Journal of Catalysis 262 (2009) 287–293

Contents lists available at ScienceDirect

Journal of Catalysis

www.elsevier.com/locate/jcat

Palladium nanoparticles supported on polyvinylpyridine: Catalytic activity in Heck-type reactions and XPS structural studies

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ARTICLE INFO

Article history:
Received 5 September 2008
Revised 29 December 2008
Accepted 5 January 2009
Available online 3 February 2009

Keywords:
Heck reaction
Palladium
Polyvinylpyridine
Metal vapour synthesis
X-ray photoelectron spectroscopy

ABSTRACT

Palladium nanoparticles, obtained by metal vapour synthesis (MVS), were deposited on cross-linked polyvinylpyridine. The Pd/PVPy system showed high catalytic activity in the Heck C–C coupling reaction of iodo- and bromo-arenes (iodobenzene, bromobenzene, *p*-nitrobromobenzene, *p*-bromoacetophenone, *p*-(methoxy)bromobenzene) with alkyl acrylates (methyl acrylate, *n*-butyl acrylate, ethylhexyl *trans*-3-(4-methoxyphenyl)acrylate) at 100 °C–175 °C working under nitrogen atmosphere as well as in air. The catalyst is stable and the leaching of metal in solution is very low. When reused, the recovered Pd/PVPy maintains the catalytic activity of the pristine material. XPS structural studies performed on the starting catalyst as well as on the recovered one indicate the presence of a interaction between the basic nitrogen of the pyridine present in the polymer and the metal.

1. Introduction

The palladium-catalyzed coupling of olefins with aryl or vinyl halides, known as the Heck reaction [1], is one of the most important reactions for the formation of C–C bonds in organic synthesis, from both the research and industrial points of view [2,3]. It enables the functionalization of sp^2 olefinic carbon atoms with a wide range of aryl and vinyl substrates in a single step under mild conditions. Homogeneous catalytic systems for the Heck reaction are generally palladium salts or organo–metallic complexes in the presence of additional ligands, such as phosphines, which prevent the formation of catalytically inactive "palladium black" [2,4]. However, the homogeneous systems present difficulties associated with the limited reusability and the removal of homogeneous materials from the reaction mixture [5]. For these reasons, there has recently been increasing interest, from both economic and environmental points of view, in the development of heterogeneous phosphine-free palladium catalysts which can be recovered from the reaction mixture by simple filtration and subsequently reused. Lately, many solid systems containing supported palladium have been studied with emphasis on the role of the procedure for the preparation of the catalyst and the kind of support (carbon, zeolite, silica, polymers, etc.) [6]. Unfortunately, in many cases, the supported systems leach palladium under the reaction conditions leading to highly active soluble palladium species. Only a few examples of leach-free heterogeneous palladium systems have been reported; they include palladium salts on zeolites [7], whose behaviour depends on the catalyst pre-treatment and on the base and solvent used, and palladium nanoparticles deposited on a particular layered double hydroxide [8] or on suitable functionalized zeolites containing primary amino [9] and SH [10] groups.

Recently [11] we reported the preparation of palladium catalysts by deposition of palladium nanoparticles, prepared by metal vapour synthesis (MVS) [12], on a commercial polyvinylpyridine crosslinked with divinylbenzene (PVPy). This system showed appreciable catalytic activity in the Heck reaction using aryl iodide and methyl acrylate as model substrates with an important contribution to the overall catalytic activity from supported palladium species. In this context it was emphasized that PVPy, thanks to its affinity with palladium, could be a very interesting catalytic support to obtain leach-free catalysts in Heck reaction. In extension of these interesting preliminary results, we report here an improved method to prepare palladium on PVPy by MVS and a more comprehensive study of its catalytic activity in the Heck reaction with a wide range of halide substrates. Moreover, in order to better understand the nature of the interaction between palladium and PVPy, a study of the structural features performed by X-Ray Photoelectron Spectroscopy (XPS) is reported.

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0021-9517/$ – see front matter
doi:10.1016/j.jcat.2009.01.005

2. Experimental

2.1. Materials and apparatus

All operations involving the MVS products were performed under a dry argon atmosphere. The co-condensation of palladium and the appropriate solvent was carried out in a static reactor as previously described [11,12]. The solvated Pd atom solutions were worked up under argon with the use of standard Schlenk techniques. The amount of palladium in the solutions was determined by atomic absorption spectrometry (AAS) in an electrochemically heated graphite furnace with a Perkin–Elmer 4100ZL instrument. The limit of detection (lod) calculated for palladium was 2 ppb. Solvents were purified by conventional methods, distilled and stored under argon. Aryl halides, alkyl acrylates, K_2CO_3, $CsCO_3$ were used as received from Aldrich. Triethylamine and tri-*n*-propylamine (from Aldrich) were distilled and stored over KOH pellets before use. The GLC analyses were performed on a Perkin–Elmer Auto System gas chromatograph, equipped with a flame ionization detector (FID), using a SiO_2 column (BP-1, 12 m × 0.3 mm, 0.25 μm) and helium as carrier gas. ^1H- and ^{13}C-NMR spectra were measured on Varian Gemini 200 spectrometer at 200 and 50.3 MHz, respectively, using chloroform-*d* as solvent; chemical shifts are relative to internal $Si(CH_3)_4$. XPS was performed on an instrument of our own design and construction, consisting of a preparation and an analysis UHV chamber, equipped with a 150 mm mean radius hemispherical electron analyser with a four-element lens system with a 16-channel detector giving a total instrumental resolution of 1.0 eV as measured at the Ag $3d_{5/2}$ core level. Mg$K\alpha$ non-monochromatised X-ray radiation ($h\nu = 1253.6$ eV) was used for acquiring core level spectra of all samples (C 1s, Pd 3d, O 1s and N 1s). The energies were referenced to the C 1s signal of the aromatic C atoms having a binding energy BE = 284.70 eV. Atomic ratios were calculated from peak intensities by using Scofield's cross section values and calculated λ factors [13]. Curve-fitting analysis of the C 1s, Pd 3d, O 1s and N 1s spectra was performed using Voigt profiles as fitting functions, after subtraction of a Shirley-type background [14].

2.2. Preparation of palladium catalysts

2.2.1. Preparation of the solvated Pd atoms

In a typical experiment, Pd vapour, generated at 10^{-4} Bar by resistive heating of the metal (500 mg) in an alumina-coated tungsten crucible, was co-condensed at liquid nitrogen temperature with a 1:1 mixture of mesitylene (30 ml) and 1-hexene (30 ml) in a glass reactor described elsewhere [11,12]. The reactor chamber was heated to the melting point of the solid matrix (−40 °C), and the resulting red-brown solution was siphoned and handled at low temperature (−30/−40 °C) with the Schlenk tube technique. For AAS, the metal-containing mesitylene/1-hexene solution (1 ml) was heated over a heating plate in a porcelain crucible, in the presence of *aqua regia* (2 ml), four times and the solid residue was dissolved in 0.5 M aqueous HCl. The palladium content of the solvated metal solution was 2.8 mg/ml.

2.2.2. Preparation of palladium on polyvinylpyridine, Pd/PVPy (1 wt% Pd)

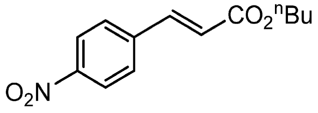
The mesitylene-1-hexene Pd atom solution (36 ml, 101 mg Pd) was added to a suspension of PVPy (10 g) in mesitylene (40 ml). The mixture was stirred for 12 h at room temperature. The colourless solution was removed and the light-brown solid was washed with pentane and dried under reduced pressure. The metal content of the Pd on PVPy catalyst (1 wt% Pd) was determined by AAS analysis, as reported in Section 2.2.1.

2.3. Catalytic reactions

2.3.1. Heck reaction between phenyl halide derivatives and alkyl acrylates to substituted trans-cinnamates: general procedure

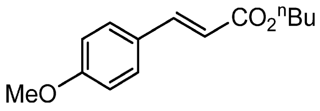
1-Methyl-2-pyrrolidinone (NMP) (9 ml), alkyl acrylate (10 mmol), phenyl halide derivatives (5 mmol), base (5 mmol) and 53 mg of Pd/PVPy catalyst (containing 5×10^{-3} mg atom of Pd) were introduced under argon atmosphere into a 25-ml round-bottomed, two-necked flask equipped with a stirring magnetic bar, a bubble condenser, and a silicon stopper. The reaction mixture was magnetically stirred at the required temperature (see Table 1, Section 3.2). When needed, small samples of the reaction mixture were taken from the stoppered side neck. For GC analysis the samples were treated with either water or 0.5 M aqueous HCl. The organic products were then extracted with diethyl ether, dried over anhydrous sodium sulfate and analyzed by GLC. The coupling product was purified by column chromatography (silica, solvent: *n*-hexane/ethylacetate). The reaction was interrupted at the time reported in Table 1 (Section 3.2).

Trans-4-nitrocinnamic acid *n*-butyl ester:



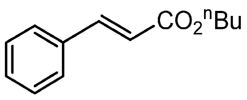
^1H NMR ($CDCl_3$, 200 MHz, ppm): δ 8.18 (d, 2H, $J = 8.8$ Hz), 7.65 (d, 1H, $J = 16.4$ Hz), 7.65 (d, 2H, $J = 8.8$ Hz), 6.50 (d, 1H, $J = 16.0$ Hz), 4.18 (t, 2H, $J = 6.7$ Hz), 1.65 (quint, 2H, $J = 5.4$ Hz), 1.42 (sextet, 2H, $J = 7.5$ Hz), 0.92 (q, 3H, $J = 7.3$ Hz); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm): δ 165.9, 148.4, 141.4, 140.5, 128.5, 124.0, 122.5, 64.8, 30.6, 19.1, 13.6; GC-MS (EI) m/z (%): 249 (M^+, 100).

Trans-4-methoxylcinnamic acid *n*-butyl ester:



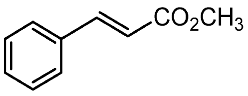
^1H NMR ($CDCl_3$, 200 MHz, ppm): δ 7.61 (d, 1H, $J = 16.0$ Hz), 7.45 (d, 2H, $J = 8.7$ Hz), 6.87 (d, 2H, $J = 8.8$ Hz), 6.28 (d, 1H, $J = 15.9$ Hz), 4.18 (t, 2H, $J = 6.8$ Hz), 3.80 (s, 3H), 1.66 (quint, 2H, $J = 5.8$ Hz), 1.41 (sextet, 2H, $J = 7.6$ Hz), 0.94 (t, 3H, $J = 7.3$ Hz); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm): δ 167.3, 161.3, 144.1, 129.6, 127.2, 115.8, 114.3, 64.2, 55.3, 30.8, 19.2, 13.7; GC-MS (EI) m/z (%): 234 (M^+, 100).

Trans-cinnamic acid *n*-butyl ester:

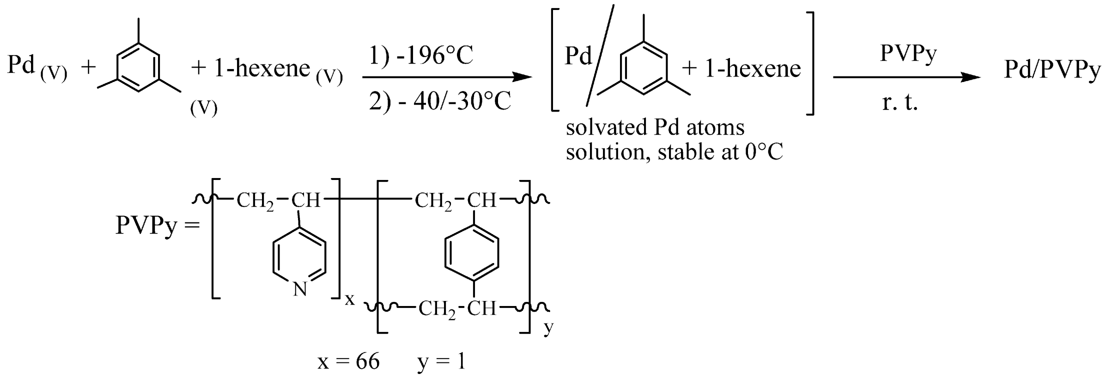


^1H NMR ($CDCl_3$, 200 MHz, ppm): δ 7.67 (d, 1H, $J = 16.0$ Hz), 7.49–7.52 (m, 2H), 7.34–7.37 (m, 3H), 6.42 (d, 1H, $J = 16.0$ Hz), 4.20 (t, 2H, $J = 6.7$ Hz), 1.69 (quint, 2H, $J = 7.2$ Hz), 1.44 (sextet, 2H, $J = 7.5$ Hz), 0.95 (t, 3H, $J = 7.4$ Hz); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm): δ 167.0, 144.5, 144.5, 134.5, 130.1, 128.8, 128.0, 118.3, 64.3, 30.8, 19.2, 13.7; GC-MS (EI) m/z (%): 204 (M^+, 100).

Trans-methyl cinnamate:



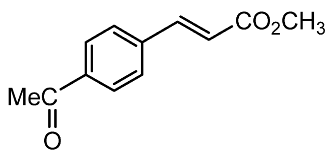
^1H NMR ($CDCl_3$, 200 MHz, ppm): δ 7.64(d, 1H, $J = 16.0$ Hz), 7.51–7.54 (m, 2H), 7.33–7.39 (m, 3H), 6.45 (d, 1H, $J = 16.0$ Hz), 3.78 (s,



Scheme 1. Preparation of the Pd/PVPy catalyst by metal vapour synthesis technique.

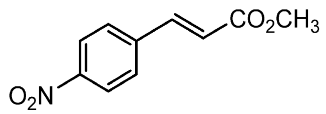
3H); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm): δ 167.0, 144.2, 144.5, 135.2, 128.9, 127.2, 118.3, 52.0; GC-MS (EI) m/z (%): 162 (M^+, 100).

Trans-methyl 3-(4-acetylphenyl)acrylate:



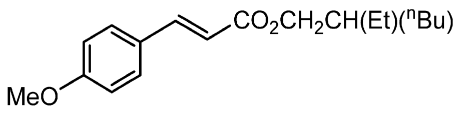
^{1}H NMR ($CDCl_3$, 200 MHz, ppm): δ 7.88 (d, 2H, $J = 8.3$ Hz), 7.53 (d, 2H, $J = 8.3$ Hz), 7.44 (d, 1H, $J = 16.2$ Hz), 6.69 (d, 1H, $J = 16.2$ Hz), 2.52 (s, 3H), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm): δ 197.9, 197.1, 141.5, 138.6, 137.9, 128.9, 128.7, 128.2, 27.6, 26.6; GC-MS (EI) m/z (%) 188 (M^+, 100).

Trans-4-nitrocinnamic acid methyl ester:



^{1}H NMR ($CDCl_3$, 200 MHz, ppm): δ 8.21 (d, 2H, $J = 8.8$ Hz), 7.77 (d, 1H, $J = 16.3$ Hz), 7.65 (d, 2H, $J = 8.8$ Hz), 6.50 (d, 1H, $J = 16.0$ Hz), 3.85 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm): δ 166.6, 148.9, 141.3, 129.3, 124.7, 123.2, 51.5; GC-MS (EI) m/z (%): 207 (M^+, 100).

Trans-4-methoxylcinnamic acid 2′-ethyl hexyl ester:



^{1}H NMR ($CDCl_3$, 200 MHz, ppm): δ 7.61 (d, 1H, $J = 16.0$ Hz), 7.45 (d, 2H, $J = 8.7$ Hz), 6.87 (d, 2H, $J = 8.7$ Hz), 6.30 (d, 1H, $J = 15.9$ Hz), 4.15 (m, 2H), 3.82 (s, 3H), 1.30–1.59 (m, 9H), 0.92 (m, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm): δ 167.9, 161.5, 144.3, 130.0, 127.4, 116.1, 114.5, 67.2, 55.7, 39.3, 30.8, 29.4, 24.3, 23.4, 14.5, 11.3; GC-MS (EI) m/z (%): 290 (M^+, 100).

3. Results and discussion

3.1. Preparation of the polyvinylpyridine supported palladium catalyst, Pd/PVPy

The polyvinylpyridine supported palladium catalyst, Pd/PVPy, has been prepared by depositing Pd nanoparticles, obtained by the metal vapour synthesis technique [12,15], on PVPy. Using the MVS apparatus, palladium atoms, produced by resistive heating of the metal under high vacuum, are co-condensed at liquid nitrogen temperature (−196 °C) with a 1:1 mixture of 1-hexene and mesitylene on the cooled wall of the reactor. On warming until the solid matrix melts (−30 °C to −40 °C), a brown solution, the so-called solvated palladium atoms solution, is obtained. It contains palladium atoms and/or palladium nanoclusters, which are solubilized and stabilized by the excess of the organic solvents acting as weakly coordinating ligands. It behaves as a source of metal nanoparticles. On warming the solution to room temperature in the presence of PVPy, the nanoclusters agglomerate with subsequent deposition of palladium nanoparticles on PVPy (Scheme 1).

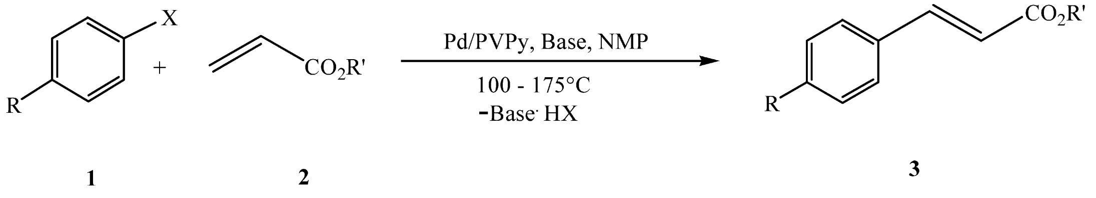
The mesitylene-1-hexene solvated Pd atom solution is stable up to 0 °C. It is more stable than the mesitylene solvated Pd atom solution that has been employed previously in the preparation of the palladium on polyvinylpyridine catalyst, which decomposes at −30 °C [11]. The high stability of the first solution allows a more controlled deposition of the metal particles on the PVPy.

3.2. Palladium on polyvinylpyridine, Pd/PVPy, as a catalyst in the Heck reaction of bromoarene and chloroarene derivatives with acrylates

As previously reported [11] the Pd/PVPy catalyst, prepared from the mesitylene solvated Pd atom solution, showed good catalytic activity in the C–C coupling reaction of iodobenzene and methyl acrylate, used as the standard reaction, giving selectively *trans*-methyl cinnamate in 60% yield after 4 h at 75 °C. The performance of the catalytic system Pd/PVPy, prepared following the improved procedure as reported in Section 3.1, has been compared with that discussed above and it has been also examined in the C–C coupling reaction of both activated and deactivated bromoarene and chloroarene derivatives with alkyl acrylates (Scheme 2).

The cross-coupling reactions have been performed at different temperatures (100–175 °C) in *N*-methylpyrrolidinone (NMP) as solvent using a molar ratio aryl halide/Pd = 100 or 1000 and an excess of alkyl acrylate with respect to aryl halide (molar ratio = 2) to avoid the formation of twofold coupling byproducts [2a]. The alkyl acrylates employed were methyl acrylate, *n*-butyl acrylate and ethylhexyl acrylate. Different bases (Et_3N, $^nPr_3N$, K_2CO_3, $CsCO_3$) were used; the base reacts with the hydrohalic acid, formed in the course of the reaction, thus shifting the equilibrium toward the products. The reaction mixture was easily separated from the solid catalyst by filtration and the organic products were extracted with diethyl ether. Pure coupling products were obtained by column chromatography and characterized by NMR spectroscopy and mass spectrometry. These compounds were selectively obtained with *trans* stereochemistry. The results are reported in Table 1.

The Pd/PVPy catalyst, prepared from a Pd/1-hexene-mesitylene solution, showed high catalytic activity in the C–C coupling re-



R = H, NO_2 , COMe, OMe
X = I, Br, Cl
R' = Me,^{n}Bu, $CH_2CH(Et)(^nBu)$
Base = NEt_3, $N(^nPr)_3$, K_2CO_3, Cs_2CO_3

Scheme 2. Heck reaction of aryl halide derivatives with alkyl acrylates.

Table 1
Reaction between aryl halide derivatives and alkyl acrylates giving substituted *trans*-cinnamates catalyzed by palladium on polyvinylpyridine, Pd/PVPy.[a]

Run	1	2	T (°C)	Time (h)	Yield of product 3 (%)[b]	Specific activity (h^{-1})[c]
1[d]	R = H, X = I	$R' = CH_3$	100	3	93 (90)	310
2	R = NO_2 X = Br	$R' = CH_3$	125	3 6	55 95 (93)	158
3[e]	R = NO_2 X = Br	$R' = CH_3$	125	3 6	25 47	78
4[f]	R = NO_2 X = Br	$R' = CH_3$	125	3 6	30 65	108
5	R = NO_2 X = Br	$R' = CH_3$	150	4	82	205
6	R = NO_2 X = Br	$R' = {}^n$Bu	150	4	90 (87)	225
7	R′ = COMe X = Br	$R' = CH_3$	125	4 8	36 65 (62)	82
8	R′ = COMe X = Br	$R' = {}^n$Bu	150	4	75 (72)	188
9	R = H X = Br	$R' = {}^n$Bu	150	4	10	25
10	R = H X = Br	$R' = {}^n$Bu	175	4 24	17 90 (85)	38
11[g]	R = OCH_3 X = Br	$R' = {}^n$Bu	175	4 24	7 34 (30)	2
12[g]	R = OCH_3 X = Br	$R' = CH_2CH(Et)(^nBu)$	175	24	37 (34)	2
13[g]	R = NO_2 X = Cl	$R' = {}^n$Bu	175	24	20	–
14[g]	R = H X = Cl	$R' = {}^n$Bu	175	24	15	–

[a] Reaction conditions: aryl halide (5 mmol); acrylate (10 mmol); base (5 mmol), $N(^nPr)_3$ (unless otherwise stated); 1-methyl-2-pyrrolidinone, NMP (9 ml); catalyst 53 mg (5×10^{-3} mg-atom Pd) (unless otherwise stated).

[b] Yield of the substituted *trans*-cinnamate determined by GLC. The yield of the isolated products are in parenthesis.

[c] Calculated as moles of aryl halide converted/g-atom of metal *per* hour.

[d] Base = Et_3N.

[e] Base = K_2CO_3.

[f] Base = Cs_2CO_3.

[g] Catalyst 5×10^{-2} mg-atom Pd.

action of iodobenzene with methyl acrylate to methyl *trans*-cinnamate at 100 °C in the presence of Et_3N (SA = 310 h^{-1}, run 1). It was more active than the analogous catalyst prepared from the mesitylene-solvated Pd atom solution (SA = 168 h^{-1}) [11].

For the reactions with bromoarene derivatives, *p*-nitrobromobenzene was chosen as the reference compound to establish the reaction conditions. The strongly electron-withdrawing nitro group in *para* position to bromine should weaken the C–Br bond, so *p*-nitrobromobenzene should, in principle, react more rapidly than bromobenzene or other mono substituted bromoarenes. The reaction of *p*-nitrobromobenzene with methyl acrylate, at 125 °C in the presence of $^nPr_3N$, gives selectively methyl *trans*-4-nitrocinnamate, after 6 h in 95% yield (SA = 158 h^{-1}, run 2). Inorganic bases, such as K_2CO_3 or Cs_2CO_3, which are often employed in the Heck reaction, furnish lower yields of the C–C coupling product (47% after 6 h, TOF = 78 h^{-1}, run 3; and 65% after 6 h, SA = 108 h^{-1}, run 4, respectively). With $^nPr_3N$ at 150 °C the yield becomes 82% after 4 h (SA = 205 h^{-1}, run 5). At this temperature, using the high boiling *n*-butyl acrylate, the yield is 90% after 4 h (SA = 225, entry 6) and it is quantitative after ca. 6 h.

p-Bromoacetophenone is slightly less reactive than *p*-nitrobromobenzene. At 125 °C its reaction with methyl acrylate in the presence of $^nPr_3N$ gives *trans*-methyl 3-(4-acetylphenyl)acrylate in 65% yield after 8 h (SA = 82 h^{-1}, run 7). At 150 °C, using *n*-butyl acrylate, the reaction furnishes *trans*-butyl 3-(4-acetylphenyl)acrylate in good yield (75%, SA = 188 h^{-1}, run 8).

Bromobenzene is less reactive than either *p*-nitrobromobenzene or *p*-bromoacetophenone, the Heck reaction with *n*-butyl acrylate at 150 °C giving *n*-butyl *trans*-cinnamate in low yield (10% after 4 h, SA = 25 h^{-1}, run 9). Raising the temperature to 175 °C gives *n*-butyl *trans*-cinnamate in good yield after 24 h (90%, SA = 38 h^{-1}, run 10). *p*-(Methoxy)bromobenzene was the least reactive of the bromo derivatives examined. The reaction with *n*-butyl acrylate was performed using a molar ratio *p*-(methoxy)bromobenzene/Pd = 100. At 175 °C, *n*-butyl *trans*-4-methoxycinnamate was obtained in low yield (7%) after 4 h, and in 34% yield after 24 h (SA = 2 h^{-1}, run 11).

The cross-coupling reaction of *p*-(methoxy)bromobenzene with 2-ethylhexyl acrylate was also examined, because the product, ethylhexyl *trans*-3-(4-methoxyphenyl)acrylate, is used as a sunscreen agent in the cosmetic industry [16]. At 175 °C, after 24 h, ethylhexyl *trans*-3-(4-methoxyphenyl) acrylate was obtained in 37% yield (SA = 2 h^{-1}, run 12).

As far as the Heck reaction with chloroarene derivatives is concerned, *p*-nitrochlorobenzene and chlorobenzene were examined using a molar ratio substrate/Pd = 100. These compounds react with *n*-butyl acrylate at 175 °C furnishing, after 24 h, respectively, *n*-butyl *trans*-4-nitrocinnamate and *n*-butyl *trans*-cinnamate in low yield (20%, run 13; and 15%, run 14) and low specific activity. The observed reactivity of the halo compounds, aryl iodide > aryl bromide > aryl chloride is that expected considering the stability of the carbon (sp^2)-halogen bond and it is in agreement with the data reported in the literature [17].

It is now well known that one of the principal disadvantages associated with the use of Pd supported catalysts in the Heck reaction is leaching of the metal into the solution, resulting in contamination of the product with metal that is difficult to remove.

Table 2
XPS data for pure PVPy, pristine Pd-containing catalyst and recovered catalyst.

Sample	Signal	BE (eV)	FWHM (eV)	$N_{i(\text{tot})}/N_{\text{N(tot)}}$	
PVPy	C 1s	284.70	2.08	34.00	
		286.20	2.08		
		288.51	2.08		
	N 1s	399.26	1.77	1.00	$Na/Nb = 9.2$
		401.61	1.77		

Sample	Signal	Starting catalyst				Recovered catalyst			
		BE (eV)	FWHM (eV)	$N_{i(\text{tot})}/N_{\text{N(tot)}}$		BE (eV)	FWHM (eV)	$N_{i(\text{tot})}/N_{\text{N(tot)}}$	
Pd/PVPy 1%	C 1s	284.70	2.27	30.27		284.70	2.16	25.7	
		286.36	2.27			286.01	2.16		
		288.44	2.27			288.28	2.16		
	N 1s	399.07	2.08	1.00	$Na/Nb = 1.2$	399.28	2.08	1.00	$Na/Nb = 3.5$
		401.97	2.08			401.75	2.08		
	O 1s	531.35	2.66	10.08		530.26	2.28	21.74	
		532.70	2.66			532.42	2.28		
		534.20	2.66			534.40	2.28		
	Pd $3d_{5/2}$	335.27	1.90	1.56	Pd(0)/Pd(II)	335.36	2.06	0.29	Pd(0)/Pd(II)
		337.21	1.90		7.2	337.19	2.06		6.3
Pd/PVP 5%	C 1s	284.70	2.06	30.50		284.70	2.09	33.43	
		286.43	2.06			285.90	2.09		
		288.67	2.06			288.10	2.09		
	N 1s	398.80	1.97	1.00	$Na/Nb = 1.3$	399.45	1.77		$Na/Nb = 3.3$
		399.95	1.97			400.70	1.77	1.00	
	O 1s	531.31	2.50	9.66		530.63	2.21	29.49	
		532.35	2.50			532.42	2.21		
		534.04	2.50			534.40	2.21		
	Pd $3d_{5/2}$	335.16	1.90	1.58	Pd(0)/Pd(II)	335.39	1.92	1.08	Pd(0)/Pd(II)
		337.09	1.90		4.6	337.14	1.92		5.2

For these reasons leaching of the metal from Pd/PVPy catalyst has been examined. The reaction between iodobenzene and methyl acrylate and between *p*-nitrobromobenzene and *n*-butyl acrylate (run 1 and run 6, respectively), which present high conversion and different reaction temperature, have been examined in detail. In the case of run 1, performed at 100 °C, the amount of Pd leached during the reaction (3 h) ranged between 0.5–0.9% of the total available metal, corresponding to 0.4–0.6 ppm in solution; in the case of run 6, performed at 150 °C for 4 h, the Pd leached was 1.0–1.3%, corresponding to 0.6–0.7 ppm. Moreover, on the isolated products, obtained by purification on silica column chromatography, very low palladium amount (<0.5 ppm) was detected. It is worth noting that these low Pd level satisfy specifications required by the pharmaceutical industry regarding the final purity of the products (Pd <2 ppm) [6a,18].

As far as the properties of the Pd/PVPy catalyst are concerned, it is interesting to note that the Pd leaching is less than that previously observed using the similar catalyst prepared from the Pd/mesitylene solvated atom solution, even at lower reaction temperature (1.3–1.9% at 75 °C and 4.2–5.2% at 125 °C) [11]. This demonstrates the high stability of the Pd/PVPy catalyst obtained by the modified procedure in which the Pd/mesitylene-1-hexene solution is the source of metal nanoparticles.

The reactions between iodobenzene and methyl acrylate and between *p*-nitrobromobenzene and *n*-butyl acrylate gave the same results regarding conversion and Pd leaching in air as under argon (run 1 and run 6), indicating that these processes do not require the use of an inert atmosphere. For this reason, the experiments on the recycle of the Pd/PVPy catalyst have been performed under air. The catalysts in runs 1, 5, 6, 8, 11 and 12 were recovered from the reaction mixture and reused in the same reactions showing the same catalytic activity as that of the starting material. In particular, the catalyst in run 1 was reused 5 times without an appreciable decline of its catalytic activity indicating the high stability of Pd/PVPy system even in air.

4. Structural studies of the Pd/PVPy catalyst by X-ray photoelectron spectroscopy (XPS)

To obtain information on the structural features of the Pd/PVPy catalyst, X-ray photoelectron spectroscopy (XPS) studies have been performed on the pristine catalyst as well as on the catalyst recovered from the catalytic test. The system examined was Pd/PVPy, containing 1 wt% Pd, employed in the reaction between *p*-nitrobromobenzene and *n*-butyl acrylate at 150 °C (run 6). The Pd/PVPy catalyst, containing 5 wt% Pd, employed in the same reaction, has been also studied to investigate the influence of the amount of metal on the structure of the catalyst.

The C 1s, Pd 3d, N 1s and O 1s core level spectra have been collected and analysed. The core level binding energy (BE) and full width at half-maxima (FWHM) were analysed with particular attention to the Pd 3d spin–orbit components, which are of major interest for the assessment of the Pd–pyridine interaction in the catalyst and for the investigation of its role in the catalytic process. BE, FWHM and atomic ratio $N_{i(\text{tot})}/N_{\text{N(tot)}}$ values observed for both the pristine and the recovered catalysts are collected and compared in Table 2, together with the XPS data collected on a pure PVPy sample, which will be taken as reference in the following discussion about the chemical structure of the organic moiety of the composite Pd/PVPy catalysts.

All the XPS spectra were calibrated in energy using the main component of the C 1s signal, attributed to aromatic carbons, at 284.70 eV. The N 1s spectra as detected for the pure PVPy, for the pristine sample and after catalytic test, appeared quite similar in structure due to the presence of multiple features. Two components were evident from peak fitting analysis; the compo-

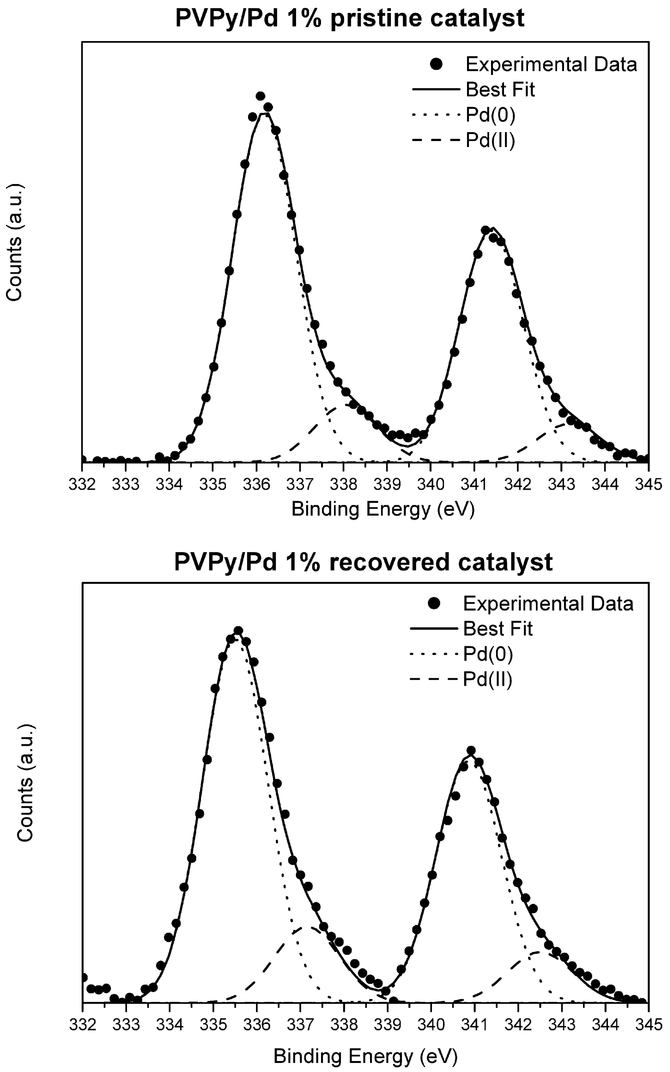


Fig. 1. XPS Pd 3d spectra of Pd/PVPy 1% both pristine and recovered from the catalytic test.

nent at about 399.0 eV BE (referred as N*a* in Table 2) was assigned to the nitrogen atoms of the pyridine rings [19]; the peak of lower intensity at 400.0–401.0 eV (N*b* in Table 2), conversely, was ascribed to positively charged N atoms. A similar structured N 1s spectrum has already been observed for the polyvinylpyridine sample itself, and is attributed in the literature to "strongly" H-bonded pyridine (400.4–400.9 eV) [20] or protonated pyridine (401.4–402.4 eV) [19,21]. As reported in Table 2, the C/N_{TOT} atomic ratios are in good agreement with the molecular stoichiometry expected and experimentally found for the pure PVPy, and are strictly similar for the two composite Pd/PVPy samples (1 wt% and 5 wt% Pd content), both pristine and after recovery from the catalytic test.

The Pd 3d spectrum shows the presence of a main contribution together with a minor component at higher BE values. Curve-fitting analysis showed that the Pd 3d spectra of the pristine catalysts resulted from two pairs of spin-orbit components, as shown in Fig. 1 (sample Pd/PVPy 1 wt%). On the basis of previous measurements, the Pd $3d_{5/2}$ peak found at BE = 335.5 eV has been attributed to metallic palladium (Pd(0)) in agreement with literature reports [22]; the second Pd $3d_{5/2}$ signal occurring at higher BE values (BE = 337.21 eV for sample 1 wt% Pd; BE = 337.09 eV for sample 5 wt% Pd) is due to Pd atoms with lower charge density. The origin of such palladium species is not completely clear; one possible hypothesis considers a perturbation occurring during the dispersion process of Pd clusters in PVPy matrix. For comparison, the Pd $3d_{5/2}$ signal for PdO is reported in the literature at 337.0 eV [21]. However, if PdO were present, we would expect also to observe a O 1s signal at about 529.3 eV, which is not present. On this basis, therefore, it is reasonable to exclude the presence of palladium oxide. On the other hand, Pd $3d_{5/2}$ BE values associated with Pd atoms covalently bonded to carbon were found at 338.2 eV in Pd(II)-diethynylbenzene poly-ynes [23], and BE values of about 337.8 eV are reported in the literature for similar systems [18]. Although this palladium species is present in only small amount, it could play a role in the grafting of the palladium nanospheres. We suggest that the low charge density Pd atoms detected in the composite samples may interact with the nitrogen atoms of the PVPy rings; in this picture, there may be an electrostatic interaction between the Pd atoms and the nitrogen atoms of the pyridine rings, which will lead to an increase of the higher BE N 1s component (N*b*) ascribed to positively charged N atoms. In fact, as reported in Table 2, the N*b* component intensity is negligible in the pristine PVPy sample ($Na/Nb = 9.2$) and grows in the composite Pd/PVPy samples ($Na/Nb \sim 1.3$). Semi-quantitative analysis of the XPS signals enabled the Pd(0)/Pd(II) atomic ratio to be estimated as 6.0:1 for the 1 wt% Pd and 5.0/1 for the 5 wt% Pd samples. The observed discrepancy between the Pd(0)/Pd(II) atomic ratio values founded for sample of different Pd% is, however, extremely small, suggesting that the two samples are completely similar.

Both qualitative and semi-quantitative analysis performed on the recovered catalysts are in excellent agreement with the data already discussed for the pristine Pd/PVPy samples, as shown in Table 2. Moreover, the Pd 3d spectrum of Pd/PVPy 1 wt% sample as recovered from the catalytic test is displayed in Fig. 1, together with the curve fitting results, and can be easily compared with the same spectrum collected on the pristine catalyst, reported in the same Fig. 1. The C 1s, N 1s, O 1s and Pd 3d spectra of the pristine and the recovered samples do not show appreciable BE differences, indicating that the chemical and electronic structure of the catalyst is not modified by the catalytic process.

In conclusion, comparison of the XPS spectra of the pure PVPy and Pd/PVPy samples show that the chemical structure of PVPy is not appreciably affected by the presence of metallic Pd atoms. Furthermore, from the comparison between pristine and recovered catalysts, we assume that the catalytic process does not induce permanent modification in the chemical and/or electronic structure of the catalyst; therefore, the material appears to be almost completely and efficiently recovered unchanged after the catalytic tests. Moreover, the, Pd(0)/Pd($\delta+$) atomic ratios as estimated by the XPS semiquantitative analysis are 6.3/1 for the 1 wt% Pd and 5.2/1 for the 5 wt% Pd recovered samples. They show only a negligible variation and are consistent with the values calculated for the pristine systems.

5. Conclusions

The Pd/PVPy system, prepared by the MVS technique, is an efficient and stable catalyst for the C–C coupling reaction of iodo- and bromoarenes with alkyl acrylates. The corresponding *trans*-cinnamates are obtained with yields in the range 35–95% at 100–175 °C depending on the substituent present on the aromatic ring of the aryl halide. The catalyst is particularly stable and the leaching of palladium into the solution is very low. It works well also in air, thus simplifying the work-up of the catalytic process. In addition, the catalyst can be recovered and reused without loss of catalytic activity. XPS structural studies indicate the presence of interactions between the basic nitrogen atoms of the pyridine moieties present in the polymer and the metal. Such interactions are present in the starting material as well as in the catalyst recovered after the catalytic reaction, thus accounting for the high stability of this catalytic system.

These results suggest that the Pd/PVPy system may be more generally useful, for example, in other Heck-type reactions of interest to chemical industry. The very low palladium leaching observed for Pd/PVPy is a particular advantage, in view of the high price of the metal and because the products should be ready for use without the need for cleaning with metal scavengers. It is also worth highlighting the versatility of the MVS technique to prepare even more stable and efficient catalysts.

Acknowledgment

The authors thank Dr. Emanuela Pitzalis (IPCF-CNR, Pisa, Italy) for AAS analyses.

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