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New route to synthesis of PVP-stabilized palladium(0) nanoclusters and their enhanced catalytic activity in Heck and Suzuki cross-coupling reactions

Feyyaz Durap^{a*}, Önder Metin^b, Murat Aydemir^a and Saim Özkar^b

Herein we report a new method for the synthesis and characterization of PVP-stabilized palladium(0) nanoclusters and their enhanced catalytic activity in Suzuki coupling and Heck reactions of aryl bromides with phenylboronic acid and styrene, respectively, under mild conditions. The PVP-stabilized palladium(0) nanoclusters with a particle size of 4.5 ± 1.1 nm were prepared using a new method: refluxing a mixture of potassium tetrachloropalladate(II) and PVP in methanol at 80 °C for 1 h followed by reduction with sodium borohydride. Palladium(0) nanoclusters prepared in this way were stable in solution for weeks, could be isolated as solid materials and were characterized by TEM, XPS, UV-vis, and XRD techniques. The PVP-stabilized palladium(0) nanoclusters were active catalysts in Heck and Suzuki coupling reactions of arylbromides with styrene and phenylboronic acid affording stilbenes and biphenyls, respectively, in high yield. Recycling experiments showed that PVP-stabilized palladium(0) nanoclusters could be used five times with essentially no loss in activity in the Heck and Suzuki coupling reactions. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: palladium; PVP; nanoclusters; Suzuki coupling; Heck reaction

Introduction

Controlling catalyst particle size is of vital importance in heterogeneous catalysis because only the surface atoms can provide catalytic activity.^[1] As the particle size decreases, the fraction of surface atoms over the total increases and, thus, the catalytic activity per mass of catalyst increases. In this context, nanoclusters have attracted great attention in the past two decades due to their large surface-to-volume ratio.^[2] However, nanoclusters must be surrounded by a shell of an adequate protecting agent that prevents their agglomeration. Some of the well-known protecting agents provide steric stabilization through a functional group with high affinity for metals.^[3–5] Steric stabilization by the presence of polymers is the general method for the preparation of stable and catalytically active colloidal nanoclusters. The use of polymeric matrix as stabilizer improves some properties of the nanoclusters such as the solubility, thermal stability and catalytic activity.^[6] Nanoparticles, in particular of palladium, have been used as catalysts in C–C coupling reactions^[7–10], a versatile tool in C–C bond formation reactions in organic synthesis.^[11–13] Reactions of aryl halides with boronic acid (the Suzuki coupling reaction) and with olefins (the Heck reaction) have been widely used in the C–C bond formation.^[14–17] PVP-stabilized palladium(0) nanoparticles have already been tested as catalysts in Suzuki coupling reactions of iodobenzene with phenylboronic acid.^[18] The PVP-stabilized palladium nanoparticles used were prepared using an alcohol reduction method which involves the refluxing a mixture of metal precursor and poly(*N*-vinyl-2-pyrrolidone) (PVP) in water–ethanol mixture for 3–4 h.^[19,20] The effects of stabilizer concentration and other chemicals present in the reaction medium on the particle

size, shape and catalytic activity of palladium nanoparticles have been studied using Suzuki coupling between phenylboronic acid and iodobenzene under reflux conditions as a test reaction.^[21–23] PVP-stabilized palladium(0) nanoparticles with 19.8 nm diameters have also been prepared in the presence of tetrabutylammonium bromide, which provides additional stability for the nanoparticles. These particles were used as catalysts in the Heck coupling of bromobenzene with butylacrylate and methoxycarbonylation of iodobenzene.^[24] All these results have shown that the method used for the preparation of nanoparticles and the reaction conditions have an effect on their catalytic activity. A recent paper has reported the development of a new method for the synthesis of PVP-stabilized nickel(0) nanoclusters which have high catalytic activity in the hydrolysis of sodium borohydride.^[25] We were successful in applying the new method for the synthesis of PVP-stabilized palladium(0) nanoclusters and employing them as catalysts in the Suzuki coupling and Heck reactions. Here, we report the synthesis of the PVP-stabilized palladium(0) nanoclusters using this new method, their characterization by TEM, XPS, UV-vis, and XRD techniques, and their employment as catalysts in the Suzuki coupling and Heck reactions of aryl bromides with phenylboronic acid and styrene, respectively, under milder reaction conditions compared to those in the previous studies.

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Results and Discussion

Synthesis and Characterization of PVP-stabilized Palladium(0) Nanoclusters

PVP-stabilized palladium(0) nanoclusters were prepared following the two-step procedure described elsewhere for the synthesis of PVP-stabilized nickel(0) nanoclusters.^[25] First, the palladium(II) precursor complex, potassium tetrachloropalladate(II), and the polymeric stabilizer were refluxed for 1 h in methanol solution. The UV–vis electronic absorption spectrum taken from the refluxed solution shows that no reduction of Pd(II) species to Pd(0) occurs during the reflux. We also performed experiments to understand the effect of methanol reflux on the reduction of palladium(II) precursor varying the reflux time up to 3 h, but there was no reduction observed. It is clearly seen that methanol reflux alone is not enough to reduce palladium(II) precursor to zerovalent palladium. Therefore, sodium borohydride solution in methanol was added dropwise to the mixture to reduce palladium(II) precursors. An abrupt color change was observed from pale yellow to dark brown immediately upon addition of sodium borohydride, indicating the formation of palladium(0) nanoclusters. One hour reflux was found to be necessary for good dispersion of the polymer in solution to provide better interaction between the metal and the stabilizer to prevent agglomeration after reduction.^[26] This is illustrated by the fact that addition of NaBH₄ without refluxing the methanol solution resulted in the formation of palladium nanoparticles which precipitate out of solution. The palladium(0) nanoclusters formed from the borohydride reduction of potassium tetrachloropalladate(II) in the presence of PVP after refluxing are stable in solution and no bulk metal formation was observed after the solution was left for weeks at room temperature. The PVP-stabilized palladium(0) nanoclusters could be isolated as a dark-brown solid from the reaction mixture by removing the volatiles in vacuum. The residuals were removed by washing with acetone. The isolated nanoclusters were stable in an inert gas atmosphere for months. The Pd content of the isolated PVP-stabilized palladium(0) nanoclusters was determined as 36 wt% Pd by ICP-OES. The particle size of the PVP-stabilized palladium(0) nanoclusters was determined from TEM (Fig. 1) as 4.5 ± 1.1 nm.

Figure 2 shows the XPS spectrum of the obtained PVP-stabilized palladium(0) nanoclusters. The spectrum exhibits two prominent signals at 335.8 and 341.4 eV, readily assigned to Pd(0) 3d_{5/2} and Pd(0) 3d_{3/2}, respectively, by comparing with the values of metallic palladium.^[27] However, there are two additional bands observed at 337.5 and 343.2 eV which indicate the formation of higher oxidation states of palladium, probably PdO. Additionally, two other weak bands are observed at 339.8 and 344.8 eV, which most probably belong to a higher oxidation state of palladium, PdO_x.^[28] Since the nanoclusters are prepared from the reduction of potassium tetrachloropalladate(II) by sodium borohydride in the presence of PVP as stabilizer, palladium(0) might be oxidized on the surface of nanoclusters during the XPS sample preparation due to the air exposure.

Figure 3 shows powder XRD diffraction patterns obtained for the PVP-stabilized palladium(0) nanoclusters. Four peaks are observed in the XRD pattern at 2 θ of 39, 41, 59 and 69° that could be attributed to 111, 200, 220 and 311 facets of elemental palladium.^[29] Other undefined less intense peaks were most probably due to residuals such as borate species remaining on the surface of the nanoclusters. The broadening observed for the 111 peak is characteristic of the materials having nanometer particle size.^[30]

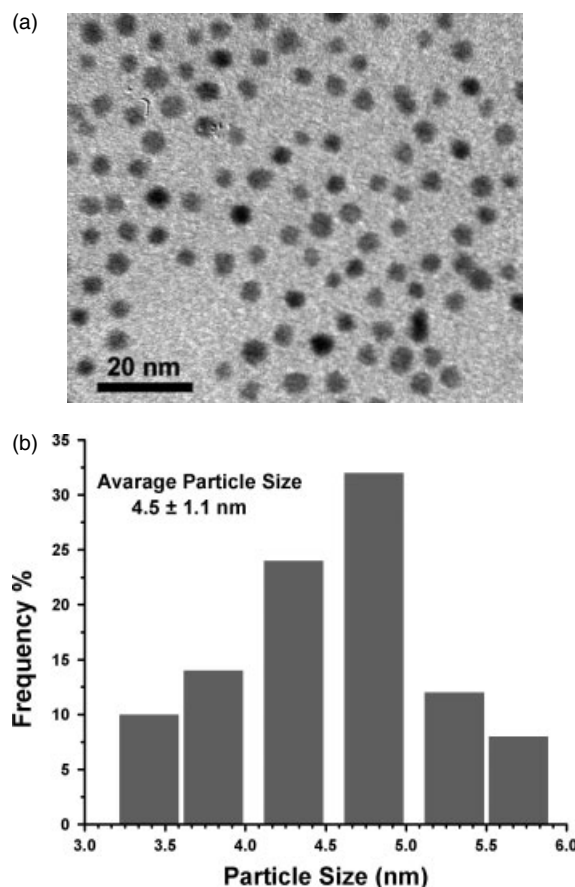


Figure 1. (a) TEM image and (b) associated histogram for PVP-stabilized palladium(0) nanoclusters formed from the reduction of potassium tetrachloropalladate(II) (3 mM) in the presence of PVP (15 mM) by sodium borohydride (150 mM) after one hour reflux in methanol at 80 °C.

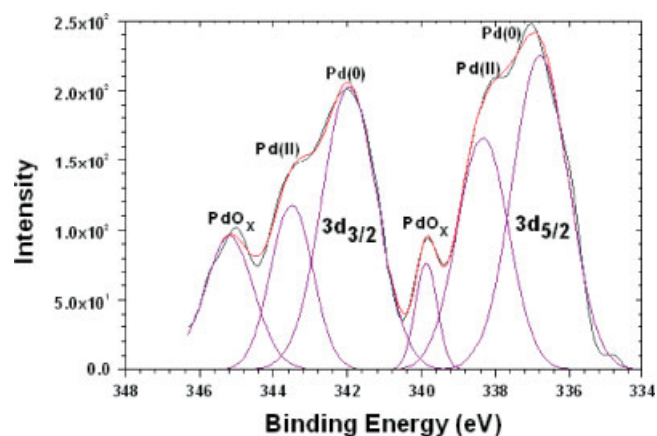


Figure 2. X-Ray photoelectron spectrum of PVP-stabilized palladium(0) nanoclusters formed from the reduction of potassium tetrachloropalladate(II) (3 mM) in the presence of PVP (15 mM) by sodium borohydride (150 mM) after one hour reflux in methanol at 80 °C.

Figure 4 shows the UV–vis electronic absorption spectra of potassium tetrachloropalladate(II) and PVP mixture in methanol before and after addition of sodium borohydride. The two absorption bands observed at 250 and 325 nm, attributed to the [PdCl₄]²⁻ anion, disappeared when sodium borohydride was

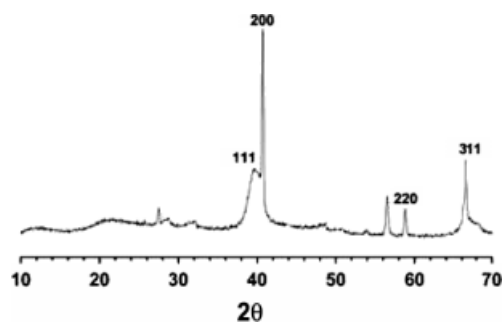


Figure 3. Powder XRD pattern of PVP-stabilized palladium(0) nanoclusters showing the facets of the palladium.

added to the solution. This disappearance indicates the reduction of palladium(II) precursor to palladium(0).

Catalytic Activity of PVP-stabilized Pd(0) Nanoclusters in the Suzuki Coupling Reaction

The catalytic activity of PVP-stabilized palladium(0) nanoclusters was first examined in the Suzuki coupling reaction, which has become, over the last ten years, the method of choice for biaryl and heterobiaryl synthesis.^[31,32] The Suzuki coupling requires harsh conditions: refluxing the mixture at 100 °C for 12 h. Suzuki coupling reaction of aryl iodides and bromides occurs in high yields only in the presence of a suitable catalyst, base and solvent. In order to find the optimum reaction conditions for the Suzuki coupling reactions catalyzed by PVP-stabilized palladium(0) nanoclusters, the test reaction was performed using different bases (Cs_2CO_3 , K_2CO_3 and KO^tBu) and different solvents (DMF and dioxane). It was found that the Suzuki coupling reaction catalyzed by PVP-stabilized Pd(0) nanoclusters gave the highest yield when using DMF as solvent and Cs_2CO_3 as a base at 110 °C. We initially

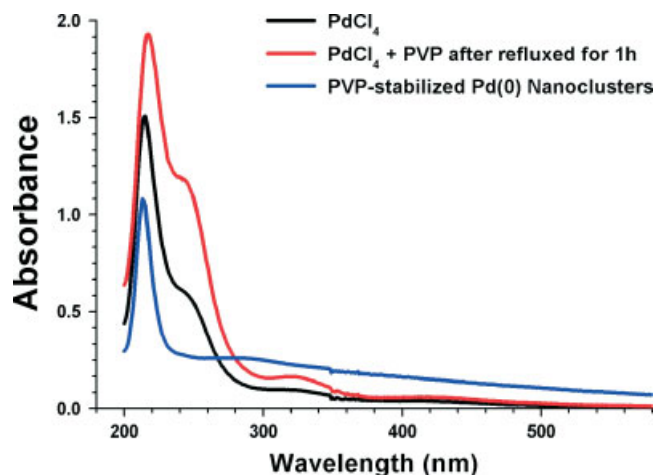


Figure 4. UV-Visible spectra of (a) potassium tetrachloropalladate(II) (b) palladium chloride and PVP mixture refluxed for 1 h at 80 °C and (c) PVP-stabilized palladium(0) nanoclusters taken from the methanol solutions.

tested the catalytic activity of the PVP-stabilized palladium(0) nanoclusters for the coupling of *p*-bromoacetophenone with phenylboronic acid. Control experiments showed that the coupling reaction did not occur in the absence of the catalyst. Under the optimized conditions, reaction of *p*-bromoacetophenone, *p*-bromobenzaldehyde, *p*-bromobenzene, *p*-bromoanisole and *p*-bromotoluene with phenylboronic acid gave high yield in 1 h without an induction time period in the presence of PVP-stabilized Pd(0) nanoclusters (Table 1). Of the five different aryl bromides used in the Suzuki coupling with phenylboronic acid, the ones with electron-withdrawing substituents were found to give the highest yields (Table 1, entries 1 and 2). We also tested PVP-stabilized palladium(0) nanoclusters as catalyst in the coupling of aryl

Table 1. The Suzuki coupling reactions of aryl bromides with phenylboronic acid catalyzed by PVP-stabilized palladium(0) nanoclusters

$\text{C}_6\text{H}_5\text{B(OH)}_2 + \text{Br-C}_6\text{H}_4\text{-R} \xrightarrow[\text{Cs}_2\text{CO}_3 (2 \text{ equiv.})]{\text{Pd-PVP (0.01 mmol)}} \text{C}_6\text{H}_5\text{-C}_6\text{H}_4\text{-R}$						
Entry	R	Cat	Product	Conv.(%)	Yield(%)	TOF(h ⁻¹)
1	4-CH ₃ C(O)-	Pd-PVP		99.55	98.54	98
2	4-CH(O)-	Pd-PVP		99.68	99.11	99
3	4-H	Pd-PVP		53.38	47.67	48
4	4-CH ₃ O-	Pd-PVP		39.82	37.67	38
5	4-CH ₃ -	Pd-PVP		50.73	48.08	48

Reaction conditions: 1.0 mmol of *p*-R-C₆H₄Br aryl bromide, 1.5 mmol of phenylboronic acid, 2.0 mmol Cs₂CO₃, 0.01 mmol (1%) Pd (Cat.), DMF 3.0 (ml). Purity of compounds was checked by NMR and yields are based on arylbromide. All reactions were monitored by GC; 110 °C. 1.0 h. TOF = (mol product/mol cat) h⁻¹.

chlorides with phenylboronic acid, but as expected no coupling product was observed because C–C coupling reactions of aryl chlorides with phenylboronic acid are more difficult than those of aryl bromides under the same reaction conditions.^[31]

Catalytic Activity of PVP-stabilized Palladium(0) Nanoclusters in the Heck Reaction

The Heck reaction, a Pd catalyzed C–C coupling between aryl or vinyl halides and triflates with alkenes, has been extensively explored and used in diverse areas such as the preparation of hydrocarbons, novel polymers, pharmaceuticals, agrochemicals, dyes and new enantioselective syntheses of natural products because of the mild conditions required for the reaction.^[33–37]

The rate of coupling is dependent on a variety of parameters such as temperature, solvent, base and catalyst loading. Again, we surveyed Cs₂CO₃, K₂CO₃ and KO^tBu as base and dioxane and DMF as solvent in the reaction of *p*-bromoacetophenone with styrene at 120 °C. Finally, we found that use of 0.01 mmol PVP-stabilized palladium(0) nanoclusters and 2 equivalents of K₂CO₃ per substrate in DMF at 120 °C led to the highest conversion within 45 min without induction time periods. A control experiment indicated that no coupling reaction product was observed in the absence of PVP-stabilized palladium(0) nanoclusters. Under the optimized reaction conditions, a wide range of aryl bromides bearing electron-donating and electron-withdrawing groups reacted with styrene, affording the coupled products in high yield. As expected, aryl bromides with electron-deficient substituents were beneficial for the conversions (Table 2). Using aryl chlorides instead of aryl bromides yielded only small amount of stilbene derivatives under the same conditions used for bromides.

Catalyst Recycling in Suzuki Cross-coupling and Heck Reaction

Reusability of PVP-stabilized palladium(0) nanoclusters catalyst was explored in Suzuki coupling and the Heck reaction. For the recycling experiment in Suzuki coupling and the Heck reaction, *p*-bromobenzaldehyde with phenylboronic acid and *p*-bromobenzaldehyde with styrene were used, respectively, in the presence of 0.01 mmol PVP-stabilized palladium(0) nanoclusters. The PVP-stabilized palladium(0) nanoclusters could be used in five successive runs with essentially no loss in activity in Heck reaction and Suzuki coupling reaction, as seen in Fig. 5a and b, respectively.

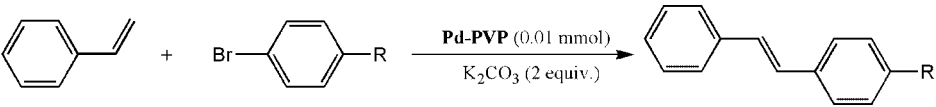
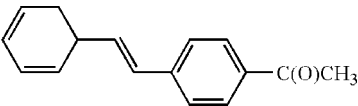
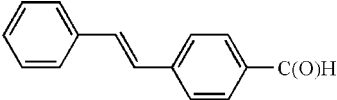
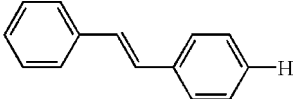
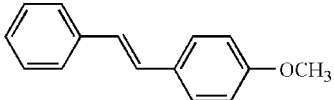
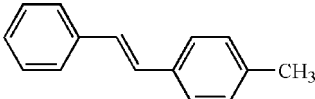
Experimental

Potassium tetrachloropalladate(II) (99%), poly(*N*-vinyl-2-pyrrolidone) (PVP-40, average molecular weight 40 000) and sodium borohydride (98%) were purchased from Aldrich®. Methanol was purchased from Riedel-De Haen AG Hannover, and used as received.

GC analysis

GC analyses were performed on a HP 6890N instrument equipped with a capillary column (5% biphenyl, 95% dimethylsiloxane; 30 m × 0.32 mm i.d. × 0.25 µm film thickness). The GC parameters were as follows: for Suzuki coupling reactions, initial temperature, 50 °C; initial time, 1 min; solvent delay, 3.70 min; temperature ramp 1, 10 °C/min; final temperature, 150 °C; temperature ramp 2, 15 °C/min; final temperature, 250 °C; final time, 20.67 min; injector

Table 2. The Heck coupling reactions of aryl bromides with styrene catalyzed by PVP-stabilized palladium(0) nanoclusters

						
Entry	R	Cat	Product	Conv.(%)	Yield(%)	TOF(h ⁻¹)
1	4-CH ₃ C(O)-	Pd-PVP		92.82	90.25	125
2	4-CH(O)-	Pd-PVP		99.90	97.70	130
3	4-H	Pd-PVP		38.74	35.75	48
4	4-CH ₃ O-	Pd-PVP		34.32	30.04	40
5	4-CH ₃ -	Pd-PVP		35.08	33.62	45

Reaction conditions: 1.0 mmol of *p*-R-C₆H₄Br aryl bromide, 1.5 mmol of styrene, 2.0 mmol K₂CO₃, 0.01 mmol (1%) Pd (Cat.), DMF 3.0 (ml). Purity of compounds was checked by NMR and yields are based on arylbromide. All reactions were monitored by GC; 120 °C, 45 min (0.75 h). TOF = (mol product/mol cat) h⁻¹.

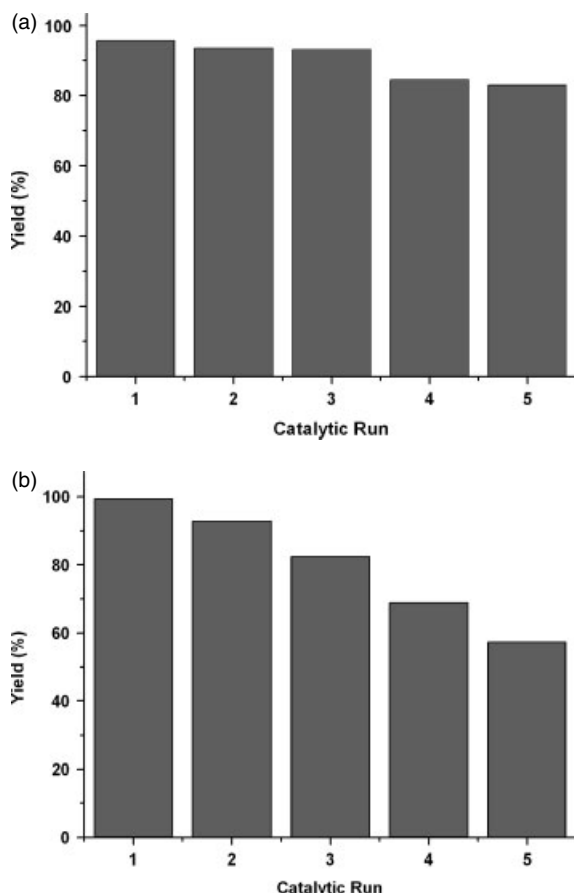


Figure 5. Recycling of PVP-stabilized palladium(0) nanoclusters a) Heck reaction *p*-bromobenzaldehyde with styrene, conditions are the same as given in Table 2, b) Suzuki coupling reaction *p*-bromobenzaldehyde with phenylboronic acid, conditions are the same as given in Table 1.

port temperature, 250 °C; detector temperature, 250 °C, injection volume, 2.0 μ L; for Heck coupling reactions, initial temperature, 50 °C; initial time, 1 min; solvent delay, 3.53 min; temperature ramp, 13 °C/min; final temperature, 300 °C; final time, 40.46 min; injector port temperature, 250 °C; detector temperature, 250 °C, injection volume, 2.0 μ L.

Preparation of the PVP-stabilized Palladium(0) Nanoclusters

PVP-stabilized palladium(0) nanoclusters were prepared by using a method used for the synthesis of PVP-stabilized nickel(0) nanoclusters in our previous paper.^[25] In a typical procedure, in a 250 ml three-necked round bottom flask, 100 mg (0.3 mmol) of K_2PdCl_4 and 167 mg (1.5 mmol monomer unit) of PVP-40 were dissolved in 100 ml of methanol (mol PVP: mol Pd = 5). The mixture of metal precursor (K_2PdCl_4) and polymer (PVP-40) in methanol was refluxed at 80 °C (oil bath temperature) for 1 h. Then, 5 ml of 150 mM (0.75 mmol) solution of sodium borohydride was added into metal–polymer mixture dropwise immediately after the reflux. The abrupt color change from pale yellow to dark brown indicates that the formation of PVP-stabilized palladium(0) nanoclusters was completed. Then, the solution was refluxed for an additional 30 min. Methanol was removed from the solution by evaporation in a rotavap (Heidolph Laborata-4000). The palladium nanoclusters were collected in solid form from the residue after evaporation in the round bottom flask. The solid

palladium nanoclusters in solid form were washed with excess acetone to remove the excess PVP and other residuals.

Characterization of PVP-stabilized Palladium(0) Nanoclusters

The TEM images were obtained using a JEM-2010 (JEOL) TEM instrument operating at 200 kV. The nanoclusters solution, prepared as described in the section 'Preparation of the PVP-stabilized Palladium(0) Nanoclusters', was centrifuged at 8000 rpm for 8 min. The separated nanoclusters were washed with excess acetone to remove the excess PVP and other residuals. Then, the nanoclusters sample was redispersed in 5 ml methanol. One drop of the colloidal solution was deposited on the silicon oxide coated copper grid and evaporated under inert atmosphere. Samples were examined at magnifications between 100 000 and 400 000. Particle size of the nanoclusters was calculated directly from the TEM image. Size distributions are quoted as the mean diameter \pm the standard deviation. X-ray photoelectron spectra (XPS) were taken at the Middle East Technical University Central Laboratory using a SPECS spectrometer equipped with a hemispherical analyzer and using monochromatic Mg-K α radiation (1250.0 eV, the X-ray tube working at 15 kV and 350 W) and pass energy of 48 eV. To better access the metal core in the sample by scraping off the polymer matrix from the surface, the sample surface was bombarded by argon ions by passing 2000 eV energy for 3 min. Peak fittings were done according to Gaussian function by using Origin 7.0 software. Powder X-ray diffraction patterns (XRD) of PVP-stabilized palladium(0) nanoclusters were recorded on a Rigaku Miniflex diffractometer with CuK α (30 kV, 15 mA, λ = 1.54051 Å), over a 2θ range from 5 to 90° at room temperature. All measurements were made with 0.05° steps at the rate 0.5 deg min⁻¹. UV–vis electronic absorption spectra of potassium tetrachloropalladate(II) and PVP-stabilized palladium(0) nanoclusters were recorded in methanol solution on a Varian-Carry100 double beam instrument. The palladium content of the PVP-stabilized palladium nanoclusters was determined by ICP-OES (inductively coupled plasma optical emission spectroscopy, Leeman-direct reading Echelle) using a direct calibration method after the sample was completely dissolved in aqua regia.

General Procedure for the Suzuki Cross-coupling Reactions

Suzuki coupling reactions were conducted as follows: PVP-stabilized palladium(0) nanoclusters (0.01 mmol), arylbromide (1.0 mmol), phenylboronic acid (1.5 mmol), Cs_2CO_3 (2.0 mmol) and DMF (3 ml) were placed in a Schlenk tube (25 ml) under an inert atmosphere. The mixture was heated at 110 °C for 1 h. The progress of the reaction was monitored by GC. Upon completion, the mixture was cooled, the product extracted with ethyl acetate–hexane (1 : 5), filtered through a pad of silica gel with copious washing, and concentrated and purified by flash chromatography on silica gel. The purity of the compounds was checked by NMR and GC, and yields are based on arylbromide.

General Procedure for the Heck Coupling Reactions

Heck coupling reactions were conducted as follows: PVP-stabilized palladium(0) nanoclusters (0.01 mmol), arylbromide (1.0 mmol), styrene (1.5 mmol), K_2CO_3 (2.0 mmol) and DMF (*N,N*-dimethylformamide) (3 ml) were placed in a Schlenk tube (25 ml) under inert atmosphere and the mixture was heated to 120 °C for 45 min. The progress of the reaction was monitored by GC.

Upon completion, the mixture was cooled, and the product extracted with ethyl acetate–hexane (1 : 5), filtered through a pad of silica gel with copious washing, and concentrated and purified by flash chromatography on silica gel. The purity of the compounds was checked by NMR and GC, and yields are based on arylbromide.

Conclusions

In summary, our study on the synthesis and characterization of PVP-stabilized palladium(0) nanoclusters as catalysts in the Suzuki coupling and Heck reactions have led to the following conclusions and insights:

- PVP-stabilized palladium(0) nanoclusters of 4.5 ± 1.1 nm average particle size are available by using our new preparation method involving the reflux of potassium tetrachloropalladate(II) and PVP mixture in methanol at 80 °C for 1 h followed by immediate reduction by sodium borohydride.
- The use of PVP-stabilized palladium(0) nanoclusters as catalysts in the Suzuki coupling and Heck reactions gives better yields and TOF values under moderate conditions and shorter reaction times compared with those given in literature.
- Recycling experiments show that PVP-stabilized palladium(0) nanoclusters could be used five times with essentially no loss in activity in Heck coupling and Suzuki coupling reactions.

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