Colloidal Supported Metal Nanoparticles (CSMNs) as Effective Nanocatalysts for Liquid-Phase Suzuki Cross-Coupling Reactions

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ABSTRACT: We investigate the catalytic activity obtained for three types of nanocatalysts: colloidal supported metal nanoparticles (CSMNs) prepared with silica colloids in solution that are air-dried, CSMNs prepared with dry silica colloids resuspended in doubly deionized water that are air-dried, and palladium nanoparticles loaded onto bulk silica dispersed in doubly deionized water that are air-dried. The three types of catalysts are prepared with and without the aminopropyltriethoxysilane (APTES) linker for a total of six different catalysts that are tested for the liquid-phase cross-coupling reaction between phenylboronic acid and iodobenzene to form biphenyl. TEM images and EDS spectra were obtained for the six different catalysts to see if the palladium nanoparticles are covalently attached to the functionalized silica colloids and functionalized bulk silica supports and to see if the palladium nanoparticles are adsorbed onto the unfunctionalized silica colloids and unfunctionalized bulk silica supports. The six different catalysts are tested for the Suzuki reaction between phenylboronic acid and iodobenzene to form biphenyl. The CSMNs prepared using unfunctionalized wet silica colloids reacted with palladium nanoparticles that are air-dried resulted in the highest catalytic activity. In the case of the nanocatalysts prepared using the APTES linker for covalent attachment of the palladium nanoparticles to the wet silica colloids or bulk silica dispersed in doubly deionized water that are air-dried, there is lower catalytic activity compared to their counterparts prepared without the use of the APTES linker. This suggests that the APTES could be acting as a catalyst poison resulting in lower catalytic activity for the Suzuki reaction between phenylboronic acid and iodobenzene to form biphenyl compared to unfunctionalized CSMNs.

INTRODUCTION

Transition metal nanoparticles are very attractive catalysts since they have a large surface-to-volume ratio which makes their surface atoms very active. Their large surface-to-volume ratio results in higher catalytic efficiency per gram than larger bulk catalytic materials. There have been numerous review articles that have focused on the use of homogeneous catalysts (transition metal nanoparticles in colloidal solution),1–9 heterogeneous catalysts (transition metal nanoparticles adsorbed onto different supports)5,9–20 and lithographic arrays of nanoparticles21–25 for many different organic and inorganic reactions. There also have been some studies involving the use of intermediate types of supports such as the use of carbon nanotubes26–29 and carbon nanofibers30 as support materials.

Suzuki cross-coupling reactions involve reacting arylboronic acids with aryl halides to form biaryls. There have been many reports on the use of transition metal nanoparticles as catalysts for Suzuki reactions.31–36 Dendrimer supported palladium nanoparticles have been used as effective nanocatalysts for Suzuki cross-coupling reactions.37,38 Shape-dependent catalytic activity of copper oxide supported palladium nanoparticles have been tested as nanocatalysts for the Suzuki cross-coupling reactions.36 Mesoporous silica supported palladium nanoparticles have been used as catalysts for Suzuki reactions.39 The catalytic activity for the Suzuki cross-coupling reactions have been compared for the use of palladium nanoparticles in solution and those adsorbed onto carbon nanotubes.40 Palladium nanoparticles have also been used as catalysts for the Suzuki reaction using water as the solvent.41

The CSMNs have a high surface area, highly active surface atoms of the nanoparticles, can be suspended in solution during catalysis, and can be easily separated from the reaction mixture. It can be seen that the colloidal supported metal nanoparticles (CSMNs) combine the advantages of heterogeneous catalysts in a near-homogeneous format. Also, the ability to be suspended in solution is especially important for liquid-phase reactions. The CSMNs will have higher catalytic activity than homogeneous nanocatalysts (transition metal nanoparticles in colloidal solution) and heterogeneous nanocatalysts (transition metal nanoparticles adsorbed onto bulk supports). Previously, we have reported the synthesis of colloidal supported metal nanoparticles (CSMNs) prepared using mercaptopropyltrimethoxysilane (MPTMS) and aminopropyltriethoxysilane (APTES) functionalized silica colloids.42 MPTMS was chosen as the linker since it has a thiol group that the palladium nanoparticles can bind to and form the Pd–S bond. APTES was chosen as a linker since it has a nitrogen group that the palladium nanoparticles can bind to and form the Pd–N bond. Palladium nanoparticles were covalently attached onto the MPTMS or APTES functionalized silica colloids.42,43

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The preparation of the CSMNs involves four steps: synthesis of silica colloids, synthesis of palladium nanoparticles, functionalizing the silica colloids with MPTMS and APTES, and covalently attaching the palladium nanoparticles to the functionalized silica colloids. In the case of the CSMNs prepared using MPTMS functionalized silica colloids, there is no catalytic activity during the entire reaction, which was run for 24 h. The CSMNs prepared using APTES functionalized silica colloids exhibit catalytic activity during the first hour of the reaction.

In this paper, we report the use of different types of CSMNs as catalysts for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene to form biphenyl. The CSMNs that we have investigated consist of metal nanoparticles covalently bound to functionalized silica colloids or adsorbed onto unfunctionalized silica colloids. Out of the six different nanocatalysts, the CSMNs prepared using palladium nanoparticles adsorbed onto unfunctionalized wet silica colloids in solution that are air-dried results in the greatest catalytic activity. In the case of the CSMNs prepared using palladium nanoparticles covalently attached to the APTES functionalized silica colloids in solution that are air-dried and palladium nanoparticles covalently attached to the APTES functionalized bulk silica dispersed in doubly deionized water that are air-dried, the catalytic activity is smaller than their unfunctionalized counterparts. This suggests that the APTES could be acting as a catalyst poison. Also, the CSMNs prepared by using palladium nanoparticles adsorbed onto unfunctionalized silica colloids in solution that are air-dried result in lower catalytic activity than the palladium nanoparticles in colloidal solution as nanocatalysts (containing the same number of grams of palladium).

**EXPERIMENTAL SECTION**

**Synthesis of Silica Colloids.** The silica colloids were synthesized by using the Stoeber synthesis method. First, 30 mL of ethanol and 2.4 mL of ammonium hydroxide were added to an Erlenmeyer flask and stirred for 5 min. Then, 1.2 mL of tetraethoxysilicate (TEOS) was added to the solution containing ethanol and ammonium hydroxide, and this solution was stirred overnight. The solution was initially clear, and after 15–20 min, the solution starts to turn cloudy and the final solution was very turbid and consisted of a suspension of the silica colloids.

**Synthesis of PVP Stabilized Palladium Nanoparticles.** The palladium nanoparticles were synthesized by using the ethanol reduction method similar to that described previously. 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 deionized 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 suspension of Pd nanoparticles.

**Functionalization of Silica Colloids.** We have used 3-aminopropyltriethoxysilane (APTES) as the linker to functionalize the silica colloids. The functionalized silica colloids were prepared in which 100 μL of APTES was added to the silica colloid suspension and allowed to react for 6 h. We have also prepared unfunctionalized silica colloids for direct adsorption of the metal nanoparticles onto the surface of the unfunctionalized silica colloids.

**Synthesis of Colloidal Supported Palladium Nanoparticles (CSMNs) Using Functionalized and Unfunctionalized Silica Colloid Suspensions.** In the case of the functionalized wet silica colloids, 100 μL of 3-aminopropyltriethoxysilane (APTES) was added and allowed to react for 6 h. 2 mL of the centrifuged functionalized or unfunctionalized silica colloids and 4 mL of the PVP-capped palladium nanoparticles were placed into a scintillation vial, and this suspension was mixed for 24 h to allow the palladium nanoparticles to covalently bind to the functionalized silica colloids or adsorb onto the unfunctionalized silica colloids. The CSMNs prepared with palladium nanoparticles covalently attached to the functionalized silica colloids or adsorbed onto the unfunctionalized silica colloids were then centrifuged four times at 13,500 rpm for 3 min each time. During the first two centrifugation cycles, the CSMNs were redispersed in ethanol, and during the last two centrifugation cycles, they were redispersed in doubly deionized water. After the final centrifugation cycle, the supernatant was removed and the silica colloids were allowed to air-dry overnight.

In the case of the functionalized silica colloids, 0.32 g of the dried silica colloids was mixed with 30 mL of doubly deionized water and stirred overnight. To this suspension of the initial dried colloids, 100 μL of APTES was added to the silica colloid suspension and allowed to react for 6 h. In the case of the unfunctionalized silica colloids, 0.32 g of the dried silica colloids was mixed with 30 mL of doubly deionized water and stirred overnight. 2 mL of the centrifuged functionalized or unfunctionalized silica colloids and 4 mL of the PVP-capped palladium nanoparticles were placed into a scintillation vial, and this suspension was mixed for 24 h to allow the palladium nanoparticles to covalently bind to the functionalized silica colloids or adsorb onto the unfunctionalized silica colloids. The CSMNs were then centrifuged four times at 13,500 rpm for 3 min each time. During the first two centrifugation cycles, the CSMNs prepared using functionalized and unfunctionalized silica colloids were redispersed in ethanol and during the last two centrifugation cycles, they were redispersed in doubly deionized water. After the final centrifugation cycle, the supernatant was removed and the silica colloids were allowed to air-dry overnight.

**Preparation of Palladium Nanoparticles Loaded onto Functionalized and Unfunctionalized Bulk Silica Dispersed in Doubly Deionized Water.** In the case of the functionalized and unfunctionalized bulk silica, 0.32 g of the bulk dry silica and 30 mL of doubly deionized water were added to an Erlenmeyer flask and stirred overnight. In the case of the functionalized bulk silica, 100 μL of 3-aminopropyltriethoxysilane was added and
reacted for 6 h. 2 mL of the centrifuged functionalized or unfunctionalized bulk silica and 4 mL of the PVP-capped palladium nanoparticles were placed into a scintillation vial, and this suspension was mixed for 24 h to allow the palladium nanoparticles to bind to the functionalized bulk silica or adsorb onto the unfunctionalized bulk silica. The bulk silica was then centrifuged four times at 13,500 rpm for 3 min each time. During the first two centrifugation cycles, the functionalized and unfunctionalized bulk silica loaded with palladium nanoparticles were redispersed in ethanol, and during the last two centrifugation cycles, they were redispersed in doubly deionized water. After the final cycle of centrifugation, the supernatant was removed, and the functionalized and unfunctionalized bulk silica loaded with palladium nanoparticles were allowed to air-dry overnight. Then, 0.1 g of palladium nanoparticles loaded onto functionalized and unfunctionalized bulk silica was used as the catalyst for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene to form biphenyl.

Characterization Studies with TEM and EDS. One drop of dilute suspensions of colloidal supported palladium nanoparticles and palladium nanoparticles loaded onto bulk silica was placed on Formvar-coated copper grids. The drop was allowed to air-dry for ~1 h. The JEOL 2100EX TEM was used to obtain the TEM images of the colloidal supported metal nanoparticles (CSMNs) and palladium nanoparticles covalently attached or adsorbed onto silica nanoparticles. Energy dispersive spectroscopy (EDS) was used to determine what elements are present in the CSMNs.

Suzuki Cross-Coupling Reaction. The Suzuki reaction between phenylboronic acid and iodobenzene was catalyzed using the PVP—Pd nanoparticles as described previously.44,48,49 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 were added to 150 mL of 3:1 acetonitrile:water solvent. The solution was heated to 100 °C, and 0.1 g of the CSMNs or palladium nanoparticles loaded onto bulk silica was added to start the reaction. The reaction mixture was refluxed for a total of 12 h. Kinetic studies were conducted during the first hour of the reaction.

RESULTS AND DISCUSSION

The CSMNs have a high surface area, highly active surface atoms of the nanoparticles, can be suspended in solution during catalysis, and can be easily separated from the reaction mixture. The colloidal supported metal nanoparticles (CSMNs) combine the advantages of heterogeneous catalysts in a near-homogeneous format. The ability of the CSMNs to be suspended in solution is especially important for liquid-phase reactions. The CSMNs will have higher catalytic activity than homogeneous nanocatalysts (transition metal nanoparticles in colloidal solution) and heterogeneous nanocatalysts (transition metal nanoparticles adsorbed onto bulk supports). We discuss the synthesis and characterization of different types of colloidal supported metal nanoparticles (CSMNs) and palladium nanoparticles loaded onto bulk silica as catalysts for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene. We also discuss the results of the kinetics experiments using HPLC for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene to form biphenyl for the different types of nanocatalysts.

Synthesis of Different Types of CSMNs and Palladium Nanoparticles Loaded onto Bulk Silica. Six different types of nanocatalysts were synthesized as catalysts for the liquid-phase Suzuki cross-coupling reaction. The palladium nanoparticles have an average size of 2.9 nm as reported previously.42 In all cases, the palladium nanoparticles are adsorbed or covalently attached to the surface of the silica colloids. The silica colloids are not hollow or porous so the palladium nanoparticles cannot be adsorbed or covalently attached inside the silica colloids. Two types of CSMNs involve the functionalized and unfunctionalized wet silica colloids reacting with the palladium nanoparticles to form CSMNs. In these two types of CSMNs, the term wet silica colloids refers to the silica colloids being in aqueous solution. Preparing the CSMNs by adsorption of the palladium nanoparticles directly to the silica colloids were synthesized as catalysts for the liquid-phase Suzuki cross-coupling reaction. The palladium nanoparticles have an average size of 2.9 nm as reported previously.42 In all cases, the palladium nanoparticles are adsorbed or covalently attached to the surface of the silica colloids. The silica colloids are not hollow or porous so the palladium nanoparticles cannot be adsorbed or covalently attached inside the silica colloids. Two types of CSMNs involve the functionalized and unfunctionalized wet silica colloids reacting with the palladium nanoparticles to form CSMNs. In these two types of CSMNs, the term wet silica colloids refers to the silica colloids being in aqueous solution. Preparing the CSMNs by adsorption of the palladium nanoparticles directly to the silica colloids.
colloid suspensions involves fewer steps compared to covalently attaching the palladium nanoparticles to APTES functionalized silica colloid suspensions. Using the wet silica colloids involves adsorption or covalent attachment of the palladium nanoparticles to the silica colloids in its native form. Figure 1 shows a representative TEM image and EDS spectrum for the CSMNs prepared using amino-propyltriethoxysilane (APTES) functionalized suspended wet silica colloids. In this case, the palladium nanoparticles are covalently attached to the functionalized silica colloids. Figure 2 shows a representative TEM image and EDS spectrum for the CSMNs prepared using unfunctionalized suspended wet silica colloids. In this case, the palladium nanoparticles are adsorbed onto the unfunctionalized wet silica colloids. The black specks in the TEM images are the palladium nanoparticles covalently bound to APTES functionalized dried silica colloid suspensions (a) and EDS spectrum which reflects the presence of both Pd and Si (b). The Cu peaks are due to Cu TEM grids. These two CSMNs that are formed are allowed to air-dry and are used as catalysts for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene, which will be discussed later in the paper.

Another two types of CSMNs involve functionalized and unfunctionalized dried silica colloids resuspended in doubly

Figure 2. Examples of TEM images showing palladium nanoparticles directly adsorbed onto the surface of the silica colloid suspensions (a) and EDS spectrum which reflects the presence of both Pd and Si (b). The Cu peaks are due to Cu TEM grids.

Figure 3. A representative TEM image showing the palladium nanoparticles covalently bound to APTES functionalized dried silica colloid suspensions (a) and EDS spectrum which reflects the presence of both Pd and Si (b). The Cu peaks are due to the copper TEM grids.
deionized water and reacting with the palladium nanoparticles to form CSMNs. In these two cases, the silica colloids are air-dried and then resuspended in doubly deionized water. Preparing the CSMNs by adsorption of the palladium nanoparticles directly to the silica colloid suspensions involves fewer steps compared to covalently attaching the palladium nanoparticles to APTES functionalized silica colloid suspensions. Using the dry silica colloids resuspended in doubly deionized water for adsorption or covalent attachment of the palladium nanoparticles is not in its native form, which is a disadvantage of this method compared to using the wet silica colloids in their native form. Figure 3 shows a representative TEM image and EDS spectrum for the CSMNs prepared using aminopropyltriethoxysilane (APTES) functionalized dried silica colloids resuspended in doubly deionized water. In this case, the palladium nanoparticles are covalently attached to the functionalized dried silica colloids resuspended in doubly deionized water. Figure 4 shows a representative TEM image and EDS spectrum for the CSMNs prepared using unfunctionalized dried silica colloids resuspended in doubly deionized water. In this case, the palladium nanoparticles adsorb onto the surface of the dried silica colloids resuspended in doubly deionized water. The black specks in the TEM images are the palladium nanoparticles covalently attached to the functionalized silica colloids.

Figure 4. A representative TEM image showing the palladium nanoparticles adsorbed onto the unfunctionalized dried silica colloid suspensions (a) and EDS spectrum which reflects the presence of both Pd and Si (b). The Cu peaks are due to the copper TEM grids.

Figure 5. Example of TEM image showing APTES functionalized bulk silica with palladium nanoparticles covalently attached to its surface (a) and EDS spectrum which reflects the presence of both Pd and Si (c). The Cu peaks are due to the copper TEM grids.
deionized water. Adsorption of the palladium nanoparticles directly in these two cases, the bulk silica supports are dispersed in doubly deionized water were prepared. In this case, the palladium nanoparticles are covalently attached onto the functionalized bulk silica. Figure 6 shows a representative TEM image and EDS spectrum for palladium nanoparticles supported on unfunctionalized dried bulk silica dispersed in water. In this case, the palladium nanoparticles are adsorbed onto the unfunctionalized bulk silica. In the EDS spectra for both cases, the Pd and Si peaks are present confirming that the Pd NPs are loaded onto the bulk silica. The palladium nanoparticles covalently attached or adsorbed onto bulk silica are air-dried and used as catalysts for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene as discussed later in the paper.

In the case of the nanocatalysts consisting of the palladium nanoparticles adsorbing onto the unfunctionalized silica colloids, the free sites on the palladium nanoparticles (sites not occupied by the PVP stabilizer) are accessible to act as a catalyst. Also, during the adsorption process, the PVP on the nanoparticle surface can be displaced, and this results in more sites that can act as catalysts. In the case of the nanocatalysts consisting of the palladium nanoparticles covalently attached to the APTES functionalized silica colloids, the free sites on the palladium nanoparticles (sites not occupied by the PVP stabilizer) are accessible to act as a catalyst. In addition, it is possible that during the process of the palladium nanoparticles covalently binding to the APTES functionalized silica colloids some of the PVP could get displaced. This would result in more free sites available to act as catalysts.

**Nanocatalysts for Liquid-Phase Suzuki Cross-Coupling Reactions.** We have tested the use of the different types of nanocatalysts for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene to form biphenyl. The Pd content of all of the nanocatalysts is the same since we prepared them in the same way. We allowed the silica colloids and bulk silica to react with 5 mL of the palladium nanoparticles and centrifuged them. The supernatant is clear, indicating that all of the palladium nanoparticles have been adsorbed or covalently bound to the silica colloids and bulk silica. We have also compared the catalytic activity of these catalysts to that of 5 mL of the colloidal palladium nanoparticles as catalysts. We have used reversed phase HPLC to follow the kinetics during the first hour of the Suzuki reaction for the different nanocatalysts we have prepared such as wet functionalized and unfunctionalized silica colloids in solution reacted with palladium nanoparticles, dried functionalized and unfunctionalized silica colloids resuspended in water reacted with palladium nanoparticles, dry functionalized and unfunctionalized bulk silica dispersed in doubly deionized water reacted with palladium nanoparticles, and palladium nanoparticles in colloidal solution. In the six cases involving CSMNs or palladium nanoparticles loaded onto bulk silica, the nanocatalysts are allowed to air-dry and 0.1 g of each catalyst was used for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene. We have made comparisons of the catalytic activity for these different types of nanocatalysts.

We have compared the catalytic activity for CSMNs consisting of palladium nanoparticles covalently attached to APTES functionalized wet silica colloids to those of CSMNs consisting of palladium nanoparticles covalently attached to the APTES functionalized dry silica colloids resuspended in doubly deionized water and palladium

Figure 6. Example of TEM image showing unfunctionalized bulk silica with palladium nanoparticles adsorbed onto its surface (a) and EDS spectrum which reflects the presence of both Pd and Si (b). The Cu peaks that appear are due to copper TEM grids.
nanoparticles covalently attached to the APTES functionalized dry bulk silica dispersed in doubly deionized water. In all three cases, the nanocatalysts are allowed to air-dry, and 0.1 g of each catalyst was used for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene. Figure 7 compares the catalytic activity of these three types of nanocatalysts based on the HPLC kinetics study during the first hour of the reaction. The catalytic activity of the CSMNs consisting of palladium nanoparticles adsorbed onto wet silica colloids that are air-dried results in lower catalytic activity compared to that of the CSMNs consisting of palladium nanoparticles covalently attached to the APTES functionalized wet silica colloids that are air-dried as shown in Figure 7. This result suggests that the APTES could be poisoning the catalytic activity for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene. Previously, we have observed that if we use palladium nanoparticles covalently attached to mercaptopropyltrimethoxysilane (MPTMS) functionalized silica colloids, there is no catalytic activity during the first hour of the reaction. In this case, the mercapto group in the linker results in poisoning of the catalyst due to APTES, which contain an amine group which results in the lower catalytic activity that is observed.

We have also compared the catalytic activity of the CSMNs consisting of palladium nanoparticles adsorbed onto wet silica colloids to those of CSMNs consisting of palladium nanoparticles adsorbed onto the dry silica colloids resuspended in doubly deionized water, and palladium nanoparticles adsorbed onto the dry bulk silica dispersed in doubly deionized water. In all three cases, the nanocatalysts are allowed to air-dry, and 0.1 g of each catalyst was used for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene. Figure 8 compares the catalytic activity of these three types of nanocatalysts based on the HPLC kinetics study during the first hour of the reaction. The CSMNs consisting of palladium nanoparticles adsorbed onto the dry silica colloids resuspended in doubly deionized water that are air-dried and the palladium nanoparticles adsorbed onto the dry bulk silica dispersed in doubly deionized water that are air-dried, the catalytic activity is much lower than that of CSMNs consisting of palladium nanoparticles adsorbed onto the wet silica colloids that are air-dried.

The CSMNs consisting of palladium nanoparticles adsorbed onto the wet silica colloids that are air-dried as shown in Figure 8 result in higher catalytic activity compared to that of the CSMNs consisting of palladium nanoparticles covalently attached to the APTES functionalized wet silica colloids that are air-dried as shown in Figure 7. This result suggests that the APTES could be poisoning the catalytic activity for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene. Previously, we have observed that if we use palladium nanoparticles covalently attached to mercaptopropyltrimethoxysilane (MPTMS) functionalized silica colloids, there is no catalytic activity during the first hour of the reaction. In this case, the mercapto group in the linker results in poisoning of the catalyst. Nitrogen compounds result in poisoning of different catalysts. This supports the idea that in the case of the CSMNs consisting of palladium nanoparticles covalently attached to APTES functionalized silica colloids there could be some poisoning of the catalyst due to APTES, which contain an amine group which results in the lower catalytic activity that is observed.

We have also compared the catalytic activity of the CSMNs consisting of palladium nanoparticles adsorbed onto unfunctionalized wet silica colloids to that of palladium nanoparticles in colloidal solution. Both of these catalysts have the same number of grams of Pd. As can be seen in Figure 9, the CSMNs consisting of palladium nanoparticles adsorbed onto the
unfunctionalized wet silica colloids that are air-dried results in larger catalytic activity compared to the palladium nanoparticles in colloidal solution. In addition to the higher catalytic activity of the CSMNs consisting of palladium nanoparticles adsorbed onto unfunctionalized wet silica colloids, these CSMNs have additional advantages such as having high surface area and being easily separated from the reaction mixture. This makes using the CSMNs consisting of palladium nanoparticles adsorbed onto the unfunctionalized wet silica colloids very attractive to use compared to the palladium nanoparticles in colloidal solution.

We have also compared the catalytic activity of the CSMNs consisting of palladium nanoparticles adsorbed to the wet silica colloid surface that are air-dried to those of the CSMNs consisting of palladium nanoparticles covalently attached to the APTES functionalized wet silica colloids that are air-dried as can be seen in Figure 10. In all three cases, the nanocatalysts are allowed to air-dry, and 0.1 g of each catalyst was used for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene. The CSMNs consisting of palladium nanoparticles adsorbed onto the wet silica colloids that are air-dried results in higher catalytic activity compared to the CSMNs consisting of palladium nanoparticles covalently attached to the APTES functionalized wet silica colloids that are air-dried. The TEM images of the two types of nanocatalysts are similar, yet there are differences in the catalytic activity. The lower catalytic activity for the CSMNs consisting of palladium nanoparticles adsorbed onto APTES functionalized dry bulk silica dispersed in doubly deionized water that are air-dried and APTES functionalized dried Si colloids resuspended in doubly deionized water that are air-dried results in higher catalytic activity of the CSMNs consisting of palladium nanoparticles adsorbed onto unfunctionalized dried silica colloids resuspended in doubly deionized water that are air-dried as shown in Figure 11 and CSMNs consisting of palladium nanoparticles covalently attached to the APTES functionalized dried silica colloids resuspended in doubly deionized water that are air-dried as shown in Figure 11.

As can be seen in Figure 11, we have compared the catalytic activity of the CSMNs consisting of palladium nanoparticles adsorbed onto dried silica colloids resuspended in doubly deionized water that are air-dried to that of the CSMNs consisting of palladium nanoparticles covalently attached to the APTES functionalized dried silica colloids resuspended in doubly deionized water that are air-dried. In both cases, the nanocatalysts are allowed to air-dry, and 0.1 g of each catalyst was used for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene. There is very little difference in the catalytic activity for the two types of nanocatalysts for the Suzuki cross-coupling reaction between phenylboronic acid and iodobenzene to form biphenyl. As shown in Figure 8, the CSMNs consisting of palladium nanoparticles adsorbed onto unfunctionalized wet silica colloids that are air-dried have much higher catalytic activity than the CSMNs consisting of palladium nanoparticles adsorbed onto unfunctionalized dried silica colloids resuspended in doubly deionized water that are air-dried as shown in Figure 11 and CSMNs consisting of palladium nanoparticles covalently attached to the APTES functionalized dried silica colloids resuspended in doubly deionized water that are air-dried as shown in Figure 11.

We have also compared the catalytic activity of the palladium nanoparticles adsorbed onto dry bulk silica dispersed in doubly deionized water that are air-dried to that of the palladium nanoparticles covalently attached onto APTES functionalized dry bulk silica dispersed in doubly deionized water that are air-dried. In all three cases, the nanocatalysts are allowed to air-dry and 0.1 g of each catalyst was used for the Suzuki reaction between phenylboronic acid and iodobenzene. As shown in Figure 12, the palladium nanoparticles adsorbed onto dry bulk silica dispersed in doubly deionized water that are air-dried results in higher catalytic activity. It can also be seen that the palladium nanoparticles covalently attached onto APTES functionalized dry bulk silica dispersed in doubly deionized water that are air-dried.
The palladium nanoparticles covalently attached to bulk silica dispersed in doubly deionized water functionalized with 200 μL of APTES that are air-dried resulted in lower catalytic activity than palladium nanoparticles covalently attached to bulk silica dispersed in doubly deionized water functionalized with 100 μL of APTES that are air-dried. This trend supports the idea that the APTES acts as a catalyst poison, resulting in lower catalytic activity.

**Leaching Test.** In the case of transition metal nanoparticles, there have been recent studies in which it has been found that heterogeneous catalysts are not truly heterogeneous in which the catalyst leaches into solution. This raises the question about whether catalysis is homogeneous or heterogeneous. Our CSMNs combine the advantages of heterogeneous catalysts in a near-homogeneous format. We have conducted experiments to determine if leaching of the palladium atoms into solution occurs. We have refluxed the CSMNs in 3:1 acetonitrile:water mixture for 1 h. Then the solution is centrifuged to remove the CSMNs in which leached atoms would be in the supernatant solution. We used the supernatant solution as catalysts for the Suzuki reaction and compared the catalytic activity to that of the CSMNs catalyzing the Suzuki reaction. The results are shown in Figure 13, and it can be seen that while there is some catalytic activity in the case of the supernatant solution, there is a much greater amount of catalytic activity in the case of the CSMNs used as catalysts. Overall, while there is a small amount of leaching that occurs, the overall catalytic activity is much greater when the CSMNs are used as catalysts.

**CONCLUSIONS**

The catalytic activity is obtained for three types of nanocatalysts: colloidal supported metal nanoparticles (CSMNs) prepared with silica colloids in solution that are air-dried, CSMNs prepared with dry silica colloids that is resuspended in doubly deionized water that are air-dried, and palladium nanoparticles loaded onto bulk silica dispersed in doubly deionized water that are air-dried. These three types of catalysts are prepared with and without the aminopropyltriethoxysilane (APTES) linker for a total of six different catalysts that are tested for the liquid-phase cross-coupling reaction between phenylboronic acid and iodobenzene to form biphenyl. The CSMNs prepared with the silica colloids in solution without the use of the APTES linker that are air-dried results in the highest catalytic activity for the Suzuki cross-coupling reaction. In the case of the CSMNs consisting of palladium nanoparticles covalently bound to APTES functionalized wet silica colloids that are air-dried and palladium nanoparticles covalently bound to the APTES functionalized dry bulk silica dispersed in doubly deionized water that are air-dried, it is observed that there is lower catalytic activity than their counterparts prepared without the use of the APTES linker. This suggests that the APTES could be acting as a catalyst poison resulting in lower catalytic activity for the Suzuki reaction. Also, it was observed that the CSMNs prepared with the silica colloids in solution without the use of the APTES linker that are air-dried results in higher catalytic activity than the use of palladium nanoparticles in colloidal solution containing the same number of grams of palladium. On the basis of these results, it can be seen that the CSMNs prepared using the palladium nanoparticles adsorbed onto unfunctionalized silica colloids in solution that are air-dried result in the highest catalytic activity for the Suzuki reaction between phenylboronic acid and iodobenzene to form biphenyl.

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**REFERENCES**

Nanocatalysis and scope of application.


26) Bottini, M.; Dawson, M. I.; Mustelin, T. Carbon nanotube- and assembling engineered nanocrystals.


