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Polymer (fiber)-supported palladium catalyst containing imidazolinyl rings and its application to the Heck reaction

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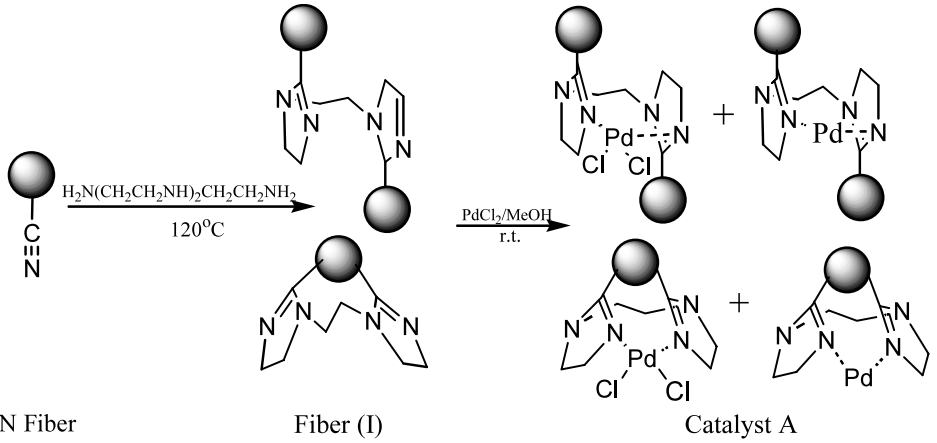
Abstract—A polymer (fiber)-supported palladium catalyst was synthesized simply from commercially available polyacrylonitrile(PAN) fiber. Its high activity and selectivity for Heck reactions were measured; its activity remained unchanged after being recycled 20 times.

Polymer-supported palladium reagents have been used extensively as important catalysts in organic synthesis since Trost and Teranishi reported their application as catalysts for the formation of carbon–carbon bonds in 1978.[1] Since then, polymer-supported palladium reagents have been used in numerous kinds of synthetic reactions with success and continue to attract much attention.[2] Although they have many advantages such as being clean and recyclable, many based on resins are phosphine-containing.[2a,b,3] Quite recently, Colacot reported Suzuki reactions promoted successfully by 'Fibercats' at room temperature.[4] In this paper we report a simple synthesis of a fiber supported palladium catalyst and its application to Heck reactions.

The following considerations prompted us to choose PAN fiber as a polymer support for our experiments. Firstly, this fiber has a larger surface area than a common resin. Secondly, the nitrile group in PAN can be easily converted to imidazoline, which facilitates coordination with palladium. Moreover, the commercially available PAN materials are somewhat cheaper than most other resins.

Scheme 1 shows the synthetic pathway to polymer-supported palladium catalyst A. This heterogeneous catalyst can be easily prepared from the commercially available PAN fiber. The grafting reaction with triethylenetetramine ($H_2N(CH_2CH_2NH)_2CH_2CH_2NH_2$)



Scheme 1.

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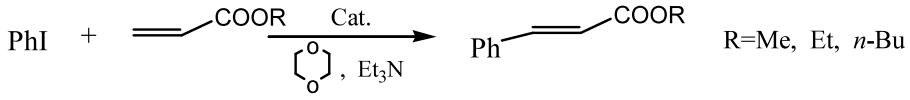

Scheme 2.

leads to the formation of imidazoline rings (Fiber I), subsequent coordination with palladium dichloride producing the palladium complex with imidazoline rings attached to the PAN backbone (Scheme 1).

The fabric palladium catalyst was characterized by elemental analysis, IR, SEM and XPS. The strong absorption at 2243 cm^{-1} indicating the presence of the nitrile group in the PAN was weak both in the fiber (I) and in the catalyst A. The absorption at 1645 cm^{-1}, corresponding to the imine groups appeared strongly in fiber (I), and shifted to 1662 cm^{-1} in catalyst A. From analysis of the surface using Scanning Electron Microscopy (SEM), we concluded that the surface of catalyst A changed significantly from ditch shape to nearly planar after reaction, and that the palladium components had dispersed on the planar surface. The XPS results show that the valencies of palladium on the fiber were Pd(II) and Pd(0); their $3d_{5/2}$ and $3d_{3/2}$ binding energies were 338.10, 337.15 and 342.30, 340.95 eV, respectively. The mechanical properties were measured on a material test instrument (Instron 4465). The Tenacity at Break of catalyst A was 2.7 CN/Dtex, 80% compared to the original 3.4 CN/Dtex of PAN.

It is well known that the commercial PAN fiber is not pure polyacrylonitrile. It contains copolymer and other additives, which make it easy for the fiber to be dyed and also enhance its stability. So, for our purposes, the coordinating ability of PAN fiber with palladium dichloride was measured. The results indicated that nitrile groups do not coordinate with Pd even under forcing conditions (refluxing in methanol for 2 days). Such results are different from those mentioned in Sherrington's reports.[5]

For the purpose of finding out which was the best catalyst or the Heck reaction, the activities (Scheme 2) of three types of palladium complex containing heterocyclic rings were examined. The results are listed in Table 1.

From Table 1, it can be seen that excellent conversions could be achieved when catalysts A and C were used (entries 1 and 3), but the activity of B was very low (entry 2). These results indicate that the reactive moiety in both catalysts A and C was a palladium complex involving imidazoline.

The results of Heck reactions promoted by catalyst A, listed in Table 2, showed: (1) The reaction did not have

Table 1. The activities of different Pd-containing catalysts[a]

Entry	Catalyst[b]	Pd in catalyst (mmol/g)	Pd used in Heck reaction (mmol)	Isolated yield[c] (%)
1	A	0.576	1%	98
2	B	3.01	2%	8
3	C	3.10	1%	100

[a] ArI: 1.0 mmol, solvent: 1,4-dioxane, base: Et_3N, temperature: 100°C, time: 1 h, R = Me.
[b] A-fiber containing palladium and imidazoline complex; B-complex obtained from the reaction of triethylenetetramine with $PdCl_2$ (2:1, mole ratio); C-complex obtained from the reaction of imidazoline with $PdCl_2$ (2:1, mole ratio).
[c] Isolated yields based on PhI.

Table 2. The results of Heck reactions catalyzed by catalyst A

Entry	PhI (mmol)	R	Cat. (mmol)	Base	Solvent	Time (h)	Yield[a] (%)	TONs[c]
1	1	Et	0.01	Et_3N	Dioxane	1	97	
2	1	Et	0.01	Et_3N	Dioxane	0.15	25	
3	1	Et	0.01	Et_3N	Dioxane	0.5	89	
4	1	Et	0.01	Na_2CO_3	Dioxane	2	72	
5	1	Et	0.01	Et_3N	Toluene	2	81	
6	1	Et	0.01	Et_3N	Benzene	3	76	
7	100	Et	0.003	Et_3N	Dioxane	130	95	31500
8	10	Me	0.001	Et_3N	Dioxane	12	92	9240
9	10	Me	0.01	Et_3N	Dioxane	2	99[b]	990
10	1	Bu	0.01	Et_3N	Dioxane	1	94	
11	1	Bu	0.01	Et_3N	Dioxane	2	100	
12	100	Bu	0.003	Et_3N	Dioxane	92	94	31233

[a] Isolated yields based on PhI.
[b] The procedure was repeated 20 times, and the catalyst showed no loss of activity after recycling 20 times.
[c] Turnover numbers.

an induction period (entries 2 and 3), because part of Pd(II) had changed into Pd(0), which was confirmed by XPS determination. (2) Addition of base was necessary (entries 1 and 4). The Heck reaction with no additional base, but using the excess basic groups on the fiber (for example, the imidazoline) was attempted, but the result were unpredictable, probably because the catalyst became coated with the salt formed. (3) The best turnover numbers (TONs) were 31,500 for a single run (entry 7). The catalyst can be reused at least 20 times without any loss of activity. The products obtained were *trans*, as determined by ^{1}H NMR spectroscopy, which is different from that reported by Bhalchandra, Bhanage and Masahik Arai.[6]

When chlorobenzene was used as a substrate, only a trace of product was obtained, even under pressure. Reaction of bromobenzene or *p*-nitrochlorobenzene with methyl acrylate using catalyst A under the same reaction conditions (Table 2, entry 9), gave yields of 47 and 8%, respectively.

In summary, we have described the synthesis of a polymer (fiber)-supported palladium catalyst and its catalytic activity in Heck reactions. The fiber catalyst can be recycled more than 20 times without any loss of activity or selectivity.[7]

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7. Typical synthetic procedure: Into a solution of triethylenetetramine (5 g) in glycol (50 mL), PAN fiber (1.0 g, 3.33 dtex, 65 mm, Kingshan Co. Ltd, Shanghai) was immersed at 120°C for 2 h. After the mixture had cooled to room temperature, the fiber was recovered by filtration, then washed with H_2O, immersed in H_2O (100 mL) for at least 30 min, and filtered. This procedure was repeated until the pH value of the H_2O washing was 7, which ensured complete removal of the amine and any soluble materials from the fiber. The fiber was then dried at 60°C in vacuo. It became yellow and contained 1.72 mmol/g imidazoline. The fiber (0.1 g) was immersed in saturated $PdCl_2$/methanol solution (ca. 100 mL) at room temperature under argon and in the dark for 2 days. When the reaction was complete, the color of the methanol solution of palladium dichloride changed from red–brown to pale brown as a result of palladium(II) loss to the fiber. After the coordination reaction, the fiber was extracted with methanol for at least 24 h at room temperature to remove any palladium complex that was not chemically bonded to the fiber. The fiber was deep-brown in color and contained 0.576 mmol/g palladium after drying in vacuo.