



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

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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 an interaction between the basic nitrogen of the pyridine present in the polymer and the metal.

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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 sp² 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, ze-

olite, 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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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 \times 0.3 mm, 0.25 μ m) 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. MgK α 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 ($-40^\circ C$), and the resulting red-brown solution was siphoned and handled at low temperature ($-30/-40^\circ C$) 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)

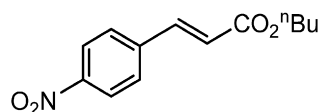
The mesitylene-1-hexene Pd atom solution (36 ml, 101 mg Pd) was added to a suspension of PVPy (10 g) in mesitylene (40 ml). The mixture was stirred for 12 h at room temperature. The colourless solution was removed and the light-brown solid was washed with pentane and dried under reduced pressure. The 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

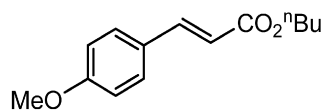
1-Methyl-2-pyrrolidinone (NMP) (9 ml), alkyl acrylate (10 mmol), phenyl halide derivatives (5 mmol), base (5 mmol) and 53 mg of Pd/PVPy catalyst (containing 5×10^{-3} mg atom of Pd) were introduced under argon atmosphere into a 25-ml round-bottomed, two-necked flask equipped with a stirring magnetic 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:



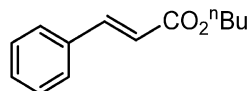
1H NMR ($CDCl_3$, 200 MHz, ppm): δ 8.18 (d, 2H, $J = 8.8$ Hz), 7.65 (d, 1H, $J = 16.4$ Hz), 7.65 (d, 2H, $J = 8.8$ Hz), 6.50 (d, 1H, $J = 16.0$ Hz), 4.18 (t, 2H, $J = 6.7$ Hz), 1.65 (quint, 2H, $J = 5.4$ Hz), 1.42 (sextet, 2H, $J = 7.5$ Hz), 0.92 (q, 3H, $J = 7.3$ Hz); ^{13}C NMR ($CDCl_3$, 50 MHz, ppm): 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-methoxycinnamic acid *n*-butyl ester:



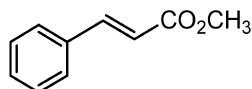
1H NMR ($CDCl_3$, 200 MHz, ppm): δ 7.61 (d, 1H, $J = 16.0$ Hz), 7.45 (d, 2H, $J = 8.7$ Hz), 6.87 (d, 2H, $J = 8.8$ Hz), 6.28 (d, 1H, $J = 15.9$ Hz), 4.18 (t, 2H, $J = 6.8$ Hz), 3.80 (s, 3H), 1.66 (quint, 2H, $J = 5.8$ Hz), 1.41 (sextet, 2H, $J = 7.6$ Hz), 0.94 (t, 3H, $J = 7.3$ Hz); ^{13}C NMR ($CDCl_3$, 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,

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