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Polyacrylonitrile fiber mat-supported palladium catalyst for Mizoroki–Heck reaction in aqueous solution

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A novel palladium catalyst immobilized on polyacrylonitrile fiber mats (Pd/PAN) was prepared by electrospinning. The catalytic activity and recyclability of the microwave-assisted Pd/PAN fiber mats were examined for the Mizoroki–Heck cross-coupling of aryl iodides with three different acrylates in aqueous solution. The morphology of the prepared Pd/PAN fiber mats was characterized by scanning electron microscopy. The large size of the PAN fiber mat-supported palladium catalyst enables much easier separation from the reaction mixture by simple filtration. Density functional theory calculation indicates that the chelation energy of palladium chloride (PdCl₂) with propionitrile (model of PAN) is considerable smaller than that of PdCl₂ with water, suggesting that the stability and reactivity of the Pd/PAN fiber mats catalyst could be improved through the surface derivatization with polar functional groups. Copyright © 2011 John Wiley & Sons, Ltd.

Keywords: heterogeneous palladium catalysis; Mizoroki – Heck cross-coupling; fiber mats; electrospinning; aryl iodides

Introduction

Palladium catalysis is one of the most important chemical transformations in synthetic organic chemistry, especially for the construction of the C–C and C–X chemical bond formations.^[1,2] Although palladium complexes such as $[Pd(OAc)_2]$ and $[Pd(PPh_3)_2Cl_2]$ have been widely used in homogeneous system for homo and crosscoupling reactions,^[3,4] the main drawback of the homogenous catalysts is the difficulty of recycling and reusing the expensive metals and ligands. Thus, it is not surprising that very few homogeneous catalytic systems have been commercialized.

Immobilization of transition metals will not only facilitate separation and reuse of the expensive and toxic catalysts, but can also reduce contamination of the heavy metal to the environment. In past few decades, a variety of heterogeneous palladium catalysts have been developed through the immobilization of transition metals on various solid supports such as alumina, silica, zeolites, active carbon and polymers.^[5-7] Owing to their excellent compatibility with organic substrates, polymeric materials have been widely used to support palladium catalysts.^[8,9] However, the heterogenization of homogeneous catalyst on insoluble solid supports generally results in reduction of the catalytic activity and selectivity. Polyacrylonitrile (PAN) is an ideal solid support to immobilize palladium catalyst because of its excellent chemical stability, anti-swelling and mechanical performances. Moreover, the abundant cyano groups of the PAN polymer chains, just like the toxic and expensive phosphine ligands, can also chelate with the palladium species to improve the stability as well as preventing the palladium black formation for the heterogeneous palladium catalyst.

Recently, we have developed an efficient heterogeneous catalyst through the immobilization of palladium species on the finely ground powders of naturally abundant pearl shells.^[10] However, it is tedious and time-consuming to separate and recycle the particulate heterogeneous palladium catalyst from the reaction mixtures by filtration owing to the sharp pressure drop. In the present paper, highly porous PAN fiber mats were prepared and

then used to immobilize the palladium catalyst. The resulting large size of the fiber mats facilitated the separation and recycling of the heterogeneous palladium catalyst. The PAN fiber mat-supported palladium catalyst (Pd/PAN fiber mats) was characterized by scanning electron microscopy (SEM) and its catalytic activity and stability were examined using the Mizoroki–Heck cross-coupling reaction of aromatic iodides with acrylates in aqueous solutions. Furthermore, DFT calculations were also used to evaluate the stability of the Pd/PAN fiber mats.

Results and Discussion

A variety of polymers and composites have been employed to fabricate porous fiber mats with high surface area to volume ratio by means of electrospinning.^[11] Acrylonitrile-based homoand copolymers are among the most used polymer substrates to be electrospun into nanofiber mats because of their excellent spinnability and chemical stability.^[12–14] In addition, PAN can form strong chelation with the palladium species owing to the abundant cyano groups, suggesting that PAN fiber mats should be an excellent solid support for the immobilization of palladium catalyst.

Substrate concentration is known to be critical for electrospinning.^[15] A series of samples with different PAN concentrations have been prepared to optimize the electrospinning conditions (Figs 1 and 2). Fiber beads (Fig. 1a and 1b) were formed at relatively lower PAN substrate concentrations, presumably owing to the jet instability of PAN polymer solution. Interestingly, the average diameter of the resulting nanofibers increases with the

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Figure 1. SEM images of PAN fiber mats electrospun at concentration of (a) 4.0 wt%, (b) 6.0 wt%, (c) 8.0 wt% and (d) palladium deposited on 8.0 wt% PAN fiber mats.



Figure 2. Dependence of PAN fiber diameter on the PAN substrate weight concentration.

PAN weight concentration until about 8.0%, as shown in Fig. 2. Therefore, 8.0% weight concentration of PAN in DMF solution was chosen for the subsequent studies.

More uniform and thinner nanofibers are generally obtained by addition of salts to increase the conductivity of the preelectrospinning solution.^[16,17] In contrast, Figs 1 and 2 show that the electrospun PAN fiber mats have relative larger diameter in the presence of palladium chloride (PdCl₂) salt. The augmentation of the fiber diameter could be attributed to the chelation of the divalent Pd²⁺ species with the cyano groups of the PAN polymer chains, which reduces the mobility of the polymer solution. In other words, the increasing conductivity is offset by reduction of the polymer solution mobility. Microwave irradiation is attractive since it can produce much more efficient internal heating than traditional conductive heating. The heating efficiency is known to be proportional to the solvent dielectric constant since microwave heating is achieved through the dielectric polarization of the solvent molecules. Microwave heating has been shown to be essentials for many types of chemical transformations, including palladium-catalyzed carbon–carbon bond couplings.^[18,19] Water is the ideal green and environmentally benign solvent for the chemical transformations, and it has the highest dielectric constant among the common solvents used.

A phase transfer agent is generally needed to facilitate reactions of organic substrates performed in polar aqueous solution, and quaternary ammonium and polyethylene glycol (PEG) polymer are the commonly used phase transfer catalysts.^[20] The initial conditions were adapted from our previous studies optimized for shell powder-supported palladium catalyst for the Mizoroki-Heck cross-coupling reaction of iodobenzene with *n*-butyl acrylate.^[10] Surprisingly, examination of entries 1 and 2 of Table 1 shows that addition of PEG does not accelerate, but instead slightly suppresses, the Mizoroki-Heck cross-coupling reaction of iodobenzene with *n*-butyl acrylate. However, addition of the quaternary ammoniums (entries 3 and 4, Table 1) results in significant improvement of the Mizoroki-Heck reaction. The quaternary ammonium salt is believed to stabilize the zero-valent palladium species generated during the Mizoroki-Heck reaction in aqueous solution.^[21] The better performance of cetryltrimethyl ammonium bromide (CATB) over tetrabutyl ammonium bromide (TBAB) could be attributed to the higher dispersion of long alkyl chains.^[22] Figure 3 shows that the cross-coupling yield increases with concentration of the phase transfer reagent (CATB) for the Mizoroki-Heck reaction of iodobenzene with *n*-butyl acrylate. Excellent yields could be obtained when CATB was added in 0.15 molar equivalents. Entries 4 and 5 of Table 1 clearly show that microwave irradiation is more effective than the conventional oil bath heating.

Table 1. Effects of heating methods and phase transfer reagents on the Mizoroki–Heck cross-coupling of iodobenzene with n-butyl acrylate^a

Entry	Heating	Phase transfer agent	Conversion ^b (%)	Yield ^b (%, <i>trans : cis</i>)
1	Microwave	None	75.5	75.1 (97.9:2.1)
2	Microwave	PEG2000	45.6	45.0 (97.4:2.6)
3	Microwave	TBAB	92.6	92.5 (99.2:0.8)
4	Microwave	CATB	96.7	96.7 (99.1:0.9)
5	Oil bath ^c	CATB	30.0	30.0 (100:0)

^a Reaction conditions: iodobenzene, 1.0 mmol; *n*-butyl acrylate, 2.0 mmol; potassium acetate, 3.0 mmol; Pd/PAN fiber mats, 0.05 mmol with or without phase transfer reagent (0.15 mmol) in 5 ml of water for 5.0 h.

^b GC-MS conversion and yield.

^c Reaction temperature was set about 100 $^\circ$ C.

CTAB, cetryltrimethyl ammonium bromide; TBAB, tetrabutyl ammonium bromide.



Figure 3. Effects of phase transfer reagent concentrations on the Pd/PAN fiber mat-catalyzed reductive cross-coupling of iodobenzene with *n*-butyl acrylate. Reaction conditions: iodobenzene, 1.0 mmol; *n*-butyl acrylate, 2.0 mmol; potassium acetate, 3.0 mmol; Pd/PAN fiber mats, 0.05 mmol; 5.0 h in 5.0 ml of water solution; microwave, 330 W. GC-MS conversion and yield.

The optimized conditions for the Pd/PAN fiber mat-catalyzed Mizoroki–Heck cross-coupling reaction of iodobenzene with *n*-butyl acrylate clearly work well for the cross-coupling of the other aryl iodides with acrylates, as evident in Table 2. Excellent cross-coupling yields (>95%) and stereoselectivity (>99%, *trans*-products) were obtained for the reactions of iodobenzene, 2-chloroiodobenzene, 3-chloroiodobenzene and 3-fluoroiodobenzene with methyl or *n*-butyl acrylate (entries 1–4 and 7). However, relatively lower cross-coupling yields were observed when the aryl iodide bore an electron-donating group (entries 5 and 6), although the excellent stereoselectivity (>99%, *trans*-product) was retained. Similarly, the cross-coupling yield was found to be only about 49% for methyl methacrylate (entry 8) under the same conditions, presumably because of steric effects.

The majority of the heterogeneous catalysts reported in the literature are prepared by the immobilization of the transition metals on particulate solid supports.^[5,6,10] Thus, it is tedious and time-consuming to separate and recycle these particulate heterogeneous catalysts by filtration. Clearly, it is much easier to separate and recycle the Pd/PAN fiber mats owing to the large fiber mat structure. Indeed, the prepared Pd/PAN fiber mats catalyst can be reused six times for the Mizoroki – Heck reaction of iodobenzene and *n*-butyl acrylate. Figure 4 presents the conversion and crosscoupling yields for the recycled Pd/PAN fiber mat catalyst. Figure 4 shows that the catalytic activities of the recycled Pd/PAN fiber mats decreased with the recycle time. Considerable swelling of the recycled PAN mat fibers was observed. For example, the diameter of the six-times-recycled Pd/PAN fiber mats was 425.5 \pm 88.6 nm, which was about twice as large as that of the unused Pd/PAN fiber mats (271.2 \pm 55.3 nm), although there was no significant morphological change in the recycled Pd/PAN fiber mats (Fig. 4). The decrease in the catalytic activities could be attributed to the gradual palladium leaching from the recycled Pd/PAN fiber mats in the polar aqueous solution under microwave heating. This conclusion is consistent with the palladium content decrease in the recycled catalyst, as shown in Table 3.

Density functional theory calculation was used to examine the stability of Pd/PAN fiber mats.^[23,24] For the sake of computational efficiency, propionitrile was used as a simple molecular model for PAN polymer. The basis sets used for calculation are $6-31G^*$ for C, H, O, N and Cl atoms, and the Hay and Wadt with a double-valence basis set (LanI2DZ) for Pd.^[25,26] Figure 5 summarizes the calculation results with polarization functions for Pd[ζ (f) = 1.472].^[27] Interestingly, the chelating energy of PdCl₂ with H₂O was found to be about 30 kJ mol⁻¹ higher than that of PdCl₂ with propionitrile, suggesting that the surface derivatization of PAN fiber mat-supported palladium catalyst.

Conclusions

In the present studies, we prepared the PAN fiber mats as a solid support to immobilize palladium catalyst. The prepared Pd/PAN fiber mats were shown to be an effective and recyclable heterogeneous palladium catalyst for the Mizoroki–Heck cross-coupling of various aryl iodides with acrylates using microwave irradiation at room temperature in aqueous solution. Excellent coupling yields (up to 95%) were obtained for the reactions of iodobenzene, 2-chloroiodobenzene, 3-chloroiodobenzene and 3-fluoroiodobenzene with methyl or *n*-butyl acrylate. Density functional theory calculation showed that the chelating energy of PdCl₂ with H₂O was about 30 kJ mol⁻¹ larger than that of PdCl₂ with propionitrile. Thus the Pd/PAN fiber mats catalyst could be further improved through introduction of strong chelating functional groups into the PAN polymer chains.

Experimental

Materials

All solvents and Chemicals were analytical grade and used without further purification. PdCl₂ was purchased from Shanghai D&R Finechem Co. Ltd. Tetrabutyl ammonium bromide and CTAB were purchased from Shanghai Zhanyun Chemical Company Ltd. Polyacrylonitrile ([η] = 157 ml g⁻¹) was synthesized and purified according to the literature procedures.^[28]

Table 2.	Pd/PAN fiber mats catalyzed Mizoroki-Heck cross-coupling reactions of various aryl iodides with acrylates ^a							
	$R_{1} \longrightarrow X + R_{2} \xrightarrow{Cat.(5 \text{ mol.}\%)/3eq \text{ KOAc}} R_{1} \xrightarrow{-R_{2}} R_{2}$							
Entry	Aryl iodide	Olefin	Time (h)	Conversion ^b (%)	Yield ^b % (<i>trans : cis</i>)			
1	C ₆ H₅I	n-Butyl acrylate	5	96.7	95.8 (99.1 : 0.95)			
2	2-CIC ₆ H ₄ I	n-Butyl acrylate	8	96.0	96.0 (100:0)			
3	3-CIC ₆ H ₄ I	n-Butyl acrylate	8	97.8	96.9 (99.1:0.91)			
4	3-FC ₆ H ₄ I	n-Butyl acrylate	8	95.6	95.1 (99.5 : 0.54)			
5	2-CH ₃ C ₆ H ₄ I	n-Butyl acrylate	8	67.5	67.3 (99.7:0.35)			
6	4-CH ₃ OC ₆ H ₄ I	n-Butyl acrylate	8	75.5	75.3 (99.7:0.31)			
7	C ₆ H ₅ I	Methyl acrylate	8	90.4	90.4 (100:0)			
8	C ₆ H ₅ I	Methyl methacrylate	8	49.1	49.1 (100:0)			

^a Reaction conditions: aryl iodide, 1.0 mmol; olefin, 2.0 mmol; potassium acetate, 3.0 mmol; CTAB, 0.10 mmol; Pd/PAN fiber mats, 0.05 mmol; in 5.0 ml of water solution under microwave irradiation (330 W).

^b GC-MS conversion and yield.



Figure 4. Catalytic activities of the recovered Pd/PAN fiber mats (left) and the SEM images of the six-times-recycled Pd/PAN fiber mats (right). Reaction conditions: iodobenzene, 1.0 mmol; *n*-butyl acrylate, 2.0 mmol; potassium acetate, 3.0 mmol; Pd/PAN fiber mats, 0.05 mmol; 5.0 h in 5.0 ml of water solution; microwave, 330 W. GC-MS conversion and yield.

Table 3. Residual palladium contents in the recovered Pd/PAN fiber mats				
Pd/PAN fiber mats	Residual palladium (%) ^a			
After first application After sixth application	$\begin{array}{c} 92.82 \pm 0.60 \\ 80.89 \pm 0.95 \end{array}$			
^a Determined by ICP-AES analysis.				

Electrospinning of the PdCl₂ and PAN Solution

Different homogeneous solutions were obtained by addition of suitable amounts of PdCl₂ and PAN polymer in DMF solution under gentle magnetically stirring, and electrospinning was carried out on purpose-made equipment.^[28] A polymer solution in a plastic syringe (20 ml) was directly delivered to the tip of the syringe needle (0.8 mm inner diameter) by a micro-infusion pump (WZ-502C, Zhejiang University Medical Instrument Co. Ltd, China)

at a feeding rate of 1.0 ml min⁻¹. The syringe needle was at a distance of 12 cm away from the collector and connected to a high-voltage supply (15 kV; GDW-a, Tianjin Dongwen High-voltage Power Supply Plant, China). A sheet of grounded aluminum foil was used as a collector. The resulting fiber mats were dried under a reduced pressure at room temperature to remove residual solvent.

General Procedure for the Pd/PAN Fiber Mat-catalyzed Cross-coupling Reactions

To a 20 ml reaction flask containing 5.0 ml water with a magnetic stir bar, aromatic iodide (1.0 mmol), acrylate (2.0 mmol), Pd/PAN fiber mats (0.05 mmol) and potassium acetate (3.0 mmol) were added. The resulting mixture was allowed to stir in an oil bath (100 °C) or in a microwave apparatus (330 W, 100 °C, WBFY-205, Henan Gongyi City Yuhua Instrument Company Ltd, China) for 5.0 h. The reaction progress was monitored by TLC and GC/MS analysis. On completion, as the volume of the Pd/PAN fiber mat in the reaction mixture was larger, the reaction mixture was added with 10 ml of water to facilitate the extraction with ethyl



Figure 5. Theoretical calculation result of the chelation of PdCl₂ with water and propionitrile.

acetate three times (3 × 20 ml). The combined organic layer was washed with water and saturated brine, and then dried over anhydrous Na₂SO₄. Solvent was removed under reduced pressure. The residue was purified to afford the cross-coupling product by silica gel chromatography with a mixture of *n*-hexane and ethyl acetate (v/v: 8/1). The spectroscopic data (¹HNMR and GC/MS) and melting points for the cross-coupling products were all consistent with the literature.^[10]

Recycling of the Pd/PAN Fiber Mat Catalyst

The heterogeneous Pd/PAN fiber mats catalyst was filtered after completion, and then washed with water, sodium acetate and ethanol. It was then dried at 30° C for 12 h under reduced pressure.

Characterizations

The quantitative analysis for the cross-coupling products was performed on an Agilent GC/MS instrument with a programmable split/splitless injector (Agilent, GC6890/5975 MSD, USA). The injector-port temperature was set at 270 °C. The oven-temperature program was initially set at 80 $^\circ$ C and ramped to 220 $^\circ$ C at 5.0 $^{\circ}$ C min⁻¹, and maintained at 220 $^{\circ}$ C for 2.0 min. ¹H NMR spectra were recorded in CDCl₃ (Bruker, Avance III 400 MHz, Switzerland) with TMS as internal standard. The morphologies of electrospun fiber mats were recorded with a scanning electron microscope (Jeol, jsm-6360lv, Japan). Samples for SEM were coated with a 2-3 nm layer of Au to make them conductive. The diameters of fibers were determined from the SEM micrographs. The contents of palladium in fresh and recovered Pd/PAN fiber mats were analyzed by ICP-AES. For the ICP-AES, the fresh and recovered Pd/PAN fiber mats were decomposed with HNO3. All of the theoretical calculations were carried out using the Gaussian 03 program.^[29]

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