

FTIR Study of the Mode of Binding of the Reactants on the Pd Nanoparticle Surface during the Catalysis of the Suzuki Reaction

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Received: November 23, 2004; In Final Form: January 12, 2005

In the Suzuki reaction between phenylboronic acid and iodobenzene catalyzed by palladium nanoparticles, our previous studies suggested that the phenylboronic acid adsorbs on the nanoparticle surface and then interacts with the iodobenzene that is present in solution. In the present study, FTIR is used to examine the change in the vibrational frequencies of phenylboronic acid in films with and without the addition of palladium nanoparticles. The large change in the B–O stretching frequency of phenylboronic acid from 1348 to 1376 cm^{-1} in the presence of sodium acetate and palladium nanoparticles strongly suggests that the mode of binding of phenylboronic acid to the Pd nanoparticle surface involves a B–O–Pd type of bonding. Shifts in the B–C stretching mode and the out-of-plane phenyl C–C ring deformation bands associated with phenylboronic acid provide additional confirmations of the binding process. It is also shown that the phenylboronic acid needs to be in the deprotonated form in the presence of sodium acetate (phenylboronate anion) to bind to the palladium nanoparticle surface. No changes in the characteristic bands of iodobenzene were observed in films made in the presence of the palladium nanoparticles. The FTIR studies provide proof of the mode of binding that occurs in the nanoparticle surface for the first time and also confirms the mechanism of the Suzuki reaction that we proposed previously.

Introduction

Studies on catalysis with transition metal nanoparticles in colloidal solution has been very active recently and is described in many review articles published during the past decade.^{1–8} There have been very few studies conducted on the stability of the nanoparticle catalysts during the course of the reaction.^{9–13} We have previously^{14–19} studied the effect of catalysis on the size and shape of transition metal nanoparticles that are used as catalysts. One particular reaction that we studied is the electron-transfer reaction between hexacyanoferrate(III) ions and thiosulfate ions using spherical,^{14–16} tetrahedral,^{15–17} and cubic^{15–17} platinum nanoparticles as catalysts. It was observed that there is a slight reduction in the size of the spherical platinum nanoparticles after the first and second cycle of the electron-transfer reaction.¹⁴ Also, there is a great reduction in the size of the nanoparticles when they are exposed to just the hexacyanoferrate(III) ions whereas they maintain their size in the presence of just the thiosulfate ions. On the basis of these observations, it was suggested that the mechanism involves the thiosulfate ions binding to the nanoparticle surface and reacting with hexacyanoferrate(III) ions in solution. We found that the catalytic activity is shape-dependent during the early stages of the reaction in which the tetrahedral nanoparticles are found to be the most catalytically active and the cubic nanoparticles are the least catalytically active for particles of comparable size.¹⁵ During the course of the reaction, it was observed that dissolution of platinum atoms occurred at the corners and edges of the tetrahedral and cubic nanoparticles, which also resulted in corresponding changes in the activation energy.¹⁶ It was also observed that the dissolution of atoms on the corners and edges

of the platinum nanoparticles occurs faster for the tetrahedral nanoparticles than the cubic nanoparticles.¹⁷

Another reaction that we studied was the Suzuki reaction between phenylboronic acid and iodobenzene using PVP–Pd nanoparticles^{18,20–22} and PAMAM-OH Generation 4 dendrimer capped Pd nanoparticles.^{19,22} We found that the size of the nanoparticles became larger as a result of Ostwald ripening processes as well as the presence of excess palladium atoms and partly reduced palladium ions. These processes occur in the presence of the solvent, sodium acetate, and iodobenzene.^{18,19} We observed that the growth process is inhibited in the presence of phenylboronic acid. Due to these observations, we proposed that when the phenylboronic acid is in the deprotonated form (due to presence of sodium acetate), it binds to the nanoparticle surface through the O^- of the OH group. We also proposed that the mechanism of the Suzuki reaction involves the phenylboronic acid binding to the nanoparticle surface and reacting with iodobenzene that is present in solution.

FTIR is used to determine the mode of binding of the phenylboronic acid to the Pd nanoparticle surface. One major characteristic vibrational mode of the phenylboronic acid that is greatly shifted upon the addition of the nanoparticles and sodium acetate is the B–O vibration. This suggests a mode of binding that involves the B–O–Pd structure. The FTIR studies provide proof of the mode of binding that occurs in the nanoparticle surface for the first time and also confirms the mechanism of the Suzuki reaction that we proposed previously.

Experimental Section

Synthesis of PVP–Pd Nanoparticles. The PVP–Pd nanoparticles are synthesized as described previously^{18,20–23} by the reduction of the Pd ions with ethanol. The palladium precursor

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TABLE 1: Frequencies of Different Vibration Modes in Phenylboronic Acid (PA), PA + Sodium Acetate (SA), PVP–Pd NPs + PA, and PVP–Pd NPs + PA + SA

vibration mode	frequency (cm ⁻¹)			
	in PA	in PA + SA	in PVP–Pd NPs + PA	in PVP–Pd NPs + PA + SA
B–O stretching	1348	1348	1349	1376
B–C stretching	1087	1087	1087	1086
B–C stretching	1102	1103	1103	1118
		1112		
out-of-plane phenyl ring deformation	700	698	700	706
shoulder next to out-of-plane phenyl ring deformation	688	687	687	681

solution (H₂PdCl₄) is 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 PVP, and 4 drops of 1 M HCl is heated. When the solution begins to reflux, 14 mL of ethanol is added. The solution is then refluxed for 3 h and a dark brown colloidal Pd solution is formed. A drop of the solution is spotted onto Formvar stabilized copper TEM grids and JEOL 100C TEM is used to characterize the size of the nanoparticles. For the FTIR studies, it is necessary to have concentrated nanoparticle solutions. As a result, the nanoparticles are rotovaped to concentrate the nanoparticle solution from 50 to 2 mL.

FTIR Studies of Dried Films. Films of sodium acetate (SA), phenylboronic acid (PA), SA + PA, PVP–Pd nanoparticles, PVP–Pd nanoparticles + PA, and PVP–Pd nanoparticles + SA + PA are prepared and dried in the oven for 30 min to investigate how the phenylboronic acid interacts with the palladium nanoparticle surface. In addition, films of iodobenzene (I), SA + I, and PVP–Pd nanoparticles + SA + I are also prepared to investigate how the iodobenzene interacts with the palladium nanoparticle surface. FTIR spectra of the films are recorded in the range 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹ using the Nicolet 860 Magna-IR with DTGS detector and zinc selenide windows.

Results and Discussion

FTIR Studies on Phenylboronic Acid. FTIR studies are conducted to find out if there are shifts in the characteristic vibrational modes associated with phenylboronic acid upon exposure to sodium acetate and the PVP–Pd nanoparticles. Table 1 summarizes the important vibrational modes and the frequencies observed in phenylboronic acid, phenylboronic acid + sodium acetate, phenylboronic acid + PVP–Pd nanoparticles, and phenylboronic acid + sodium acetate + PVP–Pd nanoparticles.

Figure 1a shows the FTIR spectra in the region of 1800–1200 cm⁻¹ obtained from dried films of sodium acetate (SA), phenylboronic acid (PA), SA + PA, PVP–Pd nanoparticles, PVP–Pd nanoparticles + PA, and PVP–Pd nanoparticles + SA + PA. Band assignments for PA are obtained from a previous infrared spectral study in the literature.²⁴ It can be seen that the B–O stretching band shifts from 1348 cm⁻¹ in the presence of PA to 1376 cm⁻¹ when the nanoparticles are added to PA + SA in solution before drying. In the spectra of PA + SA without the presence of PVP–Pd nanoparticles, it is observed that the B–O stretching band occurs at 1348 cm⁻¹, and this suggests that deprotonation does not occur in the film due to the loss of water upon drying and thus does not result in a shift in the B–O stretching mode. The large shift in the B–O stretching frequency that occurs when the PVP–Pd nanoparticles are added to PA and SA prior to evaporation of the solution is an important indication that the phenylboronate anion

(formed from PA due to the presence of SA) binds to the nanoparticle surface through the B–O⁻ group. In the case of the PVP–Pd nanoparticles + PA, it is observed that the B–O stretching mode occurs at 1349 cm⁻¹, suggesting that the addition of PA to the palladium nanoparticles prior to drying the solution into a film does not result in it binding to the

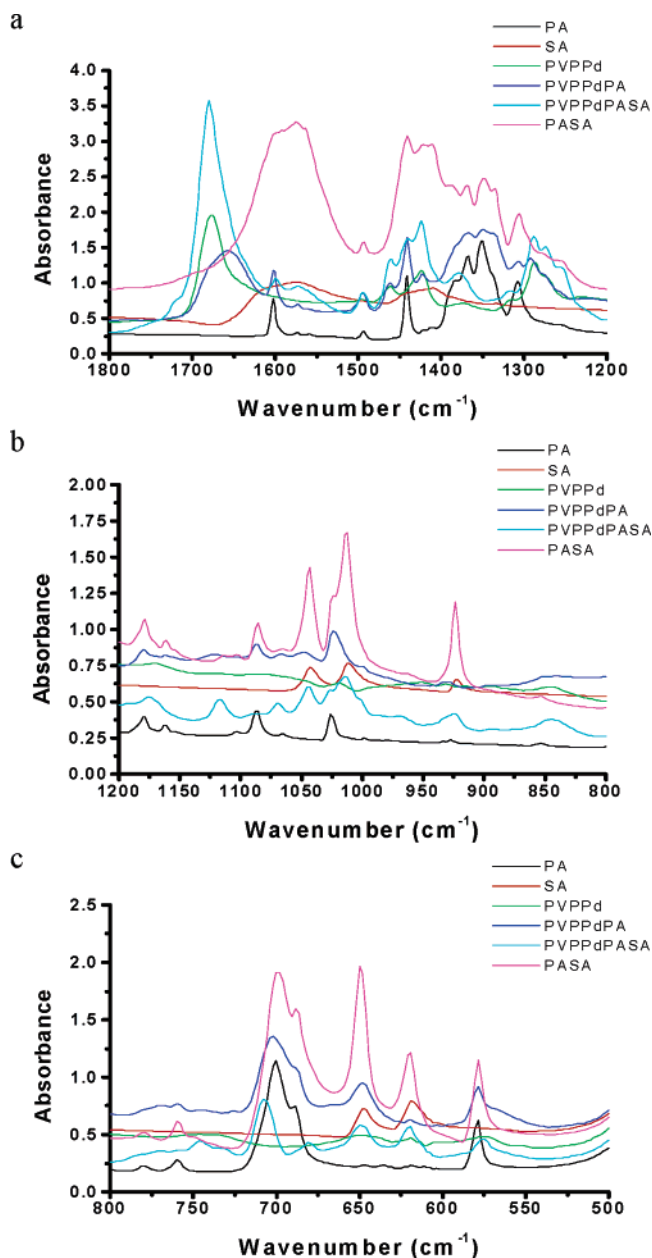
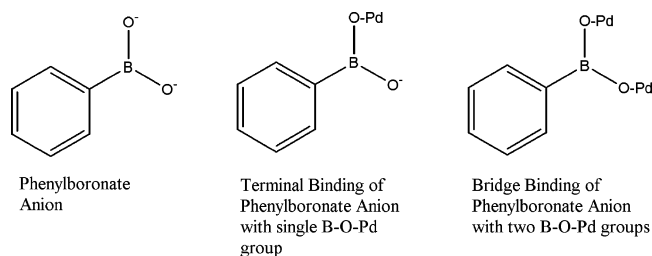


Figure 1. FTIR spectra of PA, SA, SA + PA, PVP–Pd nanoparticles, PVP–Pd nanoparticles + PA, and PVP–Pd nanoparticles + SA + PA in the 1800–1200 cm⁻¹ region (a), the 1200–800 cm⁻¹ region (b), and the 800–500 cm⁻¹ region (c).

SCHEME 1: Illustration of Phenylboronate Anion and the Two Possibilities of Binding to the Palladium Nanoparticle Surface: through One B–O– Group or through Both B–O– Groups



palladium nanoparticle surface. This provides additional evidence that the phenylboronic acid must be in the form of phenylboronate anion by the presence of sodium acetate to bind to the palladium nanoparticle surface.

An interesting question involves determining how the boronate group (BO_2^-) of phenylboronate anion binds to the nanoparticle surface and Scheme 1 illustrates two possible binding modes. The phenylboronate anion can bind to the palladium nanoparticle surface through a single bond between its B–O[−] group and the Pd atom (terminal binding) or through both of its B–O[−] groups to two Pd atoms (bridged binding). Terminal binding would result in bands existing in both the 1348 cm^{-1} and the 1376 cm^{-1} regions because one B–O[−] group would be bound to the palladium nanoparticles while the other B–O[−] group would be free. The blue shift in the B–O stretching mode that occurs when the nanoparticles are exposed to PA + SA is relatively large ($\sim 28 \text{ cm}^{-1}$). Because there is no band in the 1348 cm^{-1} region and only one shifted band is observed at 1376 cm^{-1} , the phenylboronate anion most likely binds through a bridge involving two B–O–Pd bonds.

Figure 1b shows the FTIR spectra in the region of 1200–800 cm^{-1} for the different systems. In the case of PA and PA + SA, the B–C stretching mode occurs at 1087 cm^{-1} . This suggests that deprotonation of phenylboronic acid does not occur in a film made by adding SA and then drying the solution due to the loss of water that occurs during the evaporation process. When the PVP–Pd nanoparticles are added to PA + SA prior to drying the solution into a film, it is observed that the B–C stretching mode is very weak. In the case where the PVP–Pd nanoparticles are added to PA, it is also observed that the B–C stretching mode occurs at 1086 cm^{-1} . It is also observed that the band at 1102 cm^{-1} in PA and 1103 cm^{-1} in PA + SA is shifted and enhanced when the nanoparticles are added to PA + SA before drying and appears at 1118 cm^{-1} . In the literature,^{24,25} it was shown that the infrared spectra of phenylboronic anhydride has two B–C stretching bands (doublet), one at 1087 cm^{-1} and the other at 1104 cm^{-1} . It is possible that the weak band we observe at 1102 cm^{-1} for PA by itself and 1103 cm^{-1} for PA + SA is also due to the B–C stretching mode. In the case of PA + SA, it is observed that there is also a band at 1112 cm^{-1} , which could be due to the deprotonation of the phenylboronic acid causing a shift in the B–C stretching mode. In this case, it can also be seen that the shift in the B–C stretching mode is incomplete. When the nanoparticles are added to PA + SA in solution before evaporation, the shift in the B–C stretching mode is complete with a band at 1118 cm^{-1} being present and the band at 1103 cm^{-1} being absent. The complete shift in the B–C stretching mode observed when the nanoparticles are added to PA + SA suggests that the phenylboronate anion binds to the nanoparticle surface. In the case when the nanoparticles are added to PA prior to drying the solution into

a film, there is no shift in the B–C stretching mode because it occurs at 1103 cm^{-1} . This provides additional evidence that the phenylboronate anion (formed by the presence of sodium acetate) binds to the nanoparticle surface in solution prior to drying.

Figure 1c shows the FTIR spectra in the region of 800–500 cm^{-1} . When comparing spectra obtained when the PVP–Pd nanoparticles are mixed with PA + SA to the spectra obtained of PA by itself, it is observed that there is a shift in the out-of-plane phenyl C–C ring deformation band and its shoulder from 700 and 688 cm^{-1} to 706 and 681 cm^{-1} , respectively. The shoulder has not been reported in the literature. In the spectra of PA + SA without the presence of the PVP–Pd nanoparticles, the out-of-plane phenyl C–C ring deformation band and its shoulder occur at 698 and 687 cm^{-1} . In this case, it can be seen that the ring deformation band and its shoulder occur at frequencies similar to those observed in PA. This might be explained by the fact that the OH^- is un-ionized in both cases due to the loss of water that occurs in the process of preparing dried films. This means that deprotonation of the phenylboronic acid might not occur in the films of the two samples and thus does not result in a shift in the out-of-plane phenyl C–C ring deformation band and its shoulder. In the case of PVP–Pd NPs + PA + SA, it is observed that there is a shift in the ring deformation band to higher frequencies. The shifts in the out-of-plane phenyl C–C ring deformation vibration and its shoulder could be due to the phenylboronate anion (formed from PA by the presence of SA) binding to the palladium nanoparticle surface. In the structure of the Ph-B-O-Pd , one would expect that the phenyl deformation would be different from that for the Ph-B-OH , which is present in a film made from drying a solution of PA and PA + SA. In the case of Ph-B-OH , the out-of-plane ring deformation can occur much more easily and freely than in the case of Ph-B-O-Pd , where the presence of the heavy nanoparticles makes the Ph-B bond stiffer. As a result, when the heavy phenylboronic acid is bound to the nanoparticle surface, the out-of-plane phenyl C–C ring deformation process does not occur as readily and is more difficult to do so. This would result in this vibrational mode occurring at a higher frequency, which correlates with our observation that the frequency shifts from 700 to 706 cm^{-1} . When the PVP–Pd nanoparticles are added to PA in solution before drying, it is observed that the ring deformation band occurs at 700 cm^{-1} and its shoulder occurs at 687 cm^{-1} , which is similar to that observed in PA. This shows that the phenylboronic acid does not bind to the nanoparticle surface when it is not in the presence of sodium acetate before drying. This also provides additional proof that the phenylboronate anion formed in the presence of sodium acetate binds to the nanoparticle surface.

FTIR Studies on Films of Iodobenzene and the Pd Nanoparticles. Figure 2a–c show FTIR spectra in the regions 1800–1200, 1200–800, and 800–500 cm^{-1} , respectively, for the following conditions involving iodobenzene: iodobenzene (I), sodium acetate (SA), I + SA, PVP–Pd NPs, and PVP–Pd NPs + I + SA. The band assignments for iodobenzene were obtained from infrared spectral studies conducted in the literature.²⁶ It can be seen that there are no shifts in the bands that are associated with characteristic vibrational modes of iodobenzene. There are no shifts in the four C–C stretching modes at 1571, 1471, 1438, and 1321 cm^{-1} . There are no shifts in the C–I stretching mode at 1059 cm^{-1} and the CCH in-plane bending mode at 1014 cm^{-1} . There are also no shifts in the ring breathing mode at 997 cm^{-1} or in the two CH out-of-

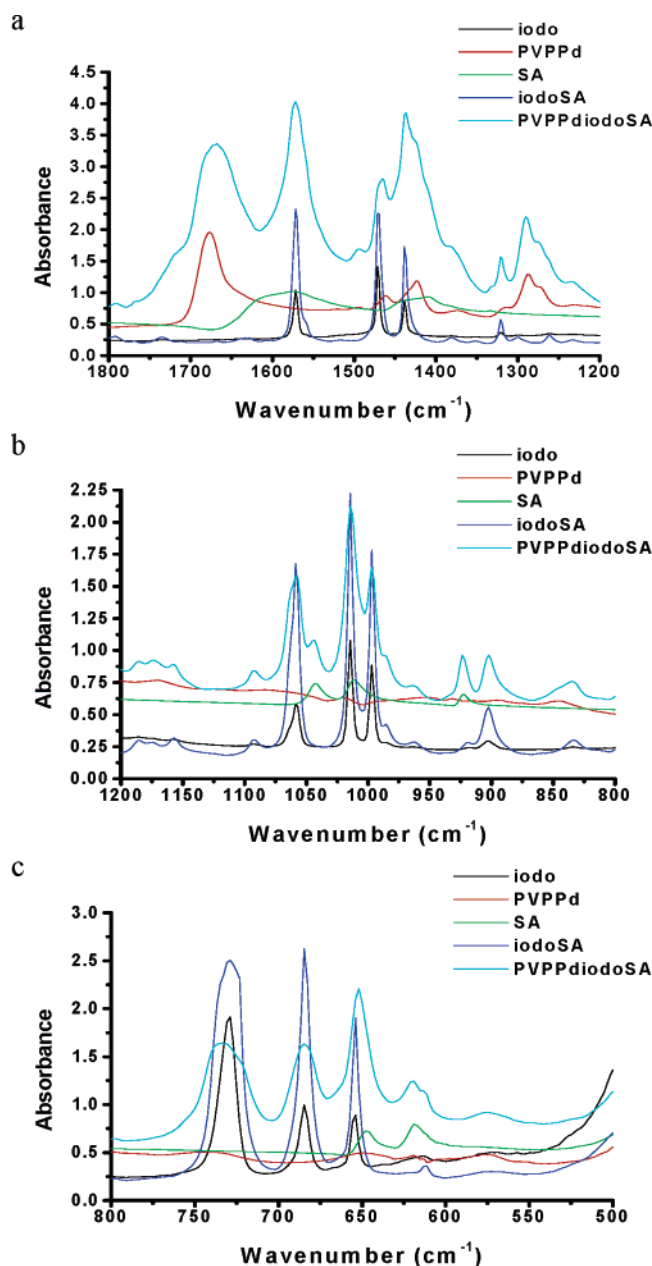


Figure 2. FTIR spectra of I, SA, SA + I, PVP-Pd nanoparticles, and PVP-Pd nanoparticles + SA + I in the 1800–1200 cm^{-1} region (a), the 1200–800 cm^{-1} region (b), and the 800–500 cm^{-1} region (c).

plane bending modes at 903 and 729 cm^{-1} . Finally, there is also no shift in the CCC nonplanar twist mode at 685 cm^{-1} . Because there are no shifts in the bands associated with the characteristic vibrational modes of iodobenzene, it is concluded that iodobenzene does not have specific bonding to the surface of the palladium nanoparticles.

Mechanism of the Suzuki Reaction. The results obtained from the FTIR studies on the interaction of phenylboronic acid and iodobenzene to the palladium nanoparticle surface show that our proposed mechanism of the Suzuki reaction reported previously^{18,19} is correct. The phenylboronate anion does indeed bind to the nanoparticle surface through both B–O[−] groups. Because the iodobenzene does not bind to the nanoparticle surface, the mechanism must involve the phenylboronic acid

binding to the nanoparticle surface in the form of phenylboronate anion followed by its reaction with the iodobenzene present in solution.

Conclusions

FTIR studies have shown that phenylboronate anion (which is formed from PA in the presence of SA) does indeed bind to the Pd nanoparticle surface. Shifts in the B–O stretching mode, the B–C stretching mode, and the out-of-plane phenyl C–C ring deformation band and its shoulder associated with phenylboronic acid are observed when the PVP–Pd nanoparticles are exposed to PA + SA. When the PVP–Pd nanoparticles are added to PA without the presence of SA, shifts in the characteristic bands associated with PA are not observed, suggesting that in this case, the phenylboronic acid must be in the protonated form and that the binding process involves its conjugate base (phenylboronate anion). The phenylboronate anion binds to the nanoparticle through a B–O–Pd bridge. It has also been shown that iodobenzene does not have specific binding to the nanoparticle surface because no shifts in the characteristic vibrational modes associated with iodobenzene are observed upon exposure to the nanoparticles. These results provide support to the surface catalytic mechanism of the Suzuki reaction that involves the phenylboronate anion binding to the nanoparticle surface and then reacting with the iodobenzene present in solution.

Acknowledgment. We thank the NSF Chemistry section (#0240380) for funding.

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