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New monodispersed palladium nanoparticles stabilized by poly-(N-vinyl-2-pyrrolidone): Preparation, structural study and catalytic properties

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ABSTRACT

Mesitylene/1-hexene solvated palladium nanoparticles, obtained by metal vapour synthesis (MVS) technique, were stabilized in solution at room temperature with poly-(N-vinyl-2-pyrrolidone) (PVP) and isolated by precipitation with a diethyl ether or THF as brown powder. HRTEM and FT-IR analyses on samples with different Pd/PVP ratio (1%, 5%, 10%, 15%, 20 w/w%) showed palladium nanoparticles with mean diameters limited in the range 1.5–2.5 nm and the presence of competitive intermolecular interactions between $>C{=}O$ groups and palladium atoms on nanoparticle surface. The Pd–PVP systems, dissolved in EtOH solvent, showed excellent catalytic activity and selectivity in the hydrogenation of aliphatic alkynes (1-hexyne, 2-hexyne, 3-hexyne, 3-hexyne-1-ol) to the corresponding (Z)-alkenes. The catalytic activity of Pd–PVP samples, dissolved in 1-methyl-2-pyrrolidinone (NMP), has been also evaluated in the Mizoroki–Heck C–C coupling reaction of iodobenzene and bromo-arenes with butyl acrylate showing high efficiency. Moreover, the catalyst can be quantitatively recovered at the end of the reaction by precipitation with diethyl ether and reused without significant loss of catalytic activity.

1. Introduction

Metal nanoparticles are of great interest in many fields of research ranging from material science and catalysis to biology thanks to their unique physical and chemical properties [1–3]. The combination of metal nanoparticles with polymeric matrix offers the possibility to obtain nanostructured metal systems with interesting additional properties for their applications in catalysis, such as thermal stability, solubility and recovery of the systems [4,5]. Poly-(N-vinyl-2-pyrrolidone) (PVP) is one of the most investigated polymer used to stabilize metal nanoparticles because of the capability of its $>N{-}C{=}O$ groups to coordinate metal atoms on nanoparticle surface [6]. Extensive studies on the preparation of palladium, rhodium and platinum nanoparticles stabilized by PVP are reported in the literature [7–9]. Generally, palladium systems were obtained by reduction of H_2PdCl_4 palladium salt in aqueous solution with primary or secondary alcohols in the presence of PVP, where the aqueous-alcoholic solution is necessary to completely dissolve PVP and palladium precursors. These palladium nanoparticles were demonstrated as active and selective catalysts in the hydrogenation of olefins and cyclic dienes (cyclopentadiene, cyclooctadiene) to the corresponding monoenes [10,11]. Teranishi and Miyake found that, by changing the amount of protective polymer and the kind and/or the concentration of alcohol in the solvent, palladium nanoparticles with diameter ranging from 2 to 3 nm and narrow size distributions can be obtained [8]. Pd–PVP systems obtained following the above described procedure were catalytically active in Suzuki cross-coupling reaction of aryl boronic acids with aryl iodides [12]. Therefore, as observed by other authors [13] with Pd colloids catalysts in C–C coupling reactions, the precipitation of inactive palladium black species that occurs during the reaction results in a decrease in catalytic activity.

Recently, PVP-stabilized palladium systems obtained by reduction of H_2PdCl_4 in the presence of PVP have been demonstrated to be active in cross-coupling reaction of aryl halides with alkyl acrylate (Mizoroki–Heck reaction) in tetrabutylammonium salts medium [14]. In this case, Pd–PVP system was recycled four times revealing a gradual decrease in the activity was explained by the contamination of liquid ionic medium with by-products.

We report here a new procedure to prepare palladium nanoparticles stabilized by PVP, as protective polymer, starting from palladium clusters obtained by metal vapour synthesis (MVS) technique [15,16]. The method allows to obtain palladium nanoparticles with Pd in reduced state and ensures the absence of impurities, such as

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residual chlorine or other ions, on surface of palladium nanoparticles. Pd–PVP systems with different Pd/PVP ratio have been isolated in solid state, and their structural features have been investigated by HRTEM and FT-IR analyses. The catalytic activity of these systems has been evaluated in the selective hydrogenation of terminal and internal alkynes to the corresponding (Z)-alkenes, a reaction very sensitive to catalyst nature. Moreover, considering the high efficiency of previously reported MVS-derived palladium systems in C–C cross-coupling reactions [17,18], the catalytic activity of Pd–PVP systems was evaluated in the coupling of aryl halide (iodobenzene and bromo-arenes) with butyl acrylate (Mizoroki–Heck reaction) evidencing a good catalytic activity and recyclability of the catalytic system.

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 described previously [15,16,19]. The solvated Pd atom solutions were worked up under argon atmosphere with the use of the standard Schlenk techniques. The amount of palladium in the above solutions was evaluated by inductively coupled plasma-optical emission spectrometers (ICP-OES) with a Spectro-Genesis instrument, using a software Smart Analyzer Vision. The limit of detection (lod) calculated for palladium was 2 ppb. Solvents were purified by conventional methods, distilled and stored under argon. Poly-(N-methyl-2-pyrrolidone) K30 was supplied from Aldrich. 1-hexyne, 2-hexyne, 3-hexyne, 3-hexyne-1-ol, iodobenzene, bromobenzene, *p*-nitrobromobenzene and *n*-butyl acrylate were supplied from Aldrich and used as received. $N(^nPr)_3$ (from Aldrich) was distilled before use.

The GLC analyses were performed on a Perkin–Elmer Auto System gas chromatograph, equipped with a flame ionisation detector (FID), using a SiO_2 column (BP-1, 12 m × 0.3 mm, 0.25 μm) and helium as carrier gas. The FT-IR spectra were carried out with a Perkin–Elmer Mod 2000 spectrometer at room temperature. One hundred scans of 2 cm^{-1} resolution were signal averaged and stored on a disc for further analysis. The catalysts were transferred into a mini agate mortar, ground with KBr for 5 min and then pellets with the same concentration (0.5% of the sample) and thickness (200 ± 10 μ) were obtained.

Electron microscopy was done with a JEOL 3010-UHR instrument with acceleration potential of 300 kV. Before being introduced into the instrument, the samples, in the form of film, were cooled to 77 K and crushed at this temperature. The obtained powders were ultrasonically dispersed in *n*-heptane, and a drop of the suspension was deposited on a copper grid covered with a lacy carbon film. Histograms of the particle size distribution were obtained by counting at least 300 particles onto the micrographs; the mean particle diameter (d_m) was calculated from the formula $d_m = d_i n_i / n_i$, where n_i is the number of particles of diameter d_i. The counting was carried out on electron micrographs obtained at 300,000 magnification, where Pd particles well contrasted with respect to the support were clearly detected. The graduation of the particle size scale was 0.5 nm.

2.1.1. Preparation of PVP-stabilized palladium nanoparticles obtained by MVS

In a typical experiment, Pd vapour generated at 10^{-4} Pa 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. The reactor chamber was heated to the melting point of the solid matrix (ca. −40 °C), and the resulting brown solution was siphoned and handled at low temperature (−20 °C) with the Schlenk tube technique. The metal content of the solution was assessed by ICP-OES analyses. 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. The solid residue was dissolved in 0.5 M aqueous HCl, and the solution was analysed by ICP-OES. The palladium content of the solvated metal solution was 1.5 mg/mL.

The above brown mesitylene/1-hexene Pd atom solution (10 mL, 15.0 mg Pd) was added to a ethanol solution of PVP (1500 mg of PVP in 9 mL EtOH, 300 mg of PVP in 3 mL EtOH, 150 mg of PVP in 1.5 mL of EtOH, 100 mg of PVP in 1 mL EtOH, 75 mg of PVP in 1 mL EtOH, for sample at 1%, 5%, 10%, 20 w/w% of palladium, respectively) obtaining Pd–PVP solutions stable at room temperature (25 °C). By adding an excess of diethyl ether, a brown solid of Pd nanoparticles dispersed in PVP which was easily re-dissolved in polar solvents such as alcohols, water or 1-methyl-2-pyrrolidinone was obtained.

2.1.2. Selective hydrogenation of aliphatic alkynes: general procedure

In a typical experiment, the acetylenic substrate (8 mmol), ethanol (10 mL), and Pd–PVP 1 w/w% catalyst (8.5 mg, 8×10^{-4} mg-atom of Pd) were introduced under argon atmosphere into a 100-mL two-necked flask equipped with a stirring magnetic bar, a silicon stopper and connected to a gas-volumetric burette containing hydrogen. The nitrogen was removed under vacuum, and hydrogen was introduced. The mixture was stirred (ca. 1500 rev/min) at room temperature (25 °C) under hydrogen (0.1 MPa). The progress of the reaction was monitored by the absorption of hydrogen in the burette, and the composition of the reaction mixture was determined by GLC analysis of liquid samples, taken at short intervals from the stoppered side neck with a syringe until complete conversion occurred.

2.1.3. Mizoroki–Heck reaction: general procedure

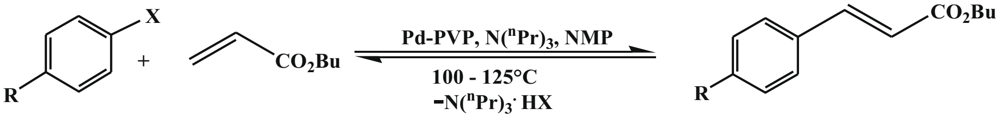
In a typical experiment, 1-methyl-2-pyrrolidinone (NMP) (15 mL), alkyl acrylate (20 mmol), aryl halide (10 mmol), $N(^nPr)_3$ (10 mmol) and Pd–PVP 1 w/w% catalyst (10 mg, containing 1×10^{-2} mg atom of Pd) were introduced under argon atmosphere into a 25-mL round-bottomed, two-necked flask equipped with a stirring magnetic bar, a bubble condenser and a silicon stopper. The reaction mixture was magnetically stirred at the required temperature (Table 1). 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 dry sodium sulphate and analysed by GLC. In some cases, the Pd–PVP catalyst was recovered at the end of the reaction by adding an excess of diethyl ether at the cooled reaction mixture. The solid was separated by filtration (0.4-μm Teflon filter) and analysed by ICP-OES. The metal content was 1 w/w% Pd, the same of the starting material, within the interval ±5%. ICP-OES analysis of the filtrate showed the presence of very low amount of palladium (0.5–2.5 ppm in solution, corresponding of 1% and 4.3% of the total available metal).

3. Results and discussion

3.1. Preparation of Pd–PVP systems

The Pd–PVP systems were prepared starting from solvated palladium atoms obtained by the metal vapour synthesis (MVS) technique [15]. According with the previously reported procedure [18],

Table 1
Carbon–carbon coupling reaction of aryl halide with *n*-butyl acrylate (Mizoroki–Heck reaction) catalysed with Pd–PVP systems obtained by MVS



Run	Catalyst	Aryl Halide	T (°C)	Yield of product[a] (%)	Specific activity (SA)[b] (h^{-1})
1	Pd(OAc)$_2$	X = I R = H	75	50	500
2	Pd–PVP (1 w/w%)	X = I R = H	75	83	830
3	Pd–PVP (1 wt.%)	X = Br R = NO$_2$	125	95	950
4[c]	Pd–PVP (1 wt.%)	X = Br R = H	125	10	4
5[c]	Pd–PVP (1 wt.%)	X = Br R = H	175	52	22
6	Pd–PVP (10 wt.%)	X = I R = H	75	81	810
7	Pd–PVP (10 wt.%)	X = Br R = NO$_2$	125	100	1000
8[c]	Pd–PVP (10 wt.%)	X = Br R = H	175	48	20
9	Pd–PVP Recovered from run 2	X = I R = H	75	78	780
10	Pd–PVP Recovered from run 3	X = Br R = NO$_2$	125	93	930

Reaction conditions: aryl halide (10 mmol); *n*-butyl acrylate (20 mmol); N(^{n}Pr)^3 (10 mmol), 1-methyl-2-pyrrolidinone, NMP (15 mL); catalyst Pd–PVP (1×10^{-2} mg-atom Pd), reaction time = 1 h.

[a] Yield of substituted (E)-cinnamate determined by GLC.

[b] Calculated as (mol product/(mol Pd × h)).

[c] Catalyst Pd–PVP (0.1 mg-atom Pd), reaction time = 24 h.

palladium vapours were co-condensed with vapours of mesitylene and 1-hexene on the cooled wall of the reactor (−196 °C). By warming until the solid matrix melts, a brown solution, the so-called solvated palladium atoms solution, was obtained. The resulting palladium-solvated solution, stable at low temperature (−20 °C), was added to PVP dissolved in EtOH, obtaining a Pd–PVP solution stable at room temperature (25 °C). By precipitation with Et$_2$O, a brown solid of Pd nanoparticles, highly dispersed in PVP, which can easily re-dissolved in polar solvents such as alcohols, water or 1-methyl-2-pyrrolidinone without formation of insoluble species was obtained (Scheme 1).

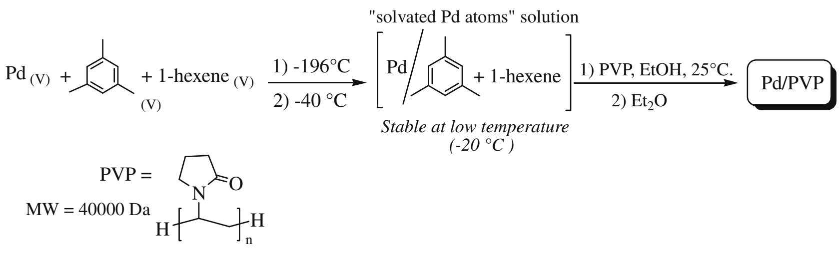
3.2. Structural studies of the Pd–PVP catalyst by HRTEM and FT-IR analyses

TEM investigations were limited to Pd–PVP systems with a metal content of 1%, 10% and 20 w/w%. A comparative view of images, representative of such materials, is displayed in Fig. 1. At the lowest Pd content (1 w/w%, panel A), only individual roundish metal nanoparticles were present (hereafter referred to as primary particles). The increase in the metal loading up to 10 w/w% (panel B) produced, as expected, more dense population of Pd particles on the polymeric support and, in addition, the formation of elongated and/or branched particles, resulted from the aggregation of some of the primary ones, was observed. At even higher Pd content (20 w/w%, panel C), the amount and size of linear/branched aggregates increased significantly, although a number of primary particles was still present.

For each of the three materials, a statistical evaluation of the size of the primary particles (both dispersed individually and partially merged in the aggregates) was carried out, and the results are reported in Fig. 2. Basically, in all cases, very narrow particle size distributions were obtained, limited in the 1.0–3.5 nm range. Likely, smaller particles, if present, escaped the detection [20].

Differences in the distribution profiles likely resulted from the fact that in Pd/PVP 1 w/w% only individual primary particles were present, with fully defined contours, whereas for the other catalysts the aggregation rendered more difficult and inaccurate the measurement of the size of the primary particles. Anyway, the standard deviations were quite close to the detection limit of the technique, and then, the three size distributions can be reasonably considered equivalent.

FT-IR spectroscopy technique was used and gave a substantial contribution to the comprehension of the interactions in different PVP–Metal and PVP–inorganic systems [21–23]. Digital subtraction, deconvolution procedure and derivative spectra technique



Scheme 1.

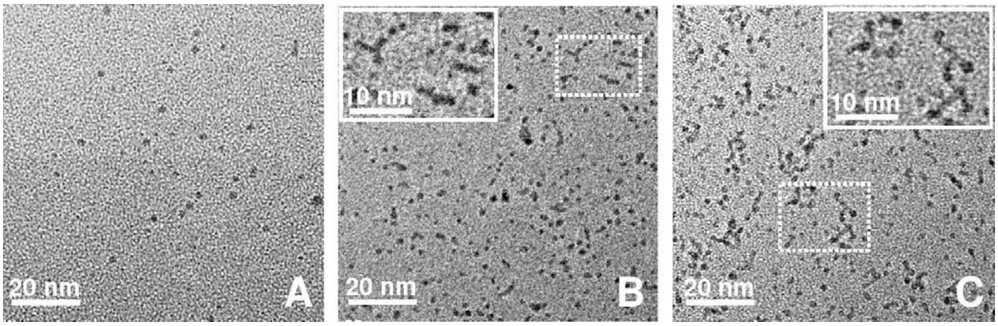


Fig. 1. Representative TEM images of: (A) Pd–PVP 1 w/w%, (B) Pd–PVP 10 w/w% and (C) Pd–PVP 20 w/w%; original magnification: 300 k. Insets in panels B and C are zoomed views of the regions unframed with the dotted line, evidencing linear/branched aggregates.

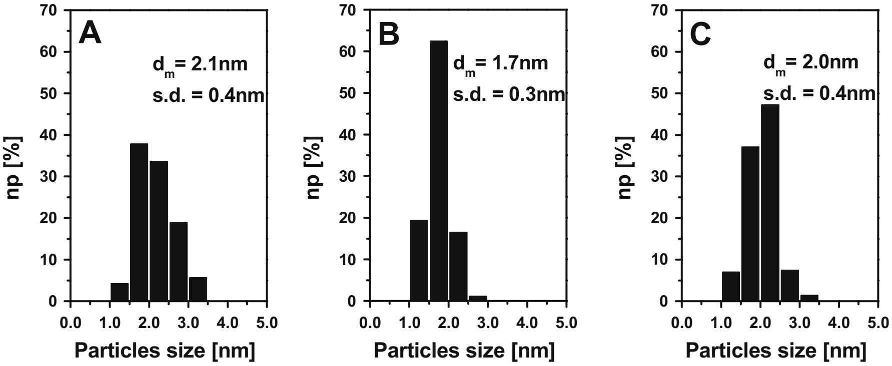


Fig. 2. Histograms of the primary particles (individual or partly merged in aggregates) of: (A) Pd–PVP 1 w/w%, (B) Pd–PVP 10 w/w% and (C) Pd–PVP 20 w/w%.

make possible the better observation of these interactions on Pd–PVP systems that showed different spectral patterns at different metal/polymer molar ratio. In particular, the absorption band due to at C=O stretching vibration showed a decrease in the width and a shift towards low frequencies vs. Pd composition.

The band of carbonyl stretching vibration of C=O in the PVP spectrum was very broad for the intermolecular interactions PVP–PVP, and many conformers appeared as more evident in the second derivative spectrum (Fig. 3A). In presence of Pd, competitive intermolecular interactions involving the C=O group of PVP and Pd occurred and a decrease in the conformers was observed. At 10 w/w% of Pd concentration, the interactions PVP–Pd prevailed on PVP–PVP and the absorption band of C=O was not broad, and we observed a minimum of conformers (Fig. 3B).

Moreover, analysing the frequency of the maximum and the broadening of the carbonyl band, as function of the Pd content, we can confirm the occurrence of the competitive intermolecular interactions involving the PVP C=O and active sites of Pd up to 10% (Fig. 4); above this concentration, interactions PVP–PVP begin to prevail again.

Similar behaviour was observed with PVP in solvents at different dielectric constant. This fact suggest that competitive intermolecular interactions occur between C=O group and active sites of the Pd.

The Pd–PVP 1 w/w% system appeared to be the more attractive material for catalytic studies thanks to the presence of highest amount of individual primary particles and the minor amount of aggregates that became more numerous by increasing the Pd loading up to 10 w/w%, as evidenced by HRTEM analyses.

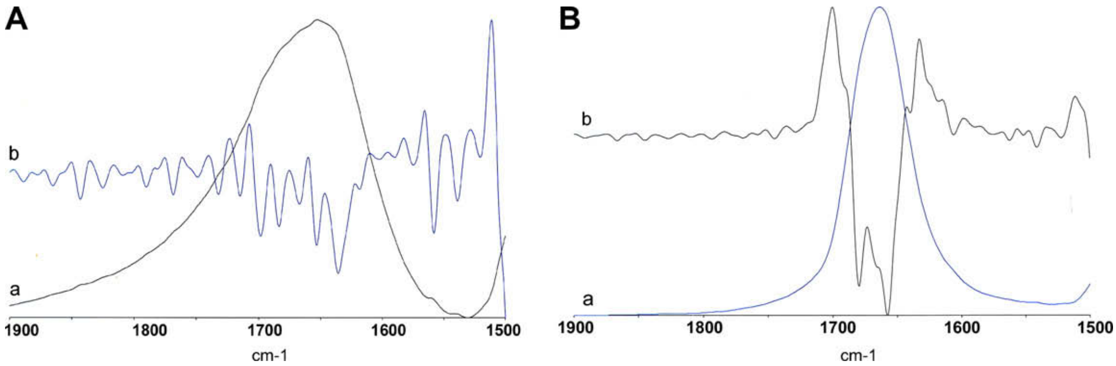


Fig. 3. (A) FTIR spectrum: (a) and FTIR second derivative (b) of PVP in the carbonyl stretching region; (B) FTIR spectrum (a) and FTIR second derivative spectrum (b) of Pd–PVP 10 w/w% in the carbonyl stretching region.

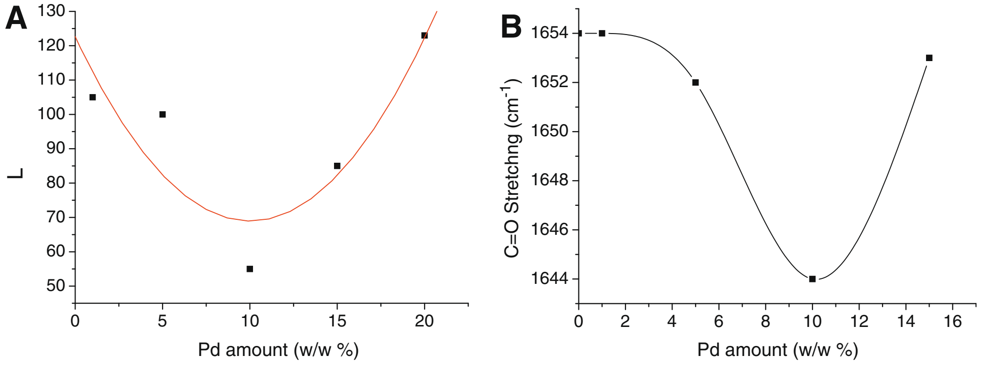


Fig. 4. (A) Plot of the width at half-height of the C═O stretching vibration as function of Pd w/w% on PVP; (B) Trend of the maximum of the carbonyl stretching band as function of Pd w/w% on PVP.

3.3. Catalytic activity of Pd–PVP system

3.3.1. Selective hydrogenation of aliphatic alkynes

The semi-hydrogenation of aliphatic alkynes is characterised by two selective parameters: a chemoselectivity towards alkene products avoiding the formation of undesired alkane and regio- and stereoselectivity towards the corresponding (Z)-alkene. Considering that nitrogen-based promoters (was used to increase) the selectivity in traditional Lindlar catalysts [24] and the positive effect of PVP polymer on Pt-based catalysts [25], PVP-stabilized palladium nanoparticles prepared by MVS, dissolved in ethanol, were tested in the selective hydrogenation of terminal and internal aliphatic alkynes (1-hexyne, 2-hexyne, 3-hexyne) to corresponding (Z)-alkenes and of 3-hexyne-1-ol to leaf alcohol 3-hexen-1-ol, a valuable compound in the chemistry of fragrances (Scheme 2, Fig. 5) [26].

It appears from the reported data that the Pd–PVP 1 w/w% system showed very high catalytic activity and selectivity, also at high substrate/Pd molar ratio (10,000 mol alkyne/mol Pd), without any additive or promoter. Hydrogenation reaction of 1-hexyne with Pd–PVP catalyst (Fig. 5A) leads to 1-hexene as main product (96%) at 95% of conversion, with the formation of hexane in very low amount (<4%) and only traces of alkenes isomers. Selectivity to (Z)-2-hexene and (Z)-3-hexene obtained from 2-hexyne and 3-hexyne, respectively, was very high (ca. 99% at 95% of alkyne conversion), and only traces of the (E)-isomer was observed (Fig. 5B and C, respectively). It is worth noting that, as previously reported for heterogeneous Pd and Pt catalysts, the sterically hindered environment, created by the PVP polymer surrounding the catalytically active metal particle, as observed by FT-IR analyses, can play an crucial role on the selectivity in the acetylenes hydrogenation reaction. It is well known that the rate of hydrogenation of internal alkynes such as 2-hexyne and 3-hexyne (SA = 210 and 390 (mol converted alkyne)/(mol Pd × min), respectively) is faster than terminal 1-hexyne (SA = 22 (mol converted alkyne)/(mol Pd × min)). As appeared from the literature, the rate of hydrogenation of terminal alkyne and the internal alkyne is expected to be different [27]. Previous studies [28,29] found a particle size effects in the selective hydrogenation of alkynes, such as small palladium particles at the high dispersion let to the faster reaction rate in the case of internal alkynes in comparison with internal ones. In this frame, the catalytic behaviour was explained by the presence of high coordinative unsaturation on the surface of small palladium nanoparticles, which can coordinate more strongly with terminal alkynes; under these conditions, the available hydrogen absorption sites decrease, reducing the reaction rate.

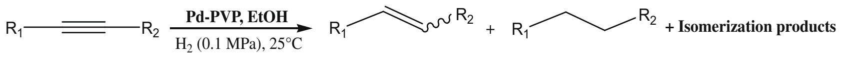
The catalytic hydrogenation of 3-hexyne-1-ol with Pd–PVP 1 w/w% system (Fig. 5D) showed high catalytic activity (SA = 180 mol converted alkyne/(mol Pd × min)) and very high selectivity (>96%), at 98% of 3-hexyne-1-ol conversion, to (Z)-3-hexene-1-ol with (E)-3-hexen-1-ol as by-product (<4%) and traces of completely saturated product. Comparable results were obtained in that reaction using Pd–PVP systems with higher metal content (10 w/w%) (Fig. 5E) evidencing not a correlation between the Pd/PVP molar ratio and the efficiency of the catalyst.

It is worth noting that the activity and selectivity of MVS-derived Pd–PVP system for the formation of (Z)-alkene is generally excellent and in many cases superior to that obtained with heterogeneous catalyst [24,30] and comparable or superior to those reported for homogeneous catalytic systems [31].

3.3.2. Pd–PVP system as “homogeneous” catalyst in Mizoroki–Heck reactions

The catalytic activity of Pd–PVP system was also evaluated in the cross-coupling of olefins with aryl halides (Mizoroki–Heck reaction), one of the most important reactions for the formation of C–C bonds in organic synthesis [32–35]. The cross-coupling reactions have been performed at different temperatures (75–175 °C) in 1-methyl-2-pyrrolidinone (NMP) as solvent, where the Pd–PVP is soluble, using N(^{n}Pr)$_3$ as base and a molar ratio aryl halide/Pd = 1000 or 100 (Table 1). An excess of *n*-butyl acrylate with respect to aryl halide (molar ratio = 2) to avoid the formation of twofold coupling by-products was used [36].

Pd–PVP system is very active and selective in coupling of iodo- and activated bromo-arenes, such as *p*-nitrobromobenzene, with *n*-butyl acrylate to the corresponding *n*-butyl (E)-cinnamate with specific activities (SA = 730 h^{-1} and 950 h^{-1}, run 2 and 3, respec-



R$_1$= H; R$_2$ = ^{n}Bu
R$_1$= Me; R$_2$ = ^{n}Pr
R$_1$= Et; R$_2$ = Et
R$_1$= Et; R$_2$ = CH$_2$-CH$_2$-OH

Scheme 2.

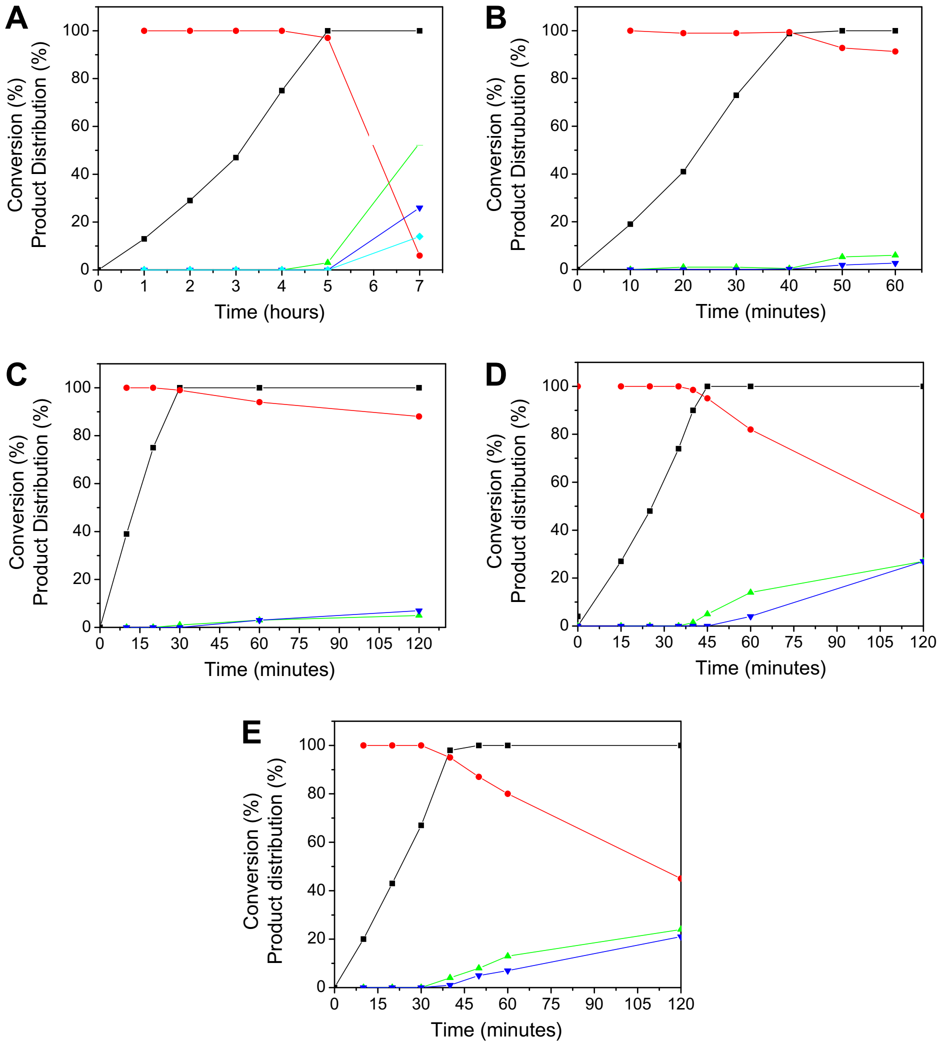


Fig. 5. Catalytic hydrogenation of alkynes with Pd–PVP 1 w/w% system obtained by MVS: (A) 1-hexyne hydrogenation, (■) 1-hexyne conversion, (●) 1-hexene, (▲) *n*-hexane, (▼) trans-2-hexene, (♦) cis-2-hexene; (B) 2-hexyne hydrogenation, (■) 2-hexyne conversion, (●) cis-2-hexene, (▲) trans-2-hexene, (▼) *n*-hexane; (C) 3-hexyne hydrogenation, (■) 3-hexyne conversion, (●) cis-3-hexene, (▲) trans-3-hexene, (▼) *n*-hexane; (D) 3-hexyne-1-ol hydrogenation, (■) 3-hexyne-1-ol conversion, (●) cis-3-hexene-1-ol, (▲) trans-3-hexene-1-ol, (▼) *n*-hexane-1-ol; (E) catalytic hydrogenation of 3-hexyne-1-ol with Pd–PVP 10 w/w%: (■) 3-hexyne-1-ol conversion, (●) cis-3-hexene-1-ol, (▲) trans-3-hexene-1-ol, (▼) *n*-hexane-1-ol.

tively) higher than commercially available $Pd(OAc)_2$ (SA = 500 h^{-1}, run 1).

The cross-coupling reaction of bromobenzene with *n*-butyl acrylate was examined at 125 °C as well as at 175 °C using a molar ratio substrate/Pd = 100. After 24 h, the yield in *n*-butyl (E)-cinnamate was 10% (T_{react} = 125 °C; Table 1, run 4) or 52% (T_{react} = 175 °C; Table 1, run 5), then indicating a quite low specific activity of the catalyst towards this reaction. In the case of the run carried out at the higher temperature (175 °C), such should be due to the instability of palladium–polymer system, which in these conditions leads to the formation of a palladium black inactive precipitate [13]. It is worth noting that, as previously observed in the selective hydrogenation of acetylenes compounds, Pd–PVP systems containing higher metal content (10 w/w%) showed catalytic efficiency comparable to that Pd–PVP 1 w/w% (runs 6–8, Table 1).

The catalysts in runs 2 and 3 were recovered by adding diethyl ether to the reaction mixture, as above reported, re-dissolved without formation of insoluble species and reused in the same reaction (runs 9 and 10, respectively). They showed very similar catalytic activity to that of the starting material (SA = 780 vs. 830 min^{-1} and SA = 930 vs. 950 min^{-1}). Moreover, the palladium amount retained in solution after the precipitation of Pd–PVP catalyst in runs 2 and 3 was examined: in both cases, very low palladium leaching was observed. In the reaction of iodobenzene with *n*-butyl acrylate performed at 75 °C (run 2), Pd leached during the reaction (1 h) was 0.9% of the total available metal, corresponding to 0.56 ppm in solution; in the case of run 2, the reaction *p*-nitrobromobenzene with *n*-butyl acrylate was carried out at 125 °C, the Pd leached was 4.3% of the total available metal corresponding to 2.53 ppm in solution.

4. Conclusions

The MVS technique has proven to be a valuable method for the preparation of peculiar PVP-stabilized palladium nanoparticles, which can be conveniently used as “homogeneous” catalytic system, quantitatively recovered at the end of the reaction and reused in additional runs. HRTEM analyses on Pd–PVP systems with different Pd content (1%, 10%, 20 w/w Pd%) showed highly dispersed palladium nanoparticles with very small mean diameters (ca. 2.0 nm) and a very narrow size distribution (1.0–3.5 nm) in comparison with the size of similar systems prepared by other routes [8,14].

FT-IR spectroscopy of Pd–PVP systems revealed the presence of intermolecular interactions between C═O groups of PVP and active sites of palladium, accounting of their thermal stability when employed in catalytic reactions at high temperature (75–125 °C).

The Pd–PVP 1 w/w% system is a very efficient catalyst in the selective hydrogenation of aliphatic alkynes (1-hexyne, 2-hexyne, 3-hexyne and 3-hexyne-1-ol) to the corresponding (Z)-alkenes that demonstrate a very high activity and selectivity, comparable or superior to that reported for homogeneous and heterogeneous catalytic systems. Interestingly, the hydrogenation of internal alkynes (2-hexyne, 3-hexyne and 3-hexyne-1-ol) was faster than terminal one (1-hexyne). It can be related to the very small particle sizes [28,29], while the presence sterical constriction of PVP surrounding Pd particles could account to the high stereoselectivity to (Z)-alkenes [25].

The Pd–PVP systems are also active in Mizoroki–Heck C–C coupling reaction of iodobenzene and *p*-bromo-nitrobenzene with butyl acrylate showing greater catalyst efficiency than commercial soluble catalysts such as $Pd(OAc)_2$. The preparation route here reported can be conveniently extended to the preparation of a wide range of PVP-stabilized metal nanoparticles (Pt, Rh, Ru, Au, etc.), pointing out the usefulness of solvated metal atoms as starting material for stabilized nanostructured metal systems.

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