Contents lists available at SciVerse ScienceDirect



Journal of Molecular Catalysis A: Chemical



journal homepage: www.elsevier.com/locate/molcata

PVP-stabilized palladium nanoparticles electrochemically obtained as effective catalysts in aqueous medium Suzuki-Miyaura reaction

Paula M. Uberman^a, Luis A. Pérez^b, Gabriela I. Lacconi^{b,*}, Sandra E. Martín^{a,*}

^a INFIQC-CONICET, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Haya de la Torre y Medina Allende, Ciudad Universitaria, X5000HUA, Córdoba, Argentina

^b INFIQC-CONICET, Departamento de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Haya de la Torre y Medina Allende, Ciudad Universitaria, X5000HUA, Córdoba, Argentina

ARTICLE INFO

Article history: Received 10 May 2012 Received in revised form 27 June 2012 Accepted 28 June 2012 Available online 7 July 2012

Keywords: Pd-nanoparticles Electrochemical synthesis Suzuki-Miyaura coupling **PVP** Aqueous medium

ABSTRACT

In this paper the synthesis of stable palladium nanoparticles (PdNPs) by electrochemical methods at room temperature is reported. Direct electroreduction of H₂PdCl₄ aqueous solution in the presence of poly-(N-vinyl-2-pirrolydone) (PVP) onto platinum electrodes was performed by the application of a constant current density pulse. By simultaneous stirring of the electrolyte, the NPs formed on the electrode surface were stabilized with PVP in the solution. The resulting PdNPs were characterized by transmission electron microscopy and the total content of palladium was analytically determined by atomic absorption measurements. The average size of the NPs (in the range of 10–22 nm) was tuned by changing the current density applied. The PdNPs prepared by this methodology exhibited highly efficient catalytic activity on Suzuki-Miyaura coupling reaction in aqueous medium. Particularly high turnover numbers (TON up to 10⁴–10⁵) were achieved by these PVP-stabilized PdNPs with aryl iodides and bromides.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Transition-metal nanoparticles (NPs) have become of increasing scientific interest due to their particular physical and chemical properties and their diverse application fields including material science, electronics, magnetism and optics [1–3]. An important field of application for NPs is that of catalysis as a result of their extremely small size and high surface-to-volume ratio. In the last decade the development of high-performance catalysts such as palladium nanoparticles (PdNPs) has been an important area of research, and consequently, the synthetic methods with a rigorous control of the NPs size has become the leading research focus [4-6].

Palladium represents one of the most used catalysts in advanced organic syntheses, which is mainly applied in the formation of C–C bonds. Thus, palladium catalyzed C–C coupling reactions are among the most useful and widely studied synthetic transformations for their remarkable chemo-, regio-, and stereoselectivities, mild reaction conditions, and high efficiency [7–10]. Among the main coupling reactions, a special place is occupied by the Suzuki-Miyaura reaction [11,12], a very attractive reaction from a

catalysis perspective. Particularly, the coupling of aryl halides and arylboronic acids provides an effective synthetic route to biaryls, which are useful as precursors to pharmaceuticals, polymers, liquid crystals, etc. [13]. Usually, the Suzuki-Miyaura reaction requires harsh conditions such as refluxing the reaction mixture at high temperature for 12-24 h in organic solvent. Under these conditions, in the presence of a suitable base and catalyst, the reaction occurs in high yields with aryl iodides and bromides. During the last decades, numerous modifications to the standard protocol have appeared either to improve its scope [14] and efficiency [15-17], or to render it more economic [18] and environmental friendly practice [19]. Most of the catalysts used in Suzuki-Miyaura coupling are based on homogeneous palladium complexes in the presence of different ligands [11]. Phosphine-based palladium catalysts are generally used [11,20], however a new type of ligands such as pincer ligands [21], N-heterocyclic carbenes [22] or palladacycles [23,24] have also been developed. Although homogeneous palladium catalysis is usually effective in this reaction, the typical problems associated with all homogeneous catalysts, that is, the separation of the catalyst from the reaction products and the catalyst recovery, are the major limitations of these catalytic systems. Alternatively, heterogeneous palladium catalysts have been developed in order to improve catalyst stability and handling during workup procedures and recycling [12]. Even though, heterogeneous supports allow efficient recycling, a decrease in the selectivity of the immobilized catalysts is frequently observed. Accordingly, PdNPs were

Corresponding author. Tel.: +54 351 4334170/73; fax: +54 351 4333030x151. E-mail addresses: glacconi@fcq.unc.edu.ar (G.I. Lacconi), martins@fcq.unc.edu.ar (S.E. Martín).

^{1381-1169/\$ -} see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.molcata.2012.06.016

introduced as an appropriate alternative, and the development of palladium nanocatalysts that combine high activity, stability and recyclability is nowadays an important goal of nanomaterials research.

In catalytic applications, the dispersity of sizes, morphology and composition of the active metals in the NPs are very important for the activity and selectivity of the catalysts. Thus, a uniform dispersion of NPs with an effective control of particles size is usually expected. However, frequently NPs aggregation produces a marked reduction of both, the catalytic activity and selectivity. Therefore, a key factor in the preparation of NPs involves the selection of a suitable stabilizing agent. PdNPs are typically formed in the presence of functionalized polymers [25–28], dendrimers [29,30], tetraalky-lammonium salts [31,32], and ionic liquids [33–35] as stabilizing agents. In some cases, Pd/C [36] systems or oxides [37,38] have also been used as supports for PdNPs immobilization.

The combination of metal nanoparticles with a polymeric matrix offers the possibility to obtain nanostructured systems with thermal stability, solubility and recovery possibilities. Steric stabilization given by the presence of polymers is a general method for the preparation of catalytically active nanoclusters. Water soluble poly-(*N*-vinyl-2-pirrolydone) (PVP) is one of the most used polymers for PdNPs stabilization [39–43].

It is well known that the size and shape of the NPs are strongly dependent on the synthetic method, as well as the experimental conditions. NPs can be prepared in solution by reduction of metal salts by a wide variety of reducing agents, or supported on a solid by metal vaporization [1]. PdNPs have been frequently obtained by reduction of H_2PdCl_4 in aqueous solution with primary or secondary alcohols in the presence of PVP [44,45]. Le Bars et al. reported the synthesis of palladium nanoclusters from Pd(dba)₂ solution in dichloromethane containing soluble PVP polymers by reduction of Pd(II) ions with hydrogen at 1–4 bar [46]. PVP-stabilized palladium nanoclusters were prepared employing K₂PdCl₄ in methanol using NaBH₄ as reducing agent [47]. Also, PdNPs were obtained by metal vapor synthesis (MVS) and stabilized in solution with PVP [48].

In addition to the chemical reduction, the electrochemical synthesis employing polymers as stabilizing agent provides a simple and effective method for PdNPs production at large scale [49-52]. Reetz and Helbig [53] reported for the first time the electrochemical preparation of a colloidal solution of PdNPs by electroreduction of metal ions in organic electrolytes. Further studies revealed that the electroreduction of Pd(II) ions in aqueous solution allowed to control the size of palladium nanoclusters [50]. Palladium structures could be formed in both potentiostatic and galvanostatic regimes of electrolysis and their formation was always accompanied by strong hydrogen co-deposition. Despite of this, in order to obtain large quantities of PdNPs in solution, it should be considered to use high current densities and very negative overpotentials in the electrochemical procedure [53]. It is important to point out that, some advantages of using electrochemical methods to obtain PdNPs can be summarized as follows: (i) direct reduction of Pd(II) ions can be performed from aqueous solution; (ii) the size of the particles is simply controlled by setting different values of current or potential in the perturbation program; (iii) colloidal solutions containing large quantities of very stable PdNPs are produced in a short time and (iv) it is a simple experimental procedure performed at room temperature. Additionally, in spite of the advance given by the electrochemical synthesis of NPs, the use of electrochemically obtained PdNPs as catalysts in coupling reactions is poorly employed [54].

A variety of PdNPs have been used as catalyst in C–C coupling reactions; however their application in Suzuki–Miyaura coupling is still not as wide as could be expected [4]. For instance, only some examples using PVP-stabilized PdNPs in the Suzuki–Miyaura reaction of aryl halide with boronic acid were reported [39,40,44,47,55,56]. In such cases, it was found that the catalytic activities of PdNPs strongly depend on the method and reactions conditions used for the NPs preparation.

In order to improve the current palladium catalyst preparation methods; herein we report the results of the synthesis of dispersed PVP-stabilized PdNPs, which were obtained by an appropriate electrochemical method. The experimental procedure was performed at room temperature by direct electroreduction of H₂PdCl₄ in aqueous solution containing PVP under vigorous stirring of the solution. Control of the NPs size, maintaining a narrow Gaussian dispersion, was regulated by changes in the applied current density. The catalytic activity of as-prepared PVP-stabilized PdNPs was evaluated in the Suzuki–Miyaura coupling reaction of aryl halides with aryl boronic acids, in aqueous medium employing very low catalysts loading.

2. Experimental

2.1. General methods

PdCl₂, KNO₃, PVP [poly-(*N*-vinyl-2-pirrolydone), Mw = 10000], HCl 35%, iodobenzene, bromobenzene, chlorobenzene, *p*-iodoanisole, *p*-bromoanisole, *p*-iodoacetophenone, *p*bromoacetophenone, *p*-iodobenzonitrile, phenylboronic acid, *o*-tolylboronic acid, *o*-methoxyphenylboronic acid, K₃PO₄, EtOH 98% and Na₂SO₄ were used without purification. All solvents were analytical grade and distilled before use. All reactions were carried out under atmosphere of nitrogen. Silica gel (0.063–0.200 mm) was used in column chromatography.

Gas chromatographic analyses were performed on a gas chromatograph with a flame ionization detector, and equipped with the following columns: HP-1 $25 \text{ m} \times 0.20 \text{ mm} \times 0.25 \mu \text{m}$ column. ¹H NMR and ¹³C NMR were conducted on a High Resolution Spectrometer Bruker Advance 400, in CDCl₃ as solvent. Gas Chromatographic/Mass Spectrometer analyses were carried out on a GC/MS QP 5050 spectrometer equipped with a VF-5ms, $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu \text{m}$ column. Melting points were performed with an electrical instrument. An Autolab PGSTAT100 (ECO CHEMIE) potentiostat was used for both, the potentiodynamic experiments (cyclic voltammetry) and the synthesis of PdNPs in the galvanostatic mode (see Supplementary material). PdNPs observation by Transmission Electron Microscopy (TEM) was performed with a JEM-Jeol 1120 microscope operating at 80 kV, at the Research Institute IFFIVE by INTA in Córdoba, Argentina. In order to characterize the NPs by TEM, samples were prepared depositing a drop of colloidal PdNPs solution on a formvar-carbon coated cooper grid and dried at room temperature. The total content of palladium was determined by Atomic Absorption in a Perkin Elmer Analyst 600, using ET (electro thermal mode with graphite furnace) at the Institute ISIDSA, Universidad Nacional de Córdoba, in Córdoba, Argentina.

2.2. Galvanostatic synthesis of PVP-stabilized PdNPs

Palladium electrodeposition on polycrystalline Pt disc electrodes (geometric area = 0.0746 cm^2) was performed in aqueous solution of H₂PdCl₄ (0.5 mM) and KNO₃ (0.1 M) containing 16 gL⁻¹ of poly-(*N*-vinyl-2-pirrolydone) polymer (PVP 10) as the stabilizing agent by application of a constant current pulse. Aqueous solutions were prepared from analytical grade chemicals and Milli-Q-Millipore water.

A volume of 50 mL of the electrolyte was prepared by mixing 0.32 g of PVP with 20 mL of the aqueous solution of H_2PdCl_4 and KNO₃. Complete dissolution of PVP required sonication of the mixture for 10 min. After that, the homogeneous yellow solution obtained was placed in a three electrodes cell and it was deoxygenated by bubbling nitrogen for about 15 min prior to each experiment. The electrochemical experiments were carried out in a glass electrochemical cell provided with a Pt disc working electrode, a very large area sheet of Pt (counter electrode) and a saturated calomel reference electrode. The Pt electrode was mechanical polished by fine grade emery paper and Al₂O₃ (0.05 µm) slurry, finally rinsed with Milli-Q water. All potentials were measured against the reference electrode. The electrochemical study of the Pt/electrolyte interface was performed by triangular potential cycling between -0.8 and 1.2 V, at a scan rate of 0.05 V s⁻¹ in aqueous solutions with different composition (see Supplementary material).

The galvanostatic synthesis of PdNPs was performed by applying to the platinum electrode a current density pulse from 0 to a cathodic value which is changed between -50 mA/cm^2 and -150 mA/cm^2 , during 600 s. Strong stirring of the solution (1000 rpm) with a magnetic stirrer was kept during the galvanostatic electrolysis. Under these conditions, an abrupt color change from yellow to a dark brown was observed since the first seconds of the galvanostatic pulse, indicating the formation of PVP-stabilized PdNPs. After completion of the reaction the aqueous dispersion of PdNPs was placed in a 25 mL volumetric flask to be used as catalyst solution for Suzuki–Miyaura coupling reaction without further purification.

Alternatively, the as-prepared PdNPs solution was centrifuged at 10000 rpm for 15 min. After that, the supernatant liquid was separated from the pellet of PdNPs and the nanoclusters sample was redispersed in water.

2.3. Characterization of PVP-stabilized PdNPs

The size and shape of the synthesized PdNPs were determined from transmission electron microscope (TEM) images. Samples were prepared by depositing a drop of the colloidal PdNPs suspension on a 300 mesh carbon and formvar-coated copper grid and dried at room temperature. The PdNPs size distribution for each sample was determined by the average over 160 PdNPs from several TEM images (different places) on the TEM grids. The size distribution plots were resolved by fitting the data with a Gaussian curve.

The total content of palladium in the colloidal suspensions was determined by Atomic Absorption using ET (electro thermal mode with graphite furnace) without previous digestion.

2.4. Representative procedure for the Suzuki–Miyaura coupling reaction

The following procedure of the reaction is representative for all Suzuki-Miyaura coupling reactions. Into a 25 mL Schlenk tube with Teflon screw-cap septum equipped with a magnetic stirrer and a nitrogen inlet, aryl halide (1a-d, 2a-c) (0.5 mmol), arylboronic acid (3a-c) (0.75 mmol) and K₃PO₄ (1.5 mmol) were added, and three cycles vacuum/nitrogen were performed to change to nitrogen atmosphere. Then, EtOH (1 mL) and water (to obtain a total volume of 3 mL taking into account the volume of PdNPs solution) were added. Finally, the required volume of the PdNPs dispersion was added. At this stage, the formation of a white precipitated was observed in the reaction mixture. The reaction mixture was heated for the required time in an oil bath at 90 °C, and the solid was dissolved within a few minutes of heating. After being cooled to room temperature, the mixture was opened to the air and diluted with water. Then the mixture was extracted three times with diethyl ether (30 mL each). The biaryl product was purified by silica-gel column chromatography after being dried with anhydrous Na₂SO₄. The products were characterized by ¹H NMR, ¹³C NMR, and GC/MS. All the spectroscopic data were in agreement with those previously reported for the following compounds: biphenyl (**4a**) [57], 4-methoxybiphenyl (**4b**) [58], 1-(biphenyl-4-yl)ethanone (**4c**) [59], 4-ciano-biphenyl (**4d**) [59], 2-methylbiphenyl (**5**) [60], 2-methoxybiphenyl (**6**) [58].

2.5. Catalyst recycling experiment in the Suzuki–Miyaura coupling reaction

In order to perform a recyclability test, the Suzuki–Miyaura coupling reaction between iodobenzene (**1a**) and 2-methoxyphenylboronic acid (**3c**) catalyzed by PdNPs with 10 nm mean diameter (0.01 mol%), was chosen (entry 8, Table 3). Initially, the reaction was carried out following the procedure descripts in Section 2.4. After the reaction mixture was refluxed for 3 h, the same mixture was used for recycling by addition of fresh amounts of reactants. The experiment was performed five times by consecutive addition of a new batch of iodobenzene (0.5 mmol), 2-methoxyphenylboronic acid (0.5 mmol), K₃PO₄ (0.5 mmol), 1 mL EtOH (1 mL) and water (1 mL). The reaction mixture was then refluxed for another 3 h. After this time, the reaction was monitored by CG analyses and no iodobenzene was observed in the reaction mixture after each catalytic cycle.

3. Results and discussion

3.1. Synthesis and structural characterization of PVP-stabilized PdNPs

It is well established that the electroreduction of metal ions in aqueous solutions at the cathode drives to the formation of a new solid phase on foreign solid substrates, being this process commonly referred to as electrochemical deposition. First steps of the electrodeposition process include the nucleation and growth of small metal clusters, that depending on the electrode metal (surface energy) and the electrolyte composition, they continue or not taking place. It is, the metal nuclei can remain or be removed from the solid surface.

In order to obtain a precise PdNPs-size control during the electrodeposition process, the presence of a stabilizer of the particles in the aqueous solution is required. PVP polymers have been demonstrated to be a high-quality stabilizing agent that promotes the formation of well-defined PdNPs during the electrochemical synthesis [50,61,62]. The electrochemical behavior of the Pt electrode, in the absence and in the presence of the PVP polymer allows to establish the potential at which the Pd(II) electroreduction can be performed (see Supplementary material).

The PVP-stabilized PdNPs were prepared by applying a galvanostatic pulse to the Pt electrode in a strongly stirred aqueous solution containing H₂PdCl₄ and the PVP water-soluble polymer. PVP10 was selected since PVP polymers with long chain are disadvantageous to electrochemical synthesis of PdNPs [50]. The presence of PVP in the stirred electrolyte is of crucial importance due to its function as stabilizer of the particles in the medium. Electrochemical reduction of Pd(II) ions at the interface Pt/electrolyte proceeded at very negative current densities and a precise PdNPs-size control could be achieved by adjusting the time and the current density of the galvanostatic pulse. The action of the PVP polymer molecules promote that small palladium clusters nucleated on the surface, and removed from it by the movement of the electrolyte, conform the monodisperse colloidal solution.

Application of a current density constant pulse to the Pt electrode, with external continuous stirring control (1000 rpm) of the electrolyte, led to the formation of nanometer-sized palladium



Data from the electrochemical synthesis of PVP-stabilized PdNPs with Pt electrodes.^a



^a Experimental conditions: Pt disc electrode; 0.5 mM H₂PdCl₄; 1.6% p/v PVP 10.000 D; 0.1 M KNO₃; room temperature; time: 600 s; stirring speed: 1000 rpm. ^b Determined by TEM analysis of a population of 160 NPs.

^c Determined by atomic absorption of the colloidal dispersion.

particles on the electrode/electrolyte interface. The particles did not remain supported on the electrode due to the convection movement of the electrolyte which mechanically carried them away from the electrode surface to the solution bulk, where they were stabilized by the polymer molecules. Under these conditions, processes such as dissolution and growth of the PdNPs at the interface were completely inhibited and colloidal solutions containing monodispersed individual-Pd particles were obtained. The formation of PdNPs in the solution was confirmed by the appearance of a dark brown color since the first seconds of the galvanostatic pulse application, which demonstrate an instantaneous formation of PdNPs. The colloidal dispersions obtained by this methodology were very stable and no aggregation was observed in several months.

Potential-time curves recorded during the application of different current pulses to the Pt electrode under continuous stirring of $0.5 \text{ mM H}_2\text{PdCl}_4 + 16 \text{ g L}^{-1} \text{ PVP} + 0.1 \text{ M KNO}_3$ solution are shown in Fig. 1. For a pulse of -150 mA/cm^2 , the formation of PdNPs occurred at -3.5 V and after the experiment time (600 s), the potential reached a value of -3.8 V. At lower current densities after 600 s of the pulse, the potential was less negative than -3.5 V. The potential evolution during the galvanostatic pulses at -50, -100 and $-150 \,\mathrm{mA/cm^2}$ changed rapidly at short times and after 600s the curves attained constant values. Thus, by increasing the deposition potentials (values more negatives), the formation of smaller particles with less dispersion in the average size was attained (Fig. 1b), as it was observed by TEM images, shown in Fig. 2. It was proposed that PdNPs obtained at low current densities consist of a small number of nuclei, while at more negative current densities, the number of metal centers increases and their dimensions decrease [63].

In Fig. 2, TEM images of PVP-stabilized PdNPs obtained by galvanostatic pulses at different values of current density are presented. The corresponding histograms are shown in Table 1.

As it is shown in Fig. 2, the PdNPs were nearly spherical, with an average diameter value which depends on the current density applied. The results obtained from the TEM images analysis are detailed in Table 1. The mean diameter of particles prepared at -50 mA/cm^2 was 22 nm, and a large dispersion of sizes was observed (entry 1, Table 1). Under these conditions the diameters of the PdNPs changed from 5 nm to 40 nm with a standard deviation of 8 nm.

When a current density pulse of -100 mA/cm^2 was applied, the mean diameter of particles was $19 \pm 7 \text{ nm}$ (entry 2, Table 1) and the particle size distribution was narrower. Finally, after a current density pulse of -150 mA/cm^2 , PdNPs with an average particle size of $10 \pm 4 \text{ nm}$ were obtained (entry 3, Table 1), and the particle size distribution was also improved. These results clearly show that the particle size is dependent of the current applied, in agreement with

the basic theory of electrochemical nucleation [51], where the critical radius of clusters of adatoms before the particle formation at the cathode/electrolyte interface depends inversely on the applied overpotential.

Some fine structure or mesoporous self-assembled PdNPs was distinguished on the Pd particles synthesized at -50 and -100 mA/cm^2 , similar to those obtained by using a Pd foil as sacrificial anode [51], possibly due to the steric repulsion force of the PVP polymer.

Generally, in the procedures for preparation of palladium nanoclusters it is assumed that all Pd(II) ions present in the original electrolyte bulk have been fully transformed to PdNPs with recovery yields of 100%. In order to approximate the results to a more real value, we decided to evaluate the effectiveness of the proposed synthesis methodology. For this reason, analytical determinations of the palladium content in the colloidal solution by atomic absorption measurements were carried out. The content of palladium in the colloidal dispersion after the galvanostatic pulse at different current densities and the corresponding NPs sizes were included in Table 1. It was found that the recovery of total Pd was close to 70% of yield for all the current densities (Table 1). This result is contradictory to that proposed by Pan et al. [50], and can be justified based on the following observations. At the final moment of the synthesis,

Table 2

Suzuki–Miyaura coupling reaction of iodobenzene $({\bf 1a})$ with phenylboronic acid $({\bf 3a})$ catalyzed by PVP-stabilized PdNPs. a

	+		[Pd]		
1a	3a		H ₂ O, 90⁰C	4a	
Entry	Catalyst		Yield	(%) ^b TON ^c	
	Pd source	Pd load (n	nol%)		
1	PdCl ₂	0.4	92	230	
2	NPs ^{22 nm}	0.4	91	228	
3	NPs ^{19 nm}	0.4	94	235	
4	NPs ^{19 nm}	0.07	79 ^d	1129	
5	NPs ^{10 nm}	0.07	97	1386	
6	NPs ^{10 nm}	0.006	97	16167	
7	NPs ^{10 nm}	0.0008	95	118750	
8 ^e	NPs ^{10 nm}	0.0008	90	112 500	
9 ^f	NPs ^{10 nm}	0.0008	94	117 500	

 a Reaction conditions: 0.5 mmol of ArX, 0.75 mmol of PhB(OH)_2, 1.5 mmol of K_3PO_4, 4 mL of the mixed H_2O:EtOH 3:1, at 90 $^\circ$ C for 24 h under nitrogen atmosphere.

^b CG yields. The yields reported represent the average of two reactions.

^c TON (turnover number, moles of product per mol of Pd).

^d The substrate was recuperated in 14% yield.

^e Reaction carried out under aerobic conditions.

^f Reaction carried out with NPs^{10nm} after they were centrifuged and redispersed in water.



Fig. 1. (a) Potential-time plots from the galvanostatic synthesis using a Pt electrode in aqueous solution containing $0.5 \text{ mM H}_2\text{PdCl}_4 + 16 \text{ gL}^{-1}$ PVP and 0.1 M KNO_3 . Galvanostatic pulses were carried out at room temperature during 600 s, under electrolyte stirring (1000 rpm), at current densities of -50 mA/cm^2 (red line); -100 mA/cm^2 (blue line) and -150 mA/cm^2 (black line) and (b) dependence of the particles size (pink symbols), from data in Fig. 2 and the final potential value reached (black symbols), with the current density of the galvanostatic pulses. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

a black deposit was observed on the working electrode surface. presumably from the formation of a layer of palladium deposited. In the global process, Pd(II) ions are electrochemically reduced at the cathode/solution interface, independently of the particles stability either on the electrode surface or in solution. Rodriguez-Sanchez et al. [61] proposed that in the presence of stabilizers, the electrochemical reduction of Ag⁺ ions occurs by two competitive processes: (i) the formation of particles by clusters formation on the electrode and their stabilization in the solution, and (ii) the formation and growth of a metal film on the electrode surface via electrodeposition. Therefore, in order to increase of colloidal particles in solution, the surface film formation should be effectively inhibited. This can be achieved for example, by choosing a cathode material with low tendency to deposit palladium over its surface. In the present case we have used Pt as the working electrode, which has structural parameters (lattice structure, atomic radii, etc.) quite similar with the palladium metal.

On the other hand, during the galvanostatic synthesis, a strong hydrogen bubbles evolution from the electrode was observed. As it was before mentioned, reduction of protons occurs simultaneously with palladium deposition, i.e., both reactions proceed at the same potentials. As a consequence, only a part of the applied current is consumed for the electrochemical reduction of Pd(II) species, and the rest is involved in the H⁺ ions discharge.

Although the yield of palladium was not complete, this methodology has the following advantages: fast and simple operation, absence of undesired byproducts, use of water as solvent, PdNPs with high purity and control of a precise particle size by adjusting the current density as experimental variable. Moreover, all the PdNPs stabilized with PVP exhibit high stability and the colloidal dispersion can be preserved for several months, without appearance of any precipitate.

3.2. Catalytic performance of PVP-stabilized PdNPs in the Suzuki–Miyaura coupling reaction

Due to the particular usefulness of the Suzuki–Miyaura coupling reaction as a method for the formation of C—C bonds [11], we choose this reaction to build the biaryl structure and examine the catalytic activity of the electrochemically synthesized PVP-stabilized PdNPs.

The use of water as a reaction medium for Pd-catalyzed reactions is very attractive for organic synthesis, due to environmental, economical, and safety reasons. Consequently, in the last decade an important number of studies related to the use of aqueous media in Suzuki–Miyaura coupling reactions has been reported [64]. Some of them were performed in the presence of NPs [65–67] such as the pioneering work of El-Sayed et al. [44].

The initial screening of catalytic efficiency of the PVP-stabilized PdNPs in the coupling reaction was carried out using iodobenzene (**1a**) and phenylboronic acid (**3a**). For this study, based on previous results [68] and after a series of initial experiments, H₂O:EtOH 75:25 was chosen as the solvent and K_3PO_4 as the base. The reactions were performed at 90 °C under nitrogen atmosphere in the presence of different ratios of PdNPs as catalyst within 24 h. Under this reaction condition we evaluated all the NPs electrochemically synthesized without any purification. In Table 2 are summarized the most relevant results for each size of PdNPs. The reproducibility of each catalytic reaction was confirmed by carrying out the catalytic reaction at least two times.

Control experiments were achieved under the optimized conditions, which have shown that the coupling reaction did not occur in the absence of PdNPs and no product was observed within 24 h. In addition, we performed a reaction using PdCl₂ as Pd source (entry 1, Table 2). The use of PdCl₂ as catalyst was already reported [69], and in few cases, the catalyst in the Suzuki–Miyaura coupling reaction



Fig. 2. TEM images of the PdNPs obtained by a galvanostatic pulse at room temperature using a Pt electrode in a stirred electrolyte (1000 rpm), after a current density pulse of (a) -50 mA/cm²; (b) -100 mA/cm² and (c) -150 mA/cm², was applied during 600 s.

Table 3

The Suzuki coupling reaction of aryl halides with boronic acid catalyzed by PVP-stabilized PdNPs.^a



Entry	Aryl halides	3a-c(R')	PdNPs (mol%)	Time (h)	Yield (%) ^b	Conv. (%) ^c	TONd
1		Н	0.0008	6	95 (4 a)	99	123750
2	0	Н	0.0008	6	96 (4b)	99	123750
3	0 1 1 c	Н	0.0008	4	91 (4c)	99	123750
4	NC 1d	Н	0.0008	24	52 (4d) ^e	99	123750
5		Me	0.0008	24	48 (5)	69	86250
6		Me	0.006	24	85 (5)	99	16500
7	1a	OMe	0.006	24	95 (6)	99	16500
8	_	OMe	0.01	3	98 (6)	99	9900
9	Br	Н	0.006	24	93 (4a)	99	16500
10	_	Н	0.003	24	87 (4a)	92	30667
11	O-Br 2b	Н	0.006	24	51 (4b)	67	11167
12	_	Н	0.07	24	89 (4b)	97	1386
13	Br 2c	Н	0.006	12	91 (4c)	99	16500

^a Reaction conditions: 0.5 mmol of ArX, 0.75 mmol of PhB(OH)₂, 1.5 mmol of K₃PO₄, 4 mL of the mixed H₂O:EtOH 3:1, at 90 °C and under nitrogen atmosphere.

^b CG yields. The yields reported represent the average of two reactions.

^c Determinate in relationship to the amount of initial substrate.

^d TON (turnover number).

^e Near a 40% yield of product biphenyl-4-carboxamide was observed.

was actually the *in situ* formed PdNPs from $PdCl_2$ and a stabilizing polymer [65,70]. Under our reaction conditions, very good yield of the biphenyl product was obtained (92%) using 0.4 mol% as a minimum load of $PdCl_2$ (entry 1, Table 2).

Furthermore, we have investigated the catalytic activity of the electrochemically synthesized PVP-stabilized NPs of different diameters. High yields were observed for the coupling reaction of iodobenzene (**1a**) and phenylboronic acid (**3a**) using all PdNPs. When PdNPs with mean diameter of 22 nm were employed as catalyst, total conversion was achieved with 0.4 mol% of Pd after 24 h (entry 2, Table 2). By decreasing the load of catalyst, the conversion and the yields of biphenyl product were lower. When the reaction was performed in the presence of PdNPs with mean diameter of 19 nm, under the same conditions, with 0.4 mol% Pd, the reaction was completed and 94% yield of biphenyl was obtained (entry 3, Table 2). Moreover, in the presence of 0.07 mol% of Pd, the biphenyl product was obtained with 79% yield and a TON of 1129, which is considerably larger for these reactions (entry 4, Table 2). However, the reaction was not completed and the substrate was recovered.

Finally, the PVP-stabilized PdNPs with mean diameter of 10 nm were examined as catalysts for the Suzuki–Miyaura reaction at

different palladium loads (entries 5-7, Table 2). At first, the reaction was performed in the presence of 0.07 mol% of Pd. After 24 h the reaction was completed and 97% yield of biphenyl was obtained (entry 5, Table 2). With 0.006 mol% of Pd, the catalyst also exhibited complete conversion and excellent yields (entry 6, Table 2). It is noticeable that the catalyst loading could be reduced to 0.0008 mol%, allowing the formation of 95% of the biphenyl product with a TON of 118750 and a turnover frequency (TOF) of $4948 \, h^{-1}$ (entry 7, Table 2). It is important to note that the extremely low Pd loading was exceptionally observed with other NPs [71-73]. In those cases the term "homeopathic dose" was used. Moreover, the obtained TOF value is considerably high for an aqueous Suzuki-Miyaura coupling reaction catalyzed by PdNPs [74]. These results demonstrated the high catalytic activity of the NPs with 10 nm mean diameter and allow us to conclude that they were the best catalysts prepared. A possible reason for the high activity of the PVP-stabilized PdNPs besides the small particles size could be a high dispersion of PVP in aqueous solution leading to an easy access of substrate to the NPs.

In addition, it should be mentioned that the PdNPs are usually used under inert atmospheres to prevent the oxidation of the



Fig. 3. Pd load (mol%) and turnover number as a function of particle size for the PdNPs given in Table 2 in the Suzuki–Miyaura coupling of iodobenzene (**1a**) and phenylboronic acid (**3a**) for 24 h.

metallic Pd which takes place under aerobic conditions. As a result of this oxidation, the catalytic activity can be reduced. However, the presence of some molecules which protect the NPs surface against the oxide formation, enables that the PdNPs can be used under aerobic conditions. In this concern, when the synthesized PVP-stabilized NPs reacted under air atmosphere, a similar behavior to that observed in nitrogen atmosphere was detected (entry 8, Table 2). Only a slight decrease in biphenyl yields was observed, indicating that the PVP molecules could avoid the oxidation of the PdNPs.

All these reactions were carried out with the aqueous dispersions of PdNPs directly obtained from the electrochemical synthesis, without further purification. In order to assess if the presence of remnant from the NPs preparation affect the catalytic activity of the PdNPs, the coupling reaction of iodobenzene with phenylboronic acid was carried out with PdNPs that were centrifuged, and the obtained pellet was redispersed in water. Under the current experimental conditions, the complete conversion of iodobenzene and 94% yields of the biaryl product were achieved with the purified PdNPs as catalyst, indicating that no considerable changes were observed (entry 9 vs. 7, Table 2). The results revealed that no further purification of the PdNPs was necessary.

The results presented in Table 2 can be summarized in Fig. 3. The observed general trend shows that the catalytic activity of NPs increases as the particle size decreases (Fig. 3). This result suggests that in the Suzuki–Miyaura reaction, the catalysis cannot be taking place over all the surface atoms of the PdNPs, since all the surface atoms on the catalyst are active sites, it should not have observed a dependence on the particle size [75].

Once the catalytic activity of the PVP-stabilized PdNPs for the Suzuki–Miyaura coupling reaction was established, the scope of this reaction was investigated. For this reason, we screened other aryl halides and boronic acids as coupling partners with the highest activity catalysts, the PdNPs with 10 nm mean diameter, as seen in Table 3.

The coupling reactions of aryl halide and arylboronic acid were carried out in the presence of K_3PO_4 using H_2O :EtOH (75:25) as environmentally benign solvents. A wide variety of aryl iodides and aryl bromides, including the deactivated aryl bromides, were readily converted to the corresponding coupled products with very good yields. After the reaction, following a simple purification procedure the biaryl products could be easily isolated.

Very good yields were achieved in the coupling reactions catalyzed by PdNPs with aryl iodides, with very low catalyst load. The Suzuki–Miyaura reaction of iodobenzene with phenylboronic acid could accomplish the total conversion in 6 h, with the corresponding TOF value being 20 625 h⁻¹ (entry 1, Table 3). This TOF value revealed that the PVP-stabilized PdNPs are effective catalysts for this kind of reaction. The effect of different functional groups in the aromatic ring was also evaluated. Electron-rich iodides and electron-deficient ones afforded the corresponding biphenyls with very good yields. An excellent yield (96%) was achieved in the coupling of phenylboronic acid with 4-iodoanisole (**1b**), with very high TON in only 6 h (entry 2, Table 3). The reaction of 4-iodoacetophenone (**1c**) and phenylboronic afforded the biphenyl product **4c** in 91% yields after 4 h with a TON of 123750 (entry 3, Table 3). When we performed the reaction with 4-iodobenzonitrile (**1d**), only 52% yields of biphenyl-4-carbonitrile product (**4c**) was obtained (entry 4, Table 3). However, the conversion of substrate was completed. As a byproduct, biphenyl-4-carboxamide was obtained from the hydrolysis of the nitrile group [76].

In addition, when the reaction between iodobenzene (**1a**) and 2-methylboronic acid (**3b**) was performed with 0.0008 mol% of catalyst the corresponding biaryl was obtained in low yields and only a 69% of conversion was observed (entry 5, Table 3). It is well known that the Suzuki–Miyaura coupling reaction with hindered arylboronic acid has traditionally proven to be a difficult challenge, particularly with substrates containing *ortho*-substituents [77,78]. However, when we used a higher catalyst loading in the reaction (0.006 mol%) the desired biaryl product **5** was obtained in high yields (entry 6, Table 3). Moreover, the coupling reaction with 2-methoxyphenylboronic acid under the same conditions was successfully carried out. The biaryl **6** was obtained in 95% yields with a TON of 16 500 (entry 7, Table 3). Total conversion and excellent yields of **6** were achieved in only 3 h with 0.01 mol% of catalyst (entry 8, Table 3).

In order to further explore the scope of the PdNPs as catalyst, the coupling reaction of substituted aryl bromides 2a-c with phenylboronic acid was carried out. Since aryl bromides are less reactive toward the oxidative addition than aryl iodides, catalyst load was increased to 0.006 mol% in order to obtain total conversion. Regardless of that, the catalytic system exhibits a remarkably high TON. When the reaction of bromobenzene (2a) and phenylboronic acid was performed, 93% yields of biphenyl 4a were achieved (entry 9, Table 3). Reducing the catalyst load (0.003 mol%) a slightly decrease on the yields was observed (entry 10, Table 3). The coupling reaction with the electron rich 4-bromoanisole (2b) provided the biaryl 4b in moderate yields (51%) (entry 11, Table 3). However, the yield of biaryl 4b was improved with 0.07 mol% of palladium (entry 12, Table 3). It is important to notice that the different reactivity of the aryl halides could be controlled by only changing the palladium load. Additionally, 4-bromoacetophenone (2c) provided the desired substituted biaryl 4c in 91% yields in 12 h (entry 13, Table 3). The TOF value of $1375 h^{-1}$ obtained for this reaction correspond to one of the highest reached for this substrate [74].

Unfortunately, the PdNPs catalytic system was less effective for the reaction of aryl chlorides. An attempt to couple chlorobenzene with phenyl boronic acid (**3a**) was not successful, and the substrate was completely recovered.

In order to establish the recycling capacity of the catalyst, the Suzuki–Miyaura cross-coupling reaction between iodobenzene (**1a**) and 2-methoxyphenylboronic acid (**3c**) in the presence of 0.01 mol% of Pd was chosen as a model reaction (entry 8, Table 3). The recycling experiment was carried out employing the PVP-stabilized PdNPs with mean diameter of 10 nm, and it was performed by repeated runs on the same batch of the catalyst. After each cycle of 3 h, fresh reactants were added to the Schlenk tube. The results of five successive runs in the recyclability test are shown in Fig. 4. The graph reveals that the PVP-stabilized PdNPs used as catalyst maintain 95% of their initial catalytic activity, at the end of the fifth cycle of Suzuki–Miyaura coupling reaction. Thus, this catalyst could be reused without any modification and with no significant loss of activity/selectivity in the Suzuki–Miyaura reaction in water.



Fig. 4. Recyclability test for the PVP stabilized PdNPs 10 nm of mean diameter in Suzuki-Miyaura cross-coupling reaction of iodobenzene (1a) and 2-methoxyphenylboronic acid (3c) for 3 h in aqueous medium.

4. Conclusions

By direct electroreduction of Pd(II) ions from aqueous solution containing PVP stabilizing agent, PdNPs with well-controlled size and shape were synthesized by a simple, mild, fast and efficient electrochemical approach. PdNPs were generated at the Pt/electrolyte interface through a galvanostatic pulse. Consequently, highly dispersed spherical PdNPs in PVP aqueous solution, with a narrow range of sizes dispersion were achieved. The PVP polymer provided a stable backbone and also assisted to control the nucleation and growth of PdNPs on the electrode. As it was demonstrated by TEM analysis, the average size of PdNPs can be conveniently controlled by the proper choice of the current densities.

The synthesized PVP-stabilized PdNPs exhibited an outstanding catalytic activity for the Suzuki-Miyaura coupling reaction under mild conditions in an environmental friendly solvent system. The PdNPs catalysts were more effective for the coupling reaction when the particles size was smaller (10 nm), providing remarkable high turnover numbers (TON up to $10^4 - 10^5$). The corresponding biaryls products could be obtained in very good yields (85–98%) from arvl iodides and arvl bromides. With the less reactive electrophiles, the catalytic performance was noticeably dependent on the palladium load. The catalyst could be reused for five times with no significant loss of activity.

In conclusion, the synthesized PdNPs have some notable features: (i) simple, fast and efficient synthesis (ii) control of NPs size by adjusting the current density, (iii) high stability, they can be preserved for several months, (iv) a great catalytic activity for the Suzuki-Miyaura coupling reaction in aqueous solvents, with remarkably high TONs and TOFs, and (v) possibility to be reused at least for five cycles, obtaining practically the same activity.

Extending the scope of applications, this type of PdNPs is expected to exhibit a broad range of usefulness for other palladium catalyzed reactions, which is underway.

Acknowledgments

This work was supported by ACC, CONICET, FONCYT and SECYT. P.M.U. and L.A.P. gratefully acknowledges CONICET and SECyT-UNC for fellowships, respectively.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. molcata.2012.06.016.

References

- [1] R.G. Finke, in: D.L. Feldheim, C.A. Foss Jr. (Eds.), Metal Nanoparticles: Synthesis, Characterization and Applications, Marcel Dekker, New York, 2002.
- D. Astruc, F. Lu, J. Ruiz Aranzaes, Angew. Chem. Int. Ed. 44 (2005) 7852.
- A. Roucoux, J. Schulz, H. Patin, Chem. Rev. 102 (2002) 3757. [3] Ì41
- Á. Molnár, Chem. Rev. 111 (2011) 2251.
- [5] I. Favier, D. Madec, E. Teuma, M. Gómez, Curr. Org. Chem. 15 (2011) 3127. D. Astruc, Inorg. Chem. 46 (2007) 1884. [6]
- N. Miyaura, in: A. de Meijere, F. Diederich (Eds.), Metal-Catalyzed Cross-[7] Coupling Reaction, vols. 1 and 2, 2nd ed., Wiley-VCH, Weinheim, 2004
- K.C. Nicolaou, P.G. Bulger, D. Sarlah, Angew. Chem. Int. Ed. 44 (2005) 4442.
- J.-P. Corbet, G. Mignani, Chem. Rev. 106 (2006) 2651. [9]
- [10] L. Yin, J. Liebscher, Chem. Rev. 107 (2007) 133
- [11] For a review, see F. Bellina, A. Carpita, R. Rossi, Synthesis 15 (2004) 2419.
- [12] N.T.S. Phan, M. Van Der Sluys, C.W. Jones, Adv. Synth. Catal. 348 (2006) 609.
- [13] E. Negishi (Ed.), Handbook of Organopalladium Chemistry for Organic Synthesis, John Wiley and Son, New York, 2002
- [14] For coupling of aryl chlorides, see F.C. Littke, G.C. Fu, Angew. Chem. Int. Ed. 41 (2002) 4176, and references cited therein.
- M. Feuerstein, H. Doucet, M. Santelli, Tetrahedron Lett. 42 (2001) 6667. [15]
- [16] J.-H. Li, W.-J. Liu, Org. Lett. 6 (2004) 2809.
- [17] D.A. Albisson, R.B. Bedford, S.E. Lawrence, P.N. Scully, Chem. Commun. (1998) 2095.
- [18] Y. Urawa, H. Naka, M. Miyazawa, S. Souda, K. Ogura, J. Organomet. Chem. 653 (2002) 269
- [19] For solvent-free coupling S.F. Nielsen, D. Peters, O. Axelsson, Synth. Commun. 30 (2000) 3501.
- [20] S.L. Buchwald, Acc. Chem. Res. 41 (2008) 1439.
- F.E. Hahn, M.C. Jankhe, T. Pape, Organometallics 26 (2007) 150. [21]
- [22] For leading review on Pd-N-heterocycliccarbene catalysis, see E.A.B. Kantchev, C.J. O'Brien, M.G. Organ, Angew. Chem. Int. Ed. 46 (2007) 276.
- C. Baleizao, A. Corna, H. Garcia, A. Leyva, Chem. Commun. (2003) 606.
- [24] F. Zeng, Z. Yu, J. Org. Chem. 71 (2006) 5275.
- [25] S. Niembro, A. Shafir, A. Vallribera, R. Alibes, Org. Lett. 10 (2008) 3215.
- [26] R. Bernini, S. Cacchi, G. Fabrizi, G. Forte, S. Niembro, F. Petrucci, R. Pleixats, A. Prastaro, R.M. Sebastián, R. Soler, M. Tristany, A. Vallribera, Org. Lett. 10 (2008) 561.
- R. Abu-Reziq, D. Wang, M. Post, H. Alper, Chem. Mater. 20 (2008) 2544. [27]
- X. Jiang, G. Wei, X. Zhang, W. Zhang, P. Zheng, F. Wen, L. Shi, J. Mol. Catal. A: [28] Chem. 277 (2007) 102.
- D. Astruc, Tetrahedron: Asymmetry 21 (2010) 1041.
- [30] M.G. Weir, M.R. Knecht, A.I. Frenkel, R.M. Crooks, Langmuir 26 (2010) 1137.
- L. Adak, K. Chattopadhyay, B.C. Ranu, J. Org. Chem. 74 (2009) 3982. [31]
- J. Liu, Y. Deng, H. Wang, H. Zhang, G. Yu, B. Wu, H. Zhang, Q. Li, T.B. Marder, Z. [32] Yang, A. Lei, Org. Lett. 10 (2008) 2661.
- [33] K.V. Kovtunov, V.V. Zhivonitko, L. Kiwi-Minsker, I.V. Koptyug, Chem. Commun. (2010) 5764.
- [34] A.D. Sawant, D.G. Raut, N.B. Darvatkar, U.V. Desai, M.M. Salunkhe, Catal. Commun. 12 (2010) 273.
- [35] G. Liu, M. Hou, J. Song, T. Jiang, H. Fan, Z. Zhang, B. Han, Green Chem. 12 (2010) 65
- [36] F.-X. Felpin, T. Ayad, S. Mitra, Eur. J. Org. Chem. 12 (2006) 2679.
- [37] M.L. Kantam, S. Roy, M. Roy, B. Sreedhar, B.M. Choudary, Adv. Synth. Catal. 347 (2005)2002
- [38] A. Cwik, Z. Hell, F. Figueras, Org. Biol. Chem. 3 (2005) 4307.
- [39] P.J. Ellis, I.J.S. Fairlamb, S.F.J. Hackett, K. Wilson, A.F. Lee, Angew. Chem. Int. Ed. 49 (2010) 1820
- [40] R. Narayanan, M.A. El-Sayed, J. Am. Chem. Soc. 125 (2003) 8340.
- Y. Li, E. Boone, M.A. El-Sayed, Langmuir 18 (2002) 4921. [41]
- B. Tamami, H. Allahyari, S. Ghasemi, F. Farjadian, J. Organometal. Chem. 696 [42] (2011)594
- A. Gniewek, A.M. Trzeciak, J.J. Ziolkowski, L. Kepinski, J. Wrzyszcz, W. Tylus, J. [43] Catal, 229 (2005) 332.
- [44] Y. Li, X.M. Hong, D.M. Collard, M.A. El-Sayed, Org. Lett. 2 (2000) 2385.
- Y. Xiong, J. Chen, B. Wiley, Y. Xia, J. Am. Chem. Soc. 127 (2005) 7332. [45]
- [46] J. Le Bars, U. Specht, J.S. Bradley, D. Blackmond, Langmuir 15 (1999) 7621.
- [47] F. Durap, Ö. Metin, M. Aydemir, S. Özkar, Appl. Organometal. Chem. 23 (2009) 498.
- [48] C. Evangelisti, N. Panziera, A. D'Alessio, L. Bertinetti, M. Botavina, G. Vitulli, J. Catal. 272 (2010) 246.
- [49] N. Cioffi, L. Torsi, L. Sabbatini, P.G. Zambonin, T. Bleve-Zacheo, J. Electroanal. Chem. 488 (2000) 42.
- [50] W. Pan, X. Zhang, H. Ma, J. Zhang, J. Phys. Chem. C 112 (2008) 2456.
- [51] C.-L. Lee, R.-B. Wu, C.-M. Syu, Electrochem. Commun. 11 (2009) 270.
- [52] J.T. Zhang, M.H. Huang, H.Y. Ma, F. Tian, W. Pan, S.H. Chen, Electrochem. Commun. 9 (2007) 1298. [53]
- M.T. Reetz, W. Helbig, J. Am. Chem. Soc. 116 (1994) 7401.
- [54] M.T. Reetz, R. Breinbauer, K. Wanninger, Tetrahedron Lett. 37 (1996) 4499. [55]
- R. Narayanan, M.A. El-Sayed, Langmuir 21 (2005) 2127.
- [56] R. Narayanan, M.A. El-Sayed, J. Catal. 234 (2005) 348.
- [57] D. Milstein, J.K. Stille, J. Am. Chem. Soc. 101 (1979) 4992. [58]
- F.-Y. Tsai, D.-N. Lin, M.-J. Chen, C.-Y. Mou, S.-T. Liu, Tetrahedron 63 (2007) 4304. [59]
- J.V. Kingston, J.G. Verkade, J. Org. Chem. 72 (2007) 2816. [60] T. Fujihara, S. Yoshida, H. Ohta, Y. Tsuji, Angew. Chem. Int. Ed. 47 (2008) 8310

- [61] L. Rodriguez-Sanchez, M.C. Blanco, M.A. Lopez-Quintela, J. Phys. Chem. B 104 (2000) 9683.
- [62] L. Rodriguez-Sanchez, M.J. Rodriguez, M.C. Blanco, J. Rivas, M.A. Lopez-Quintela, J. Phys. Chem. B 109 (2005) 1183.
- [63] H. Natter, R. Hempelmann, J. Phys. Chem. 100 (1996) 19525.
- [64] F. Alonso, P. Beletskaya, M. Yus, Tetrahedron 64 (2008) 3047.
- [65] Z. Du, W. Zhou, F. Wang, J.-X. Wang, Tetrahedron 67 (2011) 4914.
- [66] A.R. Siamaki, A.E.R.S. Khder, V. Abdelsayed, M.S. El-Shall, B.F. Gupton, J. Catal. 279 (2011) 1.
- [67] Z. Zheng, H. Li, T. Liu, R. Cao, J. Catal. 270 (2010) 268.
- [68] P.M. Uberman, M.N. Lanteri, S.C. Parajón Puenzo, S.E. Martín, Dalton Trans. 40 (2011) 9229.
- [69] C. Pan, M. Liu, L. Zhang, H. Wu, J. Ding, J. Cheng, Catal. Commun. 9 (2008) 508.
- [70] L. Tao, Y. Xie, C. Deng, J. Li, Chin. J. Chem. 27 (2009) 1365.
- [71] I.P. Beletskaya, A.V. Cheprakov, Chem. Rev. 100 (2000) 3009.
- [72] M.T. Reetz, J.G. de Vries, Chem. Commun. (2004) 1559.
- [73] A.H.N de Vries, J.M.C.A. Mulders, J.H.M. Mommers, H.J.W. Henderckx, J.G. de Vries, Org. Lett. 5 (2003) 3285.
- [74] Ö. Metin, F. Durap, M. Aydemir, S. Özkara, J. Mol. Catal. A: Chem. 337 (2011) 39.
- [75] R. Narayanan, M.A.C. Tabor, El-Sayed, Top. Catal. 48 (2008) 60.
- [76] A. Ishizuka, Y. Nakazaki, T. Oshiki, Chem. Lett. 38 (2009) 360.
- [77] A.F. Littke, C. Dai, G.C. Fu, J. Am. Chem. Soc. 122 (2000) 4020.
- [78] J. Yin, M.P. Rainka, X.-X. Zhang, S.L. Buchwald, J. Am. Chem. Soc. 124 (2002) 1162.