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FTIR Study of the Adsorption of the Capping Material to Different Platinum Nanoparticle Shapes

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FTIR spectroscopy has been used to study the binding geometry of polyacrylate capping material on cubic and tetrahedral platinum nanoparticles. It is proposed that the capping material forms an ester-like linkage to the Pt surface on the tetrahedral shapes through the hydroxyl oxygen atom of the carboxylic acid moiety of the polyacrylate (linear adsorption configuration). On the cubic particle the adsorption is through both of the carboxylic oxygen atoms (bridge adsorption configuration). These shaped nanoparticles are synthesized by changing the starting ratio of the capping material to that of the Pt salt. The results are discussed in terms of the effect of changing the concentration of the polyacrylate capping material on the mode of bonding to the surface. This might be a factor in determining the final shape formed.

Introduction

Many studies on colloidal nanoparticles have focused on the control of nanoparticle sizes and their growth kinetics and have correlated nanoparticle size to their catalytic activity[1,2] without taking into account the effect of the capping material on the surface of the nanoparticle. Previous work by this group obtained different shapes of platinum nanoparticles by changing the ratio of the concentration of the capping polymer material to that of the platinum cations used in the reductive synthesis of colloidal nanoparticles in solution at room temperature.[3] It is not known, however, how the difference in the concentration of the capping material affects the surface of the nanoparticles and, in turn, their catalytic activity. The factors controlling the shape during the growth process have been reported[4] and it was found that the polyacrylate concentration was key in this process by acting as a buffering agent during the growth period. However, it is unknown how this concentration difference affects the surface adsorption or if the polyacrylate adsorption is the same in both cases. The final arrangement of the capping material on the surface of the Pt particles has not been studied in detail until now.

Before any surface-catalyzed reactions can be studied, it is important to understand the surface of the nanoparticles in question and how a ligand may adsorb onto these different surfaces. FTIR spectroscopy can reveal information about the local molecular environment of the adsorbed polymer. It can also be an extremely powerful tool in helping to understand how the same polymer can form two different shapes (or surfaces). The polyacrylate is made up of a single-bond carbon backbone with carboxylic acid groups present on every other carbon. There is an average of approximately 20 units in the polymer, although it is not known how many of these units actually participate in the capping process (which can make the interpretation of the FTIR spectra difficult). The pH of the solution is very important in the synthesis of the final shape distribution since the polymer can act as a buffer at high concentrations during the growth process,[4] which will change the form of the polymer. Using the known ratios,[3] different shaped nanoparticles can be made only when the starting pH is 7. At lower pH (∼4), the dominant shape is truncated octrahedral (this is an intermediate shape with 6 {100} and 8 {111) facets), while at higher pH (∼9) the dominant shape is cubic for both the 1:1 and the 1:5 ratio samples.[5] Therefore, it is necessary to distinguish the carboxylate salt form and neutral carboxylic acid forms of polyacrylate. The COO^- group would have a carboxylate asymmetric ($COO^-_{(a)}$) and a symmetric stretch ($COO^-_{(s)}$) and be found in the FTIR spectrum at approximately 1560 and 1400 cm^{-1}, respectively. The acid form (COOH) has a characteristic C═O stretching vibration at ∼1750 cm^{-1}, depending on the nearest groups and degree of hydrogen bonding. Extensive hydrogen bonding can lower the frequency to around 1700 cm^{-1}.[6]

The carbonyl stretching absorption band is extremely sensitive to the surrounding structure and would be a very good monitor of changes occurring in the capping material environment.[6,7] Therefore, the carboxylic acid group itself was monitored for shifts in the carbonyl or carboxylate bands for evidence of polyacrylate groups bonding to the surface and capping the nanoparticle. The frequency shifts observed from the polyacrylate would relate to the transfer of electron density to form the new Pt−O bond in the presence of the platinum nanoparticle. Since the d-band of platinum is close to the Fermi energy level,[8] the electron density to form the new bonds will come from the carboxylic group, not from the platinum. Hence, the shifts in the carbonyl region of the spectrum will be examined for the capping material alone and for the samples where it is used to synthesize the platinum nanoparticles. These shifts will then be the clues to interpret how the adsorption occurs.

FTIR has already been used to study various small molecules on the different Pt surfaces,[9−11] but not how the capping material interacts with the surface or the different shapes of a nanoparticle. The present study will lead to a better appreciation of this adsorption.

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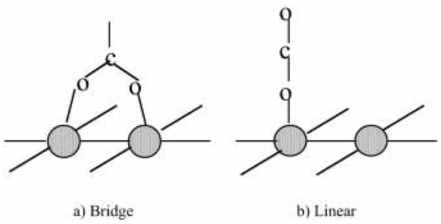
SCHEME 1. Schematic Representation of the CO_2 Configurations on the Pt Surface, Adapted from Ref 15



Structure (a) is the bridge configuration bound through two oxygen atoms to two Pt atoms, which is the most stable configuration overall for both (100) and (111) surfaces, while (b) shows the linear configuration, the most stable configuration involving only one Pt surface atom.

Experimental Section

Pt nanoparticles were prepared by using the technique of Rampino and Nord[12] and Henglein et al.[13] A 1:1 Pt/polyacrylate ratio was used for the cubic shapes and a 1:5 ratio was used to obtain the tetrahedral shapes, and the initial pH was adjusted to 7 in both cases.[3] The poly(acrylic acid), sodium salt compound (MW ∼2100) was obtained from Aldrich. Two hundred scans of the spectra were collected at a resolution of 4.0 cm^{-1} in the spectral region between 4000 and 400 cm^{-1} using a Nicolet Magna-IR 750 spectrometer equipped with a DTGS detector, potassium bromide beam splitter, and a globar source.

The films were produced by centrifuging the nanoparticle samples to concentrate the solutions from the initial 250 mL to less than 2 mL. The resulting black solution was washed several times with water to remove any excess capping material and then applied to a ZnSe window and allowed to dry. The dried films were then placed in an oven (<90 °C) overnight to remove any excess water. This temperature did not affect the nanoparticle integrity. Temperature studies were previously published on these shaped nanoparticles[14] to verify the temperatures at which the capping material would be removed and when the particle shape would be affected, and the oven temperature was kept well below those levels.

The pH of the 0.1 M polyacrylate solutions without nanoparticles was adjusted by adding 0.1 M HCl or KOH into the sample. The samples were then dried as previously described.

Results and Discussion

The possible geometries of CO_2 adsorbate on the (111) and (100) Pt cluster surfaces were calculated from a modified version of the extended Hückel molecular orbital method by Zinola, et al.[15] Although the CO_2 coordination is not exactly the same as the carboxylate group of the polyacrylate, the coordination of the CO_2 molecule with the Pt cluster surface will be used to model the carboxylic acid adsorption for this work. According to these calculations, the most stable type of CO_2 adsorption on the (100) and (111) surfaces is through the coordination of two atoms of the molecule to give a bridge configuration (this is referred to as the formate configuration in ref 15), which is shown in Scheme 1. The most stable coordination for one adsorbate atom was through the linear coordination type. The stability of these coordination types and geometries will be used to help interpret the FTIR data obtained. It is important to note that the trend of the configurations was the same for both faces.

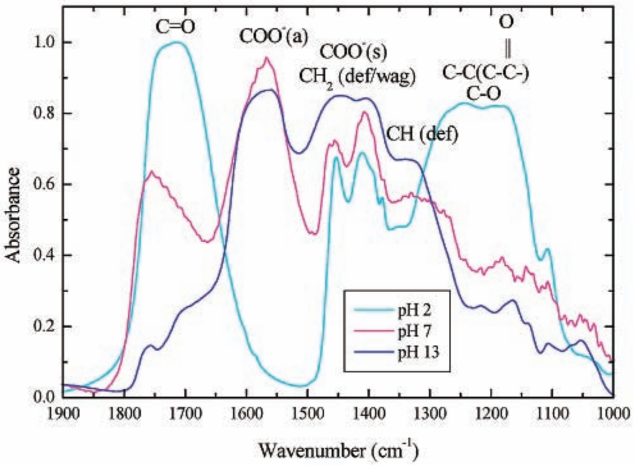


Figure 1. FTIR spectra of polyacrylate film of pH 2, 7, and 13 from 1900 to 1000 cm^{-1}.

Figure 1 shows the spectra of a 0.1 M polyacrylate solution at pH 2, 7, and 13 in the range of 1900−1000 cm^{-1} to best examine the carbonyl region. The spectra have been normalized to allow for easier analysis. At pH 2 the polymer is in its neutral form, while at pH 13 the conversion to the salt form has occurred. These two spectra will give the absolute shifts for the polymer in both its forms. Table 1 is a summary of the $C{=}O/COO^-$ of all the spectra in this work, including the pH range of 2−13 of the polyacrylate solution not shown. The trace at pH 7 is included in Figure 1 since this is the approximate pH of the platinum solutions before they are dried and made into films. There are a few observations that can be made from these figures. First, it is evident that the $C{=}O$ band intensity decreases as the pH increases. This is consistent with the chemical transformation of changing the COOH group into a COO^- group as the pH increases. Meanwhile, the $COO^-_{(a)}$ band at 1560 cm^{-1} is absent at pH 2 and increases in intensity as the pH increases. This observation is consistent with the fact that at pH 2, the acid form COOH is present, while at pH 13 the salt form (COO^-) is present. It should be mentioned that the region between 1350 and 1480 cm^{-1} results from backbone vibrations (CH_2 deformation and wagging) overlapping with the $COO^-_{(s)}$ vibration. The asymmetric and symmetric stretch of the carboxylate peaks at pH 13 would be at their maximum intensity since almost all the polymer is in the salt form. There is still some of the neutral version of the carboxylic acid, which accounts for the weak carbonyl band present and the hydrogen bonding observed. The other bands located in this region due to the carbon backbone, are not affected by the pH and can distort the intensity of the $COO^-_{(s)}$ band and make the assignments difficult. In particular, the CH_2 deformation and wag vibrations are located at approximately 1452 and 1409 cm^{-1}, respectively, for pH 2, while the CH deformation is evident at 1336 cm^{-1}. At higher pH, the overlap of the CH_2 wag and the $COO^-_{(s)}$ would not allow for the individual bands to be assigned easily. The new broad band in the pH 2 trace at 1242 and 1188 cm^{-1} is attributed to the bending and stretching of the carbonyl−carbon backbone linkage.

Lowering the pH increases the concentration of the neutral carboxylic acid, which in turn increases the amount of hydroxyl moiety present and, subsequently, the extent of hydrogen bonding in the film. This in turn shifts the carbonyl peak to lower wavenumbers and increases the intensity of the OH stretch.[7] The OH stretch region (not shown) demonstrates extensive hydrogen bonding at pH 2 and the intensity decreases with increasing pH. At a higher pH, the salt form is the most dominant. Therefore, the hydrogen bonding would not be as prevalent as in the lower pH sample. In addition, a shoulder at 2500 cm^{-1} (not shown) develops due to overtones and a

TABLE 1: Comparison of the Carbonyl and Carboxylate Stretching Frequencies in All the Samples in This Work (frequencies in cm^{-1})

sample film	C=O	COO$^-$ (asymmetric)	COO$^-$ (symmetric)[a]
polyacrylate	1759	1560	1444
pH 13	(weak)		
pH 11	1747	1583/1559 (doublet)	1406
	(medium)	(strong)	(strong)
pH 9	1759	1594	1408
	(medium)	(medium)	(medium)
pH 7	1755	1567	1407
	(medium)	(strong)	(strong)
pH 4	1716	1549	1409
	(strong)	(medium)	(medium)
pH 2	1714	N/A	N/A
	(strong)		
1:5 ratio tetrahedra	1738	1573	1391
(pH 7)	(medium)	(strong)	(medium)
1:1 ratio cubes	1701	1616	1370/1398 (doublet)
(pH 7)	(weak)	(weak)	(strong)
1:5 ratio tetrahedra	1742	1567	1401
(pH 9)	(weak)	(strong)	(medium)
1:1 ratio cubes	1696	1569	1401
(pH 9)	(weak)	(strong)	(medium)

[a] The CH_2 wag vibration overlaps with the $COO^-_{(s)}$.

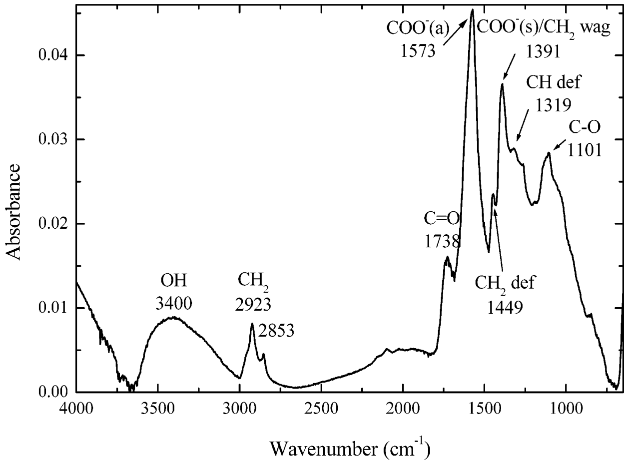


Figure 2. FTIR spectrum of a film of 1:5 ratio of platinum nanoparticles.

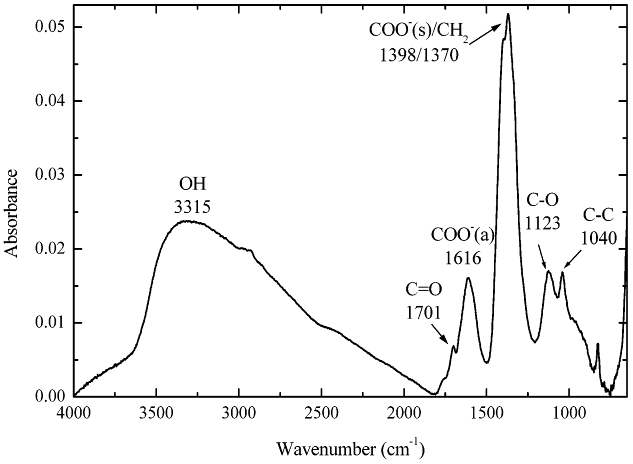


Figure 3. FTIR spectrum of a film of 1:1 ratio of platinum nanoparticles.

combination of absorptions gaining intensity from the interacting CO stretch and OH deformation vibrations, a further indication of the high degree of hydrogen bonding occurring in the pH 2 sample.

Figure 2 shows an FTIR spectrum of a 1:5 ratio film of platinum nanoparticles. This sample was washed to remove the excess polyacrylate during the sample film preparation. There is a distinct similarity between this spectrum and that of pH 7 for the polyacrylate spectrum from Figure 1. The carbonyl stretch is now shifted to 1738 cm^{-1}, while the $COO^-_{(a)}$ is now at 1573 cm^{-1} and the $COO^-_{(s)}$ (as well as the CH_2 wag) is at 1391 cm^{-1}. These factors indicate an abundance of the polymer in the salt form. The significant (~20 cm^{-1}) blue shift in the C=O band is attributed to the bonding of the hydroxyl oxygen to the platinum surface. The C=O bond would thus have less electron density as the new bond is formed, and this weakening would result in the apparent frequency shift. This binding forms an ester-like linkage between the capping material and the nanoparticle. The coordination would most likely be linear, based on the calculations of ref 15. The intensity of the C=O band has greatly decreased from that of the polyacrylate by itself, further verifying the formation of this bond. The carboxylate stretch is attributed to the noncapping units of the polymer.

The spectrum of a 1:1 ratio film of platinum nanoparticles at pH 7 is shown in Figure 3. This spectrum is quite different from those shown previously. The OH stretch region is extremely broad and much more intense than the 1:5 ratio sample, which is typical of hydrogen bonding.[7] The carbonyl region shows a slight shoulder at 1760 cm^{-1}, but the main peak has shifted to 1701 cm^{-1}, also typical for hydrogen bonding with the carbonyl. The slight shoulder at 1760 cm^{-1} may indicate some of the carbonyl not participating in the hydrogen bonding or capping. Unlike the previous spectrum, the carboxylate region has undergone a drastic change. Though the $COO^-_{(a)}$ is generally a strong band with slightly greater intensity than the symmetric stretch, as evident in the previous spectra, it is seen here at 1616 cm^{-1} with a much reduced intensity. There is now a doublet at 1398 and 1370 cm^{-1}, which makes the $COO^-_{(s)}$ difficult to assign since this also includes the CH_2 deformation and wag. Therefore, since the C=O and carboxylate bands are not evident, it is postulated that both of the carboxylic oxygens are bonded to the platinum nanoparticle surface. From the calculations in ref 15, this is possibly through bridge coordination with two Pt atoms. By having both of the oxygens capping the nanoparticle, two new bonds are formed between surface platinum atoms and the carboxylic functionality. The

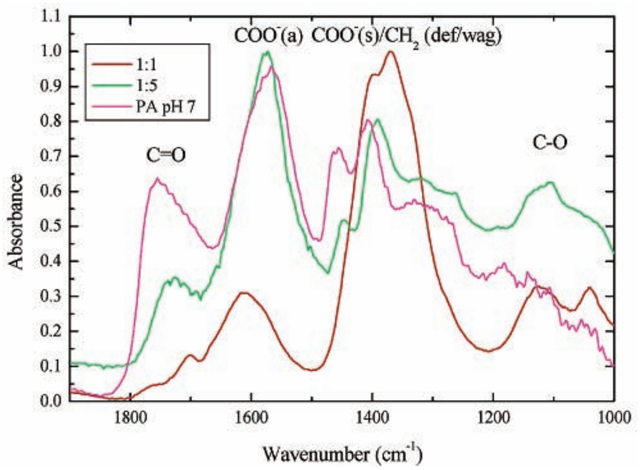


Figure 4. Comparison of the carbonyl region (1900−1000 cm^{-1}) of the FTIR spectra of the polyacrylate film at pH 7, 1:5, and 1:1 ratio films of Figures 2, 3, and 4.

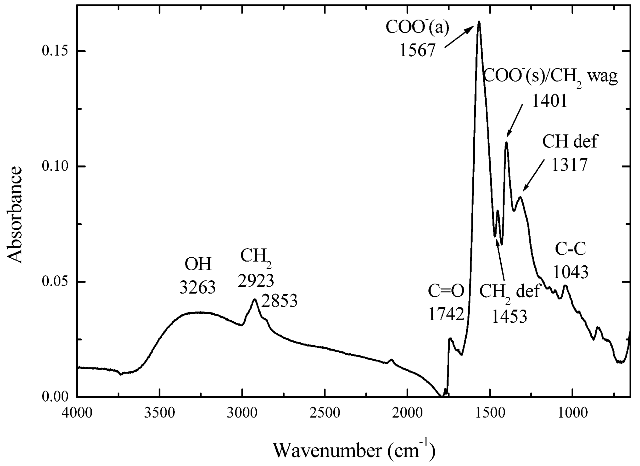


Figure 5. FTIR spectra of a 1:5 ratio of platinum nanoparticles at pH 9.

new Pt−O bond makes the C−O bond stiffer with higher frequency results, which may account for the higher frequency shift to 1616 cm^{-1}.

Figure 4 shows the carbonyl region from 1900 to 1000 cm^{-1} for the polyacrylate film at pH 7 and the 1:5 and 1:1 ratio films. They are compared here to further emphasize the shifts in the carbonyl and carboxylate bands. It is obvious looking at this figure that the polyacrylate film and the 1:5 ratio film are similar, but the 1:1 ratio film is very different from the other two.

There are two possible explanations for the difference in the adsorption of the polyacrylate on the different samples. The difference can be due to the different Pt faces of the nanoparticles in the films or the polyacrylate concentration. The question as to whether it is the polyacrylate concentration or the Pt surface is causing the difference in the capping material adsorption is answered by examining the next set of data. Cubic nanoparticles were synthesized at pH 9 in both the 1:1 and the 1:5 ratio samples. If the polyacrylate concentration determined the type of bonding with the surface, then cubic nanoparticles in the 1:5 ratio sample, although a different shape, should have a spectrum similar to that of the tetrahedral particles of the 1:5 ratio at pH 7. If the platinum surface is important to the binding, the 1:1 ratio samples should be similar, despite the difference in the capping material form (neutral vs salt) at the different pH.

The spectrum of the 1:5 ratio at pH 9 of Figure 5 has a distinct similarity to that of the 1:5 ratio sample at pH 7 (Figure 3). There is again a band at 1740 cm^{-1}, although less intense, and the carboxylate bands are located at 1565 and 1402 cm^{-1} for the asymmetric and symmetric stretches, respectively. The OH stretch region is less intense than that of the pH 7 sample, which is consistent with the higher pH, and therefore less hydrogen bonding.

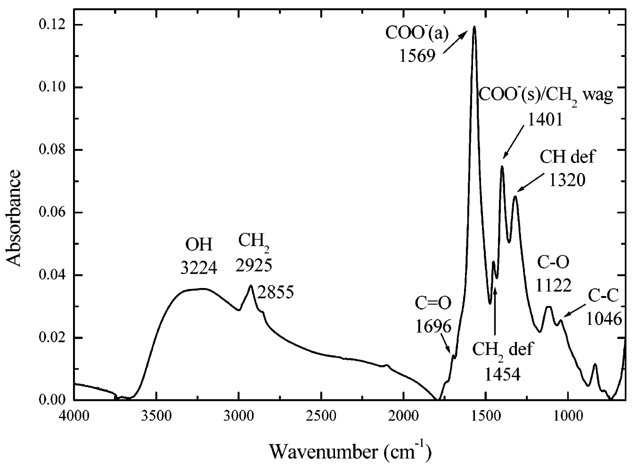


Figure 6. FTIR spectra of a 1:1 ratio of platinum nanoparticles at pH 9.

The FTIR spectrum of the 1:1 ratio pH 9 cube-shaped sample of Figure 6 again shows a similarity to the pH 7 sample. There is no peak in the carbonyl region, except for the weak band at 1696 cm^{-1}. The carboxylate stretching bands are located at 1569 and 1401 cm^{-1} for the asymmetric and symmetric stretches, respectively. At this high pH, these bands would be expected for the excess carboxylate groups that are not capping the particle surface.

Because the pH is higher in these samples, the carboxylate stretch would naturally be dominant. However, the C=O stretch is still evident in the 1:5 ratio pH 9 sample, leading to the conclusion that linear adsorption is occurring. The 1:1 ratio pH 9 sample shows very little C=O, similar to the bridge adsorption argument from the pH 7 sample. It is proposed that the binding of the capping material does not change at higher pH. From these spectra it can be concluded that the ester-like linkage of the 1:5 ratio samples is due to the high concentration of the polyacrylate capping material, independent of the particle shape or face. However, at lower polymer concentrations, the preferred binding is through both of the carboxylic oxygens. Therefore, if both of the oxygens can bind in the bridge coordination, then it will. Otherwise, if the polymer concentration is high, only one oxygen atom will form the linear bond due to the lack of space on the nanoparticle surface.

Conclusion

FTIR is a powerful tool for exploring the surface of nanoparticles. The concentration of the capping material plays an important role in how a molecule interacts with that surface. At high polymer concentration, it is proposed that linear coordination through one of the oxygen atoms of the carboxylic acid is achieved, regardless of the face of the nanoparticle. At lower concentrations of the polyacrylate capping material, a bridge coordination, where both of the carboxylic oxygen atoms adsorb to two Pt atoms on the surface, is thought to be more favorable. It is known that the shape formed of platinum nanocrystals depends on the polymer/metal cation concentration ratio, among other factors. Could the difference in binding of high and low polymer concentrations be a factor involved in the shape growth mechanism? It is obvious that more work has to be done in order to answer this question.

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