

Perspective Article

Phenanthroline functionalized polyacrylonitrile fiber with Pd(0) nanoparticles as a highly active catalyst for the Heck reaction

Jian Xiao, Haonan Zhang, Anyaegbu Chima Ejike, Lu Wang, Minli Tao*, Wenqin Zhang

Department of Chemistry, School of Sciences, Collaborative Innovation Center of Chemical Science and Engineering, Tianjin University, Tianjin 300072, PR China



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ABSTRACT

A series of polyacrylonitrile fibers (PANF) functionalized with nitrogen-containing ligands were prepared and then used to synthesize fiber-supported Pd(0) nanoparticle catalysts. The phenanthroline-functionalized PANF with immobilized Pd(0) nanoparticles (PAN_{phen}F-Pd(0)) had the best catalytic activity for the Heck reaction under solvent-free conditions. The PAN_{phen}F-Pd(0) efficiently stabilized the nanoparticles and they were well-dispersed with Pd(0) particle sizes of about 3 nm. The PAN_{phen}F-Pd(0) structure was further characterized by a variety of instrumental methods. A probable mechanism based on the fiber's microenvironment is proposed for the Heck reaction catalyzed by PAN_{phen}F-Pd(0). The PAN_{phen}F-Pd(0) catalyst is easily recovered from the reaction system and can be used up to six times with only a slight decrease in catalytic activity and with low Pd leaching. The PAN_{phen}F-Pd(0) catalyst also has excellent catalytic activity for gram-scale use.

1. Introduction

The Heck reaction is an important method for forming C—C bonds [1], and has been used for the synthesis of many new types of drugs including montelukast (asthma agent), naproxen (anti-inflammatory) [2], eletriptan (antimigraine) [3] and rilpivirine (anti-AIDS) [4]. Many organometallic catalysts have been used to efficiently catalyze Heck reactions, such as compounds containing copper [5], nickel [6,7], cobalt [8,9], and palladium [10–21]. Among them, palladium catalysis are the most efficient and have been widely studied by researchers. However, palladium is expensive and these catalysts are difficult to recycle in homogeneous reaction systems. Additionally, as a heavy metal, palladium is poisonous and can cause serious environmental problems if it is released into nature [22]. From an economical and environmental standpoint, it is of great importance to develop a recyclable palladium catalyst.

Traditionally Pd(0) has played a vital role in catalyzing Heck reactions and the preparation of catalysts with supported Pd(0) particles catalysts has found many applications [23,24]. Various carriers including silica [25], GO [26,27], polymers [28–30], magnetic Fe₃O₄ [31–33], MOFs [34–36], carbon nanotube [37] and composite materials [38–40] have all been used to prepare heterogeneous palladium catalysts. Compared with supported Pd(II) catalysts, these carriers can hold Pd(0) more tightly. Although these heterogeneous catalysts have better

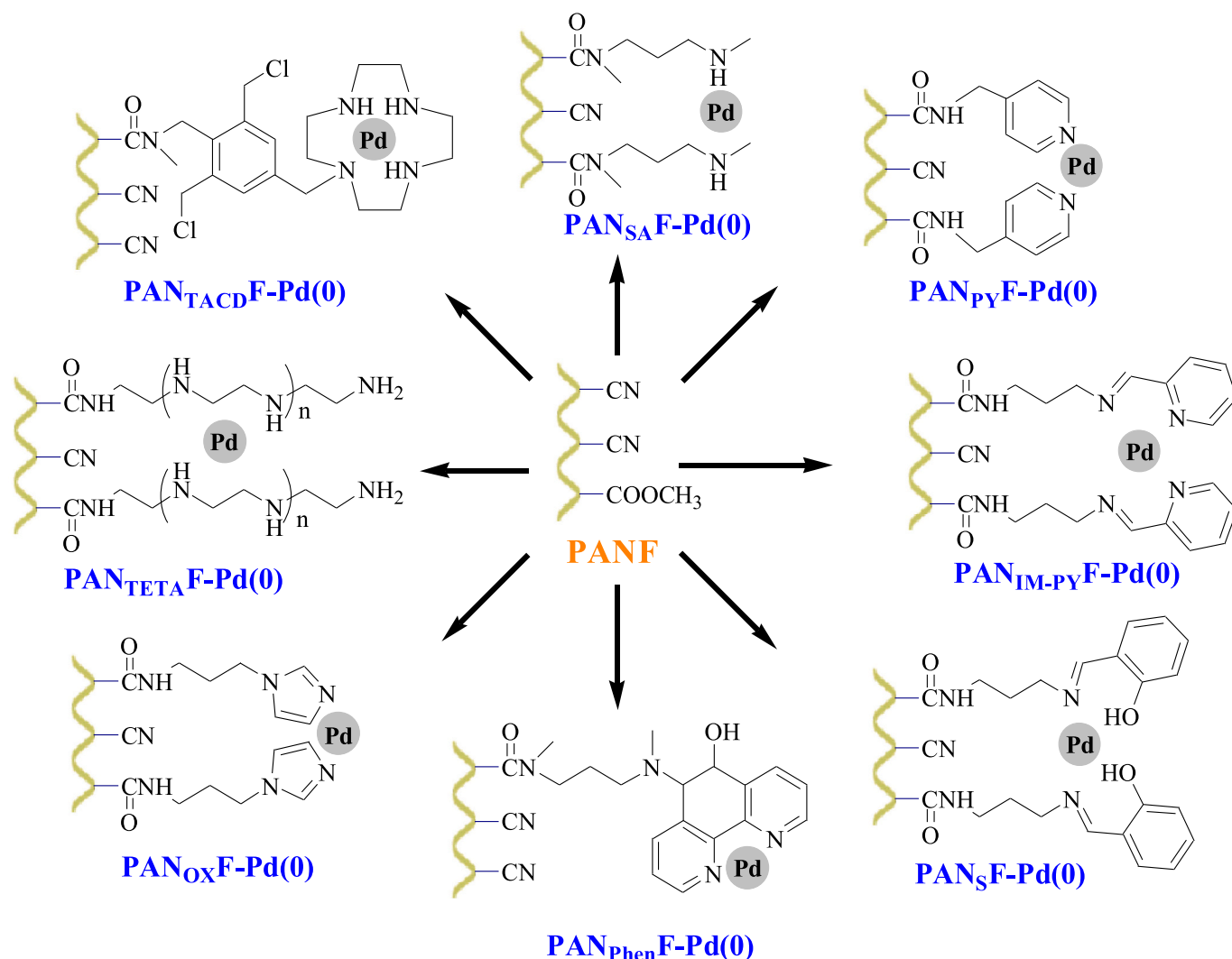
catalytic properties than homogenous catalysts, many of them have chemical stability and poor recyclability. Therefore, preparing improved supports for Pd(0) nanoparticles is a valuable research area.

Polyacrylonitrile fiber (PANF) is a cheap commercially available synthetic fiber that has a soft texture and good mechanical strength [41]. It is made from at least 85% acrylonitrile and a copolymer which produces many cyano groups in the fibers. This makes PANF easy to modify using common reactions. These excellent properties make PANF an ideal carrier for heterogeneous catalysts. In our previous work, many functionalized PANF-catalysts have been designed including PANF-supported acid and base catalysts [42–48], PANF-supported inexpensive metal catalysts [49,50], and PANF-supported phase transfer catalysts [51]. All of these catalysts have excellent catalytic abilities with good recyclability.

Interestingly, it has been shown that carriers containing organic ligands have a very positive impact on the dispersion and stability of Pd(0) nanoparticles and on the catalytic activity of these Pd catalysts [52–58]. Although aza ligands have weaker coordination abilities than phosphine ligands, they are much cheaper than phosphine ligands and can be easily immobilized on PANF [59–62]. Therefore, in this work, a series of PANFs functionalized with aza ligands were prepared using a simple method and then Pd(0) nanoparticles were stabilized on each of these samples (Scheme 1). The catalytic activities of these PANF-Pd(0) nanoparticle catalysts were investigated for the Heck reaction. The

* Corresponding author.

E-mail address: mltao@tju.edu.cn (M. Tao).



Scheme 1. PANF-supported Pd(0) nanoparticle catalysts^[a]

[a] PAN_{SA}F-Pd(0) – secondary amine functionalized PANF with Pd(0) nanoparticles; PAN_{TACD}F-Pd(0) – 1,4,7,10-tetraazacyclododecane functionalized fiber with Pd(0) nanoparticles; PAN_{Py}F-Pd(0) – pyridine functionalized fiber with Pd(0) nanoparticles; PAN_{IM-Py}F-Pd(0) – *o*-pyridyl imino functionalized fiber with Pd(0) nanoparticles; PAN_SF-Pd(0) – salen ligand functionalized fiber with Pd(0) nanoparticles; PAN_{Phen}F-Pd(0) – phenanthroline functionalized fiber with Pd(0) nanoparticles; PAN_{IM}F-Pd(0) – imidazole functionalized fiber with Pd(0) nanoparticles; PAN_{TETA}F-Pd(0) – triethylenetetramine functionalized fiber with Pd(0) nanoparticles.

Table 1
The functionalities of the different functionalized fibers.

Entry	Functionalized fibers	Functionality (mmol/g)	Entry	Functionalized fibers	Functionality (mmol/g)
1	PAN _{SA} F	1.39	10	PAN _{SA} F-Pd(0)	0.29
2	PAN _{Py} F	0.88	11	PAN _{Py} F-Pd(0)	0.28
3	PAN _{IM-Py} F	1.36	12	PAN _{IM-Py} F-Pd(0)	1.18
4	PAN _S F	1.15	13	PAN _S F-Pd(0)	0.63
5	PAN _{Phen} F	1.01	14	PAN _{Phen} F-Pd(0)	0.69
6	PAN _{Ox} F	1.01	15	PAN _{Ox} F-Pd(0)	0.42
7	PAN _{TETA} F	1.21	16	PAN _{TETA} F-Pd(0)	1.02
8	PAN _{TACD} F	0.77	17	PAN _{TACD} F-Pd(0)	0.35
9	PANF-Pd(0)	0.04			

catalysts were characterized and a possible mechanism is proposed.

2. Results and discussion

2.1. Preparation and characterization of PANF-immobilized Pd catalysts

Nine PANF-immobilized Pd(0) nanoparticle catalysts were prepared

by loading different aza ligands onto PANF and then chelating Pd(0) nanoparticles to those ligands (Scheme S1). The amount of aza ligand immobilized on the PANFs was calculated using the formula: functionality = $[w\% / (M \times (1 + w\%))] \times 1000$, where M is the molecular weight of the corresponding aza ligands and w% is the weight gain of the original fiber. The results are presented in **Table 1** (Entries 2–8). The Pd(0) content was measured by inductively coupled plasma optical emission

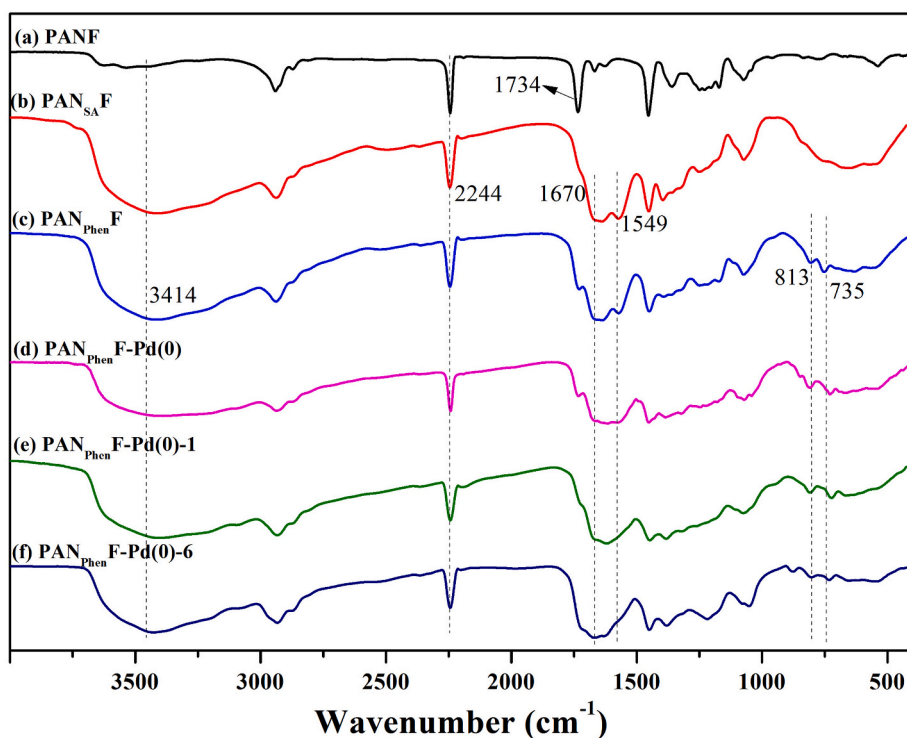


Fig. 1. The FTIR spectra of (a) PANF, (b) PAN_{SAF}, (c) PAN_{PhenF}, (d) PAN_{PhenF}-Pd(0), (e) PAN_{PhenF}-Pd(0)-1, (f) PAN_{PhenF}-Pd(0)-6.

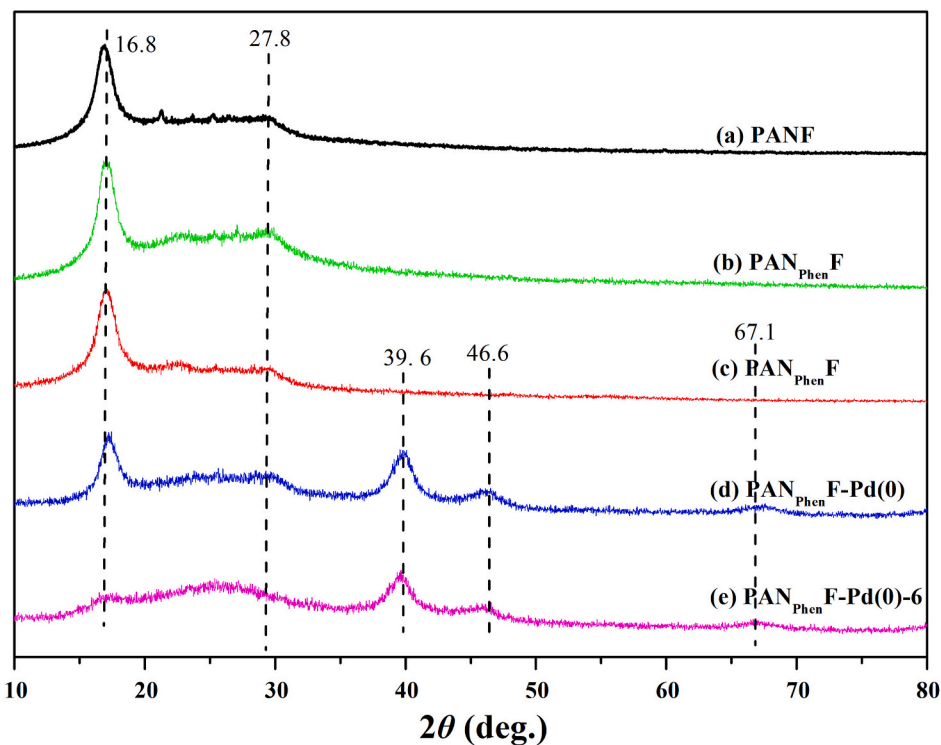


Fig. 2. The XRD spectra of (a) PANF, (b) PAN_{SAF}, (c) PAN_{PhenF}, (d) PAN_{PhenF}-Pd(0) and (e) PAN_{PhenF}-Pd(0)-6.

spectrometry (ICP-OES) and those results are also shown in Table 1 (Entries 9–17). These results show that the Pd(0) nanoparticles were immobilized on all the PANFs functionalized with aza ligands (0.28–1.18 mmol/g) but not on the original PANF.

Fourier transform infrared spectroscopy (FTIR) was used to investigate the structures of the fibers and the FTIR spectra of PANF, PAN_{SAF},

PAN_{PhenF}, PAN_{PhenF}-Pd(0), PAN_{PhenF}-Pd(0)-1 (PAN_{PhenF}-Pd(0) was used for one time) and PAN_{PhenF}-Pd(0)-6 (PAN_{PhenF}-Pd(0) used 6 times) are shown in Fig. 1. The two strong absorption peaks at 2244 and 1734 cm⁻¹ in the original fiber (Fig. 1a) can be attributed to the stretching vibrations of C≡N and C=O (in the methoxycarbonyl), respectively [44]. After the original fiber was modified by *N,N*-dimethyl-1,3-

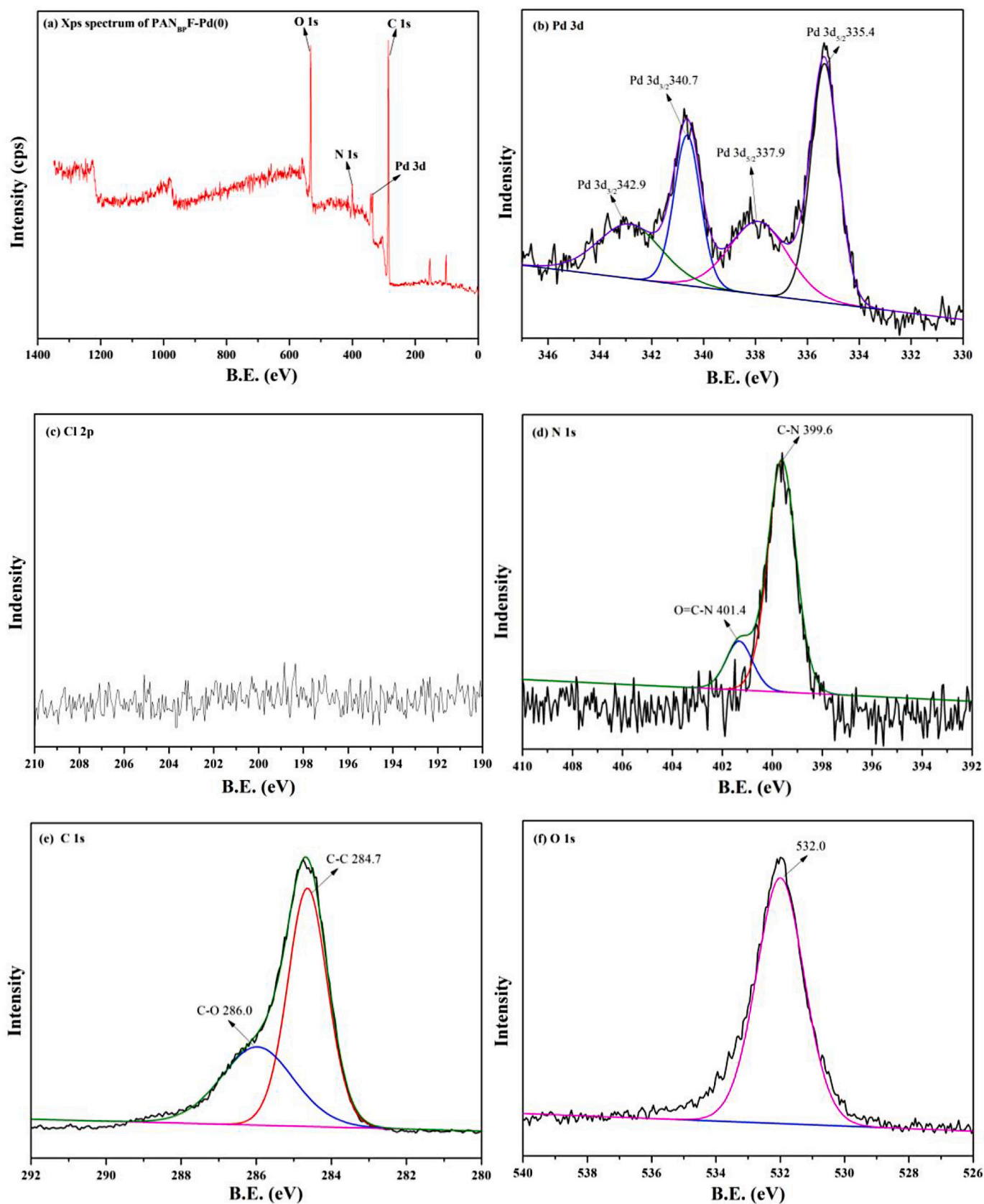


Fig. 3. XPS (a) Survey spectrum of PAN_{phen}F-Pd(0), (b) Pd 3d spectrum of PAN_{phen}F-Pd(0), (c) Cl 2p spectrum of PAN_{phen}F-Pd(0), (d) N 1s spectrum of PAN_{phen}F-Pd(0), (e) C 1s spectrum of PAN_{phen}F-Pd(0) and (f) O 1s spectrum of PAN_{phen}F-Pd(0).

Table 2
The elemental analysis data.

Entry	Fiber	Elemental analysis data		
		C (%)	H (%)	N (%)
1	PANF	66.19	5.98	24.38
2	PAN _{SA} F	58.91	6.65	20.78
3	PAN _{phen} F	60.13	6.45	20.38
4	PAN _{phen} F-Pd(0)	53.25	5.60	17.21
5	PAN _{phen} F-Pd(0)-6	53.49	5.75	17.35

propanediamine (SA), two new peaks at 3414 and 1670 cm^{-1} appear (Fig. 1b). These are due to the stretching vibrations of N—H and C=O (in the amide) respectively [44]. The peak at 1549 cm^{-1} can be attributed to interactions between the C—N stretching and the N—H bending vibrations of C-N-H. The spectrum of PAN_{phen}F has two new peaks at 813 and 735 cm^{-1} , which can be attributed to the deformation vibrations of C=C and the out-of-plane bending vibrations of the aromatic C—H respectively (Fig. 1c) [63]. There are no apparent changes in the spectra of the recycled fibers, indicating that the catalyst have not changed much after being used (Fig. 1d-f).

X-ray diffraction (XRD) was used to determine the crystal structure of the fibers and the XRD patterns of PANF, PAN_{SA}F, PAN_{BA}F, PAN_{BA}F-Pd(0) and PAN_{BA}F-Pd(0)-6 are shown in Fig. 2. The two peaks at 16.8° and 27.8° in PANF (curve a) can be attributed to the (100) and (110) crystallographic planes of the PANF hexagonal lattice [41]. The spectra for PAN_{SA}F and PAN_{BA}F (curves b and c) also contain these peaks indicating the functionalized fibers have the same structure as the unmodified PANF. The catalyst PAN_{BA}F-Pd(0) has a strong diffraction peak at 39.6° and two weak peaks at 46.6° and 67.1° (curve d), which can be attributed to the (111), (200) and (220) facets of palladium, respectively [64,65]. The reused catalysts have the same characteristic Pd diffraction peaks as the unused catalyst which demonstrates that the crystal structures of the Pd(0) nanoparticles remains the same after being used in six catalytic cycles.

X-ray photoelectron spectroscopy (XPS) was used to determine the chemical properties of the surface of PAN_{phen}F-Pd(0) and the results are shown in Fig. 3. The full range XPS spectrum contains a peak due to Pd (Fig. 3a) which proves that Pd is present in the PANF. The Pd 2d spectrum in Fig. 3b contains two strong peaks at 340.7 and 335.4 eV which corresponds to Pd 3d_{3/2} and Pd 3d_{5/2} of Pd(0), respectively [56]. The

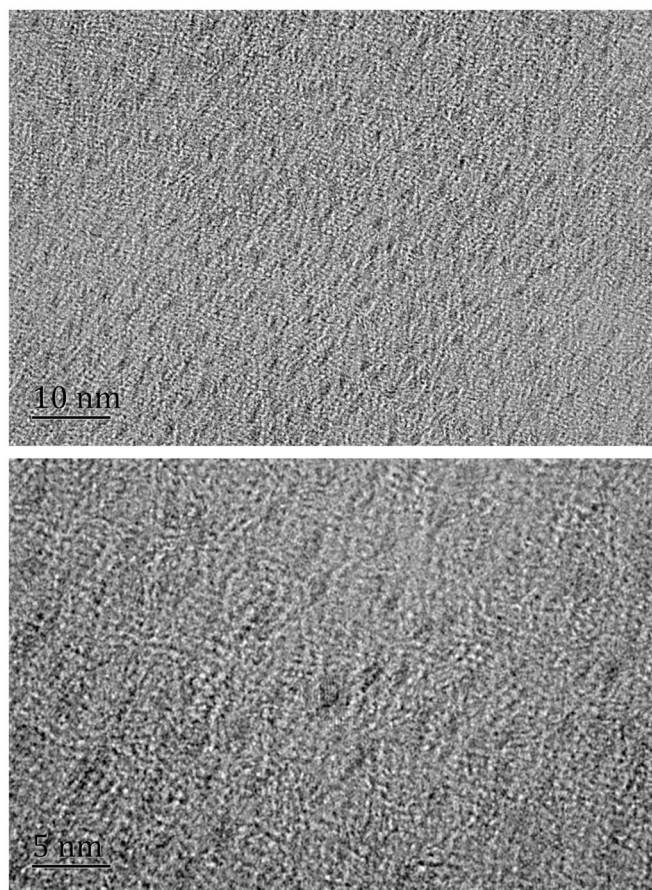


Fig. 5. The TEM images of PAN_{phen}F-Pd(0). Top row 4,000,000 \times and bottom row 8,000,000 \times magnification.

two weak peaks at 342.9 and 337.9 eV can be attributed to Pd 3d_{3/2} and Pd 3d_{5/2} from the residual Pd(II) in the fiber. The Cl 2p spectrum (Fig. 3c) contains no obvious peaks indicating that almost all the PdCl₂ in the fiber was reduced to Pd(0). The N 1s spectra (Fig. 3d) has peaks at

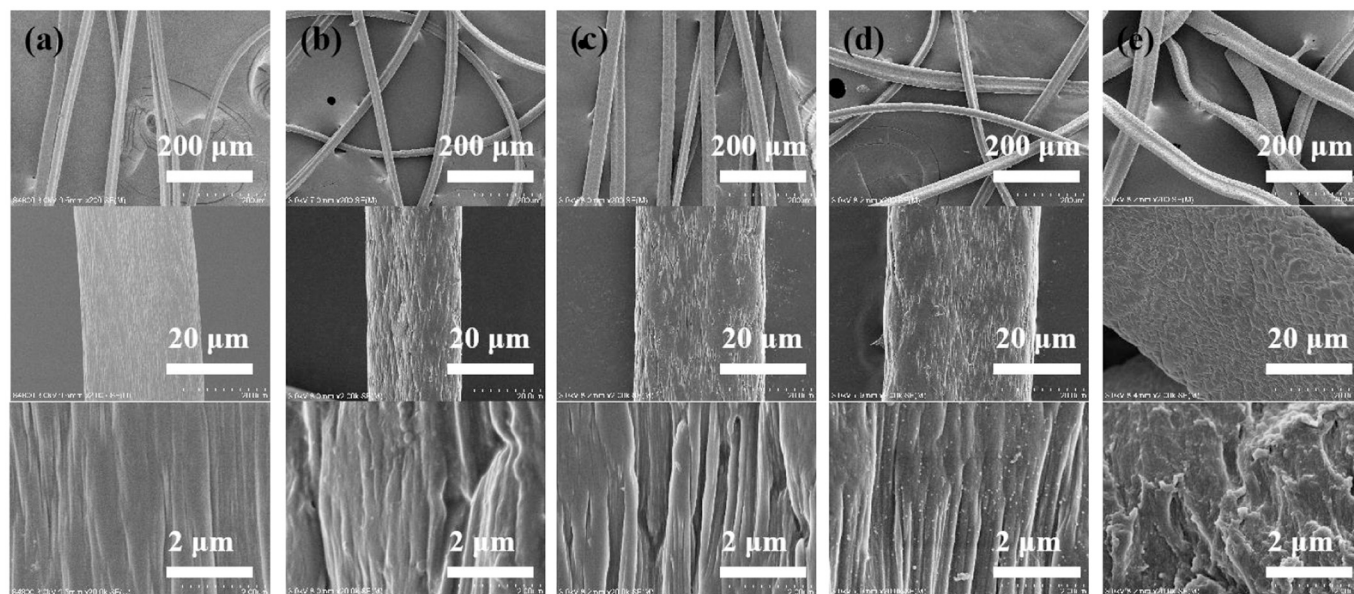


Fig. 4. The SEM images of (a) PANF, (b) PAN_{SA}F, (c) PAN_{phen}F, (d) PAN_{phen}F-Pd(0) and (e) PAN_{phen}F-Pd(0)-6. Top row 200 \times , middle row 2000 \times and bottom row 20,000 \times magnification.

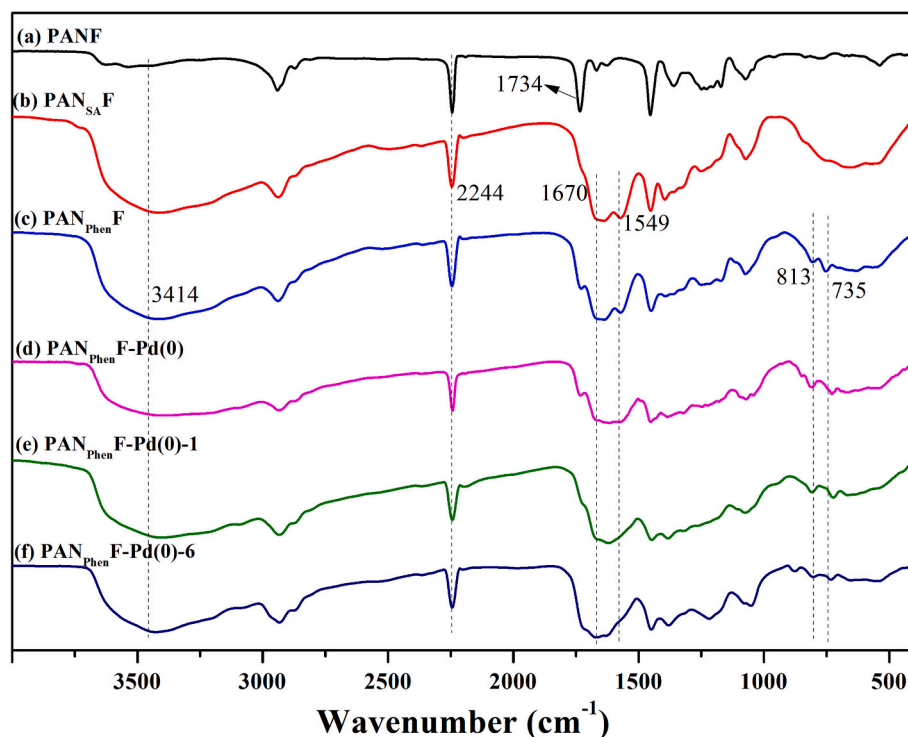


Fig. 6. The thermal stability of (a) PANF, (b) PAN_{SAF}F, (c) PAN_{PhenF} and (d) PAN_{PhenF}-Pd(0).

401.4 and 399.6 eV which can be attributed to the O=C-N and C-N bonds in the functionalized fibers. The C 1s spectrum (Fig. 3e) contains two peaks at 286.0 and 284.7 eV which are due to the C-O and C-C bonds, respectively. Finally the O 1s spectrum (Fig. 3f) has a strong peak at 532.0 eV which is from the C=O, C-O and O-H bonds in PAN_{PhenF}-Pd(0) [44]. These XPS spectra prove the successful preparation of the functionalized fiber with immobilized Pd nanoparticles.

In order to investigate the elemental composition of the fibers, elemental analysis (EA) was performed and the results for PANF, PAN_{SAF}F, PAN_{PhenF}, PAN_{PhenF}-Pd(0) and PAN_{PhenF}-Pd(0)-6 are shown in Table 2. Compared to PANF, PAN_{SAF}F has less C and N and more H (Table 2, entries 1, 2). This is because the immobilized CH₃NHCH₂CH₂CH₂N(CH₃)CO moiety contains less C and N and more H than PANF. The PAN_{PhenF} sample containing an immobilized 5,6-epoxy-5,6-dihydro-[1,10]-phenanthroline moiety has more C and less N and H than PAN_{SAF}F (entry 3) which again corresponds to the chemical makeup of the moiety. When Pd nanoparticles were immobilized on the sample to give PAN_{PhenF}-Pd(0), the amounts of C, H and N all significantly decreased (entry 4). This can be attributed to the increased proportion of palladium. The amounts of C, H and N after use in six catalytic cycles did not change significantly indicating that the Pd(0) nanoparticles in PAN_{PhenF}-Pd(0) remained relatively intact (Table 2, entry 5).

In order to observe the microscopic appearance of the fiber surfaces, scanning electron microscopy (SEM) images of PANF, PAN_{SAF}F, PAN_{PhenF} and PAN_{PhenF}-Pd(0) are shown in Fig. 4. Under a magnification of 2000, it can be seen that PAN_{PhenF} is thicker than PANF and PAN_{PhenF}-Pd(0) is even thicker (a, c and d). This indicates that the fiber is swollen by the solvent and chemical reagents during the modification process. After being used in six catalytic cycles, PAN_{PhenF}-Pd(0)-6 became rougher as seen under 20,000× magnification but no significant damage can be seen at either 200× and 2000× magnification (Fig. 4e). This proves that PAN_{PhenF}-Pd(0) has good tolerance for reuse.

Transmission electron microscopy (TEM) was used to determine the particle size of the palladium nanoparticles in the fibers. The (TEM) images of PAN_{PhenF}-Pd(0) under different magnifications are shown in Fig. 5. The average size of Pd particles was determined under

Table 3

The catalytic activities of different fiber catalysts for the Heck reaction.^{a, b}

Entry	Catalyst	Catalyst loading (mol %)	Temp. (°C)	Time (h)	Yield (%)
1	–	0.5	110	3	N.R. ^c
2	PdCl ₂	0.5	110	3	76
3	PAN _{SAF} F-Pd(0)	0.5	110	3	3
4	PAN _{PyF} -Pd(0)	0.5	110	3	76
5	PAN _{IM-PyF} -Pd(0)	0.5	110	3	86
6	PAN _{SF} -Pd(0)	0.5	110	3	79
7	PAN _{PhenF} -Pd(0)	0.5	110	3	97
8	PAN _{OXF} -Pd(0)	0.5	110	3	74
9	PAN _{TETA} F-Pd(0)	0.5	110	3	80
10	PAN _{TACD} F-Pd(0)	0.5	110	3	73

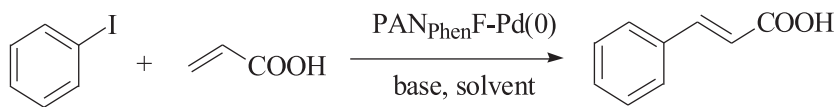
^a General conditions: iodobenzene (1 mmol), acrylic acid (1.5 mmol), N(n-C₄H₉)₃ (1.5 mmol).

^b The yields of the Heck reaction were determined using HPLC with naphthalene as the internal standard. The results are the average of three reaction results.

^c N.R. is the abbreviation for no reaction.

8,000,000× magnification to be about 3 nm. This confirms that the nano-sized Pd(0)-immobilized fiber catalyst was prepared.

The thermal stability of PANF, PAN_{SAF}F, PAN_{PhenF} and PAN_{PhenF}-Pd(0) were tested by thermogravimetric analysis (TGA) and the results are shown in Fig. 6. The functionalized fibers only have a slight mass loss below 200 °C, which is indicative of their excellent thermal stability. Both PAN_{SAF}F and PAN_{PhenF} had higher mass losses than PANF when the temperature was increased from 30 to 670 °C but they retained more mass than PANF when further heated to 800 °C. PAN_{PhenF}-Pd(0) had the

Table 4
Optimization of various parameters for the Heck reaction.^{a, b}


Entry	Solvent	Catalyst loading	Dosage of acrylic acid	Base	Temp. (°C)	Time (h)	Yield (%)	TONs ^c
1	H ₂ O	0.5 mol%	1.5 eq	N(n-C ₄ H ₉) ₃	Reflux	3	3	6
2	DMF	0.5 mol%	1.5 eq	N(n-C ₄ H ₉) ₃	110	3	96	192
3	MeOH	0.5 mol%	1.5 eq	N(n-C ₄ H ₉) ₃	Reflux	3	1	2
4	EtOH	0.5 mol%	1.5 eq	N(n-C ₄ H ₉) ₃	Reflux	3	3	6
5	CH ₃ CN	0.5 mol%	1.5 eq	N(n-C ₄ H ₉) ₃	reflux	3	4	8
6	1,4-dioxane	0.5 mol%	1.5 eq	N(n-C ₄ H ₉) ₃	reflux	3	6	12
7	Cyclohexane	0.5 mol%	1.5 eq	N(n-C ₄ H ₉) ₃	reflux	3	2	4
8	None	0.5 mol%	1.5 eq	N(n-C ₄ H ₉) ₃	110	3	97	323
9	DMF	0.1 mol%	1.5 eq	N(n-C ₄ H ₉) ₃	110	3	96	960
10	None	0.1 mol%	1.5 eq	N(n-C ₄ H ₉) ₃	110	2	89	890
11	None	0.1 mol%	1.5 eq	N(n-C ₄ H ₉) ₃	110	3	97	970
12	None	0.05 mol%	1.5 eq	N(n-C ₄ H ₉) ₃	110	3	26	520
13	None	0.1 mol%	2 eq	N(n-C ₄ H ₉) ₃	110	3	97	970
14	None	0.1 mol%	1.2 eq	N(n-C ₄ H ₉) ₃	110	3	61	610
15	None	0.1 mol%	1.5 eq	N(C ₂ H ₅) ₃	110	3	85	850
16 ^d	None	0.1 mol%	1.5 eq	N(n-C ₄ H ₉) ₃	110	3	97	970

^a General conditions: iodobenzene (1 mmol), base (1.5 mmol).^b The yields of the Heck reaction were determined using HPLC with naphthalene as the internal standard. The results are the average of three reaction results.^c The TON values were calculated by dividing the dosage of iodobenzene by the catalyst loading.^d The dosage of N(n-C₄H₉)₃ is 2 eq.

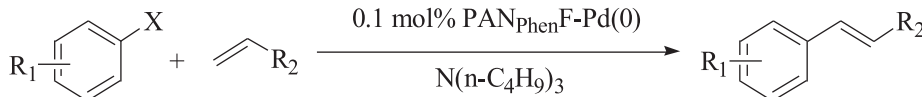
highest mass residue when heated to 800 °C, which can be attributed to the excellent thermal stability of the phenanthroline-Pd(0) complex. These results indicate that PAN_{PhenF}-Pd(0) may be potentially useful for use in heated reactions..

2.2. Catalytic activities of PANF-immobilized Pd(0) nanoparticle catalysts

2.2.1. The catalytic activities of various PANF-catalysts for the Heck reaction

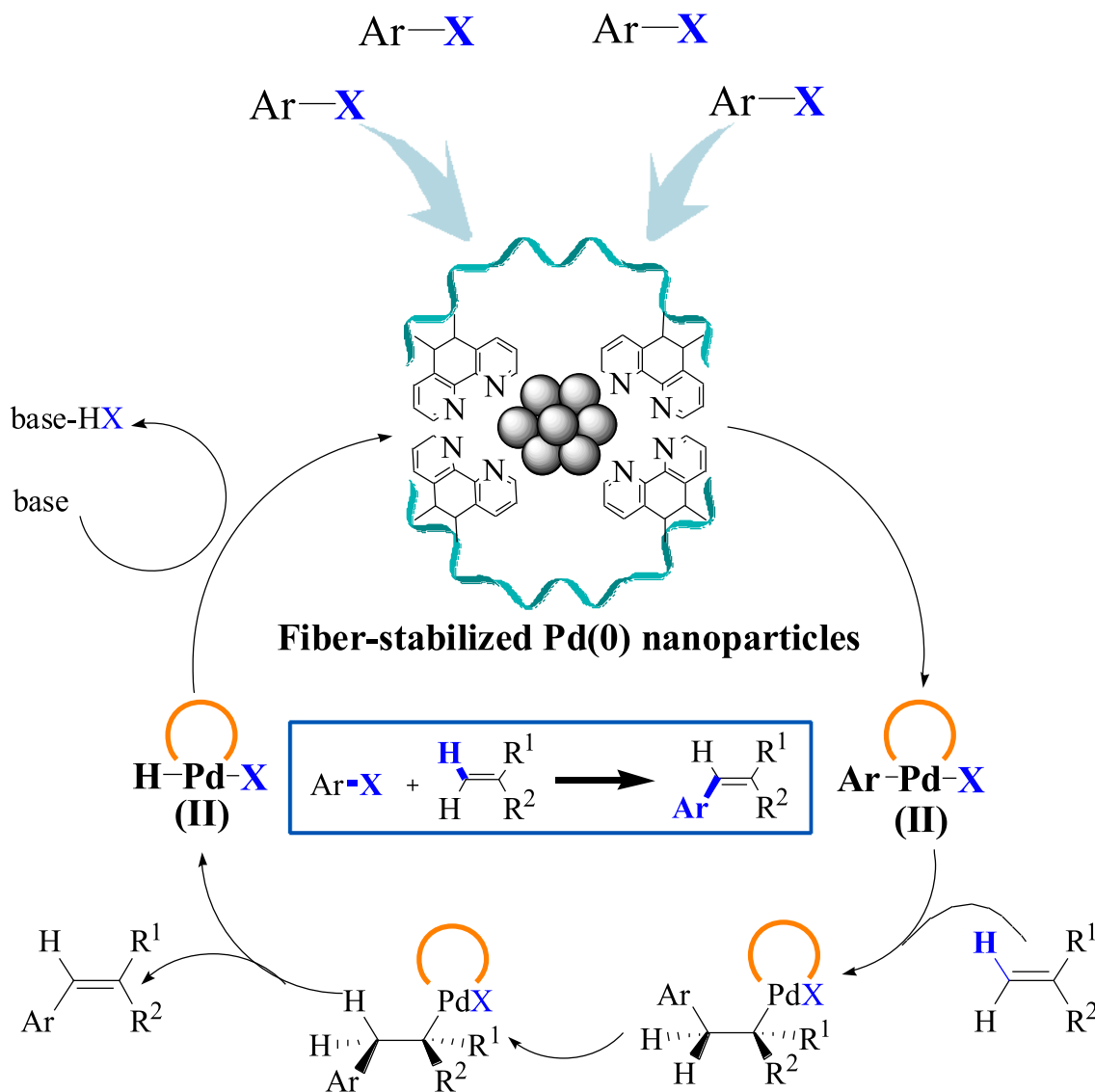
The catalytic activities of the different PANF-supported Pd(0) catalysts for the Heck reaction were investigated using solvent-free conditions and the results are shown in Table 3. The reaction did not proceed

when there was no catalyst (Table 3, entry 1). Using PdCl₂ as the catalyst gave a moderate yield of 76% (entry 2). The different fiber-supported Pd(0) nanoparticle catalysts gave yields between 3% and 99% (entries 3–11) with the highest yield being obtained for PAN_{PhenF}-Pd(0) (entry 7). The differences may be attributed to the different stabilities of the Pd(0) nanoparticles and the different Pd dispersions caused by the various aza ligands. So the TEM image of PAN_{SAF}-Pd(0) has been detected, the result is shown in Fig. S1. Compared with PAN_{PhenF}-Pd(0), it is obviously that Pd(0) nanoparticle was agglomerated and has large particle size (over than 10 nm). The test can verify the effect of ligands on Pd(0) nanoparticle. PAN_{PhenF}-Pd(0) was selected as the optimal catalyst and used for further study.

Table 5
PAN_{PhenF}-Pd(0)-catalyzed Heck reaction of various substrates.^{a, b, c}


Entry	X	R ₁	R ₂	Dosage of catalyst (mol%)	T (°C)	Time (h)	Product	Yield (%)
1	I	H	-COOH	0.1	110	3	1a	92
2	I	3-CN	-COOH	0.1	110	3	1b	90
3	I	4-CN	-COOH	0.1	110	3	1c	93
4	I	3-CF ₃	-COOH	0.1	110	3	1d	95
5	I	4-NO ₂	-COOH	0.1	110	3	1e	95
6	I	4-Br	-COOH	0.1	110	3	1f	94
7	I	3-CH ₃	-COOH	0.1	120	3	1g	91
8	I	H	-Ph	0.1	110/120	3/1	1h	43/90
9	I	H	-COOMe	0.1	110	3	1i	91
10	I	H	-COO(CH ₂) ₃ CH ₃	0.1	110	2	1j	99
11	Br	H	-COOH	1.0	140	24	1a	23
12	Br	3-CN	-COOH	0.2	140	5	1b	92
13	Br	4-CN	-COOH	0.2	140	4.5	1c	94
14	Br	4-NO ₂	-COOH	0.2/0.5	140	1/0.5	1e	97/96
15	Br	3-CH ₃	-COOH	0.2	140	5	1g	8
16	Cl	H	-COOH	1.0	140	5	1a	N.R.
17	Cl	4-NO ₂	-COOH	1.0	140	5	1e	N.R.

^a General conditions: halogenated aromatics (1 mmol), olefins (1.5 mmol), N(n-C₄H₉)₃ (1.5 mmol), PAN_{PhenF}-Pd(0) catalyst (0.1 mol%), 110 °C.^b Isolated yield.^c Reaction temperature 120 °C.



Scheme 2. Possible mechanism for PAN_{phen}F-Pd(0) catalyzed Heck reaction.

2.2.2. The optimization of Heck reaction

The conditions for the Heck reaction catalyzed by PAN_{phen}F-Pd(0) were optimized and the results shown in Table 4. First a variety of solvents were tested and the only “solvents” that gave good results were DMF and solvent-free conditions (Table 4, entries 1–9). Both N(*n*-C₄H₉)₃ and N(C₂H₅)₃ were tested as bases and with no solvent N(*n*-C₄H₉)₃ gave a higher yield (entries 11, 15). Next different catalyst loadings were evaluated and the highest TON (970) was obtained for a catalyst loading of 0.1 mol% (entry 8, 11 and 12). A longer reaction time (3 h versus 2 h) is more conducive to the reaction (entries 10, 11). Additionally, various dosages of acrylic acid were investigated and the optimal dosage is 1.5 eq (entries 12–14). Finally, different dosage of N(*n*-C₄H₉)₃ were explored, and the optimal dosage is 1.5 eq (entries 11 and 16). In summary, the highest yield and TON for the PAN_{phen}F-Pd(0) catalyst in the Heck reaction were achieved with 0.1 mol% catalyst loading, 1.5 eq alkenes, 1.5 eq base, no solvent, 110 °C and 3 h (entry 11).

2.3. Heck reaction catalyzed by PAN_{phen}F-Pd(0)

In order to determine the substrate scope for PAN_{phen}F-Pd(0) in the Heck reaction, several halogenated aromatics and olefins were tested

and the results are shown in Table 5. These results show that the reactivity of different halogenated aromatics is: iodo aromatics (entries 1 and 5) > brominated aromatics (entries 11 and 14) > chlorinated aromatics (entries 16 and 17). In all cases, iodoaromatics were produced with satisfactory isolated yields (90%–99%) (entries 1–10) under solvent-free condition. Generally, the halogenated aromatics with electron-withdrawing groups (entries 2–6, 12–14) had higher yields than the substrates with electron-donating groups (entries 7 and 15). Compared with other olefins (entries 1, 9 and 10), styrene (entry 8) with a large steric hindrance had a low yield at 110 °C (43%), but when the reaction temperature was increased to 120 °C, a satisfactory yield of 90% was obtained. PAN_{phen}F-Pd(0) can also selectively catalyze iodo-benzenes that also contain another low-activity bromine atom with a selectivity close to 100% under mild reaction conditions (entry 6). In summary, PAN_{phen}F-Pd(0) has many advantages as a catalyst such as low catalyst loading (0.1 mol%), short reaction times (1–5 h) and a wide range of substrate applicability.

2.4. Possible mechanism for PAN_{phen}F-Pd(0) catalyzed Heck reaction

A possible catalytic mechanism based on the fiber microenvironment is shown in Scheme 2. When no solvent is present, the concentration of

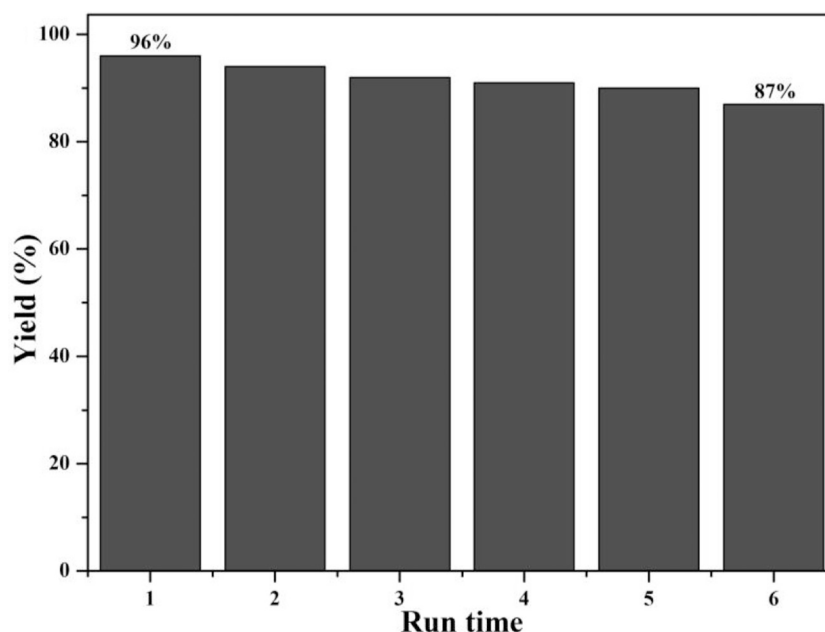
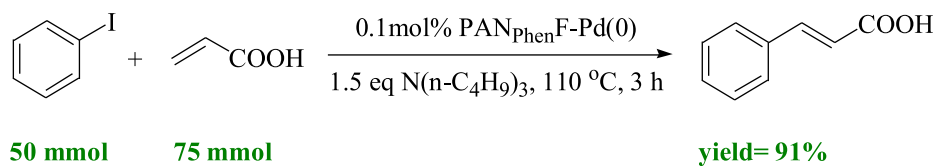


Fig. 7. Reusability test of PAN_{phen}F-Pd(0). Reaction conditions: iodobenzene (10 mmol), acrylic acid (15 mmol), 15 mmol N(n-C₄H₉)₃, 20 mL DMF, 0.1 mol% PAN_{phen}F-Pd(0), 110 °C. The yield was determined using HPLC.



Scheme 3. Gram-scale experiment of Heck reaction catalyzed by PAN_{phen}F-Pd(0).

reactant is high. The organic amine and the Brønsted acid react to generate an ionic liquid, which facilitates the reaction. The ionic liquid endows the reaction system with a high concentration of anions and cations, which can stabilize the reaction intermediates and increase the activity of the reaction. When the high-polarity solvent DMF was used, the fiber catalyst swelled causing the substrates and the Pd(0) nanoparticles to make good contact so the reaction proceed smoothly and a high yield was obtained.

2.5. Reusability and gram-scale experiments

Reusability is a vital factor in evaluating the performance of the catalyst. After each use, the fiber catalyst was taken out by tweezers, washed with ethyl acetate and dried. The fiber was then used for the next catalytic cycle. The PAN_{phen}F-Pd(0) catalyst was reused for six reaction cycles and the results are shown in Fig. 7. With each successive cycle the yield decreased slightly from 96% to 87% after six uses. The reused fiber has been characterized to determine if there were structural or chemical changes in the fiber (Figs. 1, 2 and 4; Table 2).

Then ICP-MS was used to compare the amounts of Pd in PAN_{phen}F-Pd

Table 6

Comparison of the Heck reaction of iodobenzene and acrylic acid with different catalyst systems.

Entry	Catalyst	Catalyst Amount	Solvent	T (°C)	Time (h)	Yield (%)	Reuse times ^a	Ref.	TON
1	AOFs-Pd(0)	0.8 mol%	DMF	110	3	95.5	3	[66]	119
2	Pd (PNODAM-5)	2 mol%	heptane	100	22	96	3	[67]	49.5
3	Fe ₃ O ₄ @PCA/Pd(0)-b-PEG	0.05 mol%	H ₂ O	90	2	98	10	[68]	1960
4	PdNPore	2 mol%	MeOH	80	18	94	5	[69]	47
5	Pd/APS-MIL-101	0.93 wt%	DMF	120	1	about 97	–	[70]	–
6	Pd-MPTAT-1	0.97 mol%	H ₂ O:EtOH = 1:1	reflux	6	95	2	[71]	98
7	Fe ₃ O ₄ /SiO ₂ /HPG-NCs	3 mol%	DMF	140	12	81	4	[72]	27
8	Pd-SP-CMP	0.6 mol%	1,4-dioxane/H ₂ O = 1:1	80	12	99	–	[73]	165
9	(Fe ₃ O ₄ @PUNP) magnetic microgel	0.1 mol%	H ₂ O	reflux	12	96	–	[74]	960
10	(Pd@IPN)	0.0229 mol%	H ₂ O	100	12	96	11	[75]	1266
11 ^b	SBA-15/PrSO ₃ Pd	0.5 mol%	toluene	80	4	95	9	[76]	190
12 ^b	TiO ₂ @Pd NPs	1 mol%	DMF	140	10	92	–	[77]	93
13	PAN _{phen} F-Pd(0)	0.1 mol%	Solvent-free or DMF	110	3	97	5	This work	970

^a Reuse times – number of times the catalyst can be reused before the yield drops 6%.

^b The reactants are iodobenzene and butyl acrylate.

(O) and PAN_{phen}F-Pd(O)-6. The values were 0.69 mmol/g and 0.49 mmol/g respectively so there was a decrease of Pd of 29% indicating that the fiber supported palladium catalyst still had many of its catalytic sites after reuse. All of these results indicate that PAN_{phen}F-Pd(O) has good catalytic stability for repeated use.

To demonstrate the practical applicability of this method for larger-scale use, the Heck reaction catalyzed by PAN_{phen}F-Pd(O) was carried out on a gram-scale and the results are shown in Scheme 3. The dosage of substrates were increased to 50 eq. The main product cinnamic acid was washed with water and recrystallized in petroleum ether to give the final product in 91% isolated yield.

2.6. Comparison of other catalysts for the Heck reaction

The results for PAN_{phen}F-Pd(O) in the Heck reaction are compared with results previously obtained with other catalysts in Table 6. Compared with other heterogeneous catalysts, PAN_{phen}F-Pd(O) shows good catalytic activity and remarkable overall performance. The Heck reaction catalyzed by PAN_{phen}F-Pd(O) requires only a slight excess of olefin (1.5 eq) and base (1.5 eq), which is better than all the other catalyst systems recorded below. Although some catalytic systems have reaction temperatures less than 80 °C, the corresponding reactions generally needed a longer reaction time or had lower yields (entries 2, 4, 6, 8–11). Additionally, only a small amount of PAN_{phen}F-Pd(O) is needed to efficiently catalyze the Heck reaction under mild conditions with a short time, which is better than most the other fiber catalysts (entries 1–2, 4–8 and 10). Although two catalysts have higher yields (entries 3 and 9), this aza functionalized fiber-supported Pd(O) nanoparticle catalyst exhibits high activity and may provide ideas for researchers who are interested in studying the effect of ligand functionalized materials on the stability and activity of palladium nanoparticles. Finally PAN_{phen}F-Pd(O) is easily recovered and can be reused up to six times giving the catalyst good potential for practical applications.

3. Conclusions

Various aza-ligand-functionalized PANFs with supported Pd(O) nanoparticles were prepared using a simple method and they were then used to catalyze the Heck reaction. Different ligands had different abilities to stabilize the palladium nanoparticles. Among all the prepared catalysts, PAN_{phen}F-Pd(O) had the best catalytic activity which can be attributed to its excellent dispersion of the palladium nanoparticles which was verified by TEM. The palladium nanoparticles in PAN_{phen}F-Pd(O) were as small as 3 nm. Under mild reaction conditions, PAN_{phen}F-Pd(O) efficiently catalyzed the Heck reaction with a broad range of substrates giving isolated yields of 90–99%. A catalytic mechanism based on the fiber microenvironment has been proposed. The PAN_{phen}F-Pd(O) catalyst can be used six times in the Heck reaction with only a slight decrease (9%) in catalytic activity. The catalyst can also be used on the gram-scale (50 eq) giving a yield of 91%. Thus the PAN_{phen}F-Pd(O) catalyst has excellent recyclability and good potential for practical applications.

Author statement

Xiao Jian: Conceptualization, Data curation, Formal analysis, Writing - original draft, Writing - review & editing. **Haonan Zhang, Anyaegbu Chima Ejike and Lu Wang:** Writing - review & editing. **Minli Tao:** Conceptualization, Writing - review & editing, Funding acquisition. **Wenqin Zhang:** Conceptualization, Writing - review & editing.

Declaration of Competing Interest

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.reactfunctpolym.2021.104843>.

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