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Palladium Immobilized on Aminated Polyacrylonitrile Nanofiber as an Efficient Heterogeneous Catalyst for Heck Reaction

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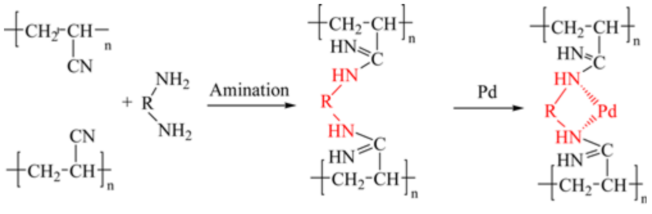
Abstract: Aminated polyacrylonitrile (PAN-NH) nanofiber mats prepared by electrospinning and then aminated by multiamines with different chemical structures have been used for the immobilization of palladium. The PAN-NH fiber morphologies were characterized by scanning electron microscopy (SEM) and the dispersion of palladium particles on the PAN-NH fiber were examined by transmission electron microscopy (TEM). The catalytic activity and recyclability of the prepared heterogeneous palladium catalysts have been evaluated by the Heck reaction of iodobenzene with *n*-butyl acrylate. It was found that the catalytic activities of PAN-NH-Pd catalysts could be correlated with the chelating energies of the PAN-NH fiber mats with Pd active species.

Keywords: Electrospinning, Heck reaction, Amination, Palladium, Density functional theory

Introduction

Palladium catalysis plays an important role in academic research and industrial application for the construction of the C-C and C-X chemical bond [1]. Homogeneous palladium catalysts such as $Pd(OAc)_2$ and $Pd(PPh_3)_2Cl_2$ have been widely used for their high catalytic activity and selectivity [2]. However, as it is not easily to separate the palladium and expansive ligands from the reaction mixture, the homogeneous palladium catalyst was very difficult to be recovered and recycled after catalysis. Moreover, the products from homogeneous palladium catalysis are usually contaminated by the palladium metal, which is a serious problem for the large scale production of pharmaceuticals, food additives and cosmetics, and so on.

Immobilization of palladium catalyst on suitable matrices will not only facilitate the separation and reuse of the expensive and toxic palladium active species, but can also reduce the contamination of palladium to the reaction products and environment. In the past decades, various inorganic and organic supports have been developed as the supporting materials of palladium catalyst [3-5]. Polymeric materials have been widely used due to their easy functionalisation and excellent compatibility with organic substrates [6-8]. Palladium leaching is a common problem for the heterogeneous palladium catalyst. Chemical modification of the solid matrix surface with suitable functional groups is an effective way to improve the interaction between sold matrices with palladium active species, ultimately reduce the palladium leaching during the catalysis process. However, it is very challenging to immobilize suitable chelating groups on solid matrices [7-11]. Herein, polyacrylonitrile (PAN) was electrospun into nanofiber mat and then chemically modified by multiamines with different chemical structure, followed by immobilization of palladium active species (Scheme 1). The catalytic performances of these novel aminated PAN fiber mats supported palladium (PAN-NH-Pd) catalyst were evaluated by the Heck reaction of iodobenzene with *n*-butyl acrylate. Density functional theory (DFT) calculation was employed to analysis the chelating energies of aminated PAN (PAN-NH) fiber with palladium and the relationship of those chelating energies with the catalytic activities of corresponding PAN-NH-Pd catalysts was investigated.



$R = -(CH_2)_2-; -(CH_2)_3-; -(CH_2)_2-NH-(CH_2)_2-; -[(CH_2)_2-NH]_3-CH_2-$

Scheme 1. Scheme representation for the synthesis of aminated PAN fiber supported Pd catalyst.

Experimental

General Remarks

All solvents and chemicals were analytical grade or the best grade available and used without further treatment. Ethylenediamine, 1,3-propanediamine, diethylenetriamine and tetraethylenepentamine were purchased from Aladdin Chemical Co. Ltd. Palladium chloride ($PdCl_2$) and palladium on carbon (Pd/C) were bought from Zhejiang Metallurgical Research Institute (Zhejiang, China). PAN fiber mat was prepared according to the literature [7].

Synthesis of Aminated Polyacrylonitrile Fiber Mat

Aminated PAN was synthesized according to the literature [12]. 0.1 g PAN fiber mat was added into the mixture of 2.0 g 1,3-propanediamine and 3.0 g ethylene glycol, and then

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*Corresponding author: 1010406319@qq.com allowed to stir at 80 °C for 6 h. After reaction, the fiber mat was filtrated and washed with H_2O (3×10 m*l*), and ethanol (3×10 m*l*). The fiber mat was dried at 60 °C under reduced pressure and named as PAN-NH fiber.

The amination process of PAN by other three multiamines was the same as that of 1,3-propanediamine.

Palladium Deposition on PAN-NH Fiber Mat (PAN-NH-Pd)

100 mg PAN-NH fiber mat was added to the aqueous solution (10 m*l*) containing 5 mg $PdCl_2$ and 4 mg NaCl. The mixture was stirred magnetically for 12 h, and the yellow solution turned into colorless, indicating the successful immobilization of Pd^{2+} on the fiber. 20 mg hydrazine was added into the solution and the PAN-NH fiber became black quickly, indicating that the Pd^{2+} was reduced into Pd^0. The PAN-NH-Pd fiber mat was filtered and washed by H_2O (3×10 m*l*), and ethanol (3×10 m*l*). The PAN-NH-Pd fiber mat was dried under reduced pressure at 30 °C for 12 h. The inductively coupled plasma-atomic emission spectroscopy (ICP-AES) characterization showed that the content of palladium in PAN-NH-Pd fiber catalyst was 3.01 %.

Immobilization process of palladium on the other three aminated PAN fiber was the same.

General Procedure for the Heck Reaction

Iodobenzene (0.7 mmol), *n*-butyl acrylate (1.4 mmol), PAN-NH-Pd catalyst (50 mg, Pd: 0.014 mmol) and CH_3COOK (5.2 mmol) were added to 3.0 g *N,N*-dimethylacetamide (DMAc) solution in a 20 m*l* round bottom flask with a magnetic stir bar. The resulting solution was allowed to stir at 110 °C for 3 h. The iodobenzene conversions and *n*-butyl cinnamate yields were determined from GC/MS measurements. The spectroscopic data (^{1}HNMR and GC/MS) for the *n*-butyl cinnamate are consistent with the literature [7].

DFT Calculation

All the calculations were performed with the Gaussian 03 programs using B3LYP method with 6-31 g(d) basis set for C, H, N and the Hay and Wadt with a double-valence basis set (LanL2DZ) for Pd [7,13]. Each optimized structure was confirmed by the frequency calculation. For computational efficiency, the 1,3-propanediamine, ethylenediamine, diethylenetriamine, tetraethylenepentamine chemically modified PAN fiber were abbreviated to N^1,N^3-diethyl-1,3-propanediamine, N^1,N^2-diethyl-ethylenediamine, N^1-ethyl-N^2-(2-(ethylamino)ethyl) ethane-1,2-diamine, N^1-ethyl-N^2-(2-(2-(2-(ethylamino)ethylamino)ethylamino)ethyl)ethane-1,2-diamine, respectively.

Characterizations

The morphologies of the electrospun mats were characterized with a scanning electron microscope (SEM) (Jeol, Jsm-6360lv, Japan). The fiber mats were analyzed by Fourier transform infrared spectroscopy (FT-IR) (Nicolet, Nexus-470, USA) with the accessories of attenuated total reflection. The quantitative analysis of the reaction products was performed on an Agilent 6890/5975 GC/MS instrument with a programmable split/splitless injector. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis was performed on a Leeman ICP-AES Prodigy XP (Leeman Labs, USA). The dispersion of palladium nanoparticles were recorded by transmission electron microscopy (TEM) (Jeol, JEM-1011, Japan).

Results and Discussion

Characterization of PAN-NH-Pd Catalyst

Electrospinning is a facile method to prepare fibers with diameters ranging from several microns to hundreds nanometers [14,15]. Due to their larger specific surface area and high flux properties, electrospun mats have been widely used as the supporting materials for transition metal catalyst and enzyme [16,17]. Moreover, compared with particle catalyst, fiber structure greatly facilitates the recovery and reuse of fiber catalyst due to the low pressure during filtration. PAN and acrylonitrile-based polymers are one of mostly widely used electrospinning materials for their excellent spinnability [18]. However, as the PAN fiber mat could be dissolved in DMSO, DMF, etc, their applications in organic solutions were limited. Herein, PAN fiber was crosslinked by multiamines and the solvent resistance of PAN fiber significantly improved (Scheme 1). Although the diameter of PAN fiber obviously increased after amination (PAN fiber diameter: 243±44 nm; PAN-NH fiber diameter: 406±102 nm), the fiber structure was well kept (Figure 1). It is interesting to find that the PAN-NH fiber diameter reduced after immobilization of palladium (PAN-NH-Pd fiber diameter: 333±92 nm). We believed that the coordination of imine groups in the PAN-NH fiber with palladium nanoparticles could increase the crosslinking degree, which resulted in the decrement of PAN-NH fiber diameter. TEM image clearly demonstrated the adsorption of palladium nanoparticles on the PAN-NH fiber (Figure 2).

The chemical structures of PAN, PAN-NH and PAN-NH-Pd fiber mat were confirmed by FT-IR spectroscopy (Figure 3). After amination, the absorption peaks at 3370 cm^{-1} and 1567 cm^{-1} assigned to secondary amine (N-H) peaks appeared and it was also found that the PAN-NH fiber mat could not be dissolved in the DMF solvent any more. These results clearly indicated that imine groups have been successfully introduced into the PAN polymer chain and PAN chain was crosslinked. After immobilization of Pd, the absorption band at 1567 cm^{-1} was blue shifted, suggesting the coordination of -NH- group with Pd. In the process of palladium immobilization, the yellow Na_2PdCl_4 aqueous solution become colorless quickly after addition of PAN-NH fiber mat while the color of Na_2PdCl_4 aqueous solution immersed

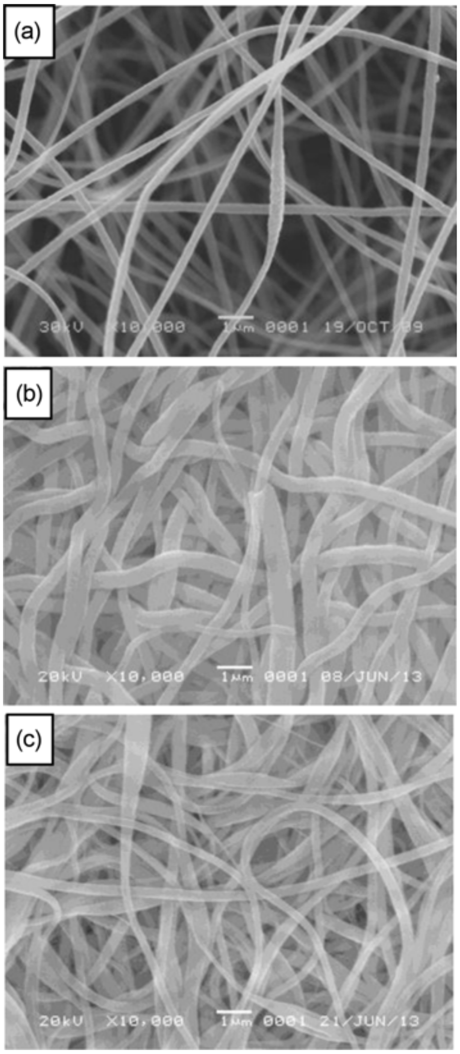

Figure 1. SEM images of (a) PAN fiber mat, (b) PAN-NH fiber mat, and (c) PAN-NH-Pd fiber mat.

with PAN fiber was unchanged, which demonstrated that the amination process is a effective way to increase the chelating properties of PAN fiber mat via the coordination of -NH- groups.

Catalytic Performance of PAN-NH-Pd Catalyst

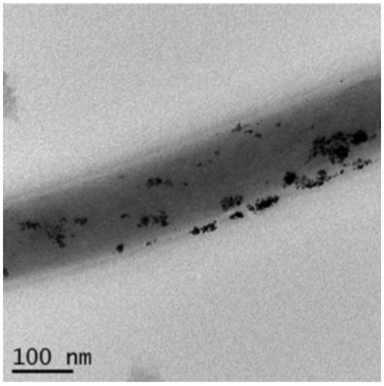

Figure 2. TEM image of PAN-NH-Pd fiber.

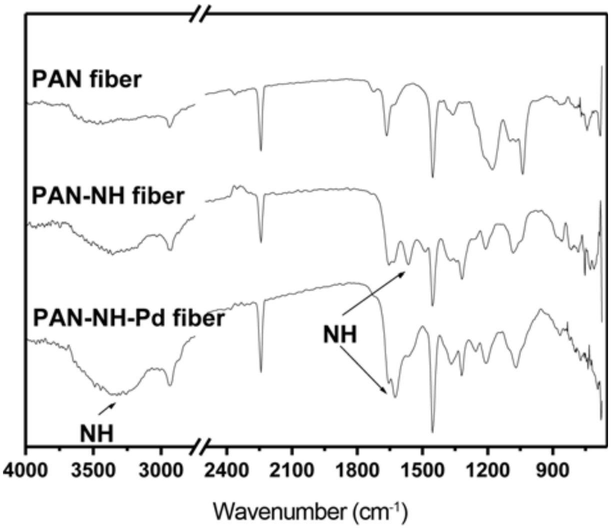

Figure 3. FT-IR spectra of the PAN fiber mat, PAN-NH fiber mat and PAN-NH-Pd fiber mat.

The catalytic performances of PAN-NH-Pd catalysts were evaluated by Heck reactions [19,20]. Examination of Table 1 showed that the catalytic activities of PAN-NH-Pd were dependent on the chemical structure of the aminated PAN fiber. Examination of entry 2-4 in Table 1 showed that the increment of coordination sites would enhance the interaction between the fibers with Pd^0 active species, which ultimately leaded to decrement of catalytic activity of corresponding palladium catalyst. Although 1,3-propanediamine derivative could form more stable complexes with Pd^{2+} ion than

Table 1. The catalytic activities and chelating energies of aminated PAN fiber mat supported palladium catalyst

Entry	Multiamines	Conversion (%)	Yield (%)	ΔH Pd^0 (kJ/mol)	ΔH Pd^{2+} (kJ/mol)
1	1,3-Propanediamine	97	97	-54	-1457
2	Ethylenediamine	90	89	-78	-1448
3	Diethylenetriamine	77	74	-116	-1680
4	Tetraethylenepentamine	75	72	-157	-1715
5	Pd/C	90	89	-	-
6	$PdCl_2$	98	98	-	-

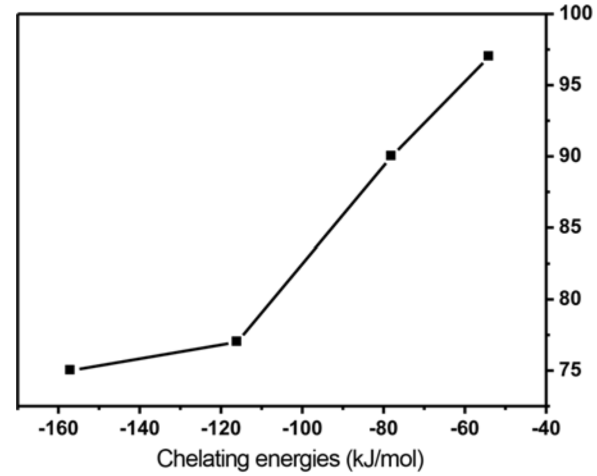

Figure 4. The correlation of chelating engergies with conversions.

ethylenediamine, the complexes of ethylenediamie derivative with Pd^0 is not as stable as that of 1,3-propanediamine derivative with Pd^0. As a result, the palladium supported on PAN-NH fiber mat (aminated by 1,3-propanediamine) was the most active catalyst among the aminated PAN fiber mat supported palladium catalyst. This PAN-NH-Pd fiber catalyst even had comparable catalytic activity with homogeneous $PdCl_2$ catalyst and considerably higher catalytic activity than that of commercial palladium heterogeneous catalyst (Pd/C). Moreover, it was found that the catalytic activities could be correlated with the chelating energies of the amianted PAN fibers with Pd^0 (Figure 4).

Reuse of the PAN-NH-Pd Fiber Catalyst

PAN fiber mat have been applied as the supporting material of palladium by coelectrospinning of PAN and $PdCl_2$ mixture by Shao *et al*. [7]. The PAN fiber mat supported Pd catalyst exhibited high catalytic activity for the Heck reaction in aqueous solution. However, due to the low chelating property of PAN fiber, the leaching of palladium was obvious and the reuse was very poor. In this article, the chelating properties of PAN fiber mat were significantly improved by introducing imine groups (Table 1). Figure 5 showed the reusability of the PAN-NH-Pd (aminated by 1,3-propanediamine) fiber catalyst. The catalytic activity of PAN-NH-Pd lost a little at the first run may be due to the desorption of the unstable Pd^0 active species (Figure 5). In the next three recycles, the catalytic activity of PAN-NH-Pd catalyst was well kept, which indicated that the chelating property of supporting materials played an important role in the stability of hetergoeneous palladium catalyst. Unfortunately, the PAN-NH fiber was frangible and a part of fibers were broken into powder after four runs, which limited its further reuse. After recycled for four runs, although some fibers of PAN-NH-Pd fiber mat were broken, the fiber structure was still well kept (Figure 6).

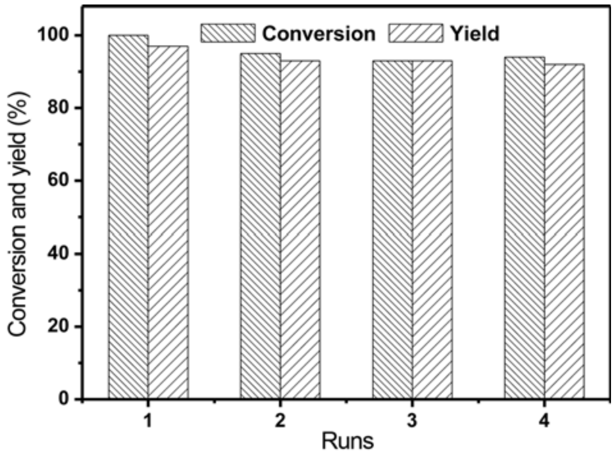

Figure 5. The reuse of PAN-NH-Pd catalyst for the Heck reaction.

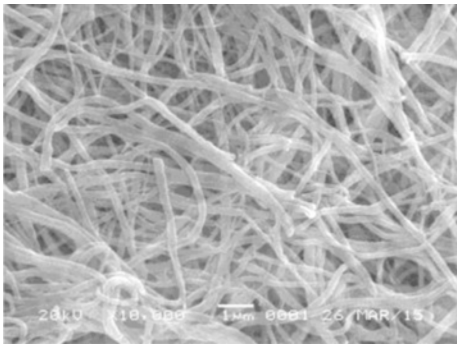

Figure 6. SEM image of PAN-NH-Pd recycled after four runs.

Conclusion

A series of novel aminated polyacrylonitrile fiber mats were synthesized and used as the supporting materials of palladium. The PAN-NH-Pd catalyst was very active and stable for the Heck reaction of iodobenzene with *n*-butyl acrylate. Furthermore, the catalytic performance could be tuned by the chelating energies of the supporting materials with Pd active species.

Acknowledgement

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