ISSN 0023-1584, Kinetics and Catalysis, 2020, Vol. 61, No. 3, pp. 480–485. © Pleiades Publishing, Ltd., 2020.

Incorporation of Palladium Catalyst Inside Cross-Linked Chitosan Hybrid Nanofibers for the Sonogashira Reaction

S. Zhong*
Department of Textile, Zhejiang Industry Polytechnic College, Shaoxing, 312000 China
**e-mail: zhaofeng08@163.com*

Received June 30, 2019; revised October 13, 2019; accepted November 28, 2019

Abstract—Nanofibers are attractive supporting matrices for catalytically active metallic catalysts. Herein, palladium species were successfully incorporated into the modified chitosan/poly(ethylene oxide)/maleic acid nanofibers by electrospinning. Then, the hybrid nanofibers were thermally cross-linked at elevated temperature to improve stable behavior in solution. X-ray diffraction and transmission electron microscopy characterizations show that the palladium nanoparticles are dispersed uniformly inside the hybrid nanofibers. This novel hybrid nanofiber mat displayed high catalytic activity for the Sonogashira coupling reaction of phenyl acetylene with aromatic iodides under copper free condition with moderate to excellent yields. Moreover, this nanofiber mat could be reused 10 times with little activity loss. Thus, we have proposed a facile way to prepare highly active and stable heterogeneous palladium catalyst.

Keywords: chitosan nanofibers, Sonogashira reaction, palladium, electrospinning

DOI: 10.1134/S0023158420030210

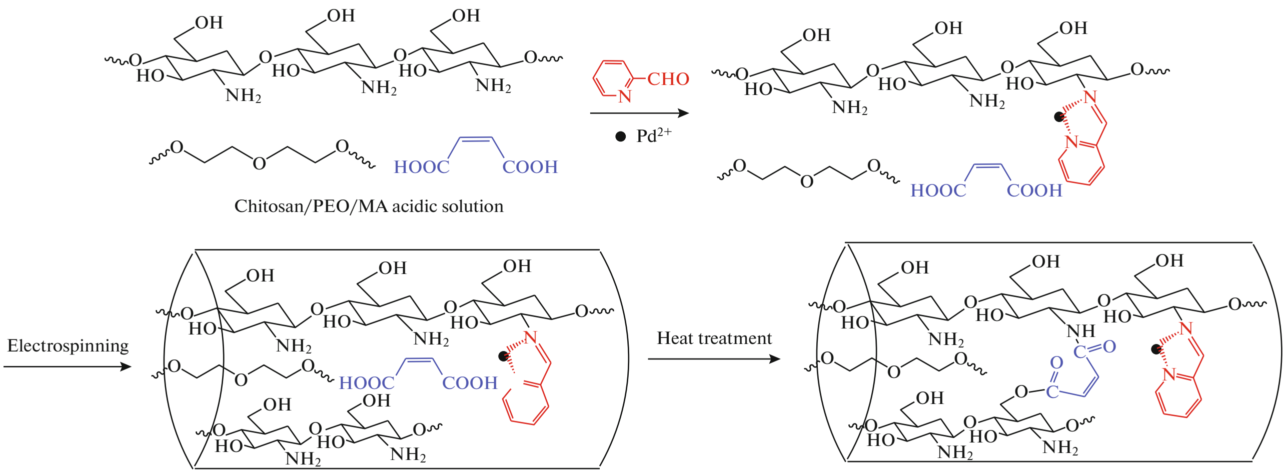
INTRODUCTION

Palladium catalysts have attracted much attention because of their high catalytic performance in organic reactions [1, 2]. Due to the high cost and toxicity, much effort has been put into immobilizing the palladium active species on/in solid matrices to facilitate recovery and recyclability [3]. To simplify the preparation procedure and ensure retention of palladium activity, Pd entities are generally deposited on solid matrices with larger specific surface area. In this way it is possible also to increase the extent of palladium dispersion [4–6]. However, severe reaction conditions (e.g. high reaction temperature and polar solvent) and destruction of solid matrices during the catalytic performance reduce the palladium-matrix bond strength, leading to the aggregation and leaching of palladium species, which in turn deteriorate the catalytic activity. Recently, highly active and stable palladium heterogeneous catalysts have been prepared by introducing the palladium species into the polymer matrices the thickness or diameter of which is ultra-small [7, 8]. The ultra-small thickness and diameter of polymer matrices can facilitate migration of reaction substrates inside the matrices to reach the palladium active species. At the same time, the steric hindrance from polymer chains can reduce the aggregation and leaching of palladium species in the course of catalytic reaction. Inspired by these literatures [7, 8], we speculated that the polymer nanofibers would be ideal supporting matrices to incorporate palladium species for their ultra-small diameter. In addition, the fiber structure could facilitate the recovery and reuse of the catalyst.

Since bioorganic polymers (e.g. gelatin, cellulose and chitosan) are biocompatible, biodegradaible and abundant in nature they attracted attention as the palladium supporting materials in recent years [9–12]. Chitosan contains considerable amounts of amino and hydroxyl functional groups, which can provide strong affinity for palladium species. However, due to the strong affinity, the chitosan solution is easily gelatinized after addition of Pd^{2+} cations, which limited the further treatment. Thus, in order to prepare chitosan supported palladium catalyst, chitosan was generally first converted into a target structure and then palladium species were deposited on the surface [13–15].

In this article, viscous Pd^{2+}/chitosan mixture solution was successfully prepared by addition of pyridine-2-formaldehyde into the mixture followed by electrospinning and thermal treatment to make uniform cross-linked chitosan hybrid nanofibers (Scheme 1). This novel hybrid nanofiber mat can be used as a highly efficient and stable catalyst for the Sonogashira coupling reaction of phenyl acetylene with aromatic halides under copper free condition.

Abbreviations: CS, chitosan; FT-IR, Fourier transform infrared spectroscopy; ICP-AES, inductively coupled plasma atomic emission spectroscopy; MA, maleic acid; PEO, polyethylene; SEM, scanning electron microscopy; TEM, transmission electron microscopy; XRD, X-ray diffraction.



Scheme 1. Scheme for the preparation of palladium incorporated chitosan composite nanofiber.

EXPERIMENTAL

Materials

Chitosan (CS) (average molecular weight of 2.0×10^5, pharmaceutical grade, deacetylated grade of 95%) was purchased from "Zhejiang Aoxing Biotechnology Co., Ltd." (China). $PdCl_2$ (chemical purity) was purchased from "Shaanxi Kaida Chemical Engineering Co., Ltd." (China). Polyethylene (PEO, average molecular weight of 1.0×10^6), maleic acid (MA, analytical grade), pyridine-2-formaldehyde (analytical grade) and substrates of Sonogashira reaction (analytical grade) were supplied by "Shanghai Aladdin Industrial Co., Ltd." (China). All the chemical reagents were directly used without further treatment.

Preparation of Palladium Incorporated Chitosan Hybrid Nanofibers

Chitosan (0.80 g), PEO (0.20 g) and maleic acid (0.20 g) were dissolved in 24 g acetic acid aqueous solution (acetic acid : H_2O = 1 : 1, w/w). The mixture was stirred vigorously for 12 h to achieve homogeneous solution.

$PdCl_2$ (25 mg) and NaCl (17 mg) was dissolved in 1.0 g H_2O to prepare Na_2PdCl_4 aqueous solution.

The Na_2PdCl_4 solution and pyridine-2-formaldehyde (0.10 g) were added into the CS/PEO/MA mixture solution and stirred for 12 h. The final homogeneous solution was subjected to electrospinning to produce the palladium embedded chitosan hybrid nanofibers through a syringe (20 mL) with a blunt-end capillary (0.91 mm ID) as spinneret at a flow rate of 1.5 mL/min (WZ-50C6, Zhejiang Smith Medical Instruments Co., Ltd., China). A voltage of 20 kV (Tianjin Dongwen High Voltage Power Supply Comp., China) was applied between the syringe tip and the collector with a distance of 15 cm. The resultant nanofibers were first dried at 100°C for 5.0 h to remove the residue solvent and then annealed separately at 160, 170 and 180°C for 10 h. The resultant nanofiber mat was labeled as Pd@CS/PEO. The content of palladium in Pd@CS/PEO (annealed at 180°C) was 1.05% as determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

General Procedure for the Sonogashira Reaction

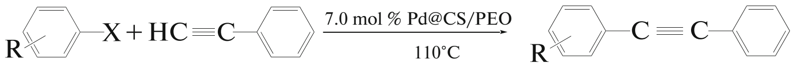
Pd@CS/PEO fiber mat (50 mg, palladium content of 4.9 μmol) was added to the N,N-dimethylacetamide solution containing glycol (0.2 g), aromatic halide (0.7 mmol), phenylene acetylene (1.4 mmol) and K_2CO_3 (3.0 mmol). The reaction was carried out at 110°C and monitored by TLC and GC-MS analysis. After completion, the reaction mixture was quenched with 10 mL H_2O. The Pd@CS/PEO was recovered by simple filtration and the filtrate was extracted three times (3 × 20 mL) by ethyl acetate. The combined organic layer was concentrated to ~5 mL and then purified by silica gel chromatography to afford the coupling product.

The recovered Pd@CS/PEO was directly used in the next run to examine its reusability.

Hot Filtration

The reaction was first carried out under the same condition as that in General procedure for the Sonogashira reaction. After reacting for 30 min, the Pd@CS/PEO was removed by vacuum filtration and the filtrate was transferred into a 25-mL flask containing 3.0 mol K_2CO_3. The reaction was then restarted at the same condition.

Table 1. Pd@CS/PEO catalyzed Sonogashira reaction of aromatic halides with phenyl acetylene



Entry	Aromatic halides	Time, h	Yield, %*
1	C_6H_5–I	5	93
2	2-F–C_6H_5–I	5	90
3	4-F–C_6H_5–I	5	94
4	4-Cl–C_6H_5–I	5	96
5	2-Br–C_6H_5–I	5	87
6	2-CH_3–C_6H_5–I	5	80
7	4-CH_3–C_6H_5–I	5	84
8	C_6H_5–Br	24	31
9	3-NO_2–C_6H_5–Br	24	38
10	4-CH_3–C_6H_5–Br	24	14

* Yields were determined from the GC-MS measurements based on the amounts of aromatic halide substrates.

Characterization

The nanofiber morphology was recorded by scanning electron microscopy (SEM, Jsm-6360 Lv, JEOL, Japan). The diameter for Pd@CS/PEO was calculated from the corresponding SEM image and fifty fibers were counted for the determination of mean fiber diameter. The dispersion of palladium species inside the nanofibers was characterized by transmission electron microscopy (TEM) (JEM-2100F, JEOL) and X-ray diffraction (XRD) (Empyrean, PANalytical, Netherlands). The chemical structure of the chitosan hybrid nanofiber mats was analyzed by Fourier transform infrared spectroscopy (FT-IR) equipped with attenuated total reflection (ATR) (Nexus-470, Nicolet, USA). The palladium content in the hybrid nanofiber mat was determined by ICP-AES. The quantitative analysis of Sonogashira reaction was performed on Agilent GC-MS instrument (USA).

RESULTS AND DISCUSSION

As the amino groups on chitosan chains held strong affinity with Pd^{2+} cations, the chitosan chains was easily physical cross-linked by Pd^{2+} cations and the chitosan solution was turned into a fixed gel after the addition of Pd^{2+} cations, which would then prevent the following electrospinning to make palladium/chitosan hybrid nanofibers. Herein, we found that the chitosan/PEO/MA solution retained flowability after additions of Pd^{2+} cations and pyridine-2-formaldehyde (Fig. 1).

Electrospinning is a facile technique to make polymer solution or melt into continuous fibers with diameter ranging from hundred nanometers to several microns [16]. Electrospinning of neat chitosan into uniform nanofibers generally needs expensive, toxic and corrosive trifluoroacetic acid as the solvent, so blending chitosan with another water-soluble polymer (e.g. PEO and poly(vinyl alcohol)) is a common

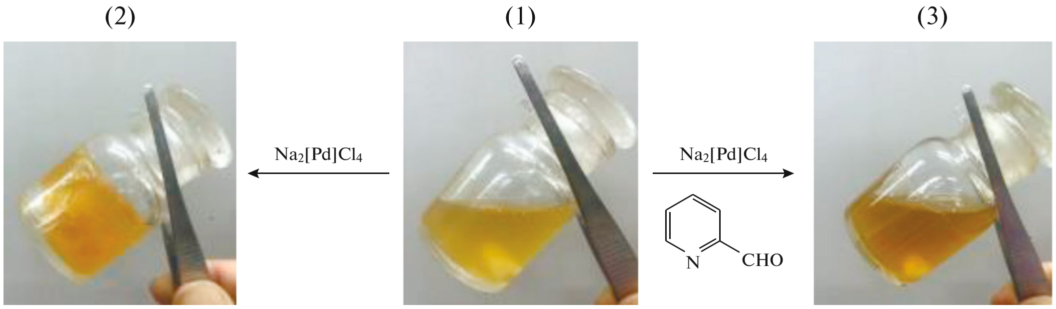


Fig. 1. The CS/PEO/MA solution (1) after addition of Na_2PdCl_4 (2), and Na_2PdCl_4 with pyridine-2-formaldehyde (3).

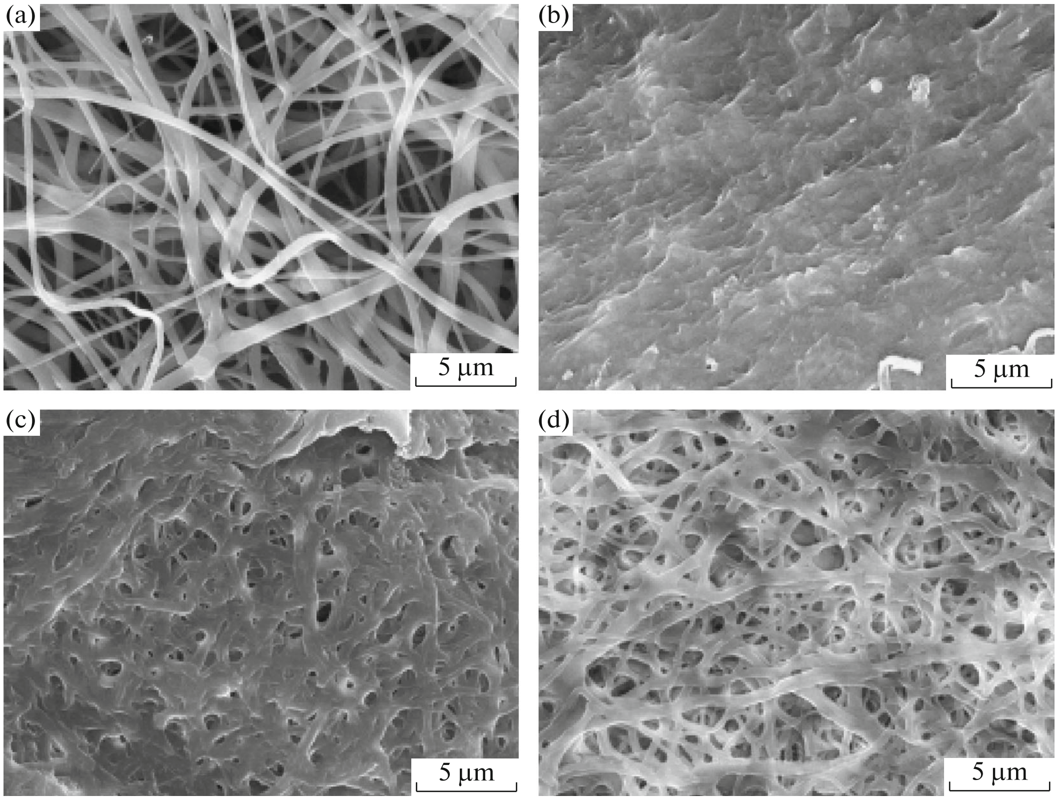


Fig. 2. SEM images of (a) Pd@CS/PEO nanofiber mat, and the swollen Pd@CS/PEO nanofiber mats after immersing in 50 wt % acetic acid aqueous solution for 24 h at different temperatures, °C: 160 (b), 170 (c), 180 (d).

method to prepare chitosan based nanofibers [17–20]. Herein, Pd@CS/PEO nanofibers with mean diameter of 430 ± 161 nm were prepared by electrospinning with total polymer concentration of 4.0 wt % and CS/PEO mass ratio of 8/2 (Fig. 2). Chitosan based nanofiber had been cross-linked with multicarboxylic acid as the in situ cross-linking agent by simple heat treatment [21, 22]. The heat treatment could induce the acylation and esterification reactions of carboxyl groups on maleic acid with the amino and hydroxyl groups on chitosan to achieve the cross-linking of chitosan chains inside the nanofibers. As shown in Fig. 2, the high temperature could reduce the swelling of Pd@CS/PEO nanofibers in 50 wt % acetic acid aqueous solution. Due to the excellent structure stability in solution, the Pd@CS/PEO fiber mat annealed at 180°C was chosen for the following study.

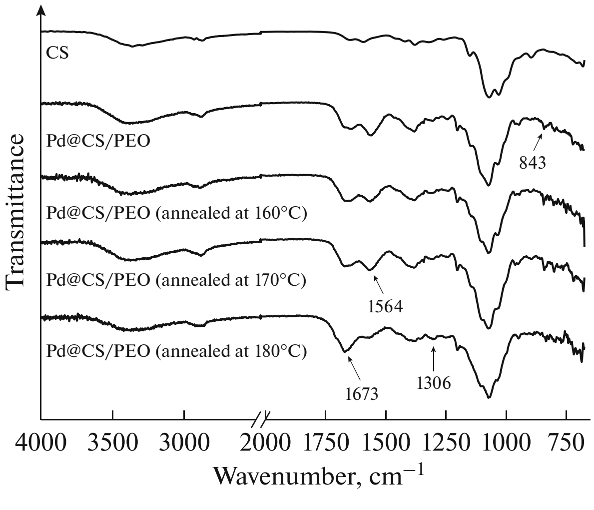


Fig. 3. FT-IR spectra of CS, Pd@CS/PEO and Pd@CS/PEO annealed at different temperatures, °C: 160, 170, 180.

The chemical structures of CS and Pd@CS/PEO nanofiber mats were characterized by FT-IR spectroscopy. Figure 3 shows that the absorption peaks at 1653 cm^{-1} (amide I) and 1306 cm^{-1} (amide III) were intensified with the increment of annealing temperature. At the same time, the absorption peak at 1563 cm^{-1} (–NH_2) was weaken after annealing treatment. In addition, the absorption at 843 cm^{-1} ascribed to prydiryl group indicated the successful modification of chitosan by 2-pyridinecarboxaldehyde. These results demonstrate that the chitosan chains inside the nanofiber have been cross-linked by the acylation reaction of carboxyl groups on maleic acid with the amino groups on the chitosan, which is consistent with the result of SEM characterization.

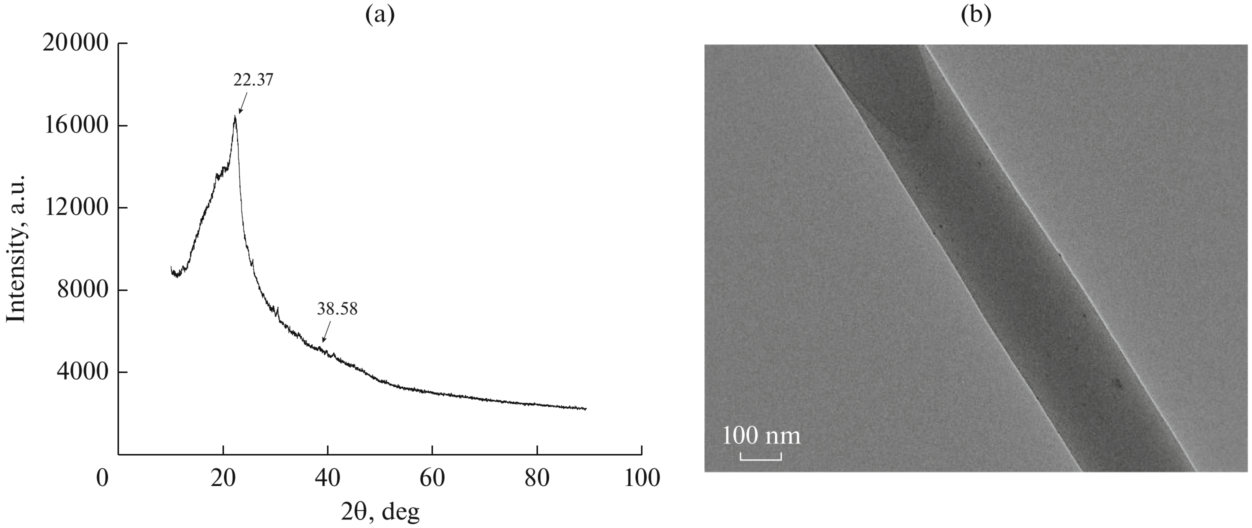


Fig. 4. XRD pattern (a) and TEM image (b) of Pd@CS/PEO nanofiber mat.

The dispersion of palladium nanoparticles inside the nanofibers was characterized by XRD and TEM. The strong reflection peak at 22.3° was signed to partially crystalline chitosan while the reflection peak attributed to palladium nanoparticles (38.6°) was very weak, indicating the uniform dispersion of palladium species inside the nanofibers (Fig. 4). The TEM image also shows that the palladium nanoparticles were dispersed very homogeneously inside the nanofibers (Fig. 4).

Sonogashira Reaction

Sonogashira reaction is the cross-coupling reaction of aromatic halides with terminal alkynes, which provides a powerful and versatile method for the construction of sp^2-sp carbon–carbon bonds [23]. In palladium catalyzed Sonogashira reaction, copper salts usually play an important role in assisting tansmetalation by the in situ generation of copper acetylide. Thus, the addition of copper salt could catalyze the Glaser-type reaction of the terminal acetylene [24]. Herein, we found that the Pd@CS/PEO could efficiently catalyze the Sonogashira reaction of iodobenzene with phenyl acetylene without the addition of copper salt (Table 1, entry 1).

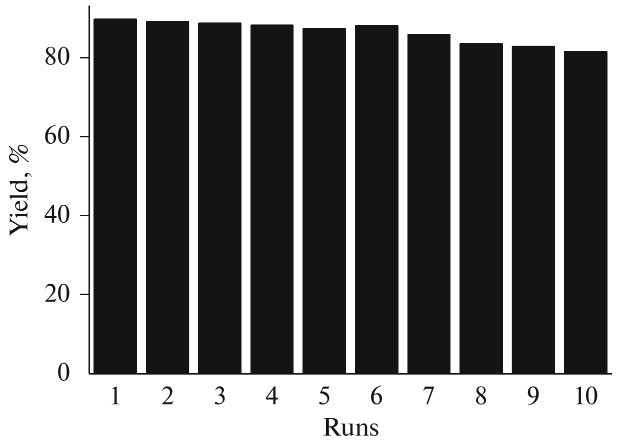


Fig. 5. The reusability of Pd@CS/PEO catalyst.

A number of Sonogashira reactions of aromatic halides with phenyl acetylene were studied by using the Pd@CS/PEO as the catalyst and the relevant results were summarized in Table 1. Examination of entries 2–7 in Table 1 shows that the Pd@CS/PEO is more active to catalyze the reaction of aromatic iodides with electron withdrawing groups than these with electron-donating groups. The yields for cross coupling of aromatic iodides with *ortho*-substituent is slightly lower that that with *para*-substituent (Table 1, entries 2, 3, 6 and 7), probably due to the steric hindrance of substituent. Due to a stronger carbon-bromine bond strength, the Pd@CS/PEO had low catalytic activity for the Sonogashira reaction of aromatic bromide with phenyl acetylene and the low yields were resulted from low substrate conversion.

The Pd@CS/PEO can be easily separated and reused due to the larger fiber structure. The reusability of Pd@CS/PEO for the Sonogashira reaction of iodobenzene with phenyl acetylene was examined (Fig. 5). The catalytic activity of the Pd@CS/PEO was retained for 10 times without obvious loss of initial activity. ICP-AES analysis shows that the palladium content in the recovered Pd@CS/PEO after 10 cycles was 0.66%, indicating that 37% of the palladium was leached in cyclic operations. The stability of Pd@CS/PEO can be attributed to the strong chelating ability of chitosan and incorporation of palladium species inside the nanofibers.

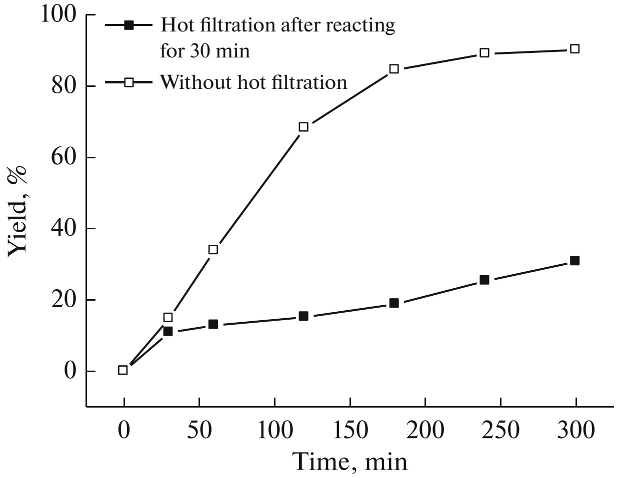


Fig. 6. Sonogashira reaction of iodobenzene with phenyl acetylene as catalyzed by Pd@CS/PEO using hot filtration (—■—) and without it (—□—).

The heterogeneity of Pd@CS/PEO catalyzed Sonogashira reaction of iodobenzene with phenyl acetylene was examined by rapid hot filtration. As shown in Fig. 6, after hot filtration test, the reaction rate was significantly reduced, indicating the Pd@CS/PEO catalyzed Sonogashira reaction mainly proceeded in a heterogeneous fashion. Moreover, a slow raise of yield after hot filtration can be ascribed to the dissolved active palladium species present in the reaction mixture.

CONCLUSIONS

A highly active and stable palladium heterogeneous catalyst (Pd@CS/PEO) was prepared by incorporating the palladium nanoparticles inside the cross-linked CS/PEO nanofibers. The Pd@CS/PEO fiber mat was very effective as the catalyst for the Sonogashira reaction of aromatic iodides with phenyl acetylene with moderate to excellent yields. Moreover, the Pd@CS/PEO fiber mat can be easily recovered and reused for 10 cycle operations with little loss of activity. A high stability and recyclability of the Pd@CS/PEO fiber mat can be attributed to the strong chelating ability of chitosan and incorporation of palladium inside the nanofibers.

FUNDING

We greatly appreciate the financial supports from Zhejiang Industry Polytechnic College.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Christoffel, F. and Ward, T.R., *Catal. Lett.*, 2018, vol. 148, p. 489.
2. Roy, D. and Uozumi, Y., *Adv. Synth. Catal.*, 2018, vol. 360, no. 4, p. 602.
3. Glasnov, T.N., Findenig, S., and Kappe, C.O., *Chem. Eur. J.*, 2010, vol. 15, no. 4, p. 1001.
4. Cui, X., Zheng, Y., Meng, T., and Dong, Z., *J. Mol. Catal.*, 2017 vol. 433, p. 202.
5. Hui, Z., Wu, C., Wu, Q., Guo, B., Liu, W., Li, G., Su, Q., and Mu, Y., *Polym. Chem.*, 2017, vol. 8, no. 9, p. 1488.
6. Veisi, H., Nikseresht, A., Mohammadi, S., and Hemmati, S., *Chin. J. Catal.*, 2018, vol. 39, no. 6, p. 1044.
7. da Costa, A.P., Rosa Nunes, D.R., Tharaud, M., Oble, J., Poli, G., and Rieger, J., *ChemCatChem*, vol. 2017, no. 12, p. 2167.
8. Li, F., Bertoncello, P., Ciani, I., Mantovani, G., and Unwin, P.R., *Adv. Funct. Mater.*, 2008, vol. 18, no. 11, p. 1685.
9. Dhanavel, S., Manivannan, N., Mathivanan, N., Gupta, V.K., Narayanan, V., and Stephen, A., *J. Mol. Liq.*, 2018, vol. 257, p. 32.
10. Li, Y., Xu, L., Xu, B., Mao, Z., Xu, H., Zhong, Y., Zhang, L., Wang, B., and Sui, X., *ACS Appl. Mater. Interfaces*, 2017, vol. 9, no. 20, p. 17155.
11. Khazaei, A., Khazaei, M., and Rahmati, S., *J. Mol. Catal. A: Chem.*, 2015, vol. 398, no. 9, p. 241.
12. Adlim, M. and Bakar, M.A., *Kinet. Catal.*, 2013, vol. 54, no. 5, p. 586.
13. Liang, L., Nie, L., Jiang, M., Bie, F., Shao, L., Qi, C., Zhang, X.M., and Liu, X., *New J. Chem.*, 2018, vol. 42, p. 11023.
14. Zhang, C., Lu, D., Jiang, P., Li, J., and Leng, Y., *Catal. Lett.*, 2017, vol. 147, p. 2534.
15. Nie, L., Liang, L., Jiang, M., Shao, L., and Qi, C., *Fibers Polym.*, 2018, vol. 19, no. 7, p. 1463.
16. Sonina, A.N., Uspenskii, S.A., Vikhoreva, G.A., Filatov, Y.N., and Gal'braikh, L.S., *Fibre Chem.*, 2011, vol. 42, no. 6, p. 350.
17. Nie, L., Liang, L., Jiang, M., Shao, L., and Qi, C., *Fibers Polym.*, 2018, vol. 19, no. 7, p. 1463.
18. Diana, S.A., Javier, G.P., Ulises, P.G., Alfredo, M.C., Reinaldo, M.O., and Ricardo, V.G., *Int. J. Mol. Sci.*, 2018, vol. 19, no. 6, p. 1718.
19. Pakravan, M., Heuzey, M.C., and Ajji, A., *Polymer*, 2011, vol. 52, no. 21, p. 4813.
20. Sun, K. and Li, Z.H., *eXpress Polym. Lett.*, 2011, vol. 5, no. 4, p. 342.
21. Pangon, A., Saesoo, S., Saengkrit, N., Ruktanonchai, U., and Intasanta, V., *Carbohydr. Polym.*, 2016, vol. 138, p. 156.
22. Shao, L., Yuan, R., Wang, Z., Qi, C., and Yao, L., *Polymer*, 2015, vol. 75, p. 168.
23. Nasrollahzadeh, M., Atarod, M., Alizadeh, M., Hatamifard, A., and Sajadi, S.M., *Curr. Org. Chem.*, 2017, vol. 21, no. 8, p. 708.
24. Han, S.C., Kwak, S.H., Yun, S.H., Jin, S.H., and Lee, J.W., *Mol. Cryst. Liq. Cryst.*, 2014, vol. 597, no. 1, p. 79.