

Fiber-Palladium Complex as Highly Active and Recyclable Catalyst for Heck Reaction in Air[†]

ZHICHUAN WU, QI WU, MENG CHEN and TINGXIAN TAO*

College of Biochemical Engineering, Anhui Polytechnic University, Wuhu 241000, P.R. China

*Corresponding author: Tel: +86 553 2871346; E-mail: tingxiantao@yahoo.cn

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A new amidoxime fibers-palladium catalyst was synthesized by the "coordination-reduction" reaction between the amidoxime groups in fibers and Pd(II) ions. The morphology, structure and composition of the as-obtained complexes were characterized by X-ray diffraction and X-ray photoelectron spectroscopy. The results indicated that the Pd(II) ions were reduced to Pd(0) nanospheres *in situ* with the diameter of about 100 nm and there were coordination interactions between the Pd nanoparticles and the amidoxime fibers. The prepared catalyst demonstrated high activities for Heck coupling reaction of aryl iodine. During the reaction, the fibers serve as both the ligand and the support. In all cases, the coupling reactions proceeded efficiently without inert atmosphere. The catalyst can be easily recycled for at least eight times.

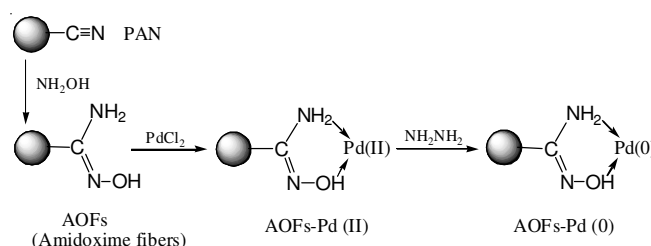
Key Words: Amidoxime fibers, Fibers-palladium complex, Palladium nanoparticles, Heterogeneous catalyst, Heck reaction.

INTRODUCTION

Palladium-catalyzed coupling of olefins with aryl or vinyl halides, known as Heck reaction, is an important and powerful reaction for the formation of C-C bond in organic synthesis¹⁻³. Many documents have reported that carboxylic acids⁴, esters⁵, amides⁶, aldehydes⁷ and ketones⁸ can be prepared by Heck reaction. In general, these reactions were homogeneously catalyzed by Pd-catalysts such as PdCl₂, Pd(OAc)₂ etc. But they suffer from drawbacks of difficult separation and limited lifetime of catalysts^{9,10}. In addition, phosphine or amine ligands are often necessary and the reactions are often sensitive to oxygen in these cases. To overcome these problems, heterogeneous palladium catalysts supported on polymers^{11,12} and inorganic solids¹³⁻¹⁵ were tentatively employed. Herein we report a new amidoxime fibers-palladium complex (Pd/AOFs) catalyst for Heck reaction. The amidoxime fibers can be easily obtained by the reaction of polyacrylonitrile (PAN) and NH₂OH. The -NH₂ and -OH in amidoxime fibers have high coordinating ability with metal cations^{16,17}.

Scheme-I shows the synthesis route of Pd/AOFs. The results of the Pd/AOFs catalyzed Heck reaction showed that the reaction could be carried out under mild conditions without protection of inert atmosphere. In addition, the catalyst is environment-friendly due to no use of phosphine or amine ligands and the catalyst can be easily recycled for at least eight times.

All these make this protocol an efficient and meaningful alternative for palladium-catalyzed Heck reactions.



Scheme-I: Synthesis route of the amidoxime fibers supported palladium complex

EXPERIMENTAL

PdCl₂, NH₂OH, HCl, 50 wt. % NH₂NH₂ aqueous solution and Na₂CO₃ were purchased from the Beijing Chemical Reagents Co. (Beijing, China). The PAN fibers were provided by the Jilin Carbon Co. Ltd., (Jilin, China).

Preparation of the catalysts: The PAN fibers (1.0 g) were first immersed in 100 mL 1 mol/L NH₂OH aqueous solution at 70 °C for 1.5 h to introduce -NH₂ and -OH groups onto the fiber surface¹⁸. The obtained fibers were termed as amidoxime fibers (AOFs). Subsequently, the amidoxime fibers were rinsed with distilled water and then immersed in 100 mL 7.05 mmol/L PdCl₂ aqueous solution at about 25 °C for 1 h to allow

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amidoxime fibers to coordinate with Pd²⁺ ions and the colour of fibers turned from colourless into yellow/orange at this stage. After being rinsed with distilled water again, these yellow/orange fibers were further immersed in 50 mL 0.344 mol/L aqueous solution of NH₂NH₂ at room temperature for 0.5 h. The products were rinsed with distilled water and dried, then black fibers of Pd/AOFs were obtained. Pd content of Pd/AOFs was measured by ICP, it is 0.6 mmol/g.

Typical procedure for the Heck reaction: In a typical reaction, 9 mmol aryl halides, 15 mmol acrylic acid, 30 mmol tributylamine and 6 mL DMF were added into a round-bottomed flask with 0.8 mol % Pd/AOFs as catalyst. The reaction was initiated at a certain temperature controlled by silicon oil bath. After completion of the reaction, the reaction mixture was cooled to room temperature. Then 50 mL of 0.38 mol/L Na₂CO₃ aqueous solution was added into the mixture under stirring for 15 min and Pd/AOFs was separated from the mixture by filtration. 15 mL 2 mol/L HCl was added in the filtrate to obtain the white precipitate, which was filtered and washed with distilled water (3 × 10 mL) and then dried to obtain the desired products.

Characterizations: Elements on the surface of samples were analyzed by X-ray photoelectron spectroscopy using a Thermo Escalab 250 X-ray photoelectron spectroscopy operating at the AlK_α radiation of 1486.6 eV. A Hitachi S-4800 field-emission scanning electron microscope was employed to examine the morphologies of samples at an accelerating voltage of 15 kV. X-ray diffraction patterns were acquired from a Bruker AXS-D8X X-ray diffractometer. A rotating X-ray generator (40 kW, 50 mA) with CuK_α radiation (λ = 1.54 Å) was used in the XRD experiments; and the XRD profiles were recorded from 10 to 80° at the scanning speed of 6° min⁻¹. The Pd(II) content of Pd-AOFs surface was obtained by IRIS INTREPID II XSP. IR measurements were performed on a WQF-300 Fourier transform infrared spectrometer (Beijing Ruili Analytical Instruments, Beijing, China). The FTIR spectra were acquired by scanning the specimens with a resolution of 4 cm⁻¹ for 64 times in the wavenumber range of 4000-400 cm⁻¹. ¹H NMR spectra were recorded on a Bruker AC-300 NMR spectrometer in CDCl₃ with tetramethylsilane as internal standards.

RESULTS AND DISCUSSION

Characterization of the catalyst: The X-ray photoelectron spectroscopy spectrum of Pd(0)/AOFs had the spin-orbital splitting peaks of Pd3d_{5/2} at the binding energy of 337.8 eV (Table-1). Compared to the standard value of Pd and PdCl₂ 3d_{5/2} at 335.4 eV and 338.3, the binding energy of Pd3d_{5/2} in Pd(0)/AOFs was higher than Pd and lower than PdCl₂, indicating that there is electronic interaction between Pd(0) and the amidoxime groups. Additionally, the binding energy values of N 1s in amidoxime fibers were 399.3 eV and 400.5 eV, corresponding to the two different nitrogen atoms in amidoxime groups¹⁹. However, the two values in Pd(0)/AOFs were 399.5 eV and 401.3 eV. The binding energy values of O 1s in amidoxime fibers was 532.4 eV, while the corresponding values were 532.2 eV and 534.0 eV in Pd(0)/AOFs. These distinguishable differences suggested that there existed coordinations between amidoxime groups and palladium nanoparticles²⁰.

TABLE-1
DATA OF XPS FOR Pd, PdCl₂, AOFs and Pd /AOFs

Samples	Pd _{3d_{5/2}} /eV	N _{1s} /eV	O _{1s} /eV
Pd	335.4		
PdCl ₂	338.0		
AOFs		399.3/400.5	532.4
Pd/AOFs	337.8	399.5/401.2	532.2/534.0

Fig. 1 showed the XRD diffraction peaks of amidoxime fibers and Pd/AOFs. Fig. 1(a) showed the diffraction peaks centered at 18.6° of amidoxime fibers. Fig. 1(b) revealed the XRD pattern of Pd/AOFs. Only the characteristic peaks of Pd(0) centered at the 2θ angles of 40.1°, 46.7° and 67.8° were observed except amidoxime fibers, which indicating that Pd(II) was reduced to palladium particles on the surface of amidoxime fibers by hydrazine hydrate and the product has a high degree of crystallinity.

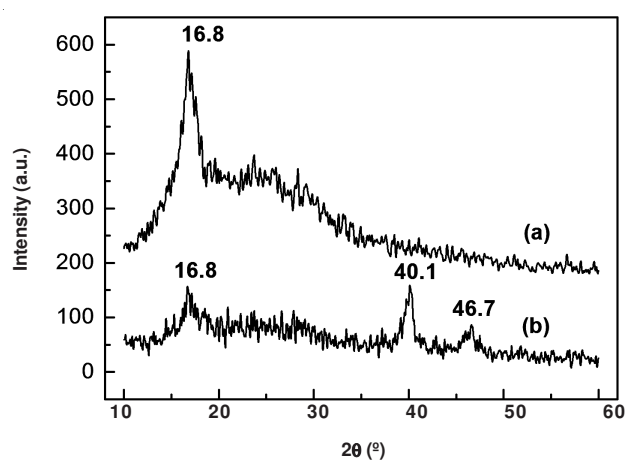


Fig. 1. XRD patterns of amidoxime fibers (a) and AOFs-Pd(0) (b)

Fig. 2 showed the SEM images of Pd/AOFs under different magnifications. It could be seen clearly that Pd particles had uniform distribution on the surface of amidoxime fibers and the average size of the Pd particles was about 100 nm.

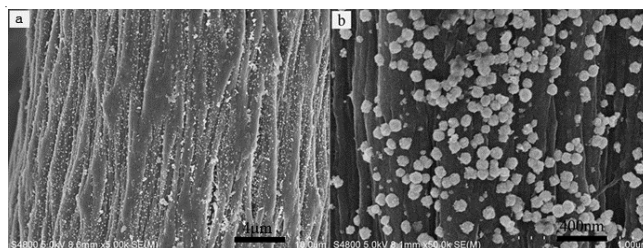


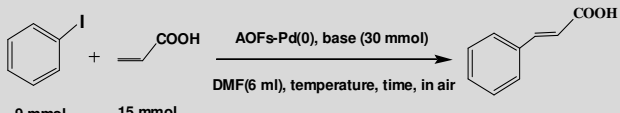
Fig. 2. SEM images of Pd/AOFs catalyst under different magnifications: (a) Low magnification; (b) high magnification.

Catalytic performances of the catalyst: Most of the Heck reactions were carried out in inert atmosphere at relatively high temperature²¹. Herein, Pd/AOFs catalyst was employed in Heck reaction efficiently in the air.

Table-2 (entry 1-6) showed the Heck reaction of iodobenzene with acrylic acid at different temperature. It can be seen that the reaction temperature has some influences on the catalytic performance. Using DMF as solvent and tributylamine as base. The Heck reaction could be carried out

at low temperature (80 °C) with the yield of 74.9 %. With the temperature increased from 80 to 110 °C, the yield increased and when the temperature was above 110 °C, the yield had hardly any change. So 110 °C was selected as the optimum reaction temperature.

TABLE-2
EFFECTS OF THE REACTION TEMPERATURE, CATALYST AMOUNT AND BASE ON CATALYTIC PERFORMANCE OF HECK REACTION OF IODOBENZENE WITH ACRYLIC ACID



Entry	Temperature (°C)	AOFs-Pd(0) (mol /%)	Base	Time (h)	Yield ^a (%)
1	80	0.2	Bu ₃ N	7	74.9
2	90	0.2	Bu ₃ N	5	78.4
3	100	0.2	Bu ₃ N	5	79.4
4	110	0.2	Bu ₃ N	5	82.1
5	120	0.2	Bu ₃ N	5	82.0
6	130	0.2	Bu ₃ N	5	82.1
7	110	0.1	Bu ₃ N	5	57.8
8	110	0.2	Bu ₃ N	5	82.1
9	110	0.4	Bu ₃ N	3	85.5
10	110	0.8	Bu ₃ N	3	90.3
11	110	1.6	Bu ₃ N	3	90.2
12	110	3.4	Bu ₃ N	3	90.3
13	110	0.8	Et ₃ N	3	95.5
14	110	0.8	Bu ₃ N	3	92.5
15	110	0.8	NaHCO ₃	3	2.3
16	110	0.8	KOH	3	1.8
17	110	0.8	Na ₂ CO ₃	3	2.5

^aIsolated yield based on the iodobenzene used

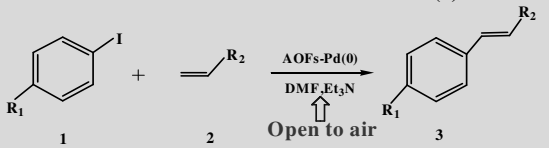
It is easy to understand that the amount of catalyst can play an important role in the catalytic performances. So we explored the reaction of iodobenzene with acrylic acid catalyzed with different amount of Pd/AOFs ranging from 0.1 to 3.4 mol % at 110 °C. The results are listed in Table-2 (entry 7-12). It could be obviously seen that the employed amount of catalyst has significant effect on this transformation. The reaction could proceed efficiently even with trace of the catalyst (entry 7, 0.1 mol %, yield 57.8 %). Increasing the amount of catalyst led to higher yield and shorter reaction time. The yield had almost no changes when the employed amount of Pd catalyst was increased to a certain value (> 0.8 mol %).

From the classical catalytic mechanism for Heck reaction of aryl halides with conjugated alkenes, it can be seen that the active site of palladium catalyst is Pd(0)²². During the reaction process, acid (HX) may be produced from the formal exchange of a hydrogen atom with an aryl or vinyl group²³, so alkaline reagents were desired to eliminate HX in time. We also investigated the influence of different alkaline reagents on Heck reaction, including tributylamine, triethylamine, sodium bicarbonate, potassium hydroxide and sodium carbonate. The corresponding yield was 95.5 %, 92.5 %, 2.3 %, 1.8 %, 2.5 %, respectively (Table-2, entry 13-17). It could be seen that organic bases is preferred, since inorganic bases (sodium bicarbonate, potassium hydroxide, sodium carbonate) are insoluble and thus can not participate in the reaction very well.

In order to experiment the catalytic activity of the AOFs-Pd(0) catalyst to other substrates, some interrelated experiments

had been employed. Results of these reactions were presented in Table-3. The identifications of compounds **3a-f** were fully established by the m.p., FT-IR and ¹H NMR. **3a**: m.p.: 133-134 °C. FT-IR (KBr, ν_{\max} , cm⁻¹): 3064, 3027, 1681, 1623, 1573, 1495, 1453, 978, 772, 708. ¹H NMR(300 MHz, CDCl₃): δ = 6.50 (d, 1H, J = 15.9 Hz), 7.84 (d, 1H, J = 15.9 Hz), 7.26-7.58 (m, 5H). **3b**: m.p.: 124-126 °C. FT-IR (KBr, ν_{\max} , cm⁻¹): 3076, 3057, 3019, 1654, 1598, 1577, 1496, 963, 764, 691. ¹H NMR (300 MHz, CDCl₃): δ = 7.13 (s, 2H), 7.28-7.55(m, 10H). **3c**: m.p.: 289-290 °C. FT-IR (KBr, ν_{\max} , cm⁻¹): 3110, 3050, 1688, 1630, 1604, 1595, 1525, 987, 840, 757. ¹H NMR (300 MHz, DMSO): δ = 6.71 (d, 1H, J = 16.0 Hz), 7.66 (d, 1H, J = 16.0 Hz), 7.93 (d, 2H, J = 7.08 Hz), 8.19 (d, 2H, J = 7.98 Hz), 12.64 (s, 1H). **3d**: m.p.: 157-159 °C. FT-IR(KBr, ν_{\max} , cm⁻¹): 3077, 3025, 1678, 1632, 1598, 1515, 971, 767, 694. ¹H NMR (300 MHz, CDCl₃): δ = 7.18 (d, 1H, J = 16.2 Hz), 7.31 (d, 1H, J = 15.8 Hz), 7.34-8.38 (m, 9H). **3e**: m.p.: 172-174 °C. FT-IR (KBr, ν_{\max} , cm⁻¹): 2973, 2938, 1682, 1624, 1598, 1510, 971, 827, 773. ¹H NMR(300 MHz, CDCl₃): δ = 3.86 (s, 3H), 6.36 (d, 1H, J = 15.9 Hz), 7.78 (d, 1H, J = 15.9 Hz), 6.94 (d, 2H, J = 8.25 Hz), 7.51 (d, 2H, J = 8.22Hz). **3f**: m.p.: 138-139 °C. FT-IR (KBr, ν_{\max} , cm⁻¹): 2962, 2935, 1686, 1598, 1566, 1515, 969, 815, 751. ¹H NMR (300 MHz, CDCl₃): δ = 3.84 (s, 3H), 6.90-7.52 (m, 11H). It can be seen from the table that the Heck reaction of acrylic acid or styrene with aryl iodides could be carried out efficiently with relatively higher yield than aryl bromides or aryl chlorides even at lower temperature. Neither electron-donating group nor electron-withdrawing group on aryl iodides has effect on the yield of the Heck reaction of aryl iodides. While the group on aryl bromides or aryl chlorides has much effect on the yield. By the way, all the reactions afforded exclusively trans products based on ¹H NMR analysis.

TABLE-3
HECK REACTION OF ARYL HALIDES WITH CONJUGATED ALKENES CATALYZED BY AOFs-Pd(0)



Entry ^a	X	R ₁	R ₂	Product ^b	T (°C)	t (h)	Yield ^c (%)
1	I	H	CO ₂ H	3a	110	3	95.5
2	I	H	Ph	3b	90	3	89
3	I	NO ₂	CO ₂ H	3c	110	7	93.7
4	I	NO ₂	Ph	3d	90	3	89.3
5	I	OCH ₃	CO ₂ H	3e	110	7	95.7
6	I	OCH ₃	Ph	3f	90	3	89.9

^aAll reactions were carried out with aryl halides (9 mmol), conjugated alkenes (15 mmol), Et₃N (30 mmol), AOFs-Pd(0) (0.8 mol %) and DMF (6 mL) in the air. ^bAll products were characterized by m.p., FT-IR and ¹H NMR. ^cIsolated yield based on the iodobenzene used

Recycling of the catalyst: The catalyst can be easily separated from the reaction mixture just by filtration during the work-up procedure. Eight recycles were carried out and the results were summarized in Table-4. It could be seen that the catalytic activities of AOFs-Pd(0) were almost unchanged

TABLE-4
ACTIVITY OF AOFs-Pd(0) AND THE EFFECT OF RECYCLES ON
THE ARYLATION OF ACRYLIC ACID WITH IODOBENZENE^a

Catalyst	Time (h)	Yield (% ^b)
Fresh catalyst	3	95.5
1 th recycle	3	95.5
2 th recycle	3	95.4
3 th recycle	3	89.5
4 th recycle	5	88.7
5 th recycle	5	86.3
6 th recycle	5	84.1
7 th recycle	5	82.8
8 th recycle	5	80.3

^aAll reactions were carried out with iodobenzene (9 mmol), acrylic acid (15 mmol), Et₃N (30 mmol), AOFs-Pd(0) (0.8 mol %) and DMF (6 mL) at 110 °C in the air. ^bIsolated yield

after second recycles. In the subsequent recycles, the catalytic performance of AOFs-Pd(0) decreased a little due to a small amount of Pd leaching^{19,20}. While even after eight recycles the reaction yield could also be 80.3 %. These can be explained that amidoxime groups had a strong complexing ability, which can formed a stable chelation with Pd.

Conclusion

In summary, AOFs-Pd(0) catalysts have been prepared and exhibit high activity for the Heck reaction of aryl iodides with conjugated alkenes without inert atmosphere. Low amount usage of palladium catalyst is required to perform the Heck reaction of aryl iodides. The catalyst can be easily separated from the reaction mixtures just by filtration and can be reused for at least eight times. It could be considered as an effective alternative heterogeneous catalyst for Heck reaction.

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