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Carbon-supported spherical palladium nanoparticles as potential recyclable catalysts for the Suzuki reaction

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Abstract

Carbon-supported PVP–Pd nanoparticles prepared by adsorption of colloidal PVP–Pd nanoparticles onto activated carbon are used as catalysts for the Suzuki reaction between phenylboronic acid and iodobenzene to form biphenyl. These carbon-supported nanoparticles result in a lower biphenyl yield during the first cycle than the colloidal Pd nanoparticles that we studied previously. The carbon-supported Pd nanoparticles retain 69% of its activity upon recycling (second cycle), which is almost double the recycling potential observed in colloidal Pd nanoparticles (37% retention of activity). In addition, the carbon-supported Pd nanoparticles retain 73 ± 3% of their catalytic activity during the second through fifth cycles of the Suzuki reaction, while the catalytic activity of the colloidal Pd nanoparticles greatly decreases during that time frame. The carbon support that the palladium nanoparticles are adsorbed onto helps to preserve its catalytic activity for longer time periods. The effect of catalysis and recycling on the nanoparticle size is also investigated. The average size of the carbon-supported palladium nanoparticles is 1.9 ± 0.1 nm initially, 2.6 ± 0.1 nm after the first cycle, and 3.1 ± 0.1 nm after the second cycle. The continued growth of the supported nanoparticles suggests that the carbon support protects the palladium nanoparticles during the harsh Suzuki reaction and prevents aggregation and precipitation unlike the colloidal palladium nanoparticles. In addition, a narrow size distribution during the growth process (Ostwald ripening) is observed for the carbon-supported nanoparticles. This could be due to the adsorption method for preparing carbon-supported Pd nanoparticles because excess unaggregated palladium atoms will not be adsorbed onto the carbon support.

Keywords: Palladium nanoparticle; Nanocatalysis; Suzuki reaction; Carbon support; Supported nanoparticle; Catalytic activity; Ostwald ripening

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1. Introduction

The nanocatalysis field has undergone explosive growth during the past decade, because nanoparticles are attractive catalysts compared to other bulk catalytic materials due to their high surface tension. Nanoparticles in colloidal solution, as well as supported nanoparticles, have been used as catalysts, and there have been more than 2800 papers published in this vast field. Approximately 15–20% of the work in this field is conducted using colloidal metal nanoparticles as catalysts. Majority of the work has been conducted using supported metal nanoparticles as catalysts for a variety of organic and inorganic reactions. Supported metal nanoparticles have been prepared by adsorption [1–10], by grafting [11,12], and by lithographic fabrication using electron beam lithography [13–16]. Numerous review articles have described the use of supported nanoparticles as catalysts for a variety of reactions [17–29].

Although the field of nanocatalysis is vast, there have not been many studies on what happens to the nanoparticles during the course of the catalytic process. A few studies have characterized nanoparticles after the catalytic process for colloidal metal nanoparticles [30–34] and supported metal nanoparticles [35–39]. Also, a few studies have investigated the recycling potential of colloidal metal nanoparticles [40–43] and supported metal nanoparticles [44–47]. Overall, however, there have not been many studies conducted on the stability of nanoparticles after their catalytic function or on

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their recycling potential in both colloidal metal nanoparticles and supported metal nanoparticles. Detailed studies are needed to determine the best catalyst to use for a particular kind of reaction.

We have previously conducted several studies on the effect of the catalytic process on the shape [49–51,54] and size [48,52,53] of colloidal metal nanoparticles. We have used tetrahedral- [49–51], cubic- [49–51], and spherical- [48–50] shaped platinum nanoparticles to catalyze the electron transfer reaction. We have found that catalysis is shape-dependent during the early stages of the reaction, in which no large shape changes take place [49]. The activation energy of the catalytic reaction decreases as the fraction of surface platinum atoms present in the corners and edges increases. During the long reaction time in the full course of the electron transfer reaction (2 days), we observe changes in the platinum nanoparticle shape and corresponding changes in the activation energy that take place [50]. Dissolution of atoms from the corners and edges of the tetrahedral and cubic platinum nanoparticles occur, resulting in the formation of distorted tetrahedral and distorted cubic platinum nanoparticles. The rate of shape change was found to occur faster for the tetrahedral platinum nanoparticles than the cubic platinum nanoparticles [51].

We also conducted studies on the effect of catalyzing the Suzuki reaction on the size of spherical palladium nanoparticles [52,53]. The Suzuki reaction is a more harsh reaction, because it requires that the reaction mixture be refluxed at 100 °C for 12 h. We observed that the spherical PVP–palladium nanoparticles grew larger after the first cycle of the Suzuki reaction because of the Ostwald ripening process. After the second cycle, the palladium nanoparticles were much smaller in size because of aggregation and precipitation of the larger nanoparticles formed during the first cycle of the reaction [52]. In the case of the dendrimer–Pd nanoparticles, it was observed that the growth process continues to occur during the second cycle, which could be because the dendrimer is a strong encapsulating agent and protects the nanoparticle surface well [53]. This makes the nanoparticles more resistant to aggregation and precipitation. We also found that the reduction method used to prepare the nanoparticles also plays an important role in the growth of the palladium nanoparticles during the Suzuki reaction. In addition, colloidal tetrahedral platinum nanoparticles have also been used as catalysts for the Suzuki cross-coupling reaction [54]. We observed that the tetrahedral platinum nanoparticles transformed into spherical-shaped platinum nanoparticles after the Suzuki reaction was complete and that these transformed spherical nanoparticles grew larger in size upon recycling (after the second cycle).

We have shown in previous studies that colloidal metal nanoparticles are unstable and undergo changes in their morphology (size and shape) to survive in the reaction mixture. As a result, there is a need to try to find better types of nanocatalysts that can withstand the reaction conditions in which catalytic processes take place. Some possibilities include the use of better stabilizers to stabilize colloidal metal nanoparticles or the use of supported metal nanoparticles as catalysts. Previously, Li et al. [55] examined the effect of the capping material in colloidal solution and found that as the capping material stabilizes the nanoparticles, it decreases its catalytic efficiency.

In the present study, we explored the possibility of using supported metal nanoparticles as good potential catalysts by using carbon-supported nanoparticles to catalyze the Suzuki reaction. Carbon is a commonly used substrate in the preparation of supported nanoparticles [56–64]. Suzuki cross-coupling reactions have traditionally been catalyzed with different phosphine-based and phosphine-free palladium complexes [65–69]. There have also been many cases of palladium complexes supported on various substrates, such as silica [70,71,73,77], resin [72,78], chitosan [74], alumina [75], carbon [76], and others, that have also been used to catalyze this type of reaction. Recently, many different types of colloidal palladium nanoparticles have been used as catalysts for the Suzuki reaction [52,53,79–87]. It is noteworthy that there have been very few cases of supported palladium nanoparticles used as catalysts for this reaction [88,89], and the substrates used in these cases were silica [88], titania [88], and alumina [89]. More importantly, there have not been any studies on using carbon-supported palladium nanoparticles as catalysts for the Suzuki cross-coupling reaction.

One aim in this paper is to determine if carbon-supported spherical PVP–Pd nanoparticles are more catalytically active for the Suzuki reaction than the colloidal spherical PVP-capped palladium nanoparticles that we studied previously [52]. Another goal is to investigate the effect of the catalytic process on the size of the carbon-supported spherical palladium nanoparticles and compare the results with those obtained for the colloidal spherical palladium nanoparticles that we studied previously [52]. We chose the Suzuki reaction to test the stability of the carbon-supported spherical nanoparticles because it is a relatively harsh reaction that takes place at 100 °C for 12 h. In addition, it is also very important to assess the recycling potential of the carbon-supported spherical palladium nanoparticles to provide additional information on its usefulness in nanocatalysis.

2. Experimental

2.1. Synthesis of colloidal spherical PVP–Pd nanoparticles

The colloidal spherical PVP–Pd nanoparticles were synthesized by reduction of the precursor Pd ions with ethanol similar to that described previously [52]. The palladium precursor solution (H_2PdCl_4) was prepared by adding 0.0887 g of $PdCl_2$ and 6 mL of 0.2 mol HCl, and diluting to 250 mL with doubly distilled water. A solution containing 15 mL of 2 mmol of H_2PdCl_4, 21 mL of doubly deionized water, 0.0667 g PVP, and 4 drops of 1 mol HCl was heated. When the solution began to reflux, 14 mL of ethanol was added. The solution was then refluxed for 3 h, and a dark-brown colloidal Pd solution was formed. A drop of the solution was spotted onto Formvar-stabilized copper transmission electron microscopy (TEM) grids, and a JEOL 100C TEM was used to characterize the size of the nanoparticles.

2.2. Synthesis of carbon-supported spherical PVP–Pd nanoparticles

The carbon-supported spherical PVP–Pd nanoparticles were prepared using the adsorption method. First, 25 mL of the nanoparticle solution was diluted to 50 mL by adding 25 mL of doubly distilled water. Next, 50 mL of the diluted palladium nanoparticles was mixed with 1.0 g of activated carbon. The solution was then stirred vigorously at room temperature for 24 h. After this, the solution was centrifuged at 19,000 rpm for 30 min at 25 °C to separate the liquid from the carbon support containing the adsorbed Pd nanoparticles. The centrifugation process was continued for two more cycles to ensure that only the adsorbed nanoparticles remained in the carbon support. The carbon support containing the adsorbed Pd nanoparticles was poured onto a piece of filter paper and allowed to dry overnight. The resulting powder is the spherical PVP–Pd nanoparticles adsorbed onto the activated carbon support. The palladium loading in terms of total weight of the supported catalyst was 4.2%. To observe the nanoparticles by high-resolution TEM (HRTEM), we placed a small amount of the powder in ethanol and sonicated it for 1 h before spotting the solution onto a Formvar-stabilized copper TEM grid. The carbon-supported palladium nanoparticles were imaged using JEM 4000EX HRTEM because HRTEM allows much clearer visualization of the supported nanoparticles than that obtained by conventional TEM.

2.3. Catalyzing Suzuki reaction

The carbon-supported spherical PVP–Pd nanoparticles were used to catalyze the Suzuki reaction between phenylboronic acid and iodobenzene to form biphenyl. In this reaction, 0.49 g sodium acetate, 0.37 g phenylboronic acid, and 0.20 g iodobenzene were added to 150 mL of the 3:1 acetonitrile:water solvent. The reaction mixture was heated to 100 °C. Once the mixture refluxed, 0.05 g of the carbon-supported spherical PVP–Pd nanoparticles was added to the reaction mixture. The reaction mixture was refluxed for a total of 12 h. The same reaction mixture solution was used for recycling after the addition of fresh amounts of the reactants. For recycling, an assumption was made that all of the iodobenzene was used up because it is the limiting reactant. Initially, there were 1 mmol iodobenzene and 3 mmol of phenylboronic acid present in the reaction mixture. After the first cycle, we assumed that no iodobenzene and 2 mmol phenylboronic acid remained. As a result, 1 mmol iodobenzene and 1 mmol phenylboronic acid were added to start the second cycle of the Suzuki reaction. The reaction mixture was then refluxed for another 12 h to complete the second cycle. A similar procedure was followed for the third, fourth, and fifth cycles of the Suzuki reaction. A control experiment was also conducted in which the Suzuki reaction mixture was refluxed for 12 h without the presence of any catalyst. In addition, another control experiment was conducted in which the Suzuki reaction mixture was refluxed for 12 h in the presence of just the activated carbon support without the nanoparticles.

2.4. High-performance liquid chromatography studies on catalytic activity of the carbon-supported spherical Pd nanoparticles

High-performance liquid chromatography (HPLC) measurements were obtained using a Hitachi-4500 HPLC unit equipped with a L4500A diode array detector in which absorbance is monitored at 254 nm. The separation was carried out on a reverse-phase packed column (Rainin Microsorb-MV C18, 300 A, dim 4.6 × 250 mm) using a 60:40 acetonitrile–water mixture and a flow rate of 1 mL/min. The area of the chromatographic peaks was calculated with a D-6000 interface-integrator. A calibration curve for determining the concentration of biphenyl was constructed by plotting the peak area versus concentration of biphenyl standards. The standards prepared were 0.0005, 0.001, 0.0015, 0.002, 0.0025, and 0.003 mol biphenyl. For HPLC measurements, all samples were diluted to 1/4 of the original concentration so that the peak areas lie within the range of the calibration curve. The actual concentration was determined by taking the concentration of the diluted sample and multiplying by 4. The concentration of biphenyl was determined before the reaction and after the first, second, third, fourth, and fifth cycles of the Suzuki reaction. In addition, the biphenyl concentration was also determined after three control experiments: Suzuki reaction with no catalyst, Suzuki reaction in the presence of the activated carbon support without the nanoparticles, and biphenyl by itself versus biphenyl in the presence of activated carbon.

2.5. HRTEM studies on the size distribution of the carbon-supported spherical palladium nanoparticles before and after catalysis and recycling

The reaction mixture solutions containing the carbon-supported spherical PVP–Pd nanoparticles were sonicated for 1 h before spotting them onto TEM grids. A drop of the solution is placed onto a Formvar-stabilized copper grid, and the drop is allowed to evaporate in air. The spotted samples take approximately 30 min to dry. Because the same deposition conditions are used for all samples, the evaporation rate of the solvent is fairly reproducible from one sample to another. For each of the experiments, the internal reproducibility of the observed size distribution was verified by spotting the sample onto three separate TEM grids. HRTEM images were also obtained from different sections of the TEM grids to verify the reproducibility of the size distribution. The general reproducibility of the size distribution was verified by conducting each of the experiments three times. The nanoparticle size distribution was determined by counting approximately 1800 nanoparticles from nine enlarged HRTEM images (approximately 200 nanoparticles from each HRTEM image). Gaussian fits of the size distributions determined from the Origin 5.0 software were used to determine the average size and the width of the size distribution.

3. Results and discussion

3.1. Catalytic activity of the carbon-supported spherical palladium nanoparticles

The catalytic activity of the carbon-supported spherical palladium nanoparticles were compared with that of the colloidal spherical palladium nanoparticles that we studied previously [52]. It is noteworthy that the palladium loading in terms of the total weight of the supported catalyst was 4.2% in the case of the carbon-supported palladium nanoparticles. In addition, control experiments in which the Suzuki reaction was conducted without the presence of any catalyst and in which the Suzuki reaction was conducted in the presence of the activated carbon support without the nanoparticles were also conducted. In both cases, we found that no biphenyl product was detected from the HPLC studies. Thus it is safe to conclude that the Suzuki reaction does not proceed without a catalyst, and that the presence of activated carbon alone does not catalyze the Suzuki reaction.

Table 1 summarizes the HPLC results on the biphenyl yields obtained during the first and second cycles of the Suzuki reaction for both the carbon-supported spherical palladium nanoparticles and the colloidal spherical palladium nanoparticles that we studied previously [52]. The HPLC results do not show the formation of any other byproducts for the Suzuki reaction between phenylboronic acid and iodobenzene, which is consistent with the previously observed results [80–82].

Table 1
Biphenyl yield obtained with the carbon-supported spherical PVP–Pd nanoparticles vs. colloidal spherical PVP–Pd nanoparticles studied previously [52]. In the case of carbon-supported spherical PVP–Pd nanoparticles, the raw biphenyl concentrations as well as the concentration corrected for biphenyl adsorbed onto the carbon support is reported

Condition	Carbon supported spherical PVP–Pd nanoparticles	Colloidal spherical PVP–Pd nanoparticles [52]
First cycle of Suzuki reaction	1.54 ± 0.07 mM 20 ± 1% Corrected for adsorption 1.76 ± 0.07 mM 23 ± 1%	3.00 ± 0.32 mM 39 ± 4%
Second cycle of Suzuki reaction	1.07 ± 0.20 mM 14 ± 3% Corrected for adsorption 1.22 ± 0.20 mM 16 ± 3%	1.11 ± 0.20 mM 15 ± 3%

It can be seen that the carbon-supported spherical palladium nanoparticles do catalyze the Suzuki cross-coupling reaction, but results in a lower amount of biphenyl formed after the first cycle compared with the amount produced with the colloidal palladium nanoparticles that we studied previously [52]. This could be a result of adsorption of some of the biphenyl on the activated carbon or that the catalytic efficiency of the nanoparticles is not as good on carbon as it is in colloidal solution. To test for the possible adsorption of biphenyl on the activated carbon, a control experiment was conducted to determine the concentration of biphenyl present in 150 mL acetonitrile:water by itself and also after refluxing the biphenyl in the presence of 0.05 g of activated carbon. We observed that the biphenyl concentration is 12.5 ± 1.4% lower after refluxing in the presence of activated carbon compared with the initial biphenyl concentration. This suggests that the activated carbon adsorbs a small quantity of biphenyl and, as a result, the actual quantity of biphenyl produced during the reaction is slightly higher. The biphenyl concentration after the first and second cycle was then corrected by multiplying by 114% to reflect the actual concentration of biphenyl present; these results are also given in Table 1. A possible reason why the catalytic efficiency of carbon-supported nanoparticles is lower than that of the colloidal nanoparticles could be better capping by large quantities of the carbon support (1 g). Thus it is possible that a much lower fraction of sites is available for the catalytic process, because many free sites are used in the adsorption process. It can be seen that even after correcting for the biphenyl adsorbed onto the carbon support, the biphenyl concentration is still lower than that observed previously for the colloidal palladium nanoparticles. This suggests that the lower catalytic efficiency of carbon-supported nanoparticles compared with colloidal nanoparticles is the dominant cause of the lower biphenyl yield observed after the first cycle.

It is interesting to note that during the second cycle of the reaction, the carbon-supported spherical palladium nanoparticles do produce a high quantity of biphenyl relative to the amount produced during the first cycle. The colloidal spherical PVP–Pd nanoparticles that we studied previously [52] did not have good recycling potential. To see whether the carbon-supported palladium nanoparticles continue to maintain their recycling potential, we determined the biphenyl yield after the third, fourth, and fifth cycles of the Suzuki reaction for both kinds of palladium nanoparticles; these findings are summarized in Table 2. In the case of the carbon-supported palladium nanoparticles, the biphenyl concentration observed was corrected for the possible adsorption of biphenyl onto the carbon support. It can be seen that the carbon-supported palladium nanoparticles maintain their catalytic activity during the second, third, fourth, and fifth cycles of the Suzuki reaction, whereas the catalytic ac-

Table 2
Biphenyl yield obtained with the carbon-supported spherical PVP–Pd nanoparticles as well as the colloidal spherical PVP–Pd nanoparticles for five cycles of the Suzuki reaction. In the case of the carbon-supported nanoparticles, the biphenyl yields are corrected for possible adsorption onto the support

Condition	Carbon supported spherical PVP–Pd NPs biphenyl yield (mM)	Colloidal spherical PVP–Pd NPs biphenyl yield (mM)
First cycle	1.76 ± 0.07	3.00 ± 0.32
Second cycle	1.22 ± 0.20	1.11 ± 0.20
Third cycle	1.31 ± 0.12	0.83 ± 0.13
Fourth cycle	1.36 ± 0.14	0.64 ± 0.09
Fifth cycle	1.25 ± 0.09	0.49 ± 0.07

Table 3
Ratio of biphenyl yields (yield in 2nd cycle/yield in 1st cycle) for the case of the carbon supported spherical PVP–Pd nanoparticles and the colloidal spherical PVP–Pd nanoparticles studied previously [52]. In the case of the carbon-supported nanoparticles, the corrected biphenyl concentrations are used for the calculation

Type of biphenyl yield ratio	Carbon-supported spherical PVP–Pd nanoparticles	Colloidal spherical PVP–Pd nanoparticles
2nd cycle/1st cycle	0.69	0.37
3rd cycle/1st cycle	0.74	0.28
4th cycle/1st cycle	0.77	0.21
5th cycle/1st cycle	0.71	0.16

tivity of the colloidal palladium nanoparticles decreases significantly during the second, third, fourth, and fifth cycles. These results suggest that the carbon-supported palladium nanoparticles maintain their recycling potential during five cycles of the Suzuki reaction, whereas the colloidal palladium nanoparticles continue to show poor recycling potential.

Table 3 summarizes the biphenyl yield ratios obtained for both types of palladium nanoparticles. The biphenyl yield ratio was calculated by dividing the biphenyl yield obtained during the second, third, fourth, or fifth cycle by that formed during the first cycle. In the case of the carbon-supported palladium nanoparticles, the biphenyl concentration corrected for the adsorption of biphenyl on the carbon was used to conduct the calculation of the biphenyl yield ratio. It can be seen that the biphenyl yield ratio (second cycle/first cycle) for the carbon-supported spherical palladium nanoparticles is quite high at 0.69. because of the relatively high recycling potential of these nanoparticles. For the colloidal spherical PVP–Pd nanoparticles that we studied previously [52], the biphenyl yield ratio of 0.37 was relatively low, suggesting that the colloidal palladium nanoparticles have a low recycling potential. The carbon-supported spherical PVP–Pd nanoparticles have almost twice the recycling potential than the colloidal spherical PVP–Pd nanoparticles [52]. In addition, the carbon-supported Pd nanoparticles maintain 73 ± 3% of their catalytic activity during the second through fifth cycles of the Suzuki reaction. The high recycling potential of the carbon-supported spherical PVP–Pd nanoparticles is probably due to the presence of a large amount of the carbon support around the palladium nanoparticles, which stabilizes the palladium nanoparticles. It is worth noting that the biphenyl product formation is 73 ± 3%, not close to 100%, which may be due to the slightly lower catalytic activity of the larger capped and stabilized palladium nanoparticles formed and also to some poisoning effect associated with the biphenyl product itself. The carbon-supported palladium nanoparticles are not as catalytically active as the colloidal nanoparticles, but their active sites are more stable. This is a result of a good stabilizing effect of the carbon around the nanoparticles.

3.2. *Effect of catalyzing the Suzuki reaction on the size of carbon-supported spherical palladium nanoparticles*

We investigated the effect of catalyzing the Suzuki reaction on the size of carbon-supported spherical palladium nanoparticles and compared it with that for colloidal spherical palladium nanoparticles. Fig. 1 shows HRTEM images and Gaussian fits of the size distributions of the carbon-supported spherical palladium nanoparticles before and after the first and second cycles of the Suzuki reaction. Table 4 summarizes the results on the center and width of the size distribution of the carbon-supported spherical palladium nanoparticles and the colloidal spherical palladium nanoparticles studied previously [52] before and after the first and second cycles.

It can be seen that the carbon-supported spherical palladium nanoparticles are monodisperse, with an average size of 1.9 ± 0.1 nm. They are similar in size to that of the colloidal spherical palladium nanoparticles that we studied previously (2.1 ± 0.1 nm) [52]. After the first cycle of the Suzuki reaction, it is observed that the nanoparticles grow in size, reaching an average size of 2.6 ± 0.1 nm. After the second cycle, the carbon-supported nanoparticles continue to grow to an average size of 3.1 ± 0.1 nm. The continued growth of the carbon-supported palladium nanoparticles and the high catalytic activity observed with these nanoparticles during the second cycle suggest that carbon support effectively prevents aggregation and precipitation of the nanoparticles, unlike the colloidal spherical palladium nanoparticles, in which the larger nanoparticles formed aggregated and precipitated out of solution, leaving the smaller nanoparticles in solution [52].

It is also noteworthy that the width of the size distribution of the carbon-supported palladium nanoparticles is not as broad as that of the colloidal spherical palladium nanoparticles. This may result from the repetitive centrifugation and decanting techniques used to prepare the nanoparticles in the carbon samples. Preparation of the carbon-supported palladium nanoparticles also results in very little, if any, free palladium atoms in the sample. This is because the centrifugation process would have effectively removed these atoms as well as unaggregated palladium atoms and colloidal palladium nanoparticles not adsorbed onto the support. In

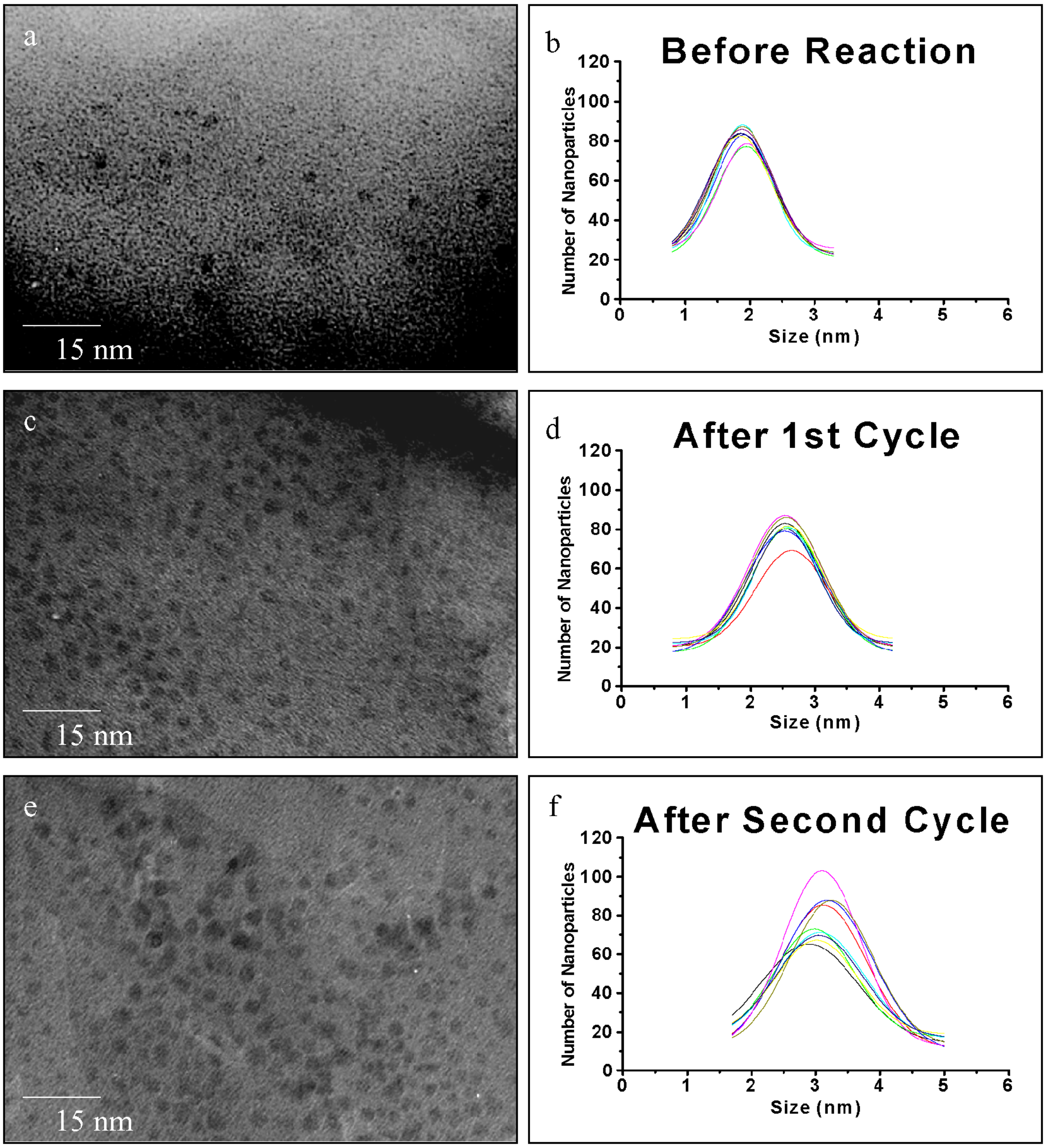

Fig. 1. HRTEM images and Gaussian fits of the size distributions of the carbon-supported spherical palladium nanoparticles before any perturbations (a, b), after the first cycle of the Suzuki reaction (c, d), and after the second cycle of the Suzuki reaction (e, f).

Table 4
Size distributions of the carbon-supported spherical PVP–Pd nanoparticles and the colloidal spherical PVP–Pd nanoparticles studied previously [52] before the reaction, after the first cycle, and after the second cycle

Condition	Carbon-supported spherical PVP–Pd NPs	Colloidal spherical PVP–Pd NPs [52]
Before Suzuki reaction	$C_D = 1.9 \pm 0.1$ nm $W_D = 0.9 \pm 0.1$ nm	$C_D = 2.1 \pm 0.1$ nm $W_D = 1.1 \pm 0.2$ nm
After first cycle of Suzuki reaction	$C_D = 2.6 \pm 0.1$ nm $W_D = 1.1 \pm 0.1$ nm	$C_D = 2.9 \pm 0.3$ nm $W_D = 2.8 \pm 0.4$ nm
After second cycle of Suzuki reaction	$C_D = 3.1 \pm 0.1$ nm $W_D = 1.3 \pm 0.1$ nm	$C_D = 2.2 \pm 0.2$ nm $W_D = 0.9 \pm 0.2$ nm

addition, ethanol is also removed during the centrifugation process, and as a result, no further reduction of any remaining palladium ions can occur. Thus the growth of nanoparticles during the reaction must then occur through the detachment of atoms from the smaller palladium nanoparticles and reattachment of these atoms to the more stable surfaces of the larger palladium nanoparticles. This mechanism would explain why the size distribution is not very broad compared with that of the colloidal spherical palladium nanoparticles that we studied previously [52].

4. Conclusions

We have observed that although the carbon-supported spherical palladium nanoparticles are less catalytically active than the colloidal spherical palladium nanoparticles that we studied previously [52], they have almost double the recycling potential. In addition, the carbon-supported palladium nanoparticles maintain 73 ± 3% of its catalytic activity during the second through fifth cycles of the reaction, whereas the colloidal palladium nanoparticles have much lower catalytic activity during the recycling process. This is probably due to the stabilizing effect of carbon as a possible capping agent. The carbon-supported spherical palladium nanoparticles grow in size during the first and second cycles of the reaction, and the width of the size distribution is not very broad. The presence of the carbon support makes the nanoparticles resistant to aggregation and precipitation and also helps preserve their catalytic activity during the second cycle. In addition, the adsorption method of preparing the supported palladium nanoparticles effectively favors the adsorption of larger palladium nanoparticles against the very small ones, as well as the palladium atoms. As a result, the Ostwald ripening growth mechanism occurs only between the nanoparticles present on the carbon support. Overall, carbon-supported spherical palladium nanoparticles are potentially better recyclable catalysts for the Suzuki reaction than colloidal palladium nanoparticles.

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