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Influence of palladium colloid synthesis procedures on catalytic activity in methoxycarbonylation reaction

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Abstract

Palladium colloids were prepared by chemical reduction of an aqueous solution of palladium dichloride with the reducing agents pyrogallol, chromium(II) acetate, and hydrazine in the presence of polyvinylpyrrolidone (PVP) as a stabilizing agent. The colloids thus obtained were characterized by means of powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and energy-dispersive X-ray microanalysis (EDX). Their catalytic activity was studied in a test reaction, methoxycarbonylation of iodobenzene. The choices of reducing agent and reduction conditions enables to synthesize colloids with various mean nanoparticle sizes (ranging from 1.9 to 19.8 nm) and nanoparticle morphologies. These two factors play a decisive role from the standpoint of catalytic activity of the systems under study.

Keywords: Pd colloid; Nanoparticles; Methoxycarbonylation; TEM; XRD

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1. Introduction

Although metal colloids have been known for more than 100 years, recently they have become an important research subject, gaining the attention of many investigative groups. Unquestionably, such great interest stems from metal colloids' unique physical properties and high catalytic activity [1–5]. Transition metal colloids, consisting of metal nanoparticles, have been successfully applied as catalysts in many reactions [6–22]. Among these, carbon–carbon bond formation processes occupy a special place. Depending on the reaction conditions, aryl halides may be transformed into carboxylic acids, esters, or amides in a one-stage carbonylation process catalyzed by transition metal colloids [6–9]. Other reactions that may also be efficiently catalyzed by palladium nanoparticles are olefination of aryl halides; the so-called "Heck reaction" [10–14]; the Sonogashira reaction, which produces phenylated alkines [15–17]; and the Suzuki process, which leads to formation of biphenyl derivates [18–20].

Metal colloids are intermediate species between single atoms and a bulk material. The essential parameter characterizing their catalytic ability is a surface-to-volume ratio. A high value of that factor is an indicator of potentially better access of substrates to the catalytic centers because a large percentage of a nanoparticle's metal atoms lie on the surface. In addition, these atoms do not necessarily order themselves in the same way that those in the bulk do [23]. Catalytic systems based on metal colloids are relatively simple, but during reaction the nanoparticles may aggregate, resulting in significant loss of their activity. However, careful selection of the reaction conditions, for instance, the introduction of tetraalkylammonium salts to the reaction medium (the so-called "Jeffery conditions" [24–26]), or the addition of ionic liquids [8,14], protects the nanoparticles against undesirable aggregation. Despite the fact that the functions of ammonium salts and ionic liquids have not been examined in detail, they are frequently considered electrostatic stabilizers of metal nanoparticles. Recently, it has also been confirmed that ammonium salts play a very important role in the solubilization of active palladium species formed in the reaction of palladium colloid with aryl halides [27,28].

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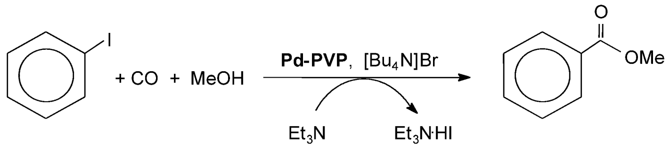


Scheme 1. Methoxycarbonylation of iodobenzene.

Transition metal colloids might be obtained by various physical or chemical methods. According to the literature [29], the four most common techniques are metal vapor condensation, thermal or photochemical decomposition of metal complexes, metal salt reduction, and electrochemical synthesis. The most frequently used method of palladium colloid preparation is palladium salt reduction in the presence of stabilizing agents, such as polymers or surfactants, which prevent the formation of "palladium black" by providing a steric barrier between particles. The reducing agents commonly used for palladium colloid synthesis are hydrogen, hydrazine, borohydrides, and alcohols [30]. Transition metal nanoparticles may also be formed in situ during the catalytic reaction and may be responsible for the activity of the considered systems [9].

Although it is well known that the size of the metal nanoparticles and the stabilizing agent used are determinants of catalytic activity [31], it is often difficult to compare synthetic methods used by different research groups. Nonetheless, the question of the size and shape dependence of the catalytic properties of platinum nanoparticles was recently addressed by Narayanan and El-Sayed [32–34]. Such a detailed study is lacking for palladium, however, prompting us to undertake an investigation into the catalytic activity of palladium colloids obtained under different conditions.

Many recent papers have described palladium nanoparticle preparation in the presence of polymers as stabilizing agents [35–40]. In this paper we report novel or improved synthesis techniques of palladium colloids by chemical reduction of an aqueous palladium dichloride solution. Polyvinylpyrrolidone (PVP) was used as the protecting agent. The reducing agents used for the synthesis were pyrogallol [28], chromium(II) acetate, and hydrazine. Through the choice of the reducing agent and reduction conditions, we were able to synthesize palladium colloids characterized by various nanoparticle sizes and morphologies. The colloids thus obtained were successfully tested as the catalysts of a simple model reaction, methoxycarbonylation of iodobenzene [8,9], and showed high activity in this process (Scheme 1).

2. Experimental

2.1. Reactants

Methanol, Et_3N, and diethyl ether were purified using standard procedures [41]. Iodobenzene and mesitylene (Acros Organics) were used without purification. Hydrazine hydrate ($N_2H_4 \cdot H_2O$) was purchased from Riedel–de Haën and used as obtained. Tetrabutylammonium bromide ($[Bu_4N]Br$), PVP K-15 ($M_W = 10{,}000$), and PVP K-30 ($M_W = 40{,}000$) were purchased from Fluka and used without purification. Chromium(II) acetate was obtained according to standard procedures [42].

2.2. Pd colloid synthesis-reducing agent: pyrogallol

The colloid was prepared as described previously [28] with slight modifications. One gram of PVP was added to 14 cm^3 of water and stirred intensively until the polymer was totally dissolved. Then 10 cm^3 of an acidic (HCl) solution of $PdCl_2$, containing 0.005 g of Pd in 1 cm^3, was added. The solution was stirred for 20 min, then heated to 85 °C. When the temperature was stabilized, 0.14 g of pyrogallol dissolved in 6 cm^3 of water was introduced, and the solution was stirred for another 20 min. During stirring, the mixture changed in color from light orange to dark brown. Once this occurred, the colloidal suspension was cooled to the ambient temperature and dried in a vacuum desiccator over molecular sieves (13X). The synthesized product, a dark-brown film of Pd-PVP colloid containing 5% Pd, was finally ground to a powder form.

2.3. Pd colloid synthesis-reducing agent: chromium(II) acetate

Palladium colloid synthesis was carried out at room temperature in a nitrogen atmosphere. One gram of PVP and 0.7 g of chromium(II) acetate were placed in a Schlenk flask and stirred intensively with 20 cm^3 of water, which had been previously kept under nitrogen flow for 5 min. After 2 h, the polymer was completely dissolved, and chromium(II) acetate remained as a suspension. Next, 20 cm^3 of an acidic (HCl) solution of $PdCl_2$, containing 0.005 g of Pd in 1 cm^3, was placed under nitrogen flow for 5 min, then introduced to the Schlenk flask. The mixture changed in color to dark brown in a few minutes, but stirring was continued for 2 h. After that, the flask was opened to expose the excess of Cr(II) to the air and allow it to oxidize to Cr(III). To separate chromium from the other components of the system, the solution was passed through a column with an ion exchanger (Dowex 50W X8). As a result, chromium(III) was bound to the cationite as a gray-blue layer. The obtained colloidal suspension was then dried in a desiccator over molecular sieves (13×). The synthesized product, a dark-brown film of Pd-PVP colloid containing 10% Pd, was finally ground to powder form.

2.4. Pd colloid synthesis-reducing agent: hydrazine

One gram of PVP was added to 20 cm^3 of water and stirred intensively until the polymer was totally dissolved. Next, 1 cm^3 of an aqueous solution containing 0.02 cm^3 of $N_2H_4 \cdot H_2O$ was added. The solution was stirred for another 20 min, then heated to the chosen temperature (with the synthesis carried out at 40, 55, 65, 75, 80, 85, 90, or 95 °C). When the temperature was stabilized, 10 cm^3 of an acidic (HCl) solution of $PdCl_2$, containing 0.005 g of Pd in 1 cm^3, was introduced, and the solution was stirred intensively for another 10 min. During stirring, the color of the mixture changed to dark brown. The colloidal suspension thus obtained was then cooled to ambient

Table 1
Synthesis parameters of palladium colloids, obtained nanoparticle size, and yield of methoxycarbonylation of iodobenzene reaction

No.	Reducing agent	PVP M_W (g/mol)	Temperature[a] (°C)	Ester yield[b] (mol%)	XRD d (nm)	TEM		
						d_m (nm)	σ	FWHM (nm)
1	Pyrogallol	40,000	85	73	17.4	19.8	0.17	8.0
2		10,000	85	62	14.2	–	–	–
3	Cr(II) acetate	40,000	Room	79	11.3	7.8	0.64	12.9
4		10,000	Room	100	7.9	6.1	0.39	5.8
5	$N_2H_4{\cdot}H_2O$	40,000	40	85	6.9	–	–	–
6			55	84	6.8	–	–	–
7			65	86	6.8	–	–	–
8			75	86	6.5	–	–	–
9			80	85	6.3	–	–	–
10			85	87	5.9	–	–	–
11			90	62[c]	6.4	–	–	–
12			95	27[c]	7.8	–	–	–
13		10,000	40	73	5.8	4.2	0.36	3.7
14			55	73	5.6	–	–	–
15			65	78	5.2	–	–	–
16			75	77	4.8	–	–	–
17			80	80	4.2	–	–	–
18			85	100	2.9	1.9	0.44	2.1
19			90	43[c]	4.0	–	–	–
20			95	10[c,d]	13.4	14.6	0.58	21.5

[a] Synthesis reaction temperature of palladium colloids.

[b] Reaction conditions: PhI 1.0 cm^3 (9.0 × 10^{-3} mol), MeOH 1.0 cm^3 (2.5 × 10^{-2} mol), NEt_3 3.0 cm^3 (3.3 × 10^{-2} mol), mesitylene 0.64 cm^3 (4.6 × 10^{-3} mol), $[Bu_4N]Br$ 0.8 g (2.5 × 10^{-3} mol), palladium colloid 0.032 g or 0.016 g (1.5 × 10^{-5} mol Pd), 2 h, 5 atm CO, 90 °C.

[c] Aggregated colloid obtained, synthesis carried out above the optimal temperature 85 °C.

[d] Yield of reaction is 46% when 0.64 g (3 × 10^{-4} mol Pd, 20 times more than usually) of the colloid is used.

temperature and dried in a vacuum desiccator over molecular sieves (13X). The synthesized product, a dark-brown film of Pd-PVP colloid containing 5% Pd, was finally ground to powder form.

2.5. Catalytic test reaction procedure

Catalytic activity of the synthesized palladium colloids was tested in methoxycarbonylation of iodobenzene, leading to the formation of benzoic acid methyl ester as the only product (Scheme 1). The catalytic reactions were carried out in a 130-cm^3 thermostatted steel autoclave with magnetic stirring. The reagents (1.0 cm^3 [9.0 × 10^{-3} mol] of iodobenzene, 1.0 cm^3 [2.5 × 10^{-2} mol] of methanol, 3.0 cm^3 [3.3 × 10^{-2} mol] of NEt_3, and 0.64 cm^3 [4.6 × 10^{-3} mol] of mesitylene as the internal standard, 0.8 g [2.5 ×10^{-3} mol] of tetrabutylammonium bromide), and palladium colloid (1.5 × 10^{-5} mol Pd) were introduced to the autoclave in a nitrogen atmosphere. Then the nitrogen was replaced with CO (5 atm). The reactions were carried out at 90 °C for 2 h, after which the autoclave was cooled and the organic components were separated by extraction with diethyl ether (3 times with 3 cm^3) and analyzed by gas chromatography–mass spectroscopy (Hewlett-Packard 8452A).

In case of catalyst recycling, the postreaction mixture was dried in vacuo after the extraction of the products. Such a residue, containing palladium colloid and ammonium salt, was placed in the autoclave and, after the addition of the liquid reagents in the amounts given above, used for the next reaction cycle.

A special sample with modified amounts of the reagents was prepared for use in transmission electron microscopy (TEM) studies of possible changes of nanoparticle size and morphology that occur during reaction. The studies used 0.15 cm^3 (1.35 × 10^{-3} mol) of iodobenzene, 1.0 cm^3 (2.5 × 10^{-2} mol) of methanol, 2.0 cm^3 (2.2 × 10^{-2} mol) of NEt_3, and 0.04 g (1.25 × 10^{-4} mol) of tetrabutylammonium bromide, together with 0.2 g (1.9 × 10^{-4} mol Pd) of the palladium colloid obtained with chromium(II) acetate (Table 1, entry 3). The reaction was carried out for 1 h at 90 °C in 5 atm of CO. The autoclave was cooled, and the solid residue was dried and used for TEM measurements.

2.6. Determination of elemental composition

The elemental composition of the obtained samples was determined by elemental analysis (using VarioEL III analyzer) and EDX. The EDX measurements were performed using a Röntec analyzer that was coupled with a LEO 435 VP scanning electron microscope.

2.7. XRD studies of palladium colloids

The size of palladium nanoparticles was determined using X-ray powder diffractograms (Fig. 1), recorded with a DRON-1 diffractometer operating with the Cu-K$_\alpha$ radiation line. The average diameter d (Table 1) of palladium crystallites was estimated from the X-ray (111) line broadening (measured at $2\theta = 40.1°$) using the Debye–Scherrer equation.

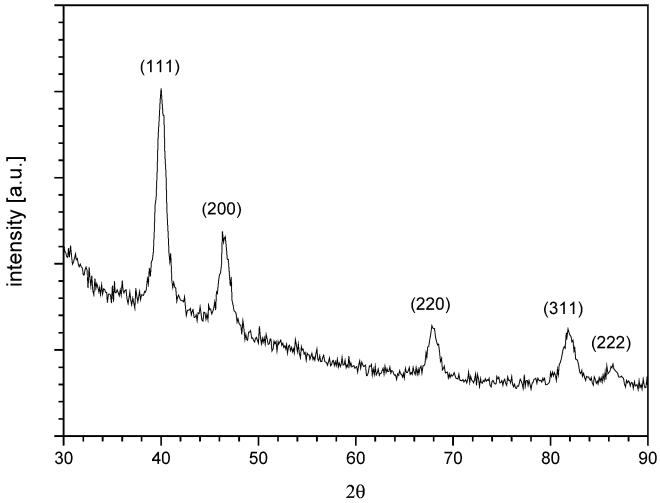


Fig. 1. Typical XRD diffractogram of a palladium colloid with the average nanoparticle diameter of 14.2 nm: colloid no. 2 (Table 1).

2.8. TEM studies of palladium colloids

TEM was performed with a Philips CM-20 Super Twin microscope operating with an acceleration voltage of 200 kV, and providing a resolution of 0.24 nm. The samples for TEM measurement were prepared by dissolving 5 mg of the colloid in 10 cm^3 of spectral-purity methanol. One drop of the solution was placed on the carbon-coated grid and dried for 40 min. The nanoparticle size distribution for each sample was determined by counting the size of approximately 400 palladium nanoparticles from several TEM images obtained from different places on the TEM carbon grids. The size d distribution plots were fitted by means of a lognormal curve approximation with the probability density function P described by

$$P(d) = \frac{1}{d\sigma\sqrt{2\pi}} \exp\left(\frac{-(\ln(d/d_m) - \sigma^2)^2}{2\sigma^2}\right). \tag{1}$$

Using such an asymmetric distribution reflects the nonzero probability of finding much larger than average colloid nanoparticles. The d_m parameter (Table 1) is the most probable particle diameter (the maximum of the distribution), and σ is the standard deviation. The full width at half maximum (FWHM) may be calculated as $f d_m - f^{-1} d_m$, where the f parameter is given by the following equation; this parameter is also used to describe the asymmetry of log-normal distributions:

$$f = \exp\left(\sigma\sqrt{2\ln 2}\right). \tag{2}$$

3. Results and discussion

Pyrogallol, chromium(II) acetate, and hydrazine were successfully used as the reducing agents in the synthesis of palladium colloids of various nanoparticle sizes. PVP was used as the stabilizing agent for all of the prepared colloids. The systems thus obtained were successfully tested as catalysts for the methoxycarbonylation of iodobenzene carried out under identical conditions.

3.1. Colloid size and morphology

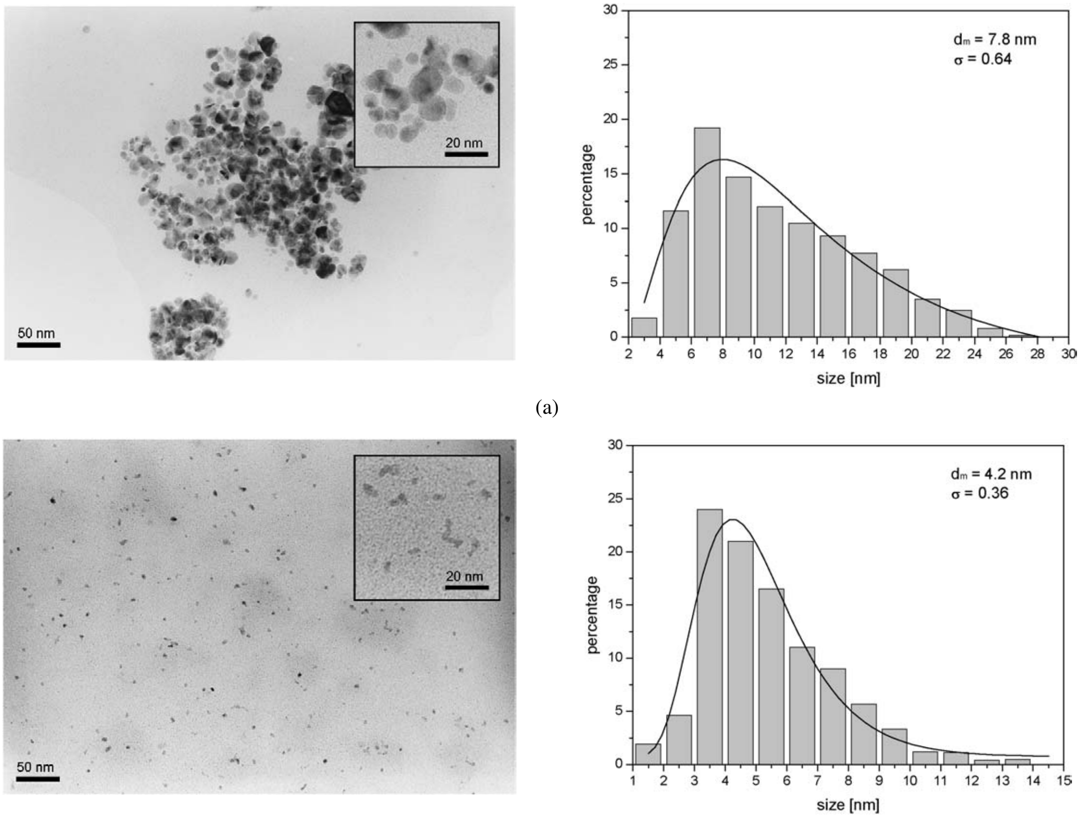
Palladium colloids synthesized using various reducing agents show differences (sometimes very significant) in nanoparticle size. The mean particle diameter ranges from almost 20 nm for pyrogallol to only about 2 nm for hydrazine. It is noteworthy that our results reflect the previous postulation that strong reducing agents lead to small colloids in a rapid reaction, whereas weaker reducing agents produce larger particles [43].

Although mean nanoparticle size is an important parameter differentiating palladium colloids synthesized using pyrogallol, chromium(II) acetate, or hydrazine as the reducing agent, it is not the only significant factor. The TEM micrographs (Fig. 2) reveal some significant morphological differences. Palladium nanoparticles prepared with pyrogallol (Table 1, entry 1) have mostly well-defined geometrical shapes, including triangular, rhomboidal or square, pentagonal, and relatively few particles with poorly defined shapes [28]. The nanoparticle size distribution is almost entirely symmetric, with a very well-developed maximum around 19.8 nm and a FWHM of 8.0 nm.

The palladium colloid prepared by reduction with chromium(II) acetate (Table 1, entry 3) reveals a highly asymmetric nanoparticle size distribution (Fig. 2a). The maximum of this distribution is located at 7.8 nm; however, particles ranging from 2 to 28 nm are observed in the system. This is the reason for the high FWHM value of 12.9 nm. The palladium particles are round; it is impossible to distinguish characteristic crystal forms like these found in the colloids prepared with pyrogallol.

Analogously, the colloid prepared using hydrazine as the reducing agent (Table 1, entry 13) is composed of nanoparticles, which do not have the characteristic shapes of crystal forms (Fig. 2b). Here the palladium particles are very small and quite irregularly shaped; some (presumably aggregates of several smaller crystals) are elongated. The size distribution is asymmetric, shifted slightly toward larger crystallites. The maximum of this distribution is at 4.2 nm, and the FWHM is 3.7 nm.

The TEM studies were also performed on palladium colloids synthesized at various temperatures using hydrazine as the reducing agent. The smallest crystallites are formed (Fig. 3a) at the optimal temperature of 85 °C (Table 1, entry 18). The nanoparticle size distribution is asymmetric, with a maximum at 1.9 nm and an FWHM of 2.1 nm. Note that in this case the particles are usually observed in closely (ca. 5 nm) spaced groups. When the synthesis is carried out at 95 °C (Table 1, entry 20), a temperature above the optimal level, the particles aggregate and form fairly large species with a highly asymmetric size distribution. The maximum distribution is located at 14.6 nm; however, particles ranging from 8 to even 48 nm are observed in the colloid. This is the reason for the very high FWHM value of 21.5 nm. Interestingly, such large aggregates in the colloid, although characterized by very irregular shapes, appear to be single crystals according to electron diffraction performed on a separated nanoparticle (see the diffractogram in the inset of Fig. 3b). This phenomenon may suggest that



(a)

(b)

Fig. 2. Morphology and nanoparticle size distributions of palladium colloids synthesized with the use of chromium(II) acetate (a) and hydrazine (b) as the reducing agents: colloids no. 3 and 13 (Table 1).

they are most likely flat species composed of many smaller palladium particles arranged in the same crystallographic direction.

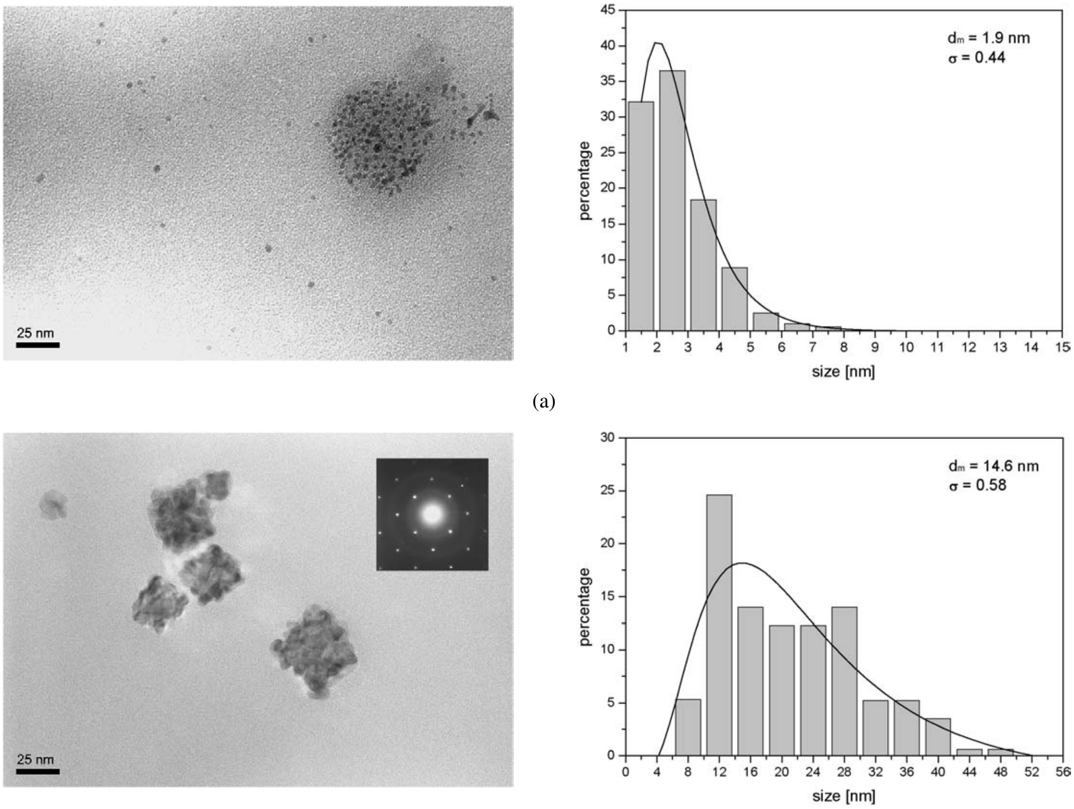
The influence of the Pd(II) reduction temperature on the nanoparticles size was further investigated for the colloids obtained using hydrazine. It was found that the higher the temperature, the smaller the average particle diameter estimated by XRD (Fig. 4). This relationship holds until the minimum is reached at 85 °C; at higher temperatures, the nanoparticles aggregate during synthesis, and much larger crystallites are formed. Note that the dependence obtained for the colloids prepared using PVP with an average molecular weight of 40,000 is smoother and has a less evident minimum than that obtained for colloids prepared using PVP with a molecular weight of 10,000.

The palladium colloids synthesized under identical conditions but using the protecting polymers of different molecular weights are also characterized by differing average particle sizes (Table 1). The nanoparticles obtained using PVP with a molecular weight of 40,000 are 20–30% larger than those obtained using PVP with a molecular weight of 10,000. Such differences, which were also observed by other researchers [44,45], may be due to the better adsorption of smaller polymer molecules on the surface of palladium particles. The colloid prepared using chromium(II) acetate also shows a significantly lower nanoparticle size dispersity (described by the FWHM parameter) when PVP with a molecular weight of 10,000 is used as the protecting agent.

3.2. Colloid activity in catalytic test reactions

Undoubtedly, as has often been postulated in the literature [46,47], nanoparticle size is a key factor affecting the catalytic activity of palladium colloids. Fig. 5 clearly shows that the yield of the product in the methoxycarbonylation reaction is dependent on the average nanoparticle size estimated by XRD. These results were obtained for the colloids synthesized using hydrazine as the reducing agent and PVP with a molecular weight of 10,000 as the protecting polymer (Table 1, entries 13–18). The relation is nonlinear; for large nanoparticles, the yield is quite similar, whereas for the smaller ones it is distinctively higher, even reaching 100% for the colloid with 2.9-nm particles.

The foregoing relationship does not take into consideration the palladium colloids obtained at temperatures above 85 °C. The synthesis carried out under such conditions leads to the formation of large, aggregated nanoparticles. But these colloids are characterized not only by the dimensions of palladium particles, but also the morphology of such nanoparticles is completely different (Fig. 3b). Thus the catalytic activity is usually significantly lower than that suggested by the average size of the Pd(0) particles. For instance, the colloid synthesized at 95 °C: $d_m = 14.6$ nm (Table 1, entry 20) allows a merely 10% product yield, and changing the amount of the catalyst to 3×10^{-4} mol Pd (20 times greater than usual) increases the yield only to 46%.



(a)

(b)

Fig. 3. Palladium colloids obtained by reduction with hydrazine at the optimal synthesis temperature 85 (a) and at 95 °C (b) when the optimal temperature is exceeded and the nanoparticles aggregated: colloids no. 18 and 20 (Table 1).

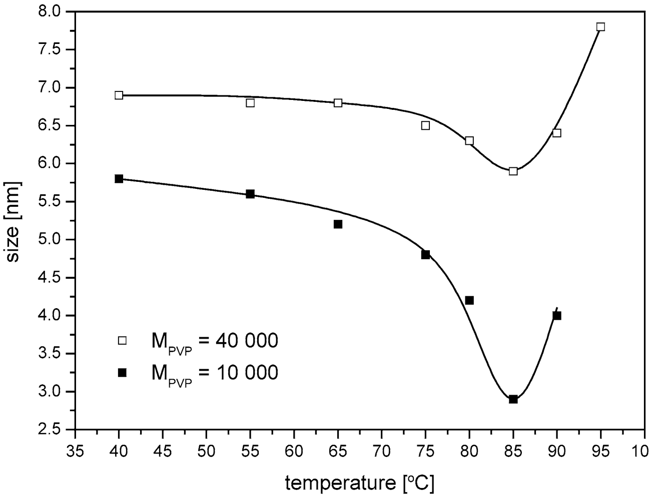


Fig. 4. Relation between nanoparticle size and synthesis temperature for palladium colloids obtained using hydrazine as the reducing agent.

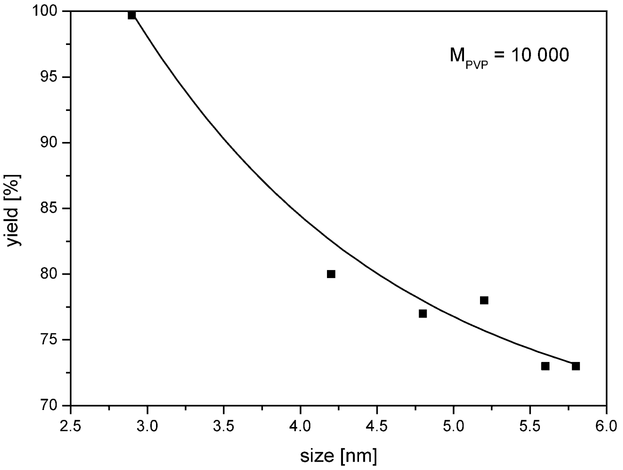


Fig. 5. Relation between methoxycarbonylation yield and nanoparticle size determined for palladium colloids prepared by reduction with hydrazine.

As mentioned above, nanoparticle size is not the only crucial factor influencing colloid catalytic activity. Colloidal systems of unlike morphologies obtained using different reducing agents cannot be compared solely on the basis of the particle size. For example, the colloid synthesized using pyrogallol, with $d_m = 19.8$ nm (Table 1, entry 1), and the colloid prepared with hydrazine, composed of smaller nanoparticles, $d_m = 4.2$ nm (Table 1, entry 13), can produce identical yields.

We have found that catalysis with palladium nanoparticles is shape-dependent. Our observations are similar to those published for platinum nanoparticles [32–34]. The authors of those earlier papers demonstrated that the activation energy of the catalytic reaction decreases as the fraction of surface atoms in the corners and edges increases. In fact, in previous studies we observed the dissolution of atoms from the corners and edges of the palladium nanoparticles under carbonylation and Heck reaction conditions [28]. This can explain the higher catalytic

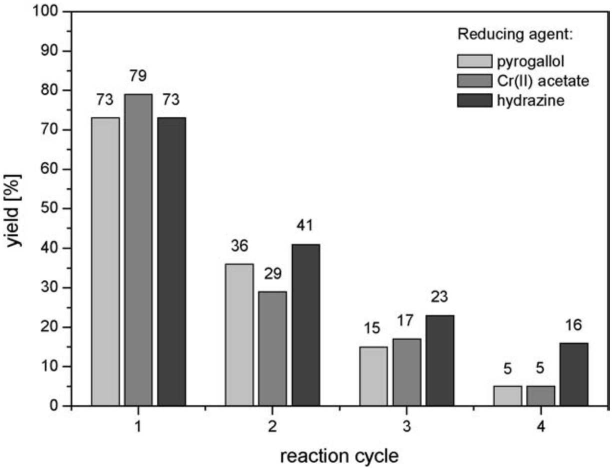


Fig. 6. Results of catalyst recycling in methoxycarbonylation of iodobenzene catalyzed by palladium nanoparticles: colloids no. 1, 3, and 13 (Table 1).

activity of palladium colloids obtained using pyrogallol, composed of rather large but well-shaped triangular and rhomboidal nanoparticles.

Note that the molecular weight of the protecting polymer also influences the yield of the reaction (Table 1). Despite the fact that palladium colloids obtained using PVP with an average molecular weight of 10,000 are composed of smaller nanoparticles, they show lower product yields than the colloids synthesized under identical conditions but using PVP with a molecular weight of 40,000. According to an earlier report [44], the magnitude of the interaction of PVP molecules with metal particles increases with decreasing molecular weight. Consequently, the polymer of lower molecular weight is strongly adsorbed on palladium nanoparticles and effectively blocks access of the reagents to the surface. Thus the catalytic activity is lower than that for heavier PVP.

The only exceptions to the rule presented above are the palladium colloids prepared by reduction with chromium(II) acetate (Table 1, entries 3 and 4); however, these systems are characterized by different average nanoparticle diameters and very distinct particle size distributions. The colloid synthesized using PVP with a molecular weight of 40,000 has a much greater nanoparticle size dispersity, characterized by the σ parameter, than the colloid synthesized using PVP with a molecular weight of 10,000. This colloid contains many larger than average palladium particles; here in effect nanoparticle size, not the kind of polymer used, plays the most important role.

The possibility of catalyst recycling in methoxycarbonylation of iodobenzene was also investigated. The catalytic reactions were carried out with colloids with similar product yields in the first cycle that had been prepared using different reducing agents, including pyrogallol, chromium(II) acetate, and hydrazine (Table 1, entries 1, 3, and 13, respectively). The results, shown in Fig. 6, demonstrate that the colloid synthesized by reduction with hydrazine preserved the highest activity while recycling. In the fourth cycle, the ester yield was about 16%, whereas the other colloids were able to catalyze methoxycarbonylation to only 5%. Also interesting is the significant drop in catalytic activity between the first and second cycles occurring for all three palladium colloids. However, similar catalyst deactivation after each reaction cycle was also observed for the methoxycarbonylation of iodobenzene catalyzed by $[Bu_4N]_2[PdBr_4]$ complex used as a precursor [28].

Table 2
Results of methoxycarbonylation of iodobenzene catalyzed by palladium colloids, duration of reaction time in second cycle elongated to 4 h

Colloid/ reducing agent	Run 1 (2 h) ester yield (mol%)[a]	Run 2 (4 h) ester yield (mol%)[a]
Pd/Cr(II) acetate[b]	79	85
Pd/hydrazine[c]	73	81

[a] Reaction conditions: PhI 1.0 cm^3 (9.0×10^{-3} mol), MeOH 1.0 cm^3 (2.5×10^{-2} mol), NEt_3 3.0 cm^3 (3.3×10^{-2} mol), mesitylene 0.64 cm^3 (4.6×10^{-3} mol), $[Bu_4N]Br$ 0.8 g (2.5×10^{-3} mol), palladium colloid 0.032 g or 0.016 g (1.5×10^{-5} mol Pd), 5 atm CO, 90 °C.

[b] Colloid no. 3 (Table 1).

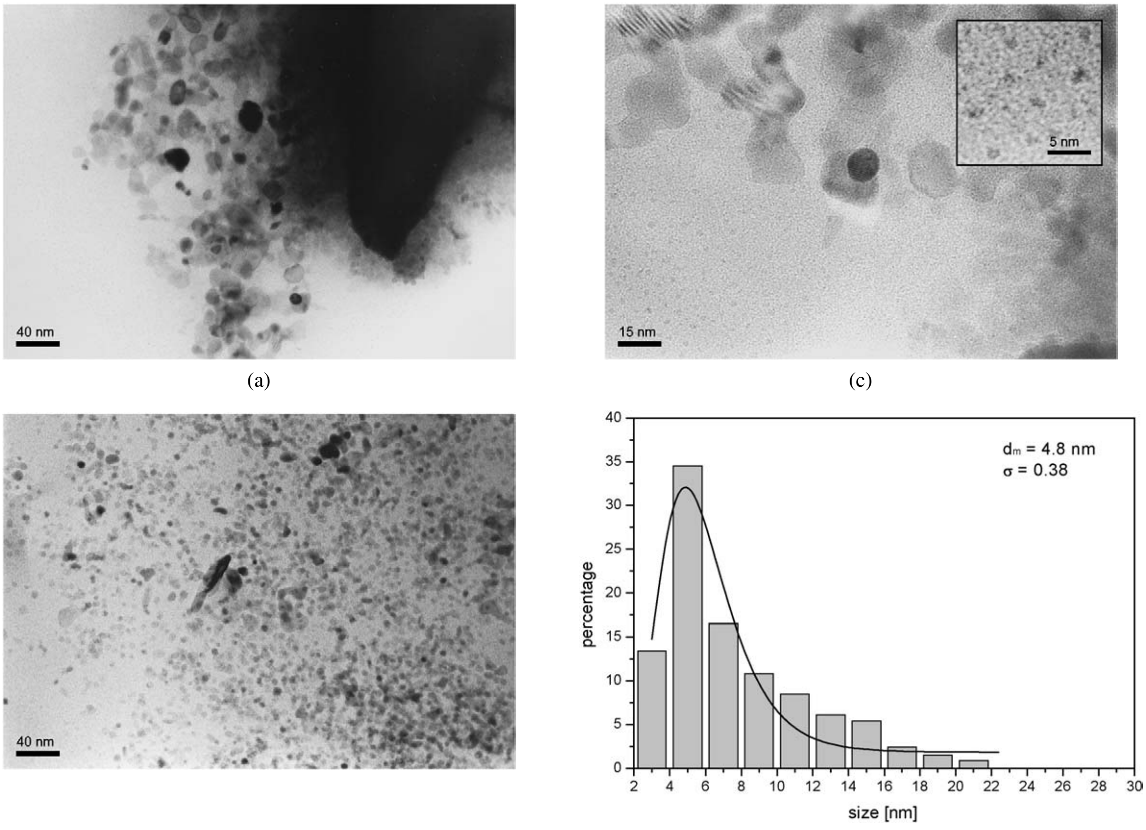
[c] Colloid no. 13 (Table 1).

Such a loss of activity could not be attributed to catalyst leaching. The diethyl ether extract of the reaction products did not contain any palladium species (analyzed by inductively coupled plasma measurements). As a result, it may be concluded that the solid residue contained all of the catalyst in the form of either palladium colloid or palladium complexes [27,28].

The stoichiometric formation and accumulation of $Et_3N{\cdot}HI$ is not responsible for the loss of catalytic activity. In a series of methoxycarbonylation reactions identical to those described herein, but carried out in an ionic liquid as the medium, only slight drops in activity were observed between cycles [8]. In our case, an elongation of the reaction time in second cycle to 4 h proved that the catalyst is still very active and that the product yield obtained in the second cycle may be even higher than in the first cycle (Table 2).

Transition metal colloids undergo changes in morphology to survive in the reaction mixture and reach their thermodynamical minimum [20]. But changes in the size and shape of nanoparticles [28] are not the only effects observed. Even though tetraalkylammonium salts are generally considered stabilizers, some authors have reported undesirable palladium colloid aggregation during catalytic reactions carried out in such media [48,49]. It is also the case here. TEM results obtained for the colloid isolated after the methoxycarbonylation reaction demonstrated that in fact a number of palladium nanoparticles aggregate and eventually form very large species (Fig. 7a).

Nevertheless, numerous particles did not suffer aggregation and are well dispersed in the reaction medium (Fig. 7b). Compared with the initial colloid (Fig. 2a), the size distribution changed significantly (Fig. 7d), and the particles became smaller as a result of the reaction. The maximum of the distribution is now located at 4.8 nm, and the FWHM is 4.4 nm. The histogram clearly shows that the palladium nanoparticles became more uniform in size here than in the starting colloid. In addition, the formation of $[Bu_4N]_2[PdBr_4]$- or $[Bu_4N]_2[Pd(Ph)Br_3]$-type complexes in the catalytic system was confirmed by XRD measurements. At the same time, the appearance of very small (ca. 1.5 nm) particles was noted (shown with enhanced contrast in the magnified fragment of



(a) (c) (b) (d)

Fig. 7. TEM micrographs showing palladium colloid recovered after methoxycarbonylation: aggregation of nanoparticles (a), nanoparticles evenly distributed in the sample (b), very small particles formed by reduction of Pd(II) species (c), and nanoparticle size distribution (d).

Fig. 7c), most likely formed by reduction of the Pd(II) species of $[Bu_4N]_2[PdBr_4]$ or $[Bu_4N]_2[Pd(Ph)Br_3]$ type.

Interesting, however, is the fact that the recycling procedure seems to mainly affect the activity of palladium colloids in the methoxycarbonylation of iodobenzene. To test the influence of catalyst handling between the cycles, a simple experiment was performed. After the first cycle of the reaction, the products were not extracted as usual with diethyl ether, but rather new portions of the liquid reagents (iodobenzene, methanol, triethylamine, and mesitylene [internal standard]) were added in the usual amounts, and the reaction was performed. Such a procedure should have led to product yields that are the average of the first and second cycles (Fig. 6). The colloid synthesized using chromium(II) acetate exhibited a noticeably higher ester yield, 68%. This observation demonstrates that the enormous drops in catalytic activity between the reaction cycles may be attributed to changes in nanoparticle size and shape during reaction, but that they are caused mainly by intensive processing of the catalyst after each cycle.

The elemental composition of the palladium colloids was also examined. According to the EDX results (Table 3) and the elemental analysis (Table 4), the colloid prepared by reduction with chromium(II) acetate contains definitely more chlorine than the other colloidal systems. This is clearly indicated by the Cl/C ratio and may be explained by the fact that HCl is always present during the preparation of palladium colloids and is easily attached to the protecting polymer. This is clearly evident in the samples prepared as described in Table 4.

Table 3
Results of X-ray microanalysis (EDX) of palladium colloids

Colloid/ reducing agent	C (at%)	N (at%)	O (at%)	Cl (at%)	Pd (at%)	Cr (at%)
Pd/Cr(II) acetate[a]	62	9	21	6.2	1.6	0.2
Pd/hydrazine[b]	65	10	22	2.1	0.9	–

[a] Colloid no. 3 (Table 1).

[b] Colloid no. 13 (Table 1).

Like the colloids prepared using pyrogallol and hydrazine, the colloid obtained by the reduction of $PdCl_2$ with chromium(II) acetate, containing 5% palladium (instead of 10%) have a much lower chlorine content (Table 4). As mentioned earlier, residual Cl is usually expected for palladium colloids prepared from $PdCl_2$ solutions, and the amount of Cl observed here may be fully justified. About 4.8% is coming from HCl attached to the protecting polymer (Table 4), whereas the remaining chlorine is most likely bounded to residual chromium, which is present in the system as $CrCl_3$.

The results of the EDX analysis (Table 3) show that the colloid obtained by reduction with chromium(II) acetate contains a small amount of chromium (atomic ratio of Pd:Cr is about 8:1), which is not removed by the ion exchanger. That quantity of chromium could not be removed even by passing the colloid several times through a column filled with the cationite. This

Table 4
Results of elemental analysis of PVP and palladium colloids stabilized with PVP

Analyzed substance	C (%)	H (%)	N (%)	Cl (%)	Ratio	
					N/C	Cl/C
PVP ($M_W = 10{,}000$)	60.72	8.89	11.91	–	0.196	–
PVP ($M_W = 40{,}000$)	61.30	8.41	11.82	–	0.193	–
Pd colloid, reduced with pyrogallol[a]	52.38	8.05	8.99	4.63	0.172	0.088
Pd colloid, reduced with Cr(II) acetate[b]	42.66	8.10	8.23	14.12	0.193	0.330
Pd colloid, reduced with hydrazine[c]	51.10	9.51	10.48	3.82	0.205	0.075
Pd colloid, reduced with Cr(II) acetate[d]	51.22	8.98	9.93	7.95	0.194	0.155
PVP-HCl[e]	58.56	8.22	11.55	4.82	0.197	0.082
PVP-HCl[f]	48.73	7.77	9.52	12.09	0.195	0.248

[a] Colloid no. 1 (Table 1).

[b] Colloid no. 3.

[c] Colloid no. 13 (Table 1).

[d] Palladium colloid synthesized according to identical procedure as described for colloid no. 3 (Table 1) but containing 5% of palladium instead of 10%.

[e] Sample preparation: 1 g of PVP dissolved in 9.9 cm^3 of H_2O and 0.1 cm^3 of HCl (HCl:PVP ratio identical as during synthesis of colloids containing 5% Pd), and dried in a vacuum desiccator over molecular sieves.

[f] Sample preparation: 1 g of PVP dissolved in 9.5 cm^3 of H_2O and 0.5 cm^3 of HCl (HCl:PVP ratio higher than during synthesis of colloids containing 5% Pd), and dried in a vacuum desiccator over molecular sieves.

Table 5
Influence of chromium additive on the yield of methoxycarbonylation reaction catalyzed by palladium colloid obtained by reduction with pyrogallol: colloid no. 2 (Table 1)

Amount of Pd ($\times 10^{-5}$ mol)	Chromium additive		Ester yield[a] (mol%)
	Type	Amount ($\times 10^{-5}$ mol)	
1.5	–	–	62
1.5	$CrCl_3 \cdot 6H_2O$	0.1	61
1.5	$CrCl_3 \cdot 6H_2O$	1	62
1.5	$Cr_2(CH_3COO)_4 \cdot 2H_2O$	1	63
–	$CrCl_3 \cdot 6H_2O$	0.1	0
–	$Cr_2(CH_3COO)_4 \cdot 2H_2O$	1	0

[a] Reaction conditions: PhI 1.0 cm^3 (9.0×10^{-3} mol), MeOH 1.0 cm^3 (2.5×10^{-2} mol), NEt_3 3.0 cm^3 (3.3×10^{-2} mol), mesitylene 0.64 cm^3 (4.6×10^{-3} mol), $[Bu_4N]Br$ 0.8 g (2.5×10^{-3} mol), palladium colloid – amount given in the table, 2 h, 5 atm CO, 90 °C.

finding may suggest that it is somehow bound in the system, for instance, complexed by the protecting polymer.

However, the presence of chromium in the system does not seem to affect the course of the methoxycarbonylation reaction. In a series of experiments catalyzed by the palladium colloid obtained using pyrogallol (Table 1, entry 2), chromium(II) and chromium(III) compounds were added to the reaction mixture. Compared with the pure palladium colloid, practically no changes in catalytic activity were noted (Table 5). The chromium compounds themselves do not catalyze this reaction either; absolutely no products of methoxycarbonylation are obtained.

Considering the colloid synthesized by reduction with hydrazine, note that the N/C ratio (Table 4) and the hydrogen content are a little higher than in the pure polymer. This implies that also in this case the reducing agent remains in the system and is not completely removed while drying.

Similarly, the colloid obtained using pyrogallol contains some quantity of the reducing agent. This is confirmed by the results of elemental analysis indicating that the N/C ratio is lower in this colloid than in the pure polymer. Such an effect may be explained by higher carbon content originating not only from the PVP, but also from pyrogallol.

4. Conclusion

Three different kinds of palladium colloids, containing nanoparticles ranging from 1.9 to 19.8 nm, were prepared by chemical reduction of an aqueous solution of palladium dichloride in the presence of PVP as the protecting polymer. Pyrogallol, chromium(II) acetate, and hydrazine were used as the reducing agents. To the best of our knowledge, using chromium(II) acetate in the preparation of palladium colloids is a novel technique published here for the first time.

The morphology and size distribution of palladium nanoparticles depend on the kind of reducing agent used. Strong reducing agents, like hydrazine, produce small Pd(0) particles. The optimal reduction temperature is 85 °C; higher temperatures lead to considerable nanoparticle aggregation. All of the palladium colloids obtained are characterized by high catalytic activity in the methoxycarbonylation of iodobenzene, enabling high product yields under mild reaction conditions. The sizes and shapes of the palladium nanoparticles, as well as the molecular weight of PVP used for their stabilization, play decisive roles in the catalytic activity of the presented systems. In most cases, higher yields of benzoic acid methyl ester (the product of methoxycarbonylation of iodobenzene) were obtained when smaller palladium nanoparticles were used.

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