

Effect of Catalysis on the Stability of Metallic Nanoparticles: Suzuki Reaction Catalyzed by PVP-Palladium Nanoparticles

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Abstract: The small size of nanoparticles makes them attractive in catalysis due to their large surface-to-volume ratio. However, being small raises questions about their stability in the harsh chemical environment in which these nanoparticles find themselves during their catalytic function. In the present work, we studied the Suzuki reaction between phenylboronic acid and iodobenzene catalyzed by PVP-Pd nanoparticles to investigate the effect of catalysis, recycling, and the different individual chemicals on the stability and catalytic activity of the nanoparticles during this harsh reaction. The stability of the nanoparticles to the different perturbations is assessed using TEM, and the changes in the catalytic activity are assessed using HPLC analysis of the product yield. It was found that the process of refluxing the nanoparticles for 12 h during the Suzuki catalytic reaction increases the average size and the width of the distribution of the nanoparticles. This was attributed to Ostwald ripening in which the small nanoparticles dissolve to form larger nanoparticles. The kinetics of the change in the nanoparticle size during the 12 h period show that the nanoparticles increase in size during the beginning of the reaction and level off toward the end of the first cycle. When the nanoparticles are recycled for the second cycle, the average size decreases. This could be due to the larger nanoparticles aggregating and precipitating out of solution. This process could also explain the observed loss of the catalytic efficiency of the nanoparticles during the second cycle. It is also found that the addition of biphenyl to the reaction mixture results in it poisoning the active sites and giving rise to a low product yield. The addition of excess PVP stabilizer to the reaction mixture seems to lead to the stability of the nanoparticle surface and size, perhaps due to the inhibition of the Ostwald ripening process. This also decreases the catalytic efficiency of the nanoparticles due to capping of the nanoparticle surface. The addition of phenylboronic acid is found to lead to the stability of the size distribution as it binds to the particle surface through the O⁻ of the OH group and acts as a stabilizer. Iodobenzene is found to have no effect and thus probably does not bind strongly to the surface during the catalytic process. These two results might have an implication on the catalytic mechanism of this reaction.

Introduction

Because of their large surface-to-volume ratio, nanoparticles offer higher catalytic efficiency per gram than larger size materials. The field of nanocatalysis has been very active lately with numerous review articles published during the past decade in both heterogeneous catalysis in which the nanoparticles are supported on solid surfaces (e.g., silica or alumina)^{1–13} and homogeneous catalysis with colloidal nanoparticles.^{14–21} Being

small in size is expected to increase the nanoparticle surface tension. This makes surface atoms very active. The question is now raised as to how active they become. Are they active beyond their catalytic function and thus become reactants rather than catalysts? Are they active enough to change the size and shape of the nanoparticles during catalysis?

The purpose of our present research is to follow the changes in the average size, size distribution, and the shape of metallic nanoparticles as they are used in different catalytic reactions. It is expected that catalysis in high-temperature colloidal solutions will affect the integrity of the particles more than gas-phase-supported solid-state nanoparticle catalysis. For this reason, we

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began examining the stability of metallic nanoparticles in catalytic reactions in colloidal solution.

In the bulk of the catalysis with colloids, TEM characterization of the nanoparticles before and after catalysis is not given. However, there are a few studies in the literature where size distribution of the nanoparticles after recycling along with the catalytic activity is reported for characterization. In these studies, reactions such as hydrogenation of ethyl pyruvate,²² hydrogenation of arenes,²³ carbonylation of methanol,²⁴ the intra- and intermolecular Paulson–Khand reactions,²⁵ and hydrogenation of alkenes²⁶ are reported. There have also been some papers that discuss the catalytic activity of the nanoparticles upon recycling, but which do not examine the stability of the nanoparticles after catalysis. Such studies were conducted for reactions such as hydrogenation of alkenes,²⁷ Heck reaction between aryl halides and *n*-butylacrylate,²⁸ hydrogenation of olefins,²⁹ and hydrogenation of unsaturated fatty acid esters.³⁰ In a review of transition metal colloids as reusable catalysts,³¹ it was pointed out that the major interest of reusability of the nanoparticle catalysts has not been systematically studied or published in the metal colloid literature.

For reactions catalyzed by metal nanoparticles in colloidal solution, there has not been any detailed examination in the literature of what causes the size distribution to change, the role of the individual chemicals present in the reaction mixture, and whether the changes in the nanoparticles affect the catalytic activity upon recycling. A detailed examination is necessary to evaluate the nanoparticles' usefulness in catalyses and to understand in detail the mechanism of "nanocatalysis". This will enable a much better understanding of what kind of nanoparticles are the best for catalysis and also provide insight on how to make the nanoparticles more stable and maintain their catalytic activity.

It is our premise that, in harsh reactions, there will be great changes in the average size (center of size distribution) and the width of the size distribution of the nanoparticles after catalysis, recycling, and in the presence of different chemicals. Also, there will be great changes in the catalytic activity of the nanoparticles upon recycling. To test this idea, the Suzuki reaction between phenylboronic acid and iodobenzene catalyzed by PVP stabilized Pd nanoparticles is chosen because it is a harsh reaction due to the need to reflux the reaction mixture at 100 °C for 12 h. The Suzuki cross-coupling reaction is an effective synthetic route toward the production of biaryls by the coupling of arylboronic acids and haloarenes. It was first discovered by A. Suzuki in 1981³² and is sometimes referred to as the Suzuki–Miyaura coupling. The Suzuki cross-coupling reactions are a method of C–C bond formation that is widely used in industry. Suzuki reactions have been traditionally catalyzed using many different kinds of phosphine-based palladium catalysts and phosphine-

free palladium catalysts such as Pd(PPh₃)₄, Pd(Oac)₂, [(η³-C₃H₅)PdCl]₂, and Pd₂(dba)₃ C₆H₆.^{33–37} The use of palladium nanoparticles as catalysts for Suzuki reactions has been a fairly recent phenomenon. Palladium nanoparticles stabilized with tetraalkylammonium salts,³⁸ PVP,^{39,40} PAMAM dendrimers,⁴¹ PS-*b*-PANa block copolymer,⁴¹ 1,5-bis(4,4'-bis(perfluorooctyl)-phenyl)-1,4-pentadien-3-one,⁴² Keggin-type polyoxometalate,⁴³ and cyclodextrin⁴⁴ have all been used to catalyze various Suzuki reactions.

In this paper, PVP-Pd nanoparticles are used to catalyze the Suzuki reaction between phenylboronic acid and iodobenzene. The aim of this study is to examine the effect of catalysis, recycling, and the different chemicals involved in the reaction on the stability and catalytic activity of the PVP-Pd nanoparticles.

Experimental Section

Synthesis of PVP-Pd Nanoparticles. The PVP-Pd nanoparticles were synthesized by the reduction of the Pd ions with ethanol similar to that described previously.^{39,40,45} The palladium precursor solution (H₂PdCl₄) was prepared by adding 0.0887 g of PdCl₂ and 6 mL of 0.2 M HCl, and diluting to 250 mL with doubly distilled water. A solution containing 15 mL of 2 mM of H₂PdCl₄, 21 mL of doubly deionized water, 0.0667 g of PVP, and 4 drops of 1 M HCl was heated. When the solution began to reflux, 14 mL of ethanol was added. The solution was then refluxed for 3 h, and this resulted in a dark brown colloidal Pd solution. A drop of the solution was spotted onto Formvar stabilized copper TEM grids, and JEOL 100C TEM was used to characterize the size of the nanoparticles.

Suzuki Reaction. The Suzuki reaction between phenylboronic acid and iodobenzene was catalyzed using the PVP-Pd nanoparticles as described previously.^{39–41} For this reaction, 0.49 g (6 mmol) of sodium acetate, 0.37 g (3 mmol) of phenylboronic acid, and 0.20 g (1 mmol) of iodobenzene was added to 150 mL of 3:1 acetonitrile:water solvent. The solution was heated to 100 °C, and 5 mL of the PVP-Pd nanoparticles was added to start the reaction. The reaction mixture was refluxed for a total of 12 h.

Recycling the PVP-Pd Nanoparticles for the Second Cycle of the Suzuki Reaction. 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 are 1 mmol of iodobenzene and 3 mmol of phenylboronic acid present in the reaction mixture. After the first cycle, it is assumed that there is no iodobenzene left and 2 mmol of phenylboronic acid left. As a result, for the second cycle, 1 mmol of iodobenzene and 1 mmol of phenylboronic acid were added. The reaction mixture was then refluxed for another 12 h to complete the second cycle.

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Table 1. Summary of Gaussian Fits Showing the Widths and Centers of Size Distributions of PVP-Pd Nanoparticles before and after Various Perturbations

condition	before width (nm)	after width (nm)	before center (nm)	after center (nm)
Suzuki reaction		after first cycle 2.8 ± 0.4		after first cycle 2.9 ± 0.3
	1.1 ± 0.2	after second cycle 0.9 ± 0.2	2.1 ± 0.1	after second cycle 2.2 ± 0.2
Suzuki reaction in the presence of PVP	1.1 ± 0.1	1.8 ± 0.4	2.1 ± 0.1	2.4 ± 0.1
reflux in solvent	1.0 ± 0.1	2.2 ± 0.4	2.1 ± 0.1	4.5 ± 0.2
reflux in solvent + PVP	1.1 ± 0.1	1.6 ± 0.1	2.1 ± 0.1	2.5 ± 0.3
reflux in solvent + sodium acetate	1.0 ± 0.1	1.7 ± 0.2	2.1 ± 0.1	3.9 ± 0.1
reflux in solvent + sodium acetate + phenylboronic acid	1.0 ± 0.1	1.5 ± 0.1	2.1 ± 0.1	2.3 ± 0.1
reflux in solvent + sodium acetate + iodobenzene	1.1 ± 0.1	1.8 ± 0.3	2.1 ± 0.1	3.6 ± 0.1

The TEM Studies To Assess Nanoparticle Stability. To examine the changes in the nanoparticles after catalysis, samples of the reaction mixture before and after refluxing for 12 h were spotted onto Formvar stabilized copper TEM grids. The JEOL 100C TEM was used to determine the changes in the width and center of the size distributions of the PVP-Pd nanoparticles. The widths and centers of the size distributions of the PVP-Pd nanoparticles during various time periods in the first cycle such as 1, 3, 6, and 10 h were also obtained. The effect of recycling on the nanoparticles was also investigated using TEM. In addition, TEM was also used to understand the roles of the different chemicals present during the Suzuki reaction. The effects of refluxing the PVP-Pd nanoparticles in the solvent, in the solvent + sodium acetate, in the solvent + sodium acetate + phenylboronic acid, and in the solvent + sodium acetate + iodobenzene were investigated. The impact of adding 0.5 g of PVP with the PVP-Pd nanoparticles solution was also investigated.

For all of the above experiments, the concentration of the Pd ions present in the nanoparticles is 6.00×10^{-4} M, and when 5 mL of the nanoparticles is added to 150 mL of the 3:1 acetonitrile:water solvent, the concentration of the Pd ions is 1.94×10^{-5} M. For the experiments, the samples were spotted by placing a drop of the solution onto a Formvar stabilized copper grid and allowing it to evaporate in air. The spotted samples take approximately 30 min to dry. Because the same deposition conditions are employed 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 particle size and distribution was verified by spotting the sample onto three separate TEM grids. TEM images were also obtained from different sections of the TEM grids to verify the reproducibility of the particle size and distribution. The general reproducibility of the observed particle size and distribution was verified by conducting each of the experiments three times. As a result, it is possible to compare the particle size and distribution changes under various conditions.

The nanoparticle size and distribution were determined by counting approximately 1800 nanoparticles from nine enlarged TEM images (approximately 200 nanoparticles from each TEM image). The size distribution plots were fit using a Gaussian model with Microcal Origin 5.0 graphing software to determine the widths and centers of the size distributions. The width of the distribution gives an idea of how narrow or wide the size distribution is, and the center of the distribution is the most probable or average size of the nanoparticles (depending on the shape of the distribution).

HPLC Experiments To Measure Catalytic Activity. HPLC measurements were conducted on a Hitachi-4500 HPLC equipped with a L4500A diode array detector in which the absorbance was monitored at 254 nm. The separation was carried out on a reversed-phase packed column (Rainin Microsorb-MV C18, 300 Å, 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 the

concentration of biphenyl standards. The standards prepared were 0.0005, 0.001, 0.0015, 0.002, 0.0025, and 0.003 M biphenyl. For HPLC measurements, all samples were diluted to $1/4$ of the original concentration so that the peak areas will be 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 first cycle, after the first cycle, before the second cycle, and after the second cycle. Also, the effect of PVP on the amount of biphenyl formed was also determined. In addition, the impact of the presence of biphenyl in the Suzuki reaction mixture on the formation of biphenyl product was also investigated using HPLC.

Results and Discussion

In this paper, a detailed examination of the stability of the PVP-Pd nanoparticles after catalyzing the Suzuki reaction between phenylboronic acid and iodobenzene, after recycling, and in the presence of chemicals has been investigated. Also, the reasons why the changes in the width and center of the size distributions occur are discussed. Table 1 summarizes the widths and centers of distributions of the PVP-Pd nanoparticles before and after various conditions.

Effect of Catalysis and Recycling. Figure 1a shows a representative TEM image of the PVP-Pd nanoparticles before the first cycle of Suzuki reaction, and Figure 1b shows the Gaussian fits of the size distributions of the nanoparticles. It can be seen that the PVP-Pd nanoparticles are monodispersed with an average size (center of distribution) of 2.1 ± 0.1 nm. Figure 1c shows a representative TEM image of the nanoparticles after the first cycle of the Suzuki reaction, and Figure 1d shows the Gaussian fits of the size distributions of the nanoparticles. By comparing the Gaussian fits before and after the first cycle in Figure 1b, Figure 1d, and Table 1, we could see that both the widths and the centers of the size distributions of the nanoparticles increase after the first cycle and that the size distribution shifts toward larger size. Also, the width of the size distribution after the first cycle is very broad. The observation of the increase in the size of the nanoparticles might be explained by the Ostwald ripening processes during the refluxing of the reaction mixture containing the nanoparticles for 12 h. The Ostwald ripening process is a mechanism for cluster growth. In this growth process, there is detachment of atoms from the smaller clusters and then reattachment on the more stable surface of the larger clusters.^{46,47} As a result, the larger clusters grow in size, while the smaller clusters shrink

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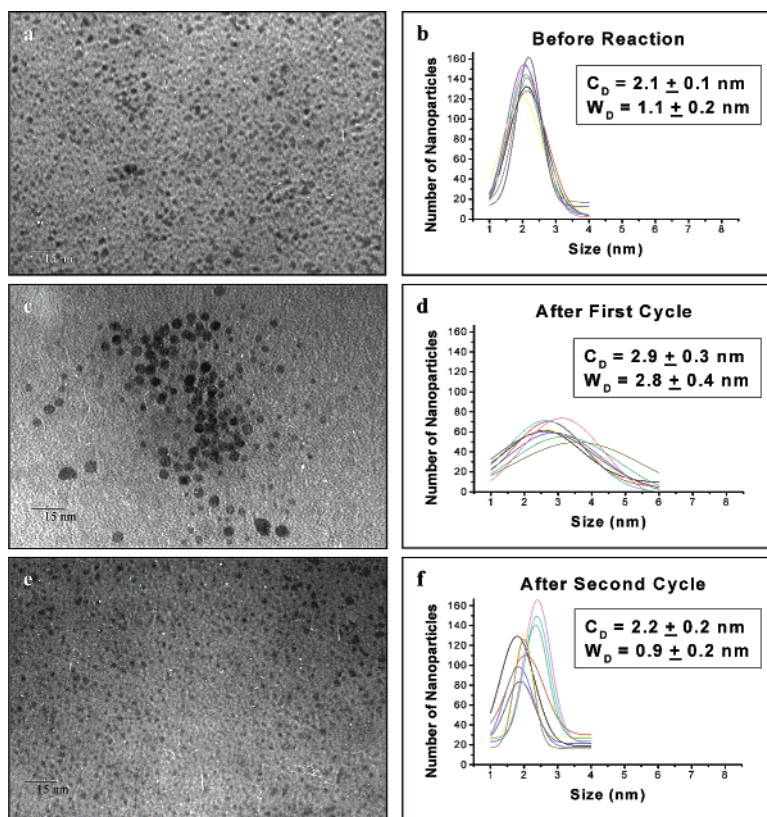


Figure 1. TEM images and Gaussian fits of the size distributions of PVP-Pd NPs before the Suzuki reaction (a,b), after the first cycle (c,d), and after the second cycle (e,f).

Table 2. Concentration of the Product Biphenyl after the Various Conditions As Determined by Using HPLC

condition	HPLC (quantitative)
after first cycle of Suzuki reaction	3.00 ± 0.32 mM biphenyl (39 ± 4% yield)
after second cycle of Suzuki reaction	4.11 ± 0.12 mM biphenyl (54 ± 2% overall yield) (15 ± 3% yield in second cycle)
after Suzuki reaction in the presence of 0.5 g of PVP	2.28 ± 0.18 mM biphenyl (30 ± 2% yield)
before Suzuki reaction in the presence of 1 mmol of biphenyl	7.61 ± 0.42 mM biphenyl (started with theoretical yield of biphenyl)
after Suzuki reaction in the presence of 1 mmol of biphenyl	10.20 ± 0.47 mM biphenyl (34 ± 6% yield)

or dissolve altogether. Furthermore, the solution itself probably has a large concentration of atomic Pd in monomeric and different polymeric forms resulting from the reduction of the salt. These will be used to allow the growth of the nanoparticles during the 12 h refluxing of the solution.

Figure 1e shows a typical TEM image of the nanoparticles after the second cycle of the Suzuki reaction, and Figure 1f shows the Gaussian fits of the size distributions of the nanoparticles. By comparing the Gaussian fits in Figure 1b, Figure 1d, Figure 1f, and Table 1, we could see that the widths and centers of the size distributions of the nanoparticles become much smaller after the second cycle of the Suzuki reaction. This observation might be due to the aggregation and precipitation of the larger nanoparticles formed during the first cycle. As a result, the average size of the nanoparticles in solution decreases.

Table 2 summarizes the concentration of biphenyl formed after the first and second cycle of the Suzuki reaction and after the Suzuki reaction in the presence of 0.5 g of PVP. The

percentage change in the biphenyl concentration formed is also compared. The catalytic activity of the nanoparticles after the first and second cycle of the Suzuki reaction is compared by using HPLC to find out if the nanoparticles remain catalytically active during the second cycle or if they become less catalytically active. A calibration curve of the peak area versus concentration of biphenyl standards was constructed. The equation, $y = (5.79 \times 10^6)x - 618422.75$, generated from the calibration curve is used to determine the concentration of biphenyl in the Suzuki reaction mixtures. HPLC chromatograms were obtained of the reaction mixtures before the first cycle, after the first cycle, before the second cycle, and after the second cycle. The concentration of biphenyl was determined after the first cycle and after the second cycle. After the first cycle of the reaction, there is a 39 ± 4% yield of biphenyl. After the second cycle of the reaction, the overall yield of biphenyl is 54 ± 2%, while the yield for the second cycle alone is 15 ± 3%. Because the amount of biphenyl formed during the second cycle is much lower than the amount formed in the first cycle, the PVP-Pd nanoparticles are definitely much less catalytically active during the second cycle of the reaction. The reason the nanoparticles are much less catalytically active during the second cycle might be due to a lower amount of nanoparticles present in the solution due to the precipitation of larger nanoparticles. Another possibility is that if the number density has not changed, but only the size is getting smaller, the smaller particles might not be as catalytically active as the larger particles. In a previous paper,⁴⁰ the catalytic activity of PVP-Pd nanoparticles of different sizes was examined. It was found that the catalytic activity increases with decreasing size of the nanoparticles.

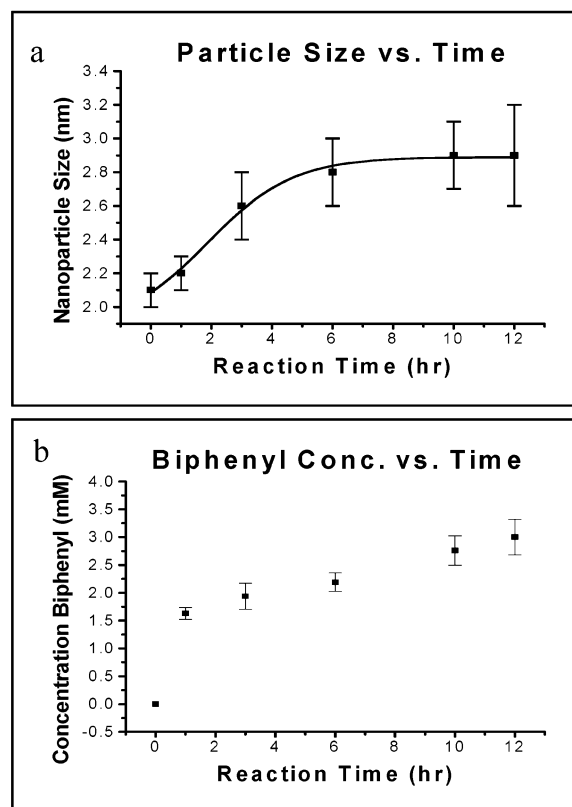


Figure 2. PVP-Pd nanoparticle size as a function of reaction time (a); biphenyl concentration as a function of reaction time (b).

Therefore, the latter explanation is ruled out. As a result, the lower catalytic activity observed during the second cycle is due to a lower amount of nanoparticles present in solution due to the larger nanoparticles aggregating and precipitating out of solution. In addition, surface poisoning by the products could be another reason. It is noticed that the yield of biphenyl in comparison to the theoretical yield is low. Experiments of conducting the Suzuki reaction in the presence of 1 mmol of biphenyl were done to find out the amount of product that forms. The reason 1 mmol of biphenyl is added is because that is the theoretical yield of biphenyl that can be formed. As seen by the HPLC results shown in Table 2, the presence of biphenyl in the reaction mixture results in inhibition of the reaction, and the yield of biphenyl is $34 \pm 6\%$. As a result, the low yield of biphenyl both in the first and in the second cycle could be due to the biphenyl product formed itself poisoning the active sites.

The stability of the PVP-Pd nanoparticles during different time periods of the first cycle of the Suzuki reaction was also investigated. Figure 2a shows the nanoparticle size as a function of time. It can be seen that the PVP-Pd nanoparticles smoothly increase in size during the beginning of the reaction from 0 to 3 h and then level off near the end of the first cycle. This suggests that the Ostwald ripening occurs during the first 3 h and then levels off toward the end of the first cycle of the Suzuki reaction due to the depletion of the small nanoparticles as well as free atoms in solution. Figure 2b shows the dependence of the concentration of product biphenyl as a function of time. It can be seen that there is rapid formation of biphenyl during the first hour of the reaction and then its rate of formation is greatly reduced. This reduction is probably a result of the surface

poisoning by the biphenyl product as well as by the increase in the nanoparticle size.

Effect of Excess PVP Stabilizer. For all of the experiments, TEM images and Gaussian fits of the size distributions were obtained before each perturbation as shown in Table 1, but to concisely summarize the results in the figure, Figure 3a and b shows a typical TEM image and Gaussian fits of the PVP-Pd nanoparticles before any perturbations. Figure 3c and d shows typical TEM image and Gaussian fits of the size distributions of the nanoparticles after the Suzuki reaction in the presence of 0.5 g of PVP. By comparing the Gaussian fits in Figure 3b, Figure 3d, and in Table 1, we could see that the widths and centers of the distributions after the reaction are slightly larger than those before the reaction, but are not as large as they are without the presence of the PVP, which is shown in Figure 1d and Table 1. Because the nanoparticles do not get as large as they do after a normal catalytic reaction, the presence of the excess PVP stabilizer probably diminishes the Ostwald ripening process by capping many of the free sites in the surface of the Pd nanoparticles. As a result, there are less free sites available for the Ostwald ripening process to occur.

The catalytic activity of the nanoparticles in the Suzuki reaction with 0.5 g of PVP present was investigated using HPLC and compared to that of a normal catalytic mixture. It was found that there is only $30 \pm 2\%$ yield of biphenyl when excess PVP was present in the reaction mixture as shown in Table 2. As a result, the presence of excess PVP results in a lower amount of biphenyl formed after the reaction. The lower catalytic activity observed when the Suzuki reaction is conducted in the presence of 0.5 g of PVP is due to the fact that there are less free metallic surface sites available for the catalysis because many of the free sites are capped by the excess PVP stabilizer.

Figure 3e shows a typical TEM image of the nanoparticles after refluxing them in the 3:1 acetonitrile:water solvent for 12 h, and Figure 3f shows Gaussian fits of the size distributions of the nanoparticles after refluxing them in the presence of 3:1 acetonitrile:water solvent. By comparing the Gaussian fits in Figure 3b, Figure 3f, and Table 1, we could see that both the widths and the centers of the size distributions of the nanoparticles become larger after just refluxing them for 12 h in the presence of the solvent. Also, the centers of the size distributions shift toward larger sized nanoparticles. The increase in the size of the nanoparticles observed is probably due to the Ostwald ripening process. The reason the process is much more prominent in this case than after the first cycle of the Suzuki reaction is because there is no phenylboronic acid present to bind to the nanoparticle surface and inhibit the Ostwald ripening process. The role of phenylboronic acid in the Ostwald ripening process of the nanoparticles is discussed later.

Figure 3g shows a typical TEM image of the nanoparticles after refluxing in the presence of solvent and 0.5 g of PVP, and Figure 3h shows Gaussian fits of the size distributions. By comparing the Gaussian fits in Figure 3f, Figure 3h, and Table 1, we could see that the widths and centers of the size distributions of the nanoparticles still get larger, but do not get as large as they do without the presence of the additional PVP, which is shown in Figure 3e,f. It can also be seen that the addition of a large quantity of PVP (0.5 g) to the mixture greatly diminishes the Ostwald ripening process because the additional

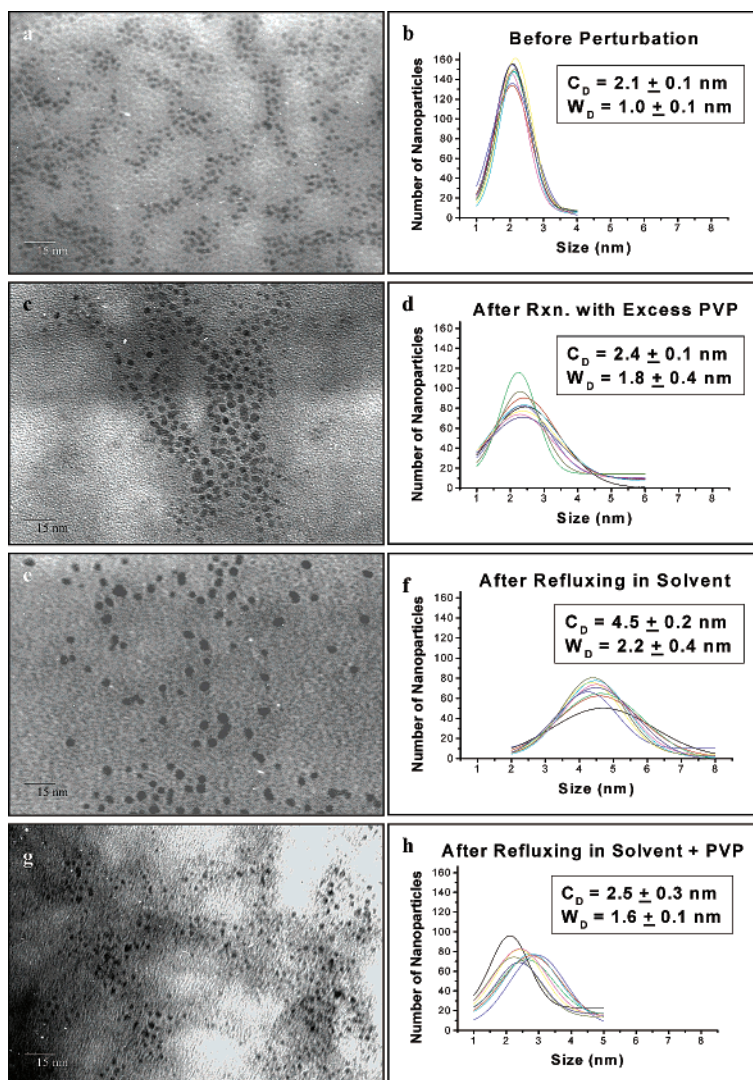


Figure 3. TEM images and Gaussian fits of PVP-Pd nanoparticles before any perturbations (a,b), after Suzuki reaction with excess PVP (c,d), after refluxing in just solvent (e,f), and after refluxing in just solvent + excess PVP (g,h).

PVP present in the solution caps many of the free metallic surface sites in the nanoparticles. Because fewer sites are available for the Ostwald ripening process, the nanoparticles do not greatly increase in size.

Effect of Chemicals. For all of the experiments, TEM images and Gaussian fits of the size distributions were obtained before each perturbation as shown in Table 1, but to concisely summarize the results in the figure, Figure 4a and b shows a typical TEM image and Gaussian fits of the PVP-Pd nanoparticles before any perturbations. Figure 4c shows a typical TEM image of the nanoparticles after refluxing them in the solvent + sodium acetate, while Figure 4d shows Gaussian fits of the size distributions of the nanoparticles. As was evident by comparing the Gaussian fits in Figure 4b, Figure 4d, and Table 1, the centers and widths of the size distributions increase after refluxing in solvent + sodium acetate. For this experiment, 0.49 g of sodium acetate was added to 150 mL of 3:1 acetonitrile: water solvent. The increase in the size of the nanoparticles observed is due to the Ostwald ripening process. Also, because there is no phenylboronic acid present to inhibit the Ostwald ripening process, the observed centers and widths of the distributions are larger than those observed after the first cycle

of the Suzuki reaction. The impact of phenylboronic acid on the Ostwald ripening process is discussed next.

Figure 4e shows a typical TEM image of the nanoparticles after refluxing them in the presence of solvent + sodium acetate + phenylboronic acid. Figure 4f shows Gaussian fits of the size distributions of the nanoparticles. By comparing the Gaussian fits in Figure 4b, Figure 4f, and Table 1, we could see that the nanoparticles increase in size only slightly. The reason for this observation is that phenylboronic acid in the presence of the base sodium acetate is in the deprotonated form and as a result binds with the O^- of the OH group to the free sites in the Pd nanoparticles and acts as a capping material. When the phenylboronic acid binds to the free sites, it acts as a stabilizer and as a result greatly diminishes the Ostwald ripening process. The presence of phenylboronic acid also plays a role in the first cycle and second cycle of the Suzuki reaction. Because of the presence of phenylboronic acid, the Ostwald ripening process is not as prominent after the first cycle of the Suzuki reaction as it is in the presence of just the solvent, solvent + sodium acetate, and solvent + sodium acetate + iodobenzene. In the second cycle of the Suzuki reaction, the catalytic activity is greatly diminished, which suggests that more phenylboronic acid is bound

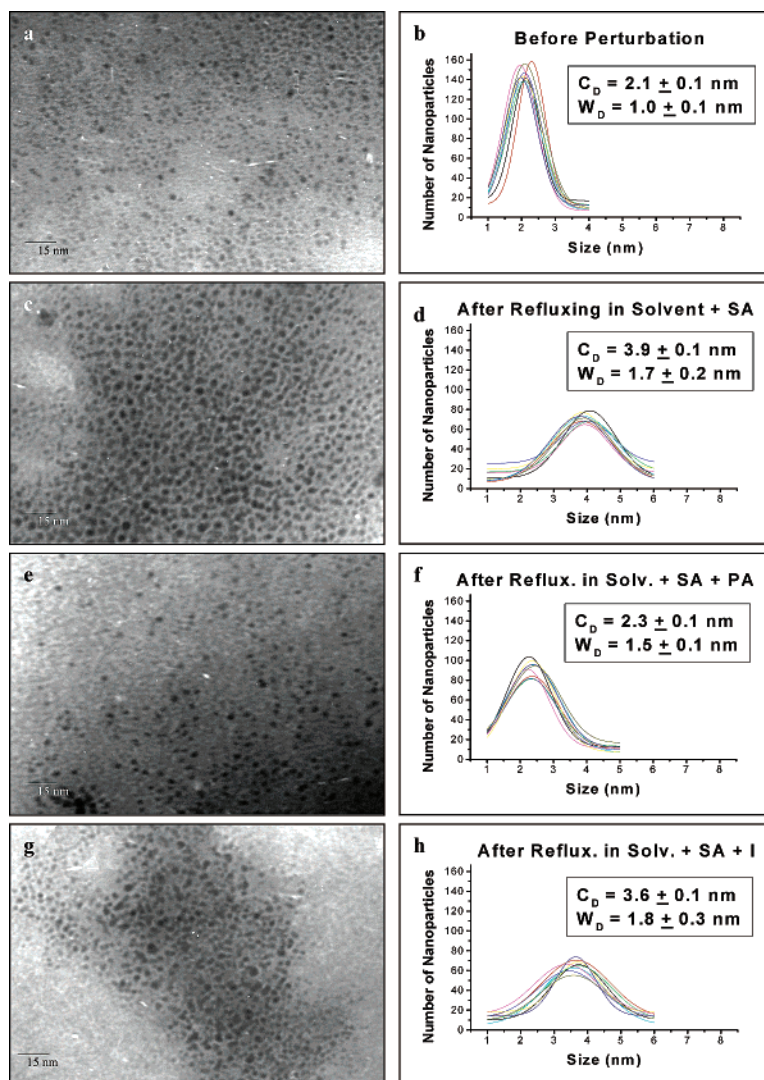


Figure 4. TEM images and Gaussian fits of PVP-Pd nanoparticles before any perturbations (a,b), after just solvent + sodium acetate (c,d), after just solvent + sodium acetate + phenylboronic acid (e,f), and after just solvent + sodium acetate + iodobenzene (g,h).

to the nanoparticles, and as a result the Ostwald ripening process is greatly diminished and the nanoparticles do not increase in size.

Figure 4g shows a typical TEM image of the nanoparticles after refluxing them in the presence of solvent + sodium acetate + iodobenzene, and Figure 4h shows Gaussian fits of the size distributions. By comparing the centers and widths of the size distributions shown in Figure 4b, Figure 4h, and Table 1, we could see that the nanoparticles do increase in size but do not get as large as they did after just refluxing in solvent. The Ostwald ripening process is responsible for the observed increase in the size of the nanoparticles. The iodobenzene does not bind to the surface of the nanoparticles and as a result does not inhibit the Ostwald ripening process. Also, phenylboronic acid is not present to inhibit the Ostwald ripening process.

It is evident that, in the Suzuki reaction, phenylboronic acid binds to the surface of the palladium nanoparticles and iodobenzene does not. As a result, any catalytic mechanism for the Suzuki reaction between phenylboronic acid and iodobenzene has to propose that phenylboronic acid binds to the surface of the nanoparticles and then the reaction with iodobenzene occurs by collisional processes.

Conclusions

The center and width of the size distribution of the PVP-Pd nanoparticles increase after the first cycle of the Suzuki reaction. The process of refluxing the nanoparticles during the Suzuki reaction seems to cause Ostwald ripening in which the size of nanoparticles increases at the expense of the smaller ones due to atomization and diffusion between particles. The nanoparticles increase in size during the beginning of the reaction and level off toward the end of the first cycle. After the second cycle of the reaction, the center and width of the size distribution of the nanoparticles become much smaller. This observation is explained by the aggregation and precipitation of the larger nanoparticles leaving the smaller nanoparticles in solution. As a result, the catalytic efficiency of the nanoparticles during the second cycle is diminished. The smaller nanoparticles in solution do not increase in size due to the presence of a greater amount of phenylboronic acid bound to the free sites which decreases their catalytic activity. It is also found that the presence of biphenyl product in the reaction mixture results in it poisoning the active sites and giving rise to a low product yield. The addition of PVP stabilizer to the reaction mixture diminishes the Ostwald ripening process as well as diminishes the catalytic

activity of the nanoparticles. This is due to the binding to the surface and prevents the adsorption of new metallic atoms or the use in catalysis.

Ostwald ripening of the nanoparticles also occurs when the sodium acetate base is present along with the solvent. The presence of phenylboronic acid, one of the reactants, inhibits the Ostwald ripening process because it binds to the nanoparticle surface through the O^- of its ionized OH group and acts as a stabilizer. Ostwald ripening of the nanoparticles occurs in the presence of iodobenzene, the other reactant. Thus, iodobenzene does not seem to strongly bind to the surface of the nanoparticles. As a result, any catalytic mechanism for the Suzuki reaction between phenylboronic acid and iodobenzene has to

consider proposing that the phenylboronic acid binds to the surface and then reacts with iodobenzene via collisional processes.

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