The Effect of Stabilizers on the Catalytic Activity and Stability of Pd Colloidal Nanoparticles in the Suzuki Reactions in Aqueous Solution†

Yin Li and Mostafa A. El-Sayed*

Laser Dynamics Laboratory, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

Received: March 8, 2001; In Final Form: May 13, 2001

Transition metal nanoparticles used in catalysis in solution are stabilized by capping the surfaces that are supposed to be used for catalysis. Determining how these two properties, that is, the catalytic activity and stability of nanoparticles, change as different capping materials are used is the aim of this work. Pd nanoparticles prepared by the reduction of metal salts in the presence of three different stabilizers—hydroxyl-terminated poly(amido-amine) (PAMAM) dendrimers (G*n*-OH, where G*n* represents the *n*th generation), block copolymer polystyrene-*b*-poly(sodium acrylate) and poly(*N*-vinyl-2-pyrrolidone) (PVP)—are used as catalysts in the Suzuki reactions in an aqueous medium to investigate the effects of these stabilizers on the metallic nanoparticle catalytic activity and stability. The stability of the Pd nanoparticles is measured by the tendency of the nanoparticles to give Pd black powder after the catalytic reaction. The Suzuki reaction is a good "acid test" for examining the stability of these nanoparticles, as it takes place when refluxed at about 100 °C for 24 h. The stability is found to depend on the type of the stabilizer, the reactant, and the base used in the reaction system. Pd nanoparticles stabilized by block copolymer, G3 dendrimer, and PVP are found to be efficient catalysts for the Suzuki reactions between phenylboronic acid (or 2-thiopheneboronic acid) and iodobenzene. G4 dendrimer is found to be an effective stabilizer; however, strong encapsulation of Pd particles in the dendrimer results in a loss of catalytic activity. The Suzuki reactions between arylboronic acids and bromoarenes catalyzed by Pd nanoparticles result in byproducts due to the homo-coupling of bromoarenes. A summary of the catalytic activity and stability of the Pd nanoparticles in these different systems is tabulated. As one would expect, these two properties are anticorrelated, that is, the most stable is the least catalytically active.

Introduction

A great interest is placed on the use of metallic nanoparticles for catalysis. In solution, the particles are always capped to stabilize them against precipitation. In this paper, we examine the stability of these particles and correlate the stability to the catalytic activity. For this, we select a very critical "acid test", the Suzuki reaction. It takes place when the reactants are refluxed at about 100 °C for 24 h. For capping materials, we select three different systems, dendrimers of different generations, block copolymer, and linear polymer.

For the past three decades, palladium catalysts have played an important role in the field of organic synthesis due to the variety of transformations they are able to catalyze.[1] One of the major contributions of zerovalent palladium catalysts in organic synthesis is the formation of carbon−carbon bonds through many coupling reactions. The cross-coupling of arylboronic acids with aryl halides, known as the Suzuki-type reaction,[2] and the coupling of aryl halides with alkenes, known as the Heck reaction,[3] are catalyzed by zerovalent palladium species and represent important synthetic methods in organic chemistry. Traditionally, these reactions are carried out in organic solvents and catalyzed by various Pd/ligand systems.[4] Phosphine-based palladium catalysts are generally used and, in most cases, the reactions are restricted to bromo or iodoarenes. The usage of chloroarenes is still a challenge due to economical considerations. To obtain high reactivity, the common phosphine-mediated catalysis must be replaced by methods involving either new types of ligands forming highly reactive but stable complexes, or new forms of palladium able to operate in the absence of tightly coordinated ligands. These new methods can be regarded as phosphine-free catalysis, and the development of new ligands has brought some promising results.[5] One important drawback of homogeneous catalysts is that they are difficult to separate from reaction mixtures and recycle. To solve this problem, studies concerning coupling reactions in aqueous media using water-soluble phosphine ligands such as sulfonated analogues of triphenylphosphine[6] have been carried out. The use of water as a reaction medium for transition-metal-catalyzed reactions is very attractive for organic synthesis due to environmental, economical, and safety reasons.

Transition metal nanoparticles are effective catalysts for chemical transformations due to their large surface area and a unique combination of reactivity, stability, and selectivity.[7] A common method to prepare metal particles involves the reduction of metal ions in the presence of stabilizers such as surfactants and polymers. Crooks et al.[8] have prepared PAMAM dendrimer-encapsulated Pd, Pt, and other metal nanoparticles that employ dendrimers as both template and stabilizer. Pd particles thus prepared show high catalytic activity for the hydrogenation of alkenes and are quite stable during the reaction.[8a,8c,8e] Mayer et al.[9] have reported that Pd nanoparticles prepared by reducing the metal precursors in the presence of protective amphiphilic block copolymer polystyrene-*b*-poly(methacrylic acid) are catalytically active for the hydro-

---

† Part of the special issue "Royce W. Murray Festschrift".

10.1021/jp010904m CCC: $20.00

genation of cyclohexene. Bronstein et al.[10] have reported that Pd colloids prepared in polystyrene-poly-4-vinylpyridine (PS-*b*-P4VP) block copolymer micelles and deposited on Al_2O_3 exhibited high activity and selectivity in hydrogenation of the triple bond of acetylene alcohols to the double bond of olefin alcohols. It has been shown that palladium colloids on the nanometer scale are effective catalysts for the Heck and Suzuki reactions in organic solvent.[11] However, poor stability of the Pd particles under these coupling reaction conditions has been reported.[11a,11c]

Recently, we reported[12] that palladium nanoparticles stabilized by PVP in colloidal aqueous solution are efficient catalysts for some Suzuki cross-couplings. By using fluorescence spectroscopy, it is shown that the initial rate of the Suzuki reactions depends linearly on the concentration of Pd catalyst, giving strong evidence that the catalysis occurs on the surface of the Pd nanoparticles. One disadvantage of this reaction system is the precipitation of Pd particles after reaction, leading to decreased catalytic activity of the Pd colloidal solution.

The development of phosphine-free palladium nanoparticle catalysis in aqueous media has brought about procedures with the catalytic efficiency and simplification of techniques with a positive impact on safety, but there are still many problems to overcome. The first is how palladium nanoparticles function in catalytic C−C bond formation reactions. The second is that the deactivation of Pd catalysts occurs due to the formation of Pd black. To increase the stability of Pd nanoparticles in catalytic C−C bond formation reactions, it is necessary to prepare Pd nanoparticles by using various kinds of stabilizers and to investigate the effect of these stabilizers on the catalytic activity and the stability of Pd nanoparticles.

In the present paper, Pd nanoparticles are prepared by the reduction of metal salts in the presence of PAMAM dendrimers, block copolymer polystyrene-*b*-poly(sodium acrylate), and PVP. The effect of these stabilizers on the catalytic activity and stability of Pd nanoparticles in the Suzuki reactions in aqueous medium is investigated.

Experimental Section

Chemicals. Poly(amido-amine) (PAMAM) dendrimers (G*n*-OH, where $n = 2,3$ and 4) were obtained in 10−20% methanol solutions from Aldrich. Prior to use, methanol was removed by rotary evaporation at room temperature. Palladium chloride ($PdCl_2$, 99%, Lancaster), Potassium tetrachloro-palladate (II) (K_2PdCl_4, 99.99%, Aldrich), poly(*N*-vinyl-2-pyrrolidone) (PVP, average molecular weight 40 000, Aldrich), polystyrene-*b*-poly(sodium acrylate) (PS-*b*-PANa, molecular weight (M_n) of PS 1800, M_n of PANa 42 500, M_w/M_n 1.06, Polymer Source), sodium borohydride ($NaBH_4$, 99%, Aldrich), hydrochloric acid (HCl, Fisher), 2-thiopheneboronic acid (Aldrich), phenylboronic acid (97%, Aldrich), iodobenzene (Eastman Kodak), bromobenzene (Fisher), 2-bromothiophene (98+%, Lancaster), triethylamine (Aldrich), sodium phosphate (J. T.Baker), sodium acetate (99+%, Fisher), and all solvents (from Aldrich) were used as received. All solutions were prepared with doubly deionized water.

Preparation of Dendrimer-Pd Nanoparticles. Pd nanoparticles in the presence of PAMAM dendrimers with different generations (G2, G3, and G4) were prepared according to the method described by Crooks et al.,[8] with some modifications. The aqueous stock solutions of 3 mM K_2PdCl_4 and 0.1 mM G*n*-OH dendrimer (from solvent-free dendrimer) were prepared separately. A solution of 30 mL of K_2PdCl_4 was mixed with 90 mL of dendrimer solution (10 Pd^{2+} ions per dendrimer, G*n*-OH(Pd^{2+})$_{10}$, $n = 3$ and 4). For G2 dendrimer-Pd particles, a solution containing an average of 5 Pd^{2+} ions per dendrimer (G2-OH(Pd^{2+})$_5$) was prepared. Prior to reduction, the pH of the dendrimer-Pd^{2+} solution was adjusted to 4.0 using 1 M HCl. The solution was purged with N_2 for 5 min. A 2 mL portion of 0.36 M $NaBH_4$ aqueous solution (the concentration of $NaBH_4$ added was 8 times that of metal ions) was then added, and the solution was vigorously stirred in N_2 for 1 h. The solution color changed from yellow to dark brown.

Preparation of PVP−Pd Nanoparticles. The method to prepare Pd nanoparticles in the presence of PVP is similar to that we[12] and Teranishi[13] et al. reported previously. H_2PdCl_4 solution (2.0 mM) was prepared by mixing 0.6 mmol of $PdCl_2$, 6.0 mL of 0.2 M HCl, and 294 mL of H_2O. A mixture of 15 mL of a 2.0 mM H_2PdCl_4 solution, 21 mL of H_2O, 14 mL of ethanol (40 vol %), and 0.0333 g of PVP (PVP/Pd (monomeric unit/metal ion) = 10) was refluxed for 3 h in air. The solution thus prepared had a dark brown color.

Preparation of Block Copolymer-Pd Nanoparticles. The method to prepare Pd nanoparticles in the presence of PS-*b*-PANa is similar to that of Mayer[9] et al. reported previously with some modifications. A sample of 0.0798 g PS-*b*-PANa was added to 21 mL of H_2O, and the solution was sonicated for about 2 h until the copolymer almost dissolved. A 15 mL portion of 2.0 mM H_2PdCl_4 solution (mass ratio of copolymer: Pd metal = 25:1) was then added, and the solution was sonicated until the copolymer dissolved completely. A solution of 14 mL of EtOH was added and the solution was refluxed in air for 3 h. The resulting dark brown solution indicated the reduction of the Pd ions.

Transmission Electron Microscopy (TEM). Pd nanoparticles were investigated by transmission electron microscopy (TEM) on a JEM 100C transmission electron microscope. The samples were prepared by placing a drop of the solution on carbon-coated Cu grids and allowed to dry in air. The particle size and standard deviation were determined by counting 200 particles from enlarged TEM images.

Pd-Catalyzed Suzuki Cross-Coupling Reactions. Suzuki coupling reactions were carried out by using different Pd catalysts. In a typical procedure (e.g., coupling of 2-thiopheneboronic acid with iodobenzene catalyzed by G3 dendrimer-Pd), 1.5% molar equiv of a dendrimer-Pd solution (100 mL) and 3 equiv (15 mmol) of $Na_3PO_4 \bullet 12H_2O$ were added to 100 mL of a 80% EtOH solution. Then, 1 equiv (5 mmol) of iodobenzene and 1.5 equiv (7.5 mmol) of 2-thiopheneboronic acid were added to the solution. The mixture was refluxed for 24 h and the extent of reaction was monitored by TLC (thin-layer chromatography) and ^1H NMR. After cooling to room temperature, the reaction mixture was extracted with petroleum ether, and the organic layers were combined and dried with anhydrous Na_2SO_4. Purification by column chromatography (silica gel/petroleum ether) gave the desired products confirmed by ^1H NMR. The other reactions followed similar procedures.

Results and Discussion

Preparation of Pd Nanoparticles. We prepare dendrimer-Pd nanoparticles based on the method described by Crooks et al.[8] In their approach, Pd^{2+} ions are sorbed into OH or NH_2-terminated PAMAM dendrimers, where they complex strongly with interior tertiary amine groups. Subsequent chemical reduction of the metal ions with BH_4- results in dendrimer-encapsulated Pd nanoparticles. Here, the dendrimers are used both as templates and stabilizers.

In the present study, Pd particles are prepared by using various generations of PAMAM dendrimers (G*n*-OH, $n = 2$, 3 and 4)

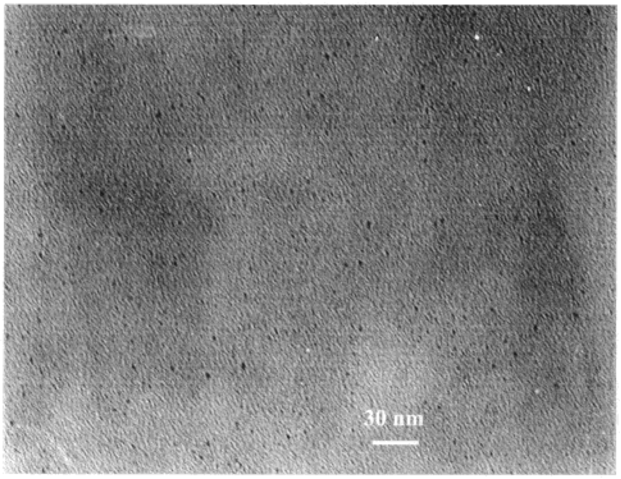


Figure 1. TEM image of Pd nanoparticles stabilized by G4-OH PAMAM dendrimer (Pd^{2+}/G4-OH dendrimer = 10).

TABLE 1: Mean Diameters of Pd Particles Stabilized by Various Generations of Dendrimers

dendrimer generation	$[Pd^{2+}]/[dendrimer]$	mean diameter (standard deviation) (nm)
G2	5	3.6 (0.8)[a]
G3	10	1.4 (0.4)
G4	10	1.4 (0.4)

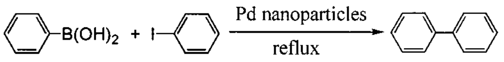
[a] The values are determined by counting un-aggregated Pd nanoparticles from TEM.

as stabilizers. Our procedure involves mixing K_2PdCl_4 with dendrimer. Before reduction, the pH of the solution is adjusted to 4.0. A clear dark brown solution is obtained after reduction of the composite with $NaBH_4$. It should be mentioned that without adjusting the pH of the solution, Pd precipitation is always observed after reduction with $NaBH_4$. This might be attributed to the coordination of palladium ions with other free ions outside the dendrimer, rather than the complexation of palladium ions with tertiary amine groups inside the dendrimer at higher pH. Reduction of palladium ions outside the dendrimer results in the precipitation of Pd particles. Adjusting the solution pH to 4.0 avoids the coordination of Pd^{2+} with other ions outside the dendrimer. Accordingly, Pd^{2+} ions bind preferentially to the interior tertiary amines and, upon reduction, the dendrimer-encapsulated Pd particles are formed. It has been demonstrated by Crooks[8c] and Tomalia[14] et al. that at pH = 4, the interior tertiary amines ($pK_a = 5.5$)[8f] of the dendrimers are almost all deprotonated and allow their coordination with Pd^{2+} ions.

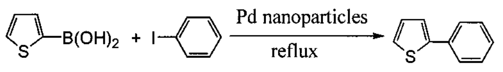
The effect of dendrimer generation on the size and stability of the Pd particles is investigated by comparing nanocomposites prepared using G2, G3, and G4 PAMAM dendrimers. Figure 1 shows the TEM micrograph of Pd particles stabilized by G4 dendrimer. It can be seen that the dendrimer-encapsulated particles are quite monodisperse, and the mean diameter of the Pd particles (G4-OH(Pd_{10})) is 1.4 ± 0.4 nm, similar to that reported previously.[8a] Table 1 gives the mean diameter with the standard deviation of Pd nanoparticles in different generation dendrimers. It can be seen from Table 1 that for G2, the particles formed are larger than those obtained with G3 or G4. The mean diameter of Pd particles in the presence of G3 or G4 dendrimer is 1.4 nm, which is smaller than the diameter of dendrimer G3 (3.6 nm) and G4 (4.5 nm),[15] indicating the formation of dendrimer-encapsulated Pd nanoparticles. Both G3 and G4 dendrimers are found to be effective stabilizers when the molar ratio of Pd^{2+} to dendrimer is 10:1. The Pd nanoparticles are stable for months, and no evidence for precipitation of Pd particles is observed, also suggesting the formation of encapsulated Pd particles. By using G3 and G4 dendrimers as stabilizers, the mean diameters of Pd nanoparticles are the same, indicating that the Pd particle size is insensitive to the generation of hydroxyl-terminated PAMAM dendrimers. G2 dendrimer does not provide an effective protective action. When the molar ratio of Pd^{2+} to dendrimer is either 10:1 or 5:1, many aggregates of Pd colloids are observed, and stable Pd particles cannot be obtained. The un-aggregated G2 dendrimer-Pd particles have a mean diameter of 3.6 nm with quite wide size distribution (Table 1, TEM not shown here). This diameter (3.6 nm) is large compared to that of dendrimer G2 (2.9 nm),[15] indicating that the Pd particles are not formed inside the dendrimer. The difference in the protective action of G2, G3, and G4 dendrimers may be due to their structures. Higher generation dendrimers (G3 and G4) have closed, increasingly compact structures and they are expected to provide effective protective action for the prepared Pd particles. Lower generation dendrimers (G2) have relatively open structures (G2 dendrimer is flat). A single G2 dendrimer cannot provide enough material to stabilize the surface of one Pd particle, and the particle stabilization by G2 dendrimer can be considered to be similar to that by conventional linear polymers: G2 dendrimers provide protective action by adsorbing on the surface of Pd particles. This behavior has been reported previously.[16]

Amphiphilic block copolymer PS-*b*-PANa consists of a hydrophobic PS block and a hydrophilic block, which by itself is a moderate to good stabilizer for metal particles. After reduction of H_2PdCl_4 by refluxing alcoholic solution in the presence of block copolymer, a clear dark-brown solution that is stable for months is obtained. The TEM picture of block copolymer-Pd nanoparticles (Figure 2) shows that the particles are quite monodispersed, and the mean diameter of the Pd particles is 3.0 ± 0.7 nm. From Figure 2 alone, it is hard to tell whether the Pd nanoparticles are actually embedded within the hydrophobic micelle core of block copolymer. However, it is expected that the Pd nanoparticles are not located exactly in the micelle core because there is very small tendency for the hydrophilic Pd precursor H_2PdCl_4 to be accumulated inside the hydrophobic micelle core. The principle for the particle stabilization here is expected to be similar to the general steric stabilization of colloidal metal nanoparticles such as homopolymers and random copolymers.

Catalytic Activity and Stability of Pd Nanoparticles in the Suzuki Reactions. The Suzuki reactions are tested using phenylboronic acid (or 2-thiopheneboronic acid) and iodobenzene in the presence of catalytic amounts of Pd nanoparticles stabilized by various generations of PAMAM dendrimers.



(1)



(2)

Table 2 gives the reaction conditions and results for these two reactions. It is seen that G4 dendrimer-encapsulated Pd nanoparticles is not an efficient catalyst for the Suzuki reactions under investigation (Table 2, entries 1−4). The product yield is affected by the bases used in the reaction system (Table 2, entries 2−4), but all these three commonly used bases result in poor yields. No Pd black is observed after the reaction; however, the color of the solution changes from dark brown before

TABLE 2: Product Yields for Suzuki Coupling Reactions Catalyzed by Dendrimer-Pd Particles (1.5 mol % of Metal) in 40% EtOH. (Temp, Reflux; Time, 24 h)

entry	reacn	catalyst	base	yield[a]	formation of Pd black	soln color after reacn
1	**(1)**	G4-OH(Pd)$_{10}$	Na_3PO_4	17%	no	light yellow
2	**(2)**	G4-OH(Pd)$_{10}$	Na_3PO_4	20%	no	light yellow
3	**(2)**	G4-OH(Pd)$_{10}$	NEt_3	35%	no	light yellow
4	**(2)**	G4-OH(Pd)$_{10}$	NaOAc	< 5%	yes	brown
5	**(1)**	G3-OH(Pd)$_{10}$	Na_3PO_4	71%	no	yellow/green
6	**(2)**	G3-OH(Pd)$_{10}$	Na_3PO_4	90%	yes	yellow/green[c]
7	**(1)**	yellow/green soln[b]	Na_3PO_4	40%	no	yellow/green
8	**(2)**	yellow/green soln[b]	Na_3PO_4	80%	yes	yellow/green[c]
9	**(1)**	G2-OH(Pd)$_5$	Na_3PO_4	69%	yes	yellow/green[c]
10	**(2)**	G2-OH(Pd)$_5$	Na_3PO_4	70%	yes	yellow/green[c]

[a] Isolated yield. [b] The clear yellow/green solution after extraction is used as the catalyst. See text for detail. [c] Solution color after filtering the Pd precipitates.

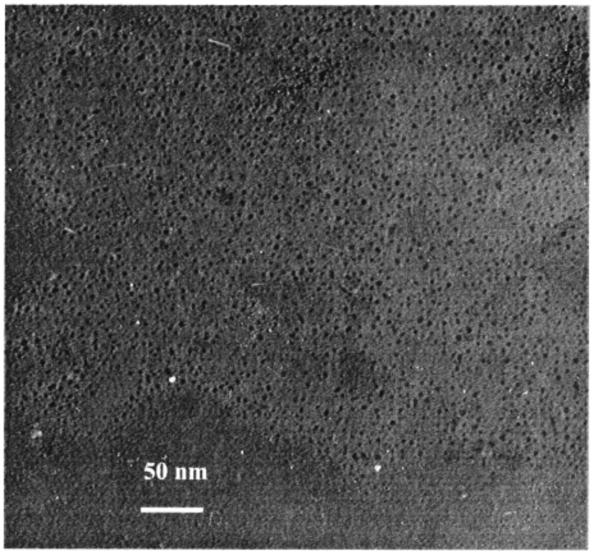


Figure 2. TEM image of Pd nanoparticles stabilized by block copolymer PS-*b*-PANa (mass ratio of copolymer:metal = 25:1).

reaction to clear light yellow after the reaction. The solution color is found to be pH-dependent. After the reaction, the solution pH is ∼10. When the pH is adjusted to ∼2, the solution color changes back to brown. It is worth noting that no color change is observed when the pH of G4 dendrimer-encapsulated Pd nanoparticle solution alone is adjusted to ∼10. This suggests that during the reaction, the initially formed nanoparticles may decompose to extremely fine particles, which are encapsulated in the dendrimers more efficiently than the initially formed particles, and/or the surface of the particles is oxidized into ionic forms that complex strongly with interior tertiary amine groups. In both cases, the surface of the particles is fully passivated, resulting in a loss of catalytic activity. When the pH of solution is adjusted to ∼2, the interior tertiary amines are protonated. As a result, palladium precipitate out of the dendrimer. More detailed studies of the identifications of reaction byproducts and their interactions with Pd particles is currently underway.

G3 dendrimer-encapsulated Pd nanoparticles is found to be an efficient catalyst for the Suzuki reactions (Table 2, entries 5 and 6). No evidence of Pd precipitation is observed in the coupling reaction **(1)**, whereas Pd black is observed in the reaction **(2)** after refluxing the solution for 24 h. In both reactions, the solution color changes from dark brown to yellow/green during the reaction. The solution color is also found to be pH-dependent. After the reaction, the pH is ∼10, and the solution color changes back to brown by adjusting the pH to ∼2. To investigate the catalytic activity of clear yellow/green solution, the following control experiment is performed. After the reaction between phenylboronic acid and iodobenzene catalyzed by G3 dendrimer-encapsulated Pd nanoparticles (Table 2, entry 5), the reaction mixture is extracted with petroleum ether, where the organic components are separated from the aqueous solution containing Pd catalyst. The resulting clear yellow/green solution is used as the catalyst for the Suzuki reactions, and it can be seen from Table 2 (entries 7 and 8) that the yellow/green solution is still catalytically active in the Suzuki reactions. It should be mentioned that for the reactions catalyzed by yellow/green solution, no Pd black is formed in reaction **(1)** whereas Pd black is observed in reaction **(2)**.

The Suzuki reactions are also tested in the presence G2 dendrimer-Pd particles. As can be seen from Table 2 (entries 9 and 10), the G2 dendrimer-Pd particles are catalytically active in the Suzuki reactions. The Pd black is formed during the reaction, which is not surprising considering that G2 dendrimer is not an effective stabilizer, as mentioned previously.

Dendrimer porosity is a function of generation; higher generation materials are less porous and thus less likely to admit the reactants to the interior metal nanoparticles.[17] On the basis of the investigation of the catalytic activity and stability of G2, G3, and G4 dendrimer-Pd nanoparticles in the Suzuki reactions, we come to the following conclusions. First, G4 PAMAM dendrimers provide an effective protective action toward Pd particles (no observable Pd black during the reaction), but strong encapsulation of Pd particles within the dendrimers results in a loss of catalytic activity; Second, G2 and G3 dendrimer-Pd particles are efficient catalysts in the Suzuki reactions. G3 dendrimers also provide effective protective action to the particles in the reaction between phenylboronic acid and iodobenzene, but the stability of Pd catalyst depends on the dendrimer generations employed as well as components in the reaction mixtures. By using dendrimers with different generations, it is possible to control the stability of Pd particles, the reaction rate and do selective catalysis. Finally, the presence of sulfur on one of the reactants seems to play a role in the formation of Pd black. Somehow, it seems to drive the particles out of their capping nest.

The catalytic activity and stability of block copolymer-stabilized Pd nanoparticles in the Suzuki reaction **(2)** is investigated. It is seen from Table 3 that block copolymer-Pd nanoparticles having a mean diameter of 3.0 nm show high catalytic activity, comparable to PVP-stabilized Pd nanoparticles. By using triethylamine as the base, no Pd precipitate is observed during the reaction. By using sodium acetate as the base, Pd nanoparticles precipitate out of the solution. The ionic strength of the solution is increased upon the addition of inorganic salt such as sodium acetate, resulting in the ineffective protective

TABLE 3: Product Yields for Suzuki Coupling Reactions Catalyzed by Pd Nanoparticles (Temp, Reflux; Time, 12 h)

entry	reacn	catalyst (mol % of metal)	base	yield[a]	formation of Pd black
1	**(2)**	block copolymer-Pd (0.6%)[b]	NEt_3	85%	no
2	**(2)**	block copolymer-Pd (0.6%)[b]	NaOAc	88%	yes
3	**(2)**	PVP-Pd (0.6%)[b]	NEt_3	80%	yes
4	**(1)**	PVP-Pd (0.3%)[c]	Na_3PO_4	95%	yes
5	**(2)**	PVP-Pd (0.3%)[c]	Na_3PO_4	92%	yes

[a] Isolated yield. [b] The reactions are carried out in 3:1 CH_3CN/H_2O. [c] The reactions are carried out in 40% EtOH. From ref 12.

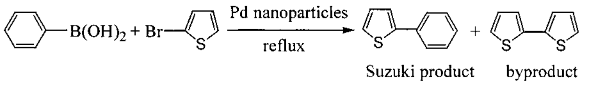
TABLE 4: Product and Byproduct Yields for Suzuki Coupling Reactions between Arylboronic Acids and Aryl Bromides Catalyzed by Pd Nanoparticles (1.0 mol % of Metal) in 3:1 CH_3CN/H_2O. (Base, NEt_3; Temp, Reflux; Time, 24 H)

entry	reacn	catalyst	suzuki product (yield %)[a]	byproduct (yield %)[a]	formation of Pd black
1	**(3)**	block copolymer-Pd	2-phenyl thiophene (16%)[b]	bithiophene (16%)[b]	no
2	**(4)**	block copolymer-Pd	2-phenyl thiophene (0%)	biphenyl (13%)	no
3	**(3)**	PVP−Pd	2-phenyl thiophene (0%)	bithiophene (18%)	a little
4	**(4)**	PVP−Pd	2-phenyl thiophene (0%)	biphenyl (10%)	a little

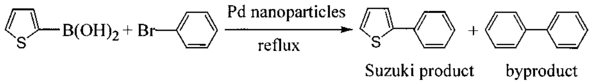
[a] Isolated yield. [b] A mixture of thiophene benzene and bithiophene are obtained (yield: 32%) which cannot be separated by column chromatography (silica gel/petroleum ether). The yield is determined by ^1H NMR ratio of these two compounds.

action of block copolymer to Pd particles. By adding triethylamine, further stabilization of Pd nanoparticles is obtained, in addition to the protection from block copolymer. The stability of the Pd particles depends on the components in the reaction mixture. The results from Table 3 (entries 1 and 3) show that block copolymer has a better protective action toward the Pd particles than PVP, although the principle for the particle stabilization here is expected to be similar to the general steric stabilization of metal particles such as PVP, as mentioned earlier. It is expected that the careful choice of polymer types, metal precursors, as well as reaction conditions will lead to the preparation of the desired catalyst type for special needs.

The catalytic activity and stability of Pd nanoparticles are also investigated in the Suzuki reactions between arylboronic acids and **aryl bromides**.



(3)



(4)

It is found that the reactions between arylboronic acids and aryl bromides are much slower than the reactions between arylboronic acids and aryl iodides. In addition, byproducts resulting from the homo-coupling of aryl bromides are obtained here. It can be seen from Table 4 that by using either block copolymer-Pd or PVP−Pd nanoparticles as the catalyst, the homo-coupling products from bromoarenes are always dominant and the yield is low. This might be attributed to the very slow rate-determining step during the Suzuki reaction between arylboronic acid and aryl bromide, where the homo-coupling reaction becomes competitive. It might be helpful to organic chemists who are performing Suzuki reactions. When byproducts are obtained, sometimes by using bromoarenes, and are hard to separate from the desired Suzuki products, iodoarenes might be an alternative to obtain the desired pure products. By using block copolymer-Pd nanoparticles as a catalyst, no precipitation of Pd particles is observed. However, by using PVP−Pd nanoparticles as a catalyst, Pd particles precipitate out of the solution during the reaction. Once again, this shows that block copolymer has a better protective action toward the Pd particles than PVP.

Conclusions

In the present paper, palladium nanoparticles are prepared in the presence of three different stabilizers, and the catalytic activity as well as the stability of Pd nanoparticles thus prepared is investigated in the Suzuki reactions in aqueous solution. It is found that the Pd nanoparticles stabilized by PVP, block copolymer, and G3 dendrimer are efficient catalysts for the Suzuki reactions between phenylboronic acid (or 2-thiopheneboronic acid) and iodobenzene. The stability of Pd particles is controlled by the type of the stabilizers, the bases, and the solvents, as well as the reactants used in the reaction system. G4 dendrimer is an effective stabilizer; however, the strong encapsulation of Pd particles within the dendrimers results in a loss of catalytic activity.

In the present study, the results of the Pd-nanoparticle-catalyzed Suzuki reactions between arylboronic acids and aryl bromides in aqueous medium are unsatisfactory, although it has been reported[11a] that Pd clusters in nanometer scale operate as an efficient catalyst in some Suzuki reactions between arylboronic acids and activated aryl bromides in organic solvent system. A general limitation is the fact that nonactivated bromoarenes do not react well.[11a−c,11f−g] Indeed, a general solution to this problem remains a challenge in organic chemistry. By carefully choosing stabilizers, bases, solvents, reactants, and reaction conditions, it is possible that both the catalytic activity and stability of Pd nanoparticles are obtained for special reactions.

Acknowledgment. We thank the support of the National Science Foundation (Grant No. CHE-9727633) and the Georgia Tech Microscopy Center for providing the research facilities used in the characterization of these samples. Y.L. wishes to gratefully acknowledge partial support of this project by the Georgia Institute of Technology Molecular Design Institute, under Prime Contract No. N00014-95-1-116 from the Office of Naval Research.

References and Notes

(1) (a) Wilkinson, G., Ed. *Comprehensive Organometallic Chemistry*; Pergamon Press: New York, 1982. (b) Tsuji, J., Ed. *Palladium Reagents and Catalysts*; Wiley: New York, 1995. (c) Malleron, J. L.; Fiaud, J. C.; Legros, J. Y., Ed. *Handbook of Palladium-Catalysed Organic Reactions*; Academic Press: London, 1997.

(2) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147. (c) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550.

(3) (a) Heck, R. F. *Org. React.* **1982**, *27*, 345. (b) Heck, R. F. In *Comprehensive Organic Synthesis*; Pergamon Press: Oxford, 1991. (c) De Meijere, A.; Meyer, F. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2379. (d) Negishi, E.; Coperet, C.; Ma, S.; Liou, S. Y.; Liu, F. *Chem. Rev.* **1996**, *96*, 5.

(4) Suzuki, A. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; VCH: Weinheim, 1998; pp 49.

(5) (a) Herrmann, W. A.; Brossmer, C.; Oefele, K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1844. (b) Beller, M.; Fischer, H.; Herrmann, W. A.; Oefele, K.; Brossmer, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1848. (c) Bei, X.; Turner, H. W.; Weinberg, W. H.; G uram, A. S. *J. Org. Chem.* **1999**, *64*, 6797.

(6) (a) Casalnuovo, A. L.; Calabrese, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 4324. (b) Genet, J. P.; Linquist, A.; Blart, E.; Mouries, V.; Savignac, M. *Tetrahedron Lett.* **1995**, *36*, 1443. (c) Genet, J. P.; Savignac, M. *J. Organomet. Chem.* **1999**, *576*, 305.

(7) Bradley, J. S. In *Clusters and Colloids: From Theory to Applications*; Schmid, G., Ed.; VCH: Weinheim, 1994; pp523.

(8) (a) Zhao, M.; Crooks, R. M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 8(3), 364. (b) Zhao, M.; C rooks, R. M. *Adv. Mater.* **1999**, *11(3)*, 217. (c) Chechik, V.; Zhao, M.; Crooks, R. M. *J. Am. Chem. Soc.* **1999**, *121*, 4910. (d) Zhao, M.; Crooks, R. M. *Chem. Mater.* **1999**, *11*, 3379. (e) Chechik, V.; Crooks, R. M. *J. Am. Chem. Soc.* **2000**, *122*, 1243. (f) Crooks, R. M.; Zhao, M.; Sun, L.; Chechik, V.; Yeung, L. K. *Acc. Chem. Res.* **2001**, *34(3)*, 181.

(9) Mayer, A. B. R.; Mark, J. E. *Colloid Polym. Sci.* **1997**, *275(4)*, 333.

(10) (a) Sulman, E.; Bodrova, Yu.; Matveeva, V.; Semagina, N.; Cerveny, L.; Kurtc, V.; Bronstein, L.; Platonova, O.; Valetsky, P. *Appl. Catal. A* **1999**, *176*, 75. (b) Sulman, E.; Matveeva, V.; Usanov, A.; Kosivtsov, Yu.; Demidenko, G.; Bronstein, L.; Chernyshov, D.; Valetsky, P. *J. Mol. Catal. A* **1999**, *146*, 265.

(11) (a) Reetz, M. T.; Breinbauer, R.; Wanninger, K. *Tetrahedron Lett.* **1996**, *37*, 4499. (b) Reetz, M. T.; Lohmer, G. *Chem. Commun.* **1996**, 1921. (c) Beller, M.; Fischer, H.; Kuehlein, K.; Reisinger, C.-P.; Herrmann, W. A. *J. Organomet. Chem.* **1996**, *520*, 257. (d) Klingelhoefer, S.; Heitz, W.; Greiner, A.; Oestreich, S.; Foerster, S.; Antonietti, M. *J. Am. Chem. Soc.* **1997**, *119*, 10 116. (e) Le Bars, J.; Specht, U.; Bradley, J. S.; Blackmond, D. G. *Langmuir* **1999**, *15*, 7621. (f) Ding, J. H.; Gin, D. L. *Chem. Mater.* **2000**, *12*, 22. (g) Yeung, L. K.; Crooks, R. M. *Nano Lett.* **2001**, *1(1)*, 14.

(12) Li, Y.; Hong, X. M.; Collard, D. M.; El-Sayed, M. A. *Org. Lett.* **2000**, *2(15)*, 2385.

(13) Teranishi, T.; Miyake, M. *Chem. Mater.* **1998**, *10*, 594.

(14) Ottaviani, M. F.; Montalti, F.; Turro, N. J.; Tomalia, D. A. *J. Phys. Chem. B* **1997**, *101*, 158.

(15) Technical data from Dendritech, Inc. (Midland, MI).

(16) (a) Esumi, K.; Suzuki, A.; Aihara, N.; Usui, K.; Torigoe, K. *Langmuir* **1998**, *14*, 3157. (b) Garcia, M. E.; Baker, L. A.; Crooks, R. M. *Anal. Chem.* **1999**, *71*, 256. (c) Gröhn, F.; Bauer, B. J.; Akpalu, Y. A.; Jackson, C. L.; Amis, E. J. *Macromolecules* **2000**, *33*, 6042. (d) Esumi, K.; Nakamura, R.; Suzuki, A.; Torigoe, K. *Langmuir* **2000**, *16*, 7842.

(17) Wells, M.; Crooks, R. M. *J. Am. Chem. Soc.* **1996**, *118*, 3988.