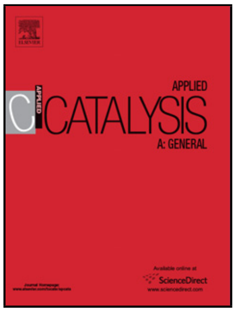

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Palladium Nanoparticles Supported on Smopex® Metal Scavengers as catalyst for Carbonylative Sonogashira Reaction: synthesis of α,β-alkynyl ketones

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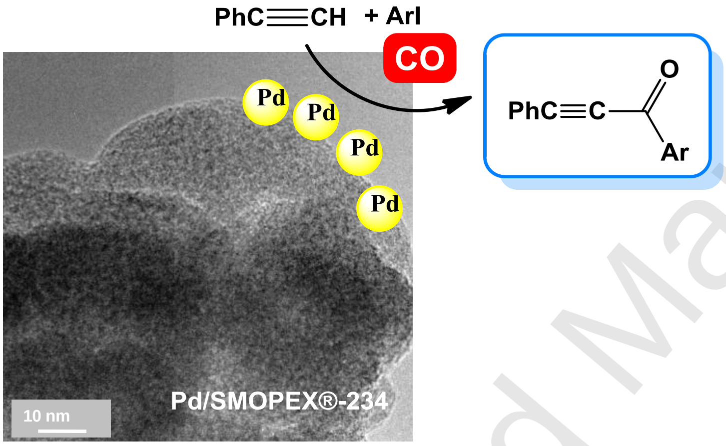
GRAPHICAL ABSTRACT:



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Research Highlights

▶ Palladium nanoparticles (Pd NP) prepared by means of metal vapour synthesis technique.

▶ Deposition of Pd NP on Smopex® metal scavengers .

▶ Pd/Smopex®-234 catalyses selectively carbonylative Sonogashira reactions.

▶ Preliminary tests indicate a heterogeneous behaviour.

Palladium nanoparticles supported on Smopex® metal scavengers as catalyst for carbonylative Sonogashira reactions: synthesis of α,β-alkynyl ketones

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Abstract

Palladium nanoparticles supported on two Smopex® commercial metal scavengers (1% w/w) have been tested in the carbonylative Sonogashira reactions of aryl iodides with phenylacetylene. Their catalytic activity has been compared with those of more common catalysts (Pd/C, Pd/γ-Al_2O_3). Pd/Smopex®-234 resulted especially effective in the synthesis of alkynyl ketones even working with a low amount of palladium (0.2-0.5 mol %). Preliminary heterogeneity tests (i.e. hot filtration test, Pd leaching and recycle of the catalyst) have been performed in order to evaluate the catalytic behavior of this system. The obtained results seem to indicate that Pd/Smopex®-234 could act as a truly heterogeneous catalyst.

Keywords

Palladium Nanoparticles, Heterogeneous catalysis, Sonogashira cross-coupling carbonylation, Metal vapour synthesis;

1. Introduction

Alkynyl ketones are contained in several biologically active molecules [1-3] and play a crucial role as key intermediates in the synthesis of natural compounds [4-8] and pharmacologically active heterocyclic systems [9-14]. In the past alkynones have been generally obtained by transition-metal-catalysed cross-coupling reactions between acid chloride and terminal acetylenes [15-20]. However, the lack of stability and the low functional group tolerance of the acid chloride have limited the application of this methodology.

Since Tanaka and coll. [21] reported the first example of carbonylative Sonogashira reaction of aryl halides with carbon monoxide and terminal alkynes, this atom economic route become the most commonly used for the synthesis of alkynyl ketones [22-30]. With respect to the Sonogashira reaction [31-32], the carbonylative version of this process is often performed in the absence of CuI which favours the formation of noncarbonylative products. Terminal alkynes are usually reacted with aryl iodide but, recently, Beller and coll. have reported the use of aryl triflates [33] and even aryl bromides [34] in the synthesis of the corresponding arylalkynyl carbonyl compounds. Several base/solvent systems (Et_3N, $(iPr)_2EtN$, NH_3aq, DBU, DABCO, K_2CO_3, $NaHCO_3$, DMF, NMP, H_2O, toluene, CH_3CN, THF, ionic liquids) have been tested in order to get mild experimental conditions and many palladium complexes ($Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, $PdCl_2$(dppf), $Pd_2(dba)_3$ etc..) have been reported to be effective in the carbonylative reaction. Even if homogeneous catalysts are generally very efficient, the use of soluble complexes makes the recovery of the metal impossible and results in palladium contamination of the product.

To date, only four examples of carbonylative Sonogashira reactions promoted by palladium supported catalysts are known, although the use of a heterogeneous species would allow simpler recovery and easier purification of the product, possible recycle of the catalyst and could assure a higher thermal stability of the catalytic species. In 2008 Xia and coll. [35] described for the first time the use of Pd/C in the carbonylative cross-coupling between phenylacetylene and aryl iodides under pressure of carbon monoxide (20 atm). The reactions afforded the carbonylated products in high yields but the catalyst could be recycled only three times before the loss of its catalytic activity. Later on, the same research group [36] investigated the activity of palladium deposited on superparamagnetic nanoparticles of Fe_3O_4. Several aryl iodides were successfully reacted with terminal acetylenes while no alkynyl ketones were formed when arylbromide or chloride were used.

As far as the catalytic mechanism is concerned, it resulted to be quasi-homogeneous since a small amount of palladium dissolved from the Pd/Fe_3O_4 catalyst and then partially re-precipitated at the end of the reaction. Nevertheless, the catalyst could be reused seven times with only a slight loss of activity. More recently, Xia and coll. [37] prepared a palladium catalyst supported on a cross-linked polymer by reaction of $Pd(OAc)_2$ with the copolymer of 3-butyl-1-vinylimidazolium iodide and divinylbenzene. The supported palladium nanoparticles (mean diameter: 20 nm) were effective catalyst for the carbonylative Sonogashira reactions. As already observed for Pd/Fe_3O_4, the catalysts could be reused 5 times but in this case AAS analysis indicated a remarkable leaching of palladium (i.e. more than 20% w/w of the metal used for the first reaction) during the recycles. Finally, Cai and coll. [38] synthesised a bidentate phosphine palladium (0) complex anchored to the mesoporous material MCM-41 and claimed it to be the first heterogeneous catalyst for the carbonylative Sonogashira reaction. The reactions were performed in Et_3N, at room temperature and under atmospheric pressure of carbon monoxide but a large amount of palladium (5 mol %) was necessary to achieve the products in good yields. The MCM-41-P-Pd(0) could be reused 10 times without loss of activity but, surprisingly, neither data on the metal leaching from the polymer were reported nor filtration tests were performed. This is quite unexpected since many authors [39-42] have demonstrated that cross-coupling reactions carried out with supported palladium catalysts often proceed via metal leached from the surface during the oxidative addition of ArI to Pd(0) which forms soluble ArPdI species.

As an alternative to supported catalyst, the problem of the palladium dissolved in reactions mixtures could be solved by employing metal scavengers. Recently, Johnson Matthey has developed and launched a new family of metal scavenger systems [43] based on a fibre technology called Smopex® which are able to recover platinum group metals (Pd, Pt, Rh) down to part per billion. In particular, Smopex®-111 and Smopex®-234, thiol-based scavengers, can absorb palladium from post-reaction solutions of cross-coupling processes such as Heck, Suzuki, and Sonogashira reactions [44-48].

Considering the high affinity between the metal and the organic resins Prasad and coll. deposited $Pd(OAc)_2$ on Smopex®-111 and used the resulting supported species in Heck and Suzuki cross-coupling reactions with good results [49]. The catalyst was recycled four times with no loss of activity and with low metal leaching.

Intrigued by the possibility of coupling the metal scavenger properties of Smopex® fibres with the high catalytic activity of metal nanoparticles (NP), we have prepared Pd(0) NP by means of Metal Vapour Synthesis (MVS) technique [50-56] which assures the formation of small dimensioned metal clusters that can be easily dispersed on several matrices. These Pd(0) NP have been deposited on Smopex®-111 and Smopex®-234 fibres. The catalysts thus prepared have been tested in the carbonylative Sonogashira reaction between iodoarenes and phenylacetylene. Here we describe the main results obtained and a detailed study on the catalytic activity of the palladium supported species. A comparison with the performances of palladium nanoparticles deposited on more traditional matrices such as carbon and alumina, will be reported too.

2. Experimental

2. 1 Catalysts preparation

All operations involving the MVS products were performed under a dry argon atmosphere. The co-condensation of palladium and mesitylene/1-hexene was carried out in a static reactor previously described [57]. The "mesitylene/1-hexene-solvated Pd atoms" solution was worked up under argon atmosphere with the use of the standard Schlenk techniques.

2.1.1 Synthesis of the solvated palladium atoms

In a typical experiment, Pd vapour generated at 10^{-3} KPa by resistive heating of 500 mg of the metal in an alumina coated tungsten crucible was co-condensed at liquid nitrogen temperature with vapour of mesitylene (30 mL, MES) and 1-hexene (30 mL) in a glass reactor. Then the reactor chamber was heated to the melting point of the solid matrix (ca −40 °C), and the resulting red-brown solution was siphoned and handled at low temperature (−30/−40 °C) with the Schlenk tube technique. The metal content of the solution was assessed by ICP spectrophotometry. The metal containing mesitylene 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 analyzed by ICP. The palladium content of the solvated metal solution was 4.8 mg/mL.

2.1.2 Preparation of Pd/γ-Al_2O_3 catalyst (1 w % Pd)

The Pd/mesitylene-1-hexene solution (2.1 mL, 10 mg Pd) was added to a suspension of γ-Al_2O_3 (1.00 g) in mesitylene (10 mL). The mixture was stirred for 24 h at room temperature. The colourless solution was removed and the grey solid, containing 1 wt. % Pd, was washed with n-pentane and dried under reduced pressure.

2.1.3 Preparation of Pd/C catalyst (1 w % Pd)

The Pd/mesitylene-1-hexene solution (2.1 mL, 10 mg Pd) was added to a suspension of carbon (1.00 g) in mesitylene (10 mL). The mixture was stirred for 24 h at room temperature. The colourless solution was removed and the solid, containing 1 wt. % Pd, was washed with n-pentane and dried under reduced pressure.

2.1.4 Preparation of Pd/Smopex®-111 catalyst (1 w % Pd)

The Pd/mesitylene-1-hexene solution (1 mL, 5 mg Pd) was added to a suspension of Smopex®-111 (0.500 g) in mesitylene (10 mL). The mixture was stirred for 24 h at room temperature. The colourless solution was removed and dark-grey the solid, containing 1 wt. % Pd, was washed with n-pentane and dried under reduced pressure.

2.1.5 Preparation of Pd/Smopex®-234 catalyst (1 w % Pd)

The Pd/mesitylene-1-hexene solution (1 mL, 5 mg Pd) was added to a suspension of Smopex®-234 (0.500 g) in mesitylene (10 ml). The mixture was stirred for 24 h at room temperature. The colourless solution was removed and dark-grey the solid, containing 1 wt. % Pd, was washed with n-pentane and dried under reduced pressure.

2.2 Catalysts characterization

The amount of palladium in the above solutions was determined by inductively coupled plasma–optical mission spectrometers (ICP–OES) with a Spectro-Genesis instrument equipped with software Smart Analyser Vision.

Electron micrographs were obtained by a Jeol 3010-UHR high resolution transmission electron microscope (HRTEM) operating at 300 kV equipped with a LaB6 filament and with an Oxford Inca Energy TEM 300 EDS X-rays analyser by Oxford Link. Digital micrographs were acquired by an Ultrascan 1000 camera and processed by Gatan digital micrograph. Before the experiments, the samples, in the form of powders, were milled in an agate mortar and deposited on a copper grid covered with a lacey carbon film. In the case of Pd/Smopex®-111 and Pd/Smopex®-234, the milling procedure was performed at low temperature (in the presence of liquid nitrogen, in order to preserve the fibres from mechanical damage).

FTIR spectra were collected using a Bruker IFS 28 spectrometer (MCT detector; resolution: 4 cm^{-1}). The samples were pressed in self supported pellets and placed in a quartz cell with KBr windows that, once connected to conventional vacuum lines (residual pressure $1.0\times10^{-}$

^{5} Torr), allowed all thermal treatments and adsorption/desorption experiments to be carried out in situ. Before the CO adsorption experiments the samples were reduced 1 hour in H_2 at RT, and then degassed for 30 min at the same temperature. High purity CO (Praxair) was used, without any further purification.

2.3. Catalytic tests

2.3.1 General procedure for Sonogashira carbonylative reactions

Sonogashira carbonylative reactions were run in a 25 mL stainless steel autoclave fitted with a Teflon inner crucible and a stirring bar. In a typical run, 2 mmol of ArI, 2. 5mmol of phenyl acetylene and 5 mL of Et_3N were put in a Pyrex “Schlenk” tube under CO atmosphere. This solution was introduced by a steel siphon into the previously evacuated (0.1 Torr) autoclave carried with 0.2 mol% of catalyst. The reactor was pressurised with carbon monoxide (20 atm) and the mixture was stirred at 100 °C for the specified time. After removal of excess CO (fume hood), the reaction mixture was diluted with CH_2Cl_2, filtered (Celite) and concentrated under vacuum. The residue was purified by column chromatography and characterized by ^{1}H-NMR and ^{13}C-NMR analysis.

All operation involving CO must be performed under fume-hood (DANGER).

2.3.2 Hot filtration test

According to the cross-coupling procedure, iodobenzene (2 mmol) and phenylacetylene (2.5 mmol) dissolved in Et_3N (5 mL) were reacted with 0.0426 g (0.2 mol%) of Pd/Smopex$^{®}$-234 at 100 °C, under CO (20 atm). After 4 h, the CO pressure was removed under fume hood, the reaction mixture was filtered at 100 °C through syringe fitted with a 0.2 μm Teflon filter, in order to remove all fine particles and the clear solution obtained was introduced into another autoclave by a steel siphon and stirred at 100°C under CO (20 atm) for further 24 h. After the usual work up, the reagents conversion (58%) was determined by GLC and ^{1}H NMR analysis.

2.3.3 Leaching Test

According to the cross-coupling procedure, iodobenzene (2 mmol) and phenylacetylene (2.5 mmol) were dissolved in Et_3N (5 mL) and reacted in the presence of 0.0426 g (2 mol%) of Pd/Smopex$^{®}$-234 at 100 °C, under CO (20 atm). After 4 h, the CO pressure was removed under fume hood, the reaction mixture was filtered at 100 °C through syringe fitted with a 0.2 μm Teflon filter. A sample (1 mL) of the clear reaction mixture was heated over a heating plate in a porcelain crucible in the presence of aqua regia (2 mL) for four times, and the solid residue was dissolved in 0.5 M aqueous HCl. The ICP–OES analysis of the solution obtained indicated that a 0.8 % ($3.4\ 10^{-3}$ mg) of the total palladium employed (0.43 mg) in the reaction was leached into solution during the reaction.

2.3.4 Recycle tests

According to the cross-coupling procedure, iodobenzene (2 mmol) and phenylacetylene (2.5 mmol) were dissolved in Et_3N (5 mL) and reacted in the presence of 0.0426 g of Pd/Smopex®-234 at 100 °C, under CO (20 atm). After 24 h excess CO (fume hood) was removed, and a fresh mixture of 2 mmol of iodobenzene, 2.5 mmol of phenylacetylene and 2 mmol of triethylamine was introduced by a steel siphon into the same autoclave which was repressurised with 20 atm of CO and stirred at 100 °C for more 24 h. After the usual work up, the reagents conversion (82%) was determined by GLC and ^{1}H NMR analysis. Analogously the autoclave was recharged two (74%, 24+24+24 h) and three times (90%, 24+24+24+24 h) with fresh reagents.

3. Results and discussion

3.1 Catalysts preparation and HR-TEM characterisation

Initially we focused our attention on the preparation and characterization of samples of palladium nanoparticles dispersed on the following supports: Smopex®-111, Smopex®-234, γ-Al_2O_3 and carbon (Table 1). Smopex®-111 and Smopex®-234 are polyolefin fibres grafted with styryl thiol and mercaptoethyl acrylate respectively (Figure 1).

Figure 1. (a) Smopex®-111, (b) Smopex®-234

The fibres are mechanically and chemically robust, air stable and may be used in organic solvents but not in water. The functional groups are easy accessible since they are located at the exterior of the fibres.

Palladium nanoparticles were prepared by means of the MVS technique. According to previously described procedures [57], Pd and a mixture of mesitylene/1-hexene were evaporated under vacuum and co-condensed on the frozen walls (-196°C) of a glass reactor, generating a brown solid matrix. During the warm-up stage from -196 to 0°C the matrix melted, and nucleation and growth processes of the metal particles took place leading to palladium(0) nanoclusters weakly stabilized by the solvent molecules. The supported catalysts (Table 1 entries 1-4) were prepared by simple addition of the Pd/Mesitylene/1-hexene solution to the chosen supports till decolourisation of the solution occurred. The catalysts thus obtained contained Pd(0) NP quantitatively deposited on the supports and were ready to use without any pre-activation step.

A sample of a commercial Pd/C was also used as reference supported specie (Table 1, entry 5).

Table 1. Supported Palladium nanoparticles

The morphology of all the supported catalysts was investigated by means of high resolution transmission electron microscopy (HR-TEM). Representative images of Pd/Smopex®-111 (section a), Pd/Smopex®-234 (section b), Pd/γ-Al_2O_3 (section c), Pd/C (MVS) (section d) and commercial Pd/C (section e) are shown in Figure 2.

Figure 2. HR-TEM micrographs and histograms of particle size distributions of palladium supported nanoparticles: a) Pd/Smopex®-111. Instrumental magnification: 60000X and 250000X, respectively; b) Pd/Smopex®-234. Instrumental magnification: 100000X and 500000X, respectively; c) Pd/γ-Al_2O_3. Instrumental magnification: 200000X; d) Pd/C (MVS). Instrumental magnification 300000X; e) Pd/C (Aldrich). Instrumental magnification: 100000X and 300000X, respectively.

It is worth noting that both Smopex®-111 and Smopex®-234 do not exhibit the expected fibres-like morphology any more after the addition of palladium nanoparticles.

In particular, Smopex®-111 appears as very large particles with globular shape and with size of about 200 nm, whereas Smopex®-234 exhibits an homogeneous population of globular particles with quite similar size, having an average diameter of 20 nm. The drastic change in morphology of both fibres is reasonably induced by the interaction of the functional groups with the Pd NP, making each fibre to wrap itself in around the metallic particles. This phenomenon seems particularly effective in the case of Smopex®-234, where the mercaptoethyl acrylate groups, due to their intrinsic structure, display a better capability to chelate the Pd nanoparticles, as confirmed by HRTEM observations which detected exclusively Pd nanoparticles embedded into the fibres (zoom in Figure 2, section b). As a consequence, on this sample Pd is highly dispersed and stabilized. An effect the electronic beam of the microscope on the change in shape of the fibres can be excluded, since the samples are stable during observation.

Moreover, a statistical evaluation of the size of the Pd particles was carried out for each material (see also Table 1). Histograms of the particle size distribution were obtained by considering at least 500 particles on the TEM images, and the mean particle diameter (d_m) was calculated as $d_m = \Sigma d_i n_i / \Sigma n_i$, where n_i was the number of particles of diameter d_i. The counting was carried out on electron micrographs acquired starting from 60,000 magnification, where Pd particles well contrasted with respect to the support were clearly detected. The graduation of the particle size distribution scale was 0.25 nm.

Due to the large contrast phase between the Smopex®-111 fibre and the metal, palladium is easily recognisable on this support. A quite low and heterogeneous dispersion of Pd NP has been observed by HR-TEM measurements when supported on Smopex®-111. Small, roundish particles with diameter ranging from 1 to 13 nm with average size 3.5 nm, as well as big nanoparticles agglomerates were detected (Figure 2, section a). Moreover, XRD measurements revealed the presence of crystalline PdO (JCPDS file number 00-46-1211 and 00-43-1024) and Pd phases (JCPDS file number 01-087-0637) (see Figure S1 in the Supporting Information section).

On the contrary, a very narrow particle size distribution was obtained for Pd/Smopex®-234 (particles with size in the 0.25-2.75 nm range have been detected). In particular, Pd particles were rather small and well dispersed with a more abundant population around 2 nm, with average size of 1.7 nm, as displayed in the inset of section b, Figure 2, where for the sake of clarity, these particles have been put in evidence by circles. In this case, two additional considerations have to be made: the former is that HR-TEM could not display a high sensitivity in revealing particles smaller than 1 nm in size, and the latter is that the occurrence of aggregation phenomena of sub-nanometric metal particles under the electron beam during HR-TEM observation cannot be excluded. As a consequence, the real mean size of MVS Pd particles on Smopex®-234 could be even smaller than that obtained from the particles size distribution. Furthermore, no diffraction peaks related to crystalline Pd phases were observed in the patterns of Pd/Smopex®-234 sample, indicating that the Smopex®-234 fibre is able to stabilise highly dispersed Pd nanoparticles (see Figure S1 in the Supporting Information section).

With the assumption that all Pd particles have spherical shape, the ‘theoretical’’ metal specific surface areas (SSA) were calculated, by applying the formula SSA= $3\ \Sigma\ n_i r_i^2 / (\rho_{Pd}\ \Sigma n_i r_i^3)$ m^2/g, where r_i was the mean radius of the size class containing n_i particles, and ρ_{Pd}

the volumetric mass of Pd (12.02 g/cm^3). Pd SSA equal to 135 m^2 g^{-1} and about 45 m^2 g^{-1} were obtained for Pd/Smopex$^{®}$-234 and Pd/Smopex$^{®}$-111, respectively.

All these results indicate that the structure of the fibre strongly influences the Pd dispersion and, in particular that Smopex$^{®}$-234 displays a greater affinity for Pd than Smopex$^{®}$-111, being able to stabilise the metal in the form of very small nanoparticles.

As far as Pd/γ-Al_2O_3 and Pd/C prepared according to the MVS technique, the analysis of the metal particles of the two systems showed the presence of palladium clusters with a small size distribution lying in the 1.5 and 7 nm range and average diameters of 3.2 and 3.6 nm respectively, while in the case of commercial Pd/C the particles size distribution is broader than the previous ones, ranging from about 2 and 23 nm approximately (as shown in section e of Figure 2). However, in this case, the largest fraction of particles has size of 3-6 nm, and an average diameter of 5.5 nm is obtained.

3.2 Carbonylative Sonogashira Reactions

The catalytic activity of the palladium supported nanoparticles was initially investigated in the Sonogashira carbonylative coupling of phenyl acetylene with iodobenzene, chosen as model compounds (Scheme 1).

Scheme 1. Carbonylative Sonogashira reaction of iodobenzene and phenylacetylene

The reactions were performed in triethylamine, used as solvent and as base, and at 100 °C, since Smopex$^{®}$ fibre can decompose at higher temperature. Moreover, organometallic complex such as $Pd(OAc)_2$ and $PdCl_2(PPh_3)_2$ were used as reference homogeneous catalysts. In a typical experiment, 2.5 mmol of PhC≡CH and 2 mmol of PhI were reacted in the presence of 0.2 mol % of palladium with respect to the iodobenzene, in a 25 mL stainless steel autoclave pressurised to 20 atm of carbon monoxide (Table 2).

Table 2.

Carbonylative Sonogashira reaction of phenyl acetylene and iodobenzene promoted by palladium catalysts

Almost all supported species were able to catalyse the carbonylative Sonogashira process with moderate to excellent conversions towards the alkynyl ketone **3a**, even if reaction times longer than $PdCl_2(PPh_3)_2$ were necessary. In particular, commercial and MVS derived Pd/C resulted highly efficient species affording the desired product **3a** with high selectivity and conversion, which slightly decreased when alumina was used as support instead of carbon (Table 2 entries 3-5).

The dramatic difference observed in the catalytic behaviour of the palladium NP supported on the two Smopex® fibres (Table 2 entries 6 vs. 7) was quite unexpected and could be firstly related to the morphological features of the two species, i.e. small particles well dispersed for Pd/Smopex®-234 and presence of big aggregates in the case of Pd/Smopex®-111 (Figure 2, a and b, respectively).

FTIR measurements of adsorbed CO at RT were undertaken to get information on the metallic exposed sites of the Pd nanoparticles supported on both Smopex® matrices. The FTIR spectra of 100 torr CO dosed at RT onto Pd/Smopex®-111 and Pd/Smopex®-234 are reported in Figure 3.

Figure 3. FTIR spectra of 100 torr CO dosed at r.t. onto a) Pd/Smopex®-111 and b) Pd/Smopex®-234.

The catalysts were previously treated with H_2 at RT in order to activate the surface towards the adsorption of probe molecules. Surprisingly, no CO adsorption took place on the surface of either Pd/Smopex®-111 or Pd/Smopex®-234 samples. This feature indicates that in dry conditions the Pd particles are covered by the fibre and remain inaccessible for CO molecules. However, the catalytic activity displayed by Pd/Smopex®-234 suggests that the Pd active sites are available in reaction conditions. It can be hypothesised that in the presence of triethylamine the interaction between the functional groups of Smopex®-234 and the Pd NP is weakened, resulting in an opening phenomenon of the fibre, which makes the Pd active phase available to the reaction. This capability is peculiar of Smopex®-234, whilst in the case of Smopex®-111, which is catalytically inactive, no opening process occurs during reaction.

Moreover, carbon monoxide seems to play an important role in the different reactivity of the two catalysts. Indeed, when Pd/Smopex®-111 and Pd/Smopex®-234 were tested in Sonogashira reactions carried out in the absence of CO (Scheme 2) no results were obtained in both cases, as described in Table 3, entries 3 and 4.

Scheme 2. Sonogashira reaction of iodobenzene and phenylacetylene

These results could be tentatively explained considering a possible ligand exchange between the carbonyl group of the Smopex®-234 and a molecule of carbon monoxide that can take place after the opening process of the fibre. As hypothesized in Scheme 3 (cycle I), after the coordination of the Pd centre with a CO molecule, the formation of an acylpalladium intermediate could occur; then the alkyne addition and the reductive elimination could generate the observed product. Alternatively, it can be postulated a competition between CO and polymer–bound thiol groups at the surfaces of the Pd nanoparticles (Scheme 3, cycle II) so that carbon monoxide displaces SH making palladium nanoparticles more accessible to the attack of the aryl halide.

On the other hand, the small amount of diphenylacetylene detected in the Sonogashira carbonylative reaction of Pd/Smopex®-234 (Table 2, entry 7) can be due to the addition of phenylacetylene to Ph-Pd-I intermediate before the formation of the acyl palladium complex; the subsequent reductive elimination would generate the Sonogashira product (Scheme 3, cycle III)

Scheme 3. Hypothesis of ligand exchange mechanism.

In order to get more information on the catalytic performances of the supported palladium nanoparticles, their specific activity (SA) was calculated as (mmol iodobenzene consumed %) / (mmol Pd), after stopping the reactions at 4h, i.e. at partial conversion of the reagents. The obtained results, described in Table 4 and Figure 4, indicated that all supported MVS catalysts showed appreciable to excellent specific activities. More in detail, Pd/C (MVS) and Pd/C (comm.) exhibit similar SA and slightly lower than SA of $PdCl_2(PPh_3)_2$ (Table 4, entries 3 and 4 vs entry 2). Analogously, Pd/Smopex®-234 showed a good specific activity in the catalysis of the reaction (Table 4, entry 6, SA = 336), even higher than SA of a homogeneous organometallic compound such as $Pd(OAc)_2$ (Table 4, entry 1, SA = 196).

Table 4. Catalytic behaviour of palladium catalysts

Figure 4. Specific Activity of Pd catalysts calculated as (mmol iodobenzene consumed %) / (mgatom Pd) (conditions in Table 4).

In the light of the promising results obtained with Pd/Smopex®-234, this catalyst has been tested in the carbonylative Sonogashira reactions of phenylacetylene with iodoarenes characterised by different steric and electronic properties (Table 5).The reactions were performed under the same experimental conditions employed with iodobenzene (5 mL Et_3N, 100 °C, 20 atm CO).

Table 5. Carbonylative Sonogashira reaction of phenyl acetylene and iodoarenes promoted by Pd/SMOPEX®- 234

From the results reported in Table 5, it is evident that Pd/Smopex®-234 resulted a good catalyst for the reactions of phenylacetylene with aryl iodides possessing both electron donating (Me, OMe, Ph) and electron withdrawing (Cl) substituents in ortho or para position. All the reactions yielded the carbonylated coupling products **3a-f** with high chemoselectivity (82-93%). A reduction of the reaction rate was observed when the steric requirements of the aryl iodide increased (Table 5, entries 3 vs 5); however, the use of a higher amount of the catalyst (0.5 mol % instead of 0.2 mol %, Table 5, entries 5,6) resulted in good conversion of the reagents.

Next, we tested the catalytic activity of Pd/Smopex®-234 in the carbonylative Sonogashira reaction of phenylacetylene and aryl bromides (Scheme 4) which offer considerable advantages with regard to availability, toxicity and costs compared with aryl iodide. The reactions were carried out under the experimental conditions previously used for the reactions of the aryl iodides (100 °C, 20 atm CO, 2.5 mmol of phenylacetylene, 2 mmol of aryl bromide and 0.2-0.5 mol% catalyst).

Scheme 4. Pd/Smopex®-234 catalysed carbonylative Sonogashira reaction of phenyl acetylene and bromoarenes

Unfortunately, no conversion towards the alkynyl ketones was observed. Indeed, the reagents were totally recovered at the end of the reactions, regardless of the long reaction times (72 h) employed and the electronic features of the aryl bromides (i.e. p- NO_2 or p-OMe). Moreover, when a stoichiometric amount of KI was added to the reaction mixture of bromobenzene and phenylacetylene in order to perform in situ a “Halex” [58] Br/I exchange, no product formation was detected.

3.3 Heterogeneity tests

In order to determine whether the catalyst or a portion thereof can be considered truly heterogeneous, we have performed some heterogeneity tests following Pagliaro's approach [59].

Firstly, the Maitlis [60] hot filtration test was carried out to look for the presence of soluble active palladium nanoparticles. Two identical reactions were performed reacting iodobenzene (2 mmol) with phenylacetylene (2.5 mmol) in Et_3N (5 mL), with 0.2 mol% of Pd/Smopex®-234, at 100 °C, under CO (20 atm) (Scheme 5).

Scheme 5. Hot filtration test.

In the first case (Scheme 5, a), after 4h, the autoclave was cooled to room temperature, CO pressure was discharged under fume hood and the reaction mixture was analysed by ^{1}H-NMR and GC analysis which indicated a 65% conversion of reagents. In the other case (Scheme 5, b), after the same time, the CO pressure was discharged under fume hood and the hot reaction mixture was filtered through a Teflon filter (0.2 μm) under CO atmosphere (DANGER!), in order to remove all suspended metal particles. Then, the clear solution obtained was introduced into another autoclave, charged with 20 atm of CO and reacted for 24 hours. If the catalysts is truly heterogeneous the conversion should not increase. To our delight, no further reaction was observed, (Scheme 5, b) and the resulting value of 58% of conversion could be ascribed to a partial decomposition of the product during the second run of reaction.

Subsequently, a leaching test was performed. Again, the autoclave was charged with iodobenzene (2 mmol), phenylacetylene (2.5 mmol), Et_3N (5 mL), and 0.2 mol% of Pd/Smopex®-234. After 4 h at 100 °C, the CO pressure was discharged (fume hood) and the hot reaction mixture was filtered (Teflon filter, 0.2 mm) under nitrogen atmosphere. The palladium content in the resulting solution was determined by ICP analysis and was found to be 0.8 w/w % of the total Pd employed. This very low value, together with the result of the hot filtration test, could reasonably suggest that even if a very small amount of Pd nanoparticles is present in the solution during the reactions they are not active, thus suggesting a heterogeneous mechanism for the Pd/Smopex®-234 catalyst.

Finally we have carried out some experiments in order to verify if the catalyst could be reused without loss of activity (Figure 5). Since Smopex® fibres cannot be treated with water in order to remove the salts that are generated during the cross coupling process, the recycle tests were performed by recharging with fresh reagents the same batch of Pd/Smopex®-234 several times. Indeed, in the first run, the autoclave was charged with the typical amount of reagents and catalyst (2 mmol of iodobenzene, 2.5 mmol of phenylacetylene, 5 mL of Et_3N and 0.2 mol% of Pd/Smopex®-234, 20 atm CO). The reaction was run for 24 h in order to get a high conversion of the PhI (80%). Then, the autoclave was cooled, the CO pressure was discharged and a fresh solution of 2 mmol of iodobenzene, 2.5 mmol of phenylacetylene and 2 mmol of triethylamine was siphoned into the same autoclave which was again pressurized with 20 atm of CO (Figure 5, recycle 1). After 24 h GC and ^{1}H-NMR analysis of the reaction mixture showed 82% conversion of iodobenzene. Analogously in the cases of recycles 2 and 3 (Figure 5) the autoclave was recharged with fresh reagents two (24+24+24 h, 76% conv.) and three times (24+24+24+24 h 90% conv.) respectively. The observed results indicated that the same batch of catalyst can be used at least four times with no significant loss of activity.

Figure 5. Recycling tests of Pd/Smopex®-234 performed under the standard reactions conditions (2 mmol of iodobenzene, 2.5 mmol of phenylacetylene, 5 mL of Et_3N and 0.2 mol% of Pd/Smopex®-234, 20 atm CO).

3. 4. Conclusions

We have demonstrated that palladium (0) nanoparticles, prepared according to the MVS technique, can be easily tethered to commercial thiol based metal scavengers Smopex®-111 and Smopex®-234. Between the two supported species obtained, only Pd/Smopex®-234 showed a good catalytic activity in the carbonylative Sonogashira reaction of iodoarenes and phenylacetylene affording the corresponding α,β-alkynyl ketones with high chemoselectivity (82-93%). The reactions can be carried out with a very small amount of catalyst (0.2-0.5 mol% Pd) and did not require phosphine ligands or CuI as co-catalyst.

The good performances observed with Pd/Smopex®-234 can be reasonably due to its very small Pd NP highly dispersed in the organic matrix as well as to the unique capability of the Smopex®-234 resin to render Pd NP accessible to the reactants in the presence of the Et_3N solvent.

The results obtained in the hot filtration test, the very low value (0.8%) of the Pd leached into solution during the reaction and the possibility of recycling the catalyst with no loss of activity seem to indicate a heterogeneous behaviour of Pd/Smopex®-234. Even if the presence of a “homeopathic” amount of homogeneous catalytic systems cannot be ruled out, the “coupling” of a metal scavenger with very active Pd(0) nanoparticles generates a promising catalyst for carbonylative Sonogashira reactions.

Acknowledgements

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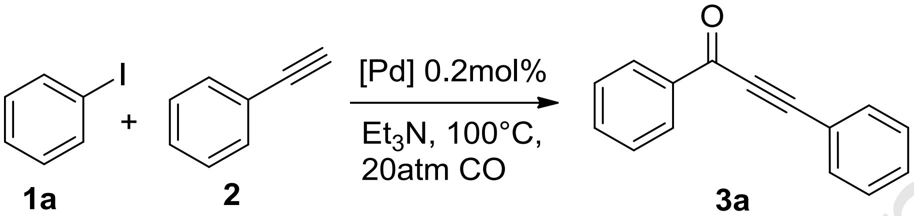
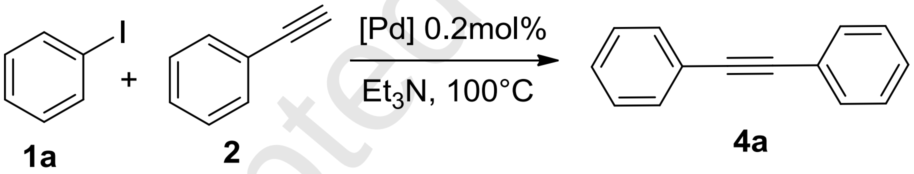
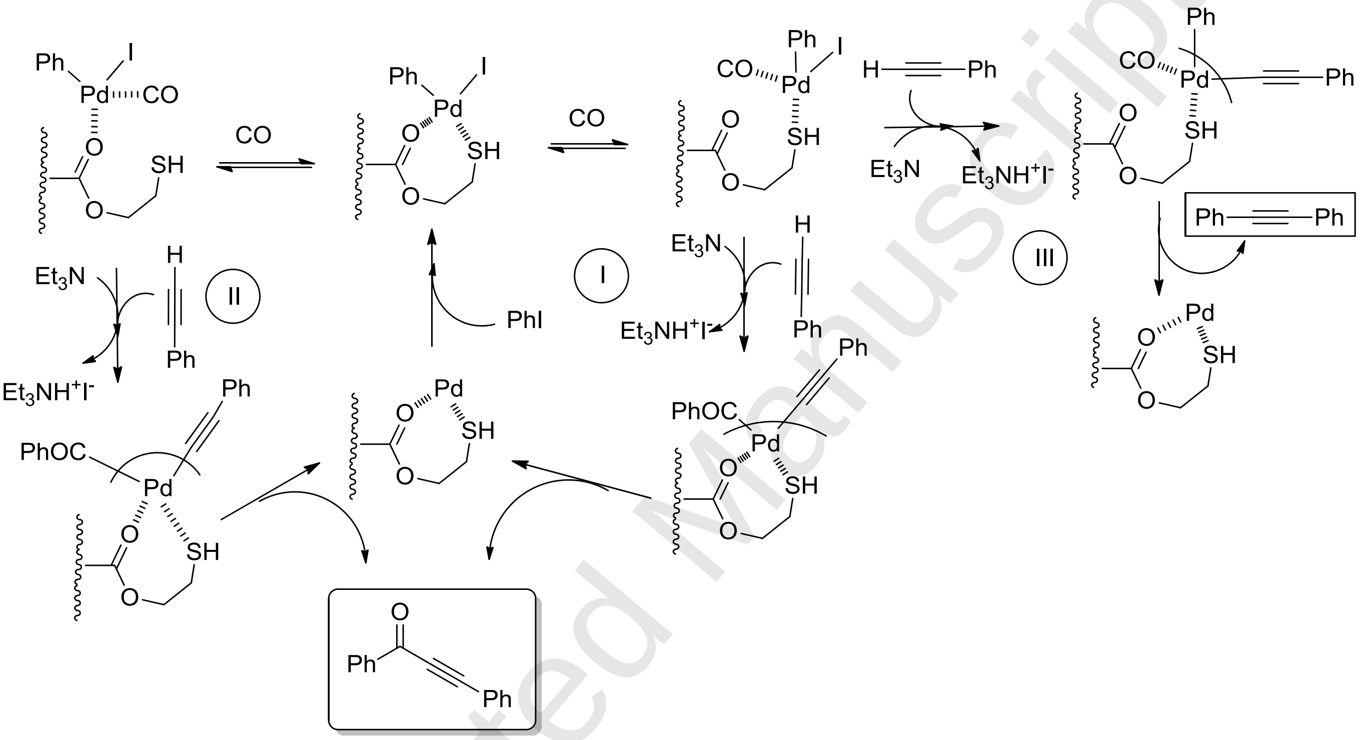
Scheme 1. Carbonylative Sonogashira reaction of iodobenzene and phenylacetylene



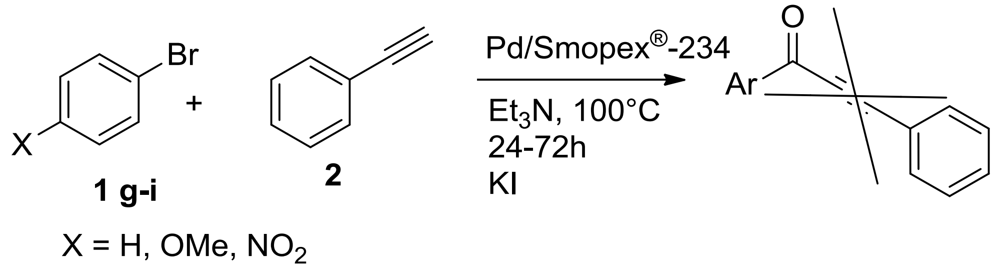
Scheme 2. Sonogashira reaction of iodobenzene and phenylacetylene



Scheme 3. Hypothesis of ligand exchange mechanism.



Scheme 4. Pd/Smopex®-234 catalysed carbonylative Sonogashira reaction of phenyl acetylene and bromoarenes



Scheme 5. Hot filtration test.

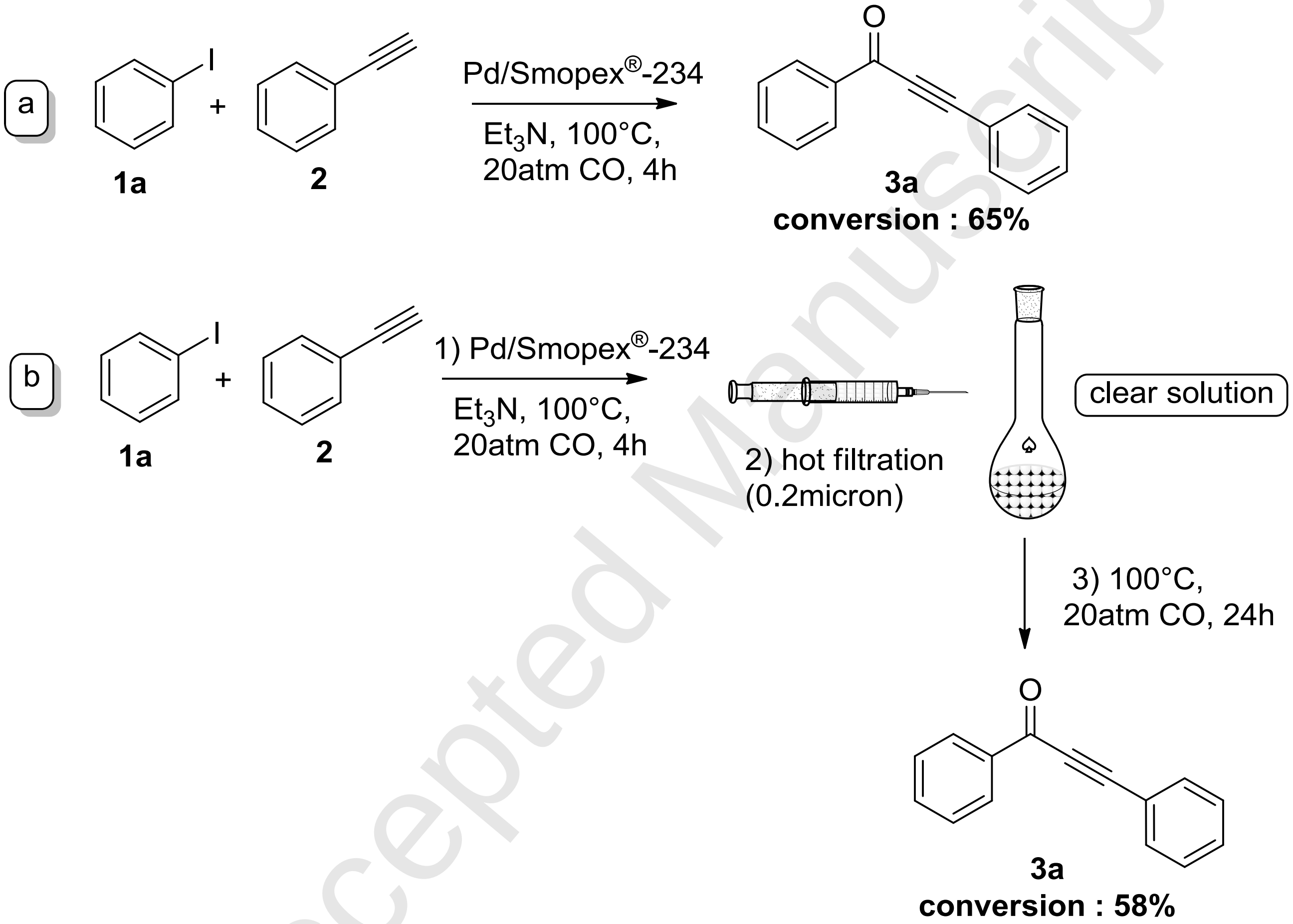


FIGURE CAPTIONS

Figure 1. (a) Smopex®-111, (b) Smopex®-234

Figure 2. HR-TEM micrographs and histograms of particle size distributions of palladium supported nanoparticles: a) Pd/Smopex®-111. Instrumental magnification: 60000X and 250000X, respectively; b) Pd/Smopex®-234. Instrumental magnification: 100000X and 500000X, respectively; c) Pd/γ-Al_2O_3. Instrumental magnification: 200000X; d) Pd/C (MVS). Instrumental magnification 300000X; e) Pd/C (Aldrich). Instrumental magnification: 100000X and 300000X, respectively.

Figure 3. FTIR spectra of 100 torr CO dosed at r.t. onto a) Pd/Smopex®-111 and b) Pd/Smopex®-234.

Figure 4. Specific Activity of Pd catalysts calculated as (mmol iodobenzene consumed %) / (mgatom Pd) (conditions in Table 4).

Figure 5. Recycling tests of Pd/Smopex®-234 performed under the standard reactions conditions (2 mmol of iodobenzene, 2.5 mmol of phenylacetylene, 5 mL of Et_3N and 0.2 mol% of Pd/Smopex®-234, 20 atm CO).

Figure S1. XRD patterns of Pd/Smopex®-111 (upper panel) and of Pd/Smopex®-234 (lower panel) before reaction. The XRD patterns of bare SMOPEX111 and SMOPEX234 have been inserted as a reference.

Palladium Nanoparticles Supported on Smopex® Metal Scavengers as catalyst for Carbonylative Sonogashira Reaction: synthesis of α,β-alkynyl ketones

Laura Antonella Aronica [a] *, Anna Maria Caporusso[a], Giulia Tuci[b], Claudio Evangelisti[c],
Maela Manzoli[d], Maria Botavina[d], Gianmario Martra[d]

Table 1.

Supported Palladium nanoparticles

n	Catalyst[a]	Type	d_m (mean diameter, nm) [b]	Particle size distribution[b]
1	Pd/Smopex®-111	MVS	3.5	0.25-12.75
2	Pd/Smopex®-234	MVS	1.7	0.25-5.00
3	Pd/γ-Al_2O_3	MVS	3.2	1.75-5.25
4	Pd/C	MVS	3.6	1.75-7.00
5	Pd/C	Comm.	5.5	1.75-23.25

[a] Metal loading: 1 % w/w.

[b] Determined by HR-TEM analysis

Table 2.

Carbonylative Sonogashira reaction of phenyl acetylene and iodobenzene promoted by palladium catalysts

n	Catalyst[a]	t(h)	Conversion (%)[b]	Selectivity **3a**[b]
1	$Pd(OAc)_2$	4	39	89
2	$PdCl_2(PPh_3)_2$	4	83	92
3	Pd/C[c]	24	79	93
4	Pd/C[d]	24	82	85
5	Pd/γ-Al_2O_3[d]	24	74	88
6	Pd/Smopex®-111[d]	24	4	67
7	Pd/Smopex®-234[d]	24	80	88

[a] Reaction conditions: Et_3N (5 ml), iodobenzene (2 mmol), phenylacetylene (2.5 mmol), catalyst (0.2 mol %), 100 °C, CO (20 atm).

[b] Determined by GC and ^{1}H-NMR analysis; remainder of product is diphenylacetylene, generated by direct Sonogashira reaction.

[c] Catalyst was purchased by Sigma Aldrich; metal loading 1 % w/w.

[d] Catalysts were prepared according to MVS technique; metal loading 1 % w/w.

Table 3. Sonogashira reaction of phenyl acetylene and iodobenzene promoted by palladium catalysts

n	Catalyst[a]	Conversion[b] (%)
1	$Pd(OAc)_2$	45
2	$PdCl_2(PPh_3)_2$	100
3	Pd/SMOPEX®-111[c]	0
4	Pd/SMOPEX®-234[c]	0

[a] Reaction conditions: Et_3N (5 ml), iodobenzene (2 mmol), phenylacetylene (2.5 mmol), catalyst (0.2 mol %), 100 °C, 24 h.

[b] Determined by GC and ^{1}H-NMR analysis.

[c] Catalysts were prepared according to MVS technique ; metal loading 1 % w/w.

.

Table 4. Catalytic behaviour of palladium catalysts

n[a]	Catalyst	Conversion[b](%)	SA[c]
1	$Pd(OAc)_2$	39	196
2	$PdCl_2(PPh_3)_2$	83	416
3	Pd/C[d]	73	364
4	Pd/C[e]	70	350
5	Pd/γ-Al_2O_3[e]	38	192
6	Pd/Smopex®-234[e]	67	336

[a] Reaction conditions: Et_3N (5 ml), iodobenzene (2 mmol), phenylacetylene (2.5 mmol), catalysts (0.2 mol %), 100 °C, 4 h, CO (20 atm).

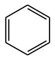
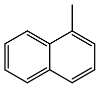
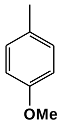
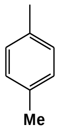
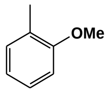
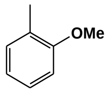
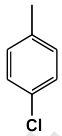
[b] Determined by GC and ^{1}H-NMR analysis.

[c] Specific Activity (SA) calculated as: (mmol iodobenzene consumed %) / (mgatom Pd).

[d] Catalyst purchased by Aldrich; metal loading 1 % w/w.

[e] Catalysts prepared according to MVS technique; metal loading 1 % w/w.

Table 5. Carbonylative Sonogashira reaction of phenyl acetylene and iodoarenes promoted by Pd/Smopex®- 234

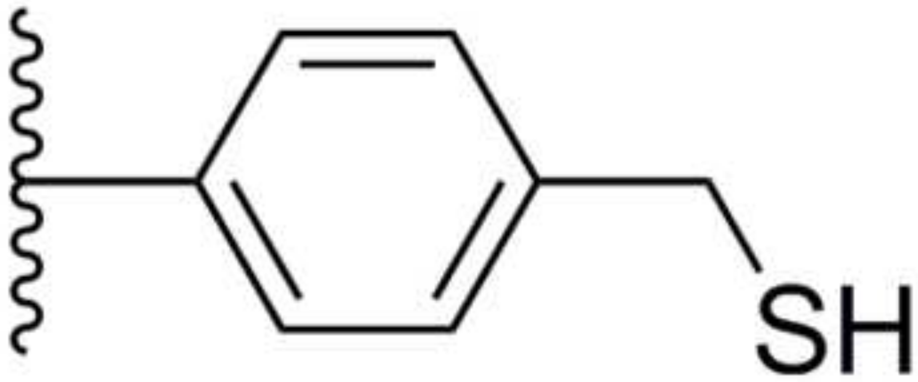
n	**1**[a]	Ar	Conversion [b] (%)	**3,4**	Selectivity[b]	
					3	**4**
1	a		80	a	88	12
2	b		71	b	88	12
3	c		81	c	93	7
4	d		68	d	89	11
5	e		49	e	89	11
6[c]	e		62	e	89	11
7[c]	f		54	f	82	18

[a] Reaction conditions: Et_3N (5 ml), iodobenzene (2 mmol), phenylacetylene (2.5 mmol), catalyst (0.2 mol%), 100 °C, 24 h, CO (20 atm).

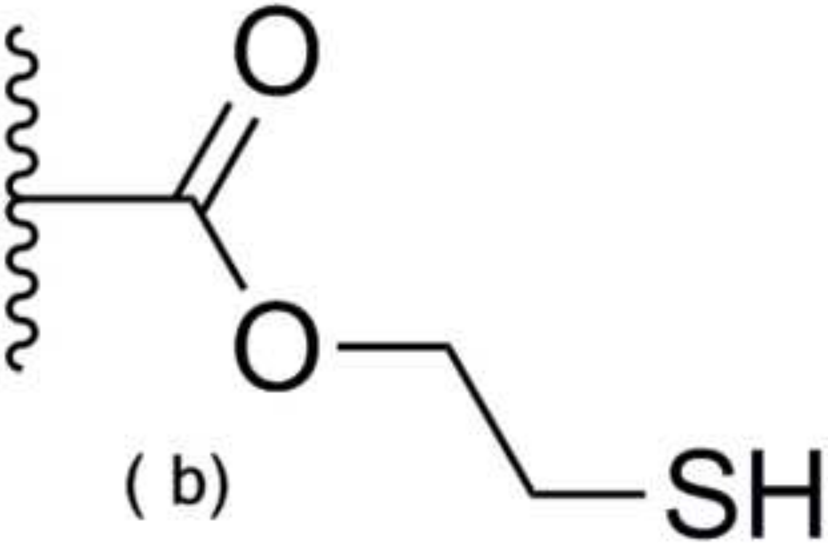
[b] Determined by GC and ^{1}H-NMR analysis.

[c] Reactions performed with 0.5 mol % of catalyst.

Figure

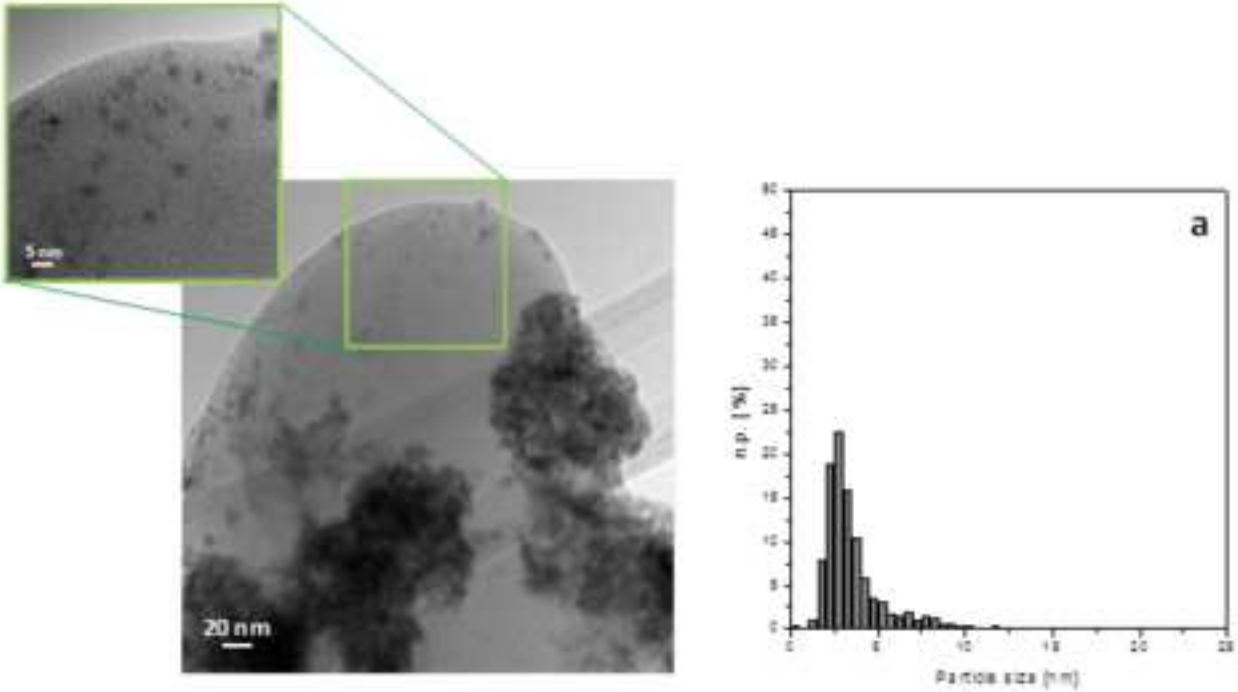


(a)

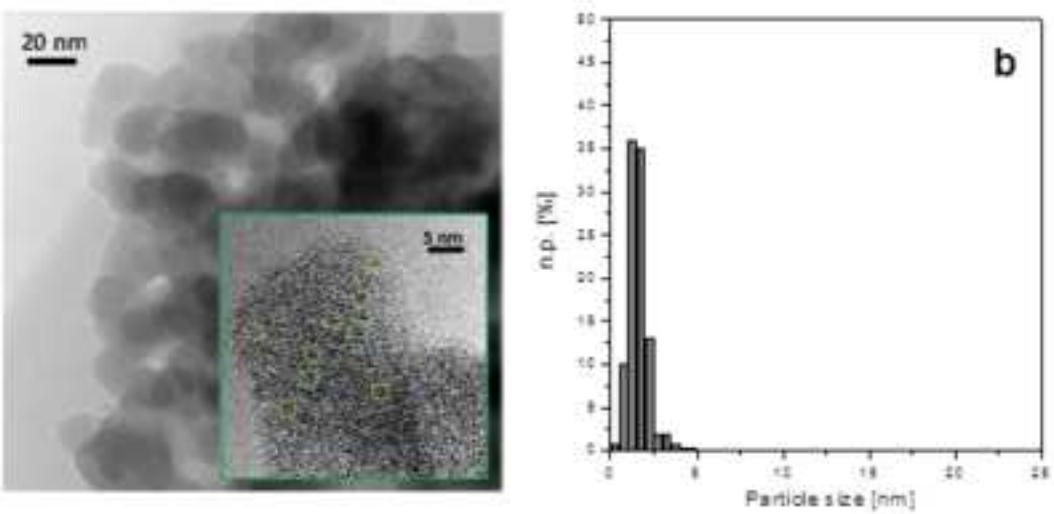


(b)

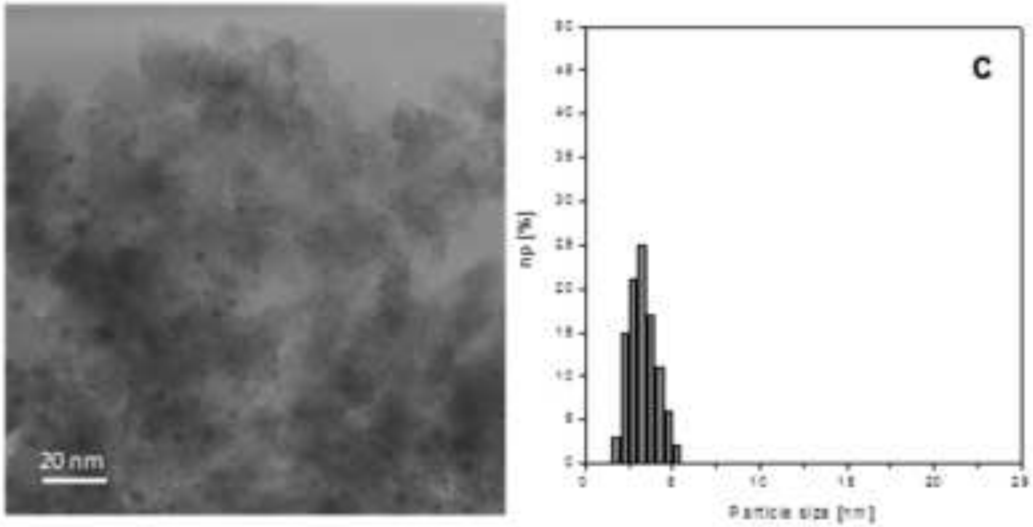
Figure


5 nm
20 nm
a
n.p. [%]
0
5
10
15
20
25
30
35
40
45
50
0
5
10
15
20
25
Particle size (nm)

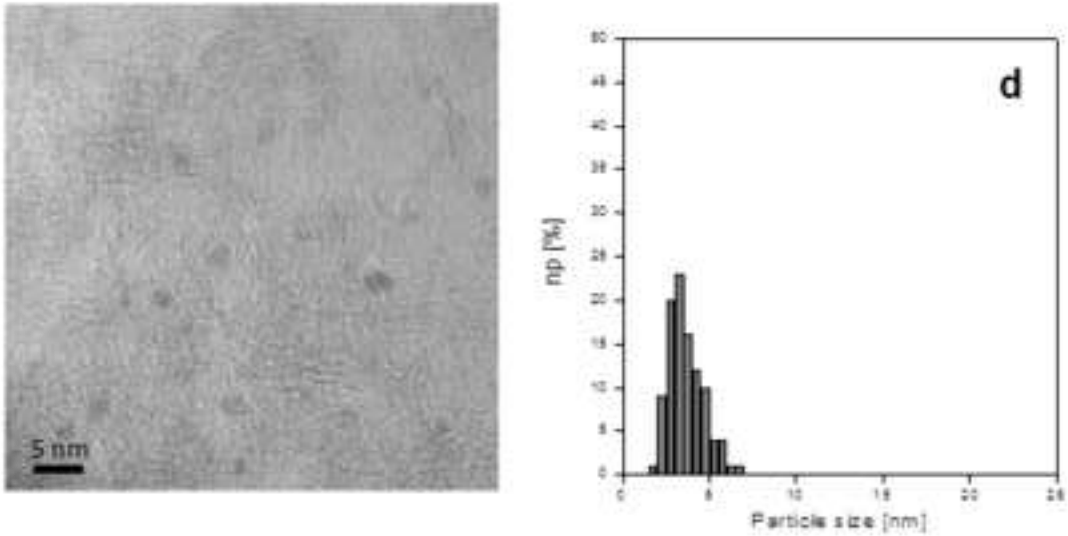
Figure


20 nm
5 nm
b
n.p. [%]
50
45
40
35
30
25
20
15
10
5
0
0
5
10
15
20
25
Particle size [nm]

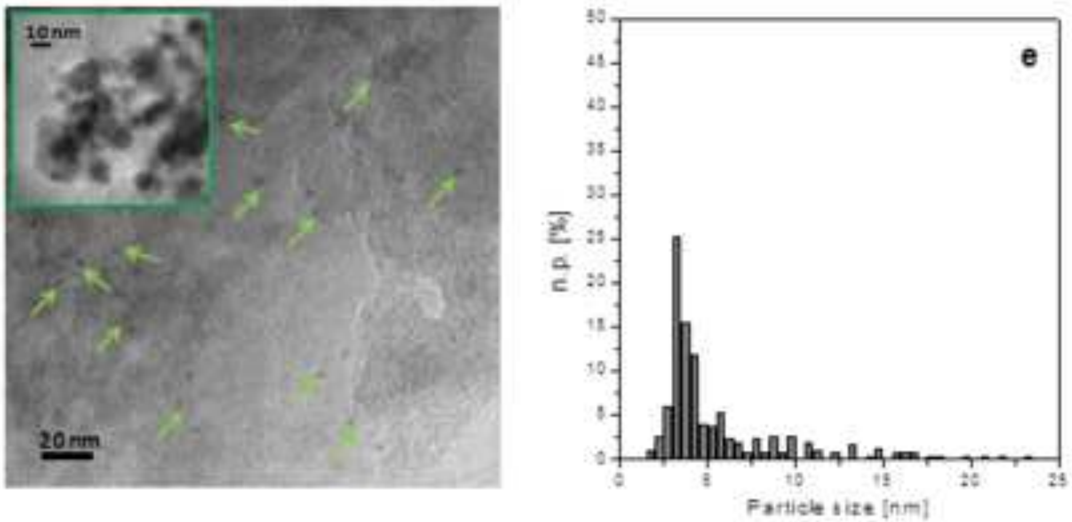
Figure


20 nm
c
np [%]
50
45
40
35
30
25
20
15
10
5
0
0
5
10
15
20
25
Particle size [nm]

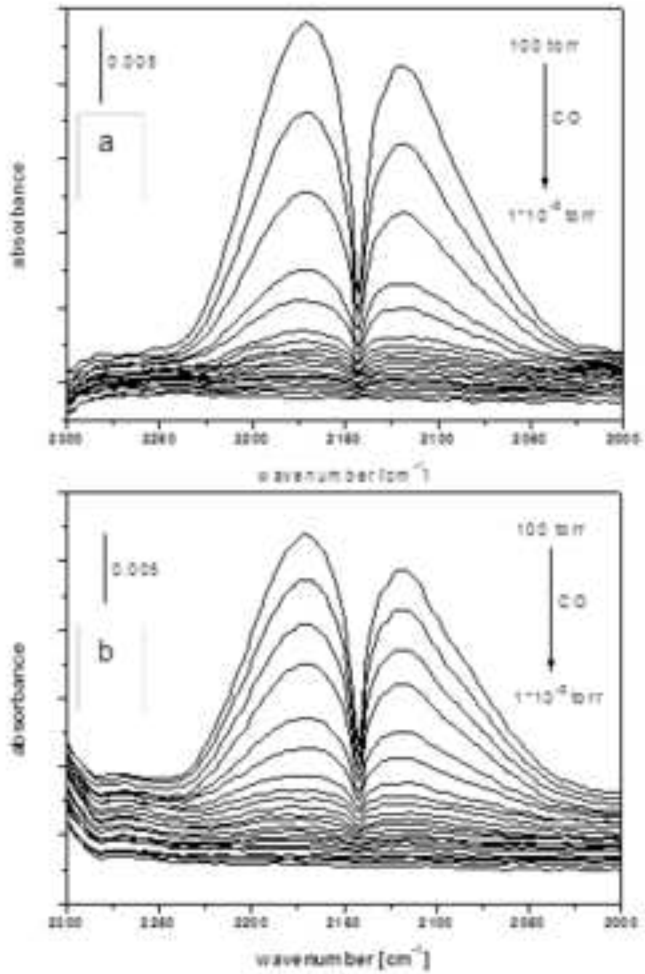
Figure


5 nm
d
np [%]
0
5
10
15
20
25
30
35
40
45
50
Particle size [nm]
0
5
10
15
20
25

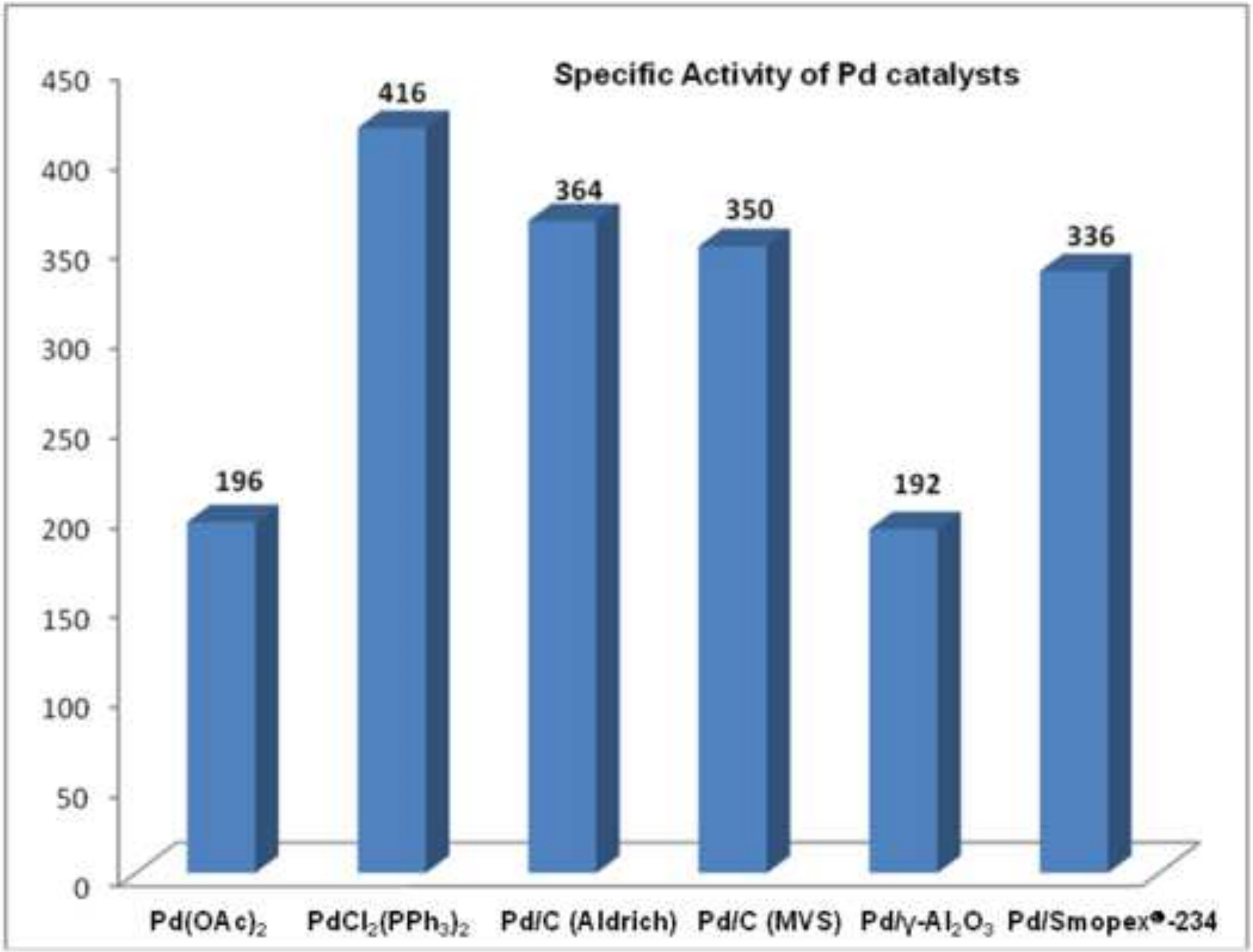
Figure


10 nm
20 nm
e
50
45
40
35
30
25
20
15
10
5
0
n.p. [%]
0
5
10
15
20
25
Particle size [nm]

Figure

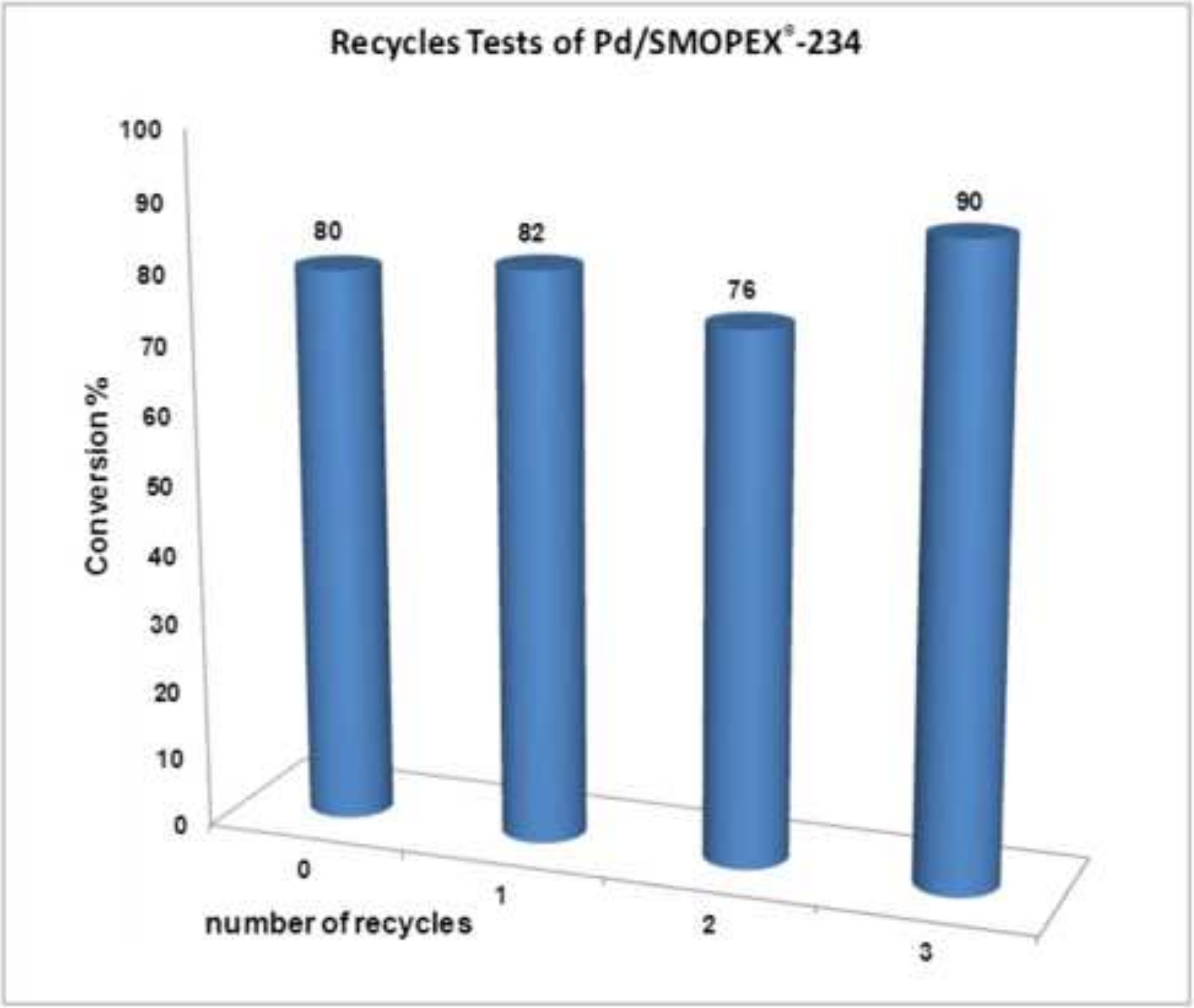

a
0.005
100 torr
CO
1*10^{-4} torr
absorbance
2300
2250
2200
2150
2100
2050
2000
wavenumber [cm^{-1}]
b
0.005
100 torr
CO
1*10^{-4} torr
absorbance
2300
2250
2200
2150
2100
2050
2000
wavenumber [cm^{-1}]

Figure



Specific Activity of Pd catalysts
450
400
350
300
250
200
150
100
50
0
196
416
364
350
192
336
Pd(OAc)$_2$
PdCl$_2$(PPh$_3$)$_2$
Pd/C (Aldrich)
Pd/C (MVS)
Pd/γ-Al$_2$O$_3$
Pd/Smopex®-234

Figure


Recycles Tests of Pd/SMOPEX®-234
Conversion %
100
90
80
70
60
50
40
30
20
10
0
80
82
76
90
0
1
2
3
number of recycles