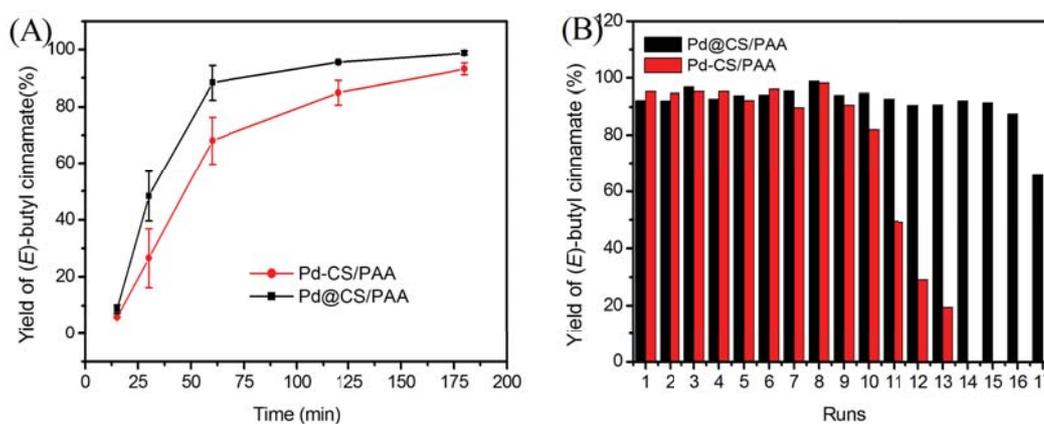


Fig. 4 Comparison of catalytic activity and reusability of Pd@CS/PAA and Pd-CS/PAA. Reaction condition: 0.7 mmol iodobenzene, 1.4 mmol *n*-butyl acrylate, 2.8 μ mol Pd catalyst and 2.0 mmol Et₃N in a solution of 3.0 g DMAc at 110 °C.

bonds [18, 19]. The catalytic activity and stability of Pd@CS/PAA and Pd-CS/PAA was examined by the Mizoroki-Heck reaction of iodobenzene with *n*-butyl acrylate (Fig. 3). As the high dispersion of palladium species could increase its catalytic activity, the Pd@CS/PAA was even more active than Pd-CS/PAA to catalyze the Mizoroki-Heck reaction of iodobenzene with *n*-butyl acrylate (Fig. 4(A)). Moreover, the Pd@CS/PAA could be reused 16 times with excellent yields while the catalytic activity of Pd-CS/PAA decreased after 10 cycles, indicating that the Pd@CS/PAA was obviously more stable than the Pd-CS/PAA (Fig. 4(B)).

3. Conclusion

Pd/chitosan composite fibers were successfully prepared with sodium polyacrylate as the co-electrospinning agent in trifluoroacetic acid/acetic acid/H₂O solution. The composite fiber mat was very efficient to catalyze the Mizoroki-Heck reaction. This is demonstrated to be a simple way to prepare an active and stable heterogeneous palladium catalyst.

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