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Preparation and Characterization of Organosols of Monodispersed Nanoscale Palladium. Particle Size Effects in the Binding Geometry of Adsorbed Carbon Monoxide

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A series of poly(vinyl pyrrolidone) (PVP) stabilized palladium colloids was prepared by the reductive decomposition of solutions of palladium complexes in the presence of PVP. The resulting colloidal clusters had diameters of ca. 60, ca. 40, and ca. 25 Å (by TEM), with polydispersities of ca. 10%, and were shown by electron diffraction to be crystalline (fcc) palladium. Carbon monoxide adsorbed on the colloidal metal, both terminal and bridged CO being observed by solution infrared spectroscopy. A size dependency is observed for the bonding mode of CO, with the smallest particles giving the highest ratio of terminal CO to bridging CO and the largest particles showing only bridging CO.

Introduction

The properties of highly dispersed transition-metal aggregates are of great interest. From the fundamental perspective of the transition from bulk properties through the intermediate quantum-size effect domain to the properties of molecular clusters,[1] metal particles with diameters of 1–10 nm (nanoscale clusters) are a relatively accessible class of materials with potentially unique electronic properties. From a more practical perspective they offer the prospect of surface chemical and physical characteristics which derive from their electronic properties, and thus they are of considerable potential in both the new technology of advanced materials and more mature applications such as catalysis.[2] If size-dependent properties are to be observed and utilized, the control of particle size, morphology, and composition is of the greatest importance. From this perspective, and as part of our continuing work on polymer stabilized metal colloids,[3–6] we have sought reliable procedures for the preparation of nanoclusters of various transition metals with high dispersion and low polydispersity in the liquid phase and methods for the characterization of their structures and surface properties. Although it is a challenge to prepare and stabilize the smallest possible particles, a study of size-dependent properties, especially surface properties, requires that monodispersed particles in a range of sizes be available, preferably stabilized by the same polymer. In this paper we report the use of palladium complexes under mild reducing conditions and in the presence of poly(vinylpyrrolidone) as stabilizing agent in the preparation of solutions of palladium clusters with approximate mean particle diameters of 25, 40, and 60 Å, each with a polydispersity of ca. 10%. In establishing the chemical and physical properties of such metal particles we use methods drawn both from the study of solid-state phases and of molecular inorganic complexes. Thus 10–100-Å particles of metallic elements can be studied as *ultradispersed metals* by the applicable techniques of metallurgy, materials science and surface chemistry, or in solution as *inorganic macromolecules* by methods usually applied in molecular cluster chemistry and coordination chemistry. Accordingly we have characterized the palladium particles in this study by transmission electron microscopy and electron diffraction and also, after the addition of carbon monoxide as a surface probe molecule, by solution infrared spectroscopy. The IR spectra of CO adsorbed on palladium and platinum organosols,[5–7] and hydrosols,[8,9] and rhodium hydrosols[10] have been the subject of previous reports.

Throughout this report we will use the term *colloid* and *colloidal solution* to describe nanoscale metal aggregates stabilized by polymers in the liquid phase. It can be argued that the term *solution* can be legitimately applied only in the case of molecular or ionic solutes, and that *suspension* is more appropriate for the systems under study. Similarly, the term colloid might be considered more appropriate for particles larger than the aggregates we describe here (20–60 Å), which should be referred to as clusters. However, we

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Table I

precursor (% w/w on polymer)	polymer (MW)	prep conditions	size (Å)	structure
$Pd(OAc)_2$				
I 2%	PVP(40k)	MeOH, 65 °C, 2 h	60	fcc (electron diff)
$Pd(dba)_2$				
IIa 2%	PVP (40k)	H_2, 3 atm, 25 °C, 1 h	40	fcc (electron diff)
IIb 5%	PVP (40k)		40	fcc (electron diff)
IIc 8%	PVP (40k)		40	fcc (electron diff)
$Pd(dba)_2$				
III 3%	PVP (40k)	H_2, 1 atm, 25 °C, 1 h	25	fcc (electron diff)
$Pd(dba)_2$				
IVa 3%	PVP (10k)	CO, 1 atm, 25 °C, 1 min	20	amorph (electron diff)
IVb 3%	PVP(24k)			amorph (electron diff)
IVc 3%	PVP(40k)		20	amorph (electron diff)
IVd 3%	PVP(90k)		20	amorph (electron diff)

prefer to reserve the term "cluster" for polynuclear metal cluster compounds, and so we consciously use the term *colloid* to describe a dispersion of closely sized metal aggregates in a liquid. *Solution* seems an adequate description for a liquid dispersion of a metal in which the particles are too small to scatter light, are stabilized in the liquid by surface interactions with the solvent analogous to solvation in molecular solutions, and from which the dispersed particles do not spontaneously sediment over a period of several weeks.

Experimental Section

General Techniques. The colloid solutions for which we report the syntheses might be expected to exhibit some degree of air sensitivity. Without determining the degree to which this is a problem, we have adopted the general precautions, such as Schlenk techniques, which are common practice[11] in the synthesis of moderately air-sensitive compounds, such as molecular carbonyl clusters. Palladium acetate (Alfa) was used as purchased. Bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) was prepared by literature methods[12] from sodium tetrachloropalladate (Alfa) and dibenzylidene acetone (1,5-diphenyl-3-pentadienone) (Aldrich). This precursor complex is slightly air sensitive and was thus stored and handled under nitrogen. The general method employed in colloid synthesis involved the arrested precipitation of palladium metal from a solution of a molecular complex precursor in the presence of a polymer stabilizer. Metal complex concentrations in the reaction mixture were $(1-2) \times 10^{-2}$ M, and polymer (as monomer) to metal molar ratios of 10–30 were used. Poly(vinylpyrrolidone) (MW 10 000, 24 000, 40 000, 90 000, Aldrich) was used as purchased. Metal particles were characterized by transmission electron microscopy and selected area diffraction on a Phillips CM12 TEM and a Phillips EM 420 ST STEM, at 100 keV. Samples were prepared by placing a drop of the colloidal metal solution, appropriately diluted, onto a holey carbon-coated copper grid, placed on a disk of absorbent paper (Whatman filter disks were effective) to remove rapidly most of the solution. The remaining adhering film of solution was allowed to evaporate on the grid, leaving a polymer film thin enough to allow transmission of the electron beam. The images reported in this paper were obtained after dilution of the colloid solution, as prepared, by a factor of 10–20 to give well-separated metal particles in a film of appropriate thickness. Infrared spectra were recorded on a Perkin-Elmer 787 grating spectrophotometer using sealed solution cells from CaF_2 windows (path length 0.1–0.5 mm). Solutions for infrared analysis were prepared by evaporation of the as-prepared colloid solutions to dryness, dilution to a standard volume and filtration through a 0.2-μM Teflon Millipore filter. The infrared spectra of these solutions, which typically contained 10–20 mg/mL palladium, were recorded as a reference, and the solutions then exposed to a stream of carbon monoxide, saturated with solvent vapor. Subtraction of the reference from the spectrum of the carbonylated solution gave clean spectra of adsorbed CO, with absorbances in the range 0.02–0.10.

Poly(vinylpyrrolidone)-Stabilized Colloidal Palladium from Palladium Acetate, $Pd(OAc)_2$. Colloid I. Palladium acetate was dissolved in a solution of PVP in methanol (150 mL), with concentrations in the range described above and refluxed under nitrogen for 2 h. During this time the solution changed in color from yellow to brown. After filtration through 1.0- and 0.2-μM Teflon millipore filters, the solution was stored under nitrogen and showed no sign of precipitation after several weeks.

Poly(vinylpyrrolidone)-Stabilized Colloidal Palladium from Bis(dibenzylideneacetone)palladium, $Pd(dba)_2$. Colloids II–IV. To a solution of poly(vinylpyrrolidone) (PVP) in dichloromethane (10 mL) was added a solution of $Pd(dba)_2$ in the same solvent, with concentrations in the range described above. Hydrogen reduction was carried out at room temperature by stirring for 1 h under a slightly elevated pressure (3 atm) in a Fischer-Porter bottle. The solution turned from purple to brown, indicating reduction of the precursor to the colloidal metal state. Filtration as for I gave a brown solution (II). When a stream of hydrogen saturated with dichloromethane was passed at 1 atm through a similar solution of $Pd(dba)_2$ and PVP in dichloromethane, the length of time necessary for reduction to occur at room temperature varied from 30 min to several hours, giving a brown solution (III) which was filtered as before. Reaction of the same precursor solution with carbon monoxide at 1 atm resulted in an immediate darkening of the solution. Colloid formation (IV) was judged to be complete in a few seconds, although the CO stream was continued for 1 min before filtration.

No sign of sedimentation of any of the colloidal solutions II–IV was apparent over a period of several weeks.

Results and Discussion

Preparative Methods, Particle Sizes, and Structures (See Table I). This study required reproducible methods of preparing monodispersed colloidal palladium in various size ranges, and a survey of the literature revealed that colloidal palladium particles have been prepared in both the presence and absence of polymer stabilizers by several authors. Esumi et al. used the thermal decomposition of bis(acetylacetonato)palladium[13] and palladium acetate[14] in various solvents at temperatures above 115 °C. The colloidal solutions produced under these conditions, in the absence of a stabilizing polymer, contained particles with sizes which varied according to the solvent used, from ca. 80 to over 1000 Å, and the palladium particles had the bulk fcc structure. Hirai has prepared colloidal palladium with particle sizes generally smaller than those found by Esumi, by reduction of palladium chloride in aqueous methanol in the presence of poly(vinyl alcohol) or poly(vinylpyrrolidone)[15] and also in aqueous higher boiling alcohols and ethers.[16] In selecting a procedure for the preparation of one of the colloids in this study, we have used a variation on these methods to produce relatively large particles from palladium acetate by reduction in refluxing methanol (functioning as both solvent and reducing agent) in the presence of PVP. The colloid particles resulting from this preparation (I) have a mean diameter of 60 Å and are clearly well facetted as shown in Figure 1. Selected area electron diffraction shows that the particles are crystalline, with the fcc structure of metallic palladium. A detailed analysis of structural data from X-ray diffraction and EXAFS experiments (which confirm the electron diffraction results)

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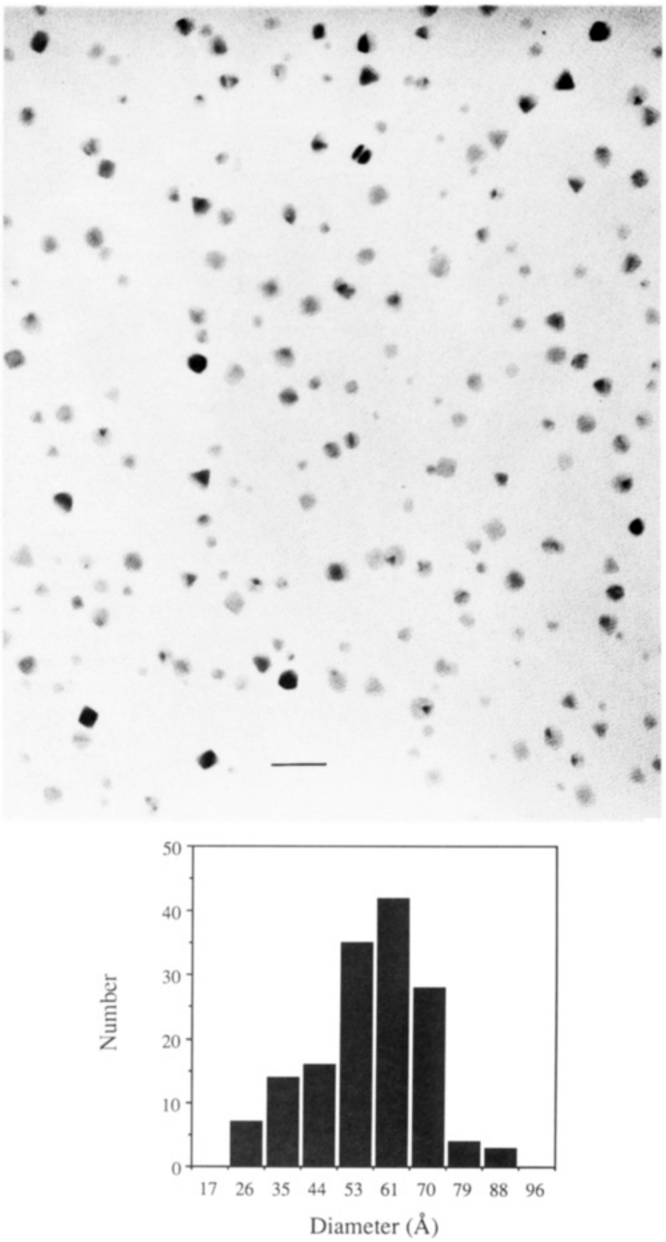

Figure 1. (a, top) Transmission electron micrograph of PVP stabilized palladium colloid I, prepared from $Pd(OAc)_2$ in refluxing methanol (scale bar = 180 Å). (b, bottom) Particle size distribution.

for this and the other palladium nanoparticles will be reported separately.

To prepare colloidal palladium in smaller size ranges, we have developed an alternative method. The zerovalent palladium complex bis(dibenzylideneacetone)palladium is known to react under mild conditions with either hydrogen or carbon monoxide with the formation of palladium metal.[12] The platinum analog of $Pd(dba)_2$ has been used as a source of highly dispersed supported platinum catalyst particles by reduction of $Pt(dba)_2$ by carbon monoxide in the presence of amorphous carbon.[17] We have found that when the reaction of $Pd(dba)_2$ in the presence of PVP (40 000 MW) with hydrogen is carried out at 3–4 atm and 25 °C, the formation of colloidal palladium takes place rapidly and yields well-crystallized fcc particles of ca. 40-Å diameter (II(a)) as shown in Figure 2. The particles shown appear to be either overlapping or slightly agglomerated, and no size distribution measurement was made. Even smaller particles were produced by the reduction of $Pd(dba)_2$ under 1 atm of hydrogen in dichloromethane in the presence of PVP at 25 °C. The reaction takes place over a period varying from 30 min to several hours, with an induction period of unpredictable duration.[18] The palladium colloid produced in this manner (III) contained particles of quite uniform size (25+/−3 Å) as shown in Figure 3. The fact that *smaller* particles are produced at the lower hydrogen pressure, i.e., by a slower reduction of the precursor, suggests that nucleation rate is not the predominant factor in determining ultimate particle size. The particles are not obviously crystalline in form—the particle images show no regular geometric features, unlike those of colloid I in Figure 1—but weak electron diffraction rings are observed by selected area diffraction on an area of the film which contains ca. 100 particles. This technique proved to be very sensitive to the imaging conditions, but by careful selection of imaging parameters, we were able reproducibly to observe diffraction rings for samples containing palladium particles in this size range indicative of the fee structure of bulk palladium. This is probably the lower limit of particle size for which crystallinity could be demonstrated by electron diffraction in these colloid systems, where polycrystallinity and twinning are common. It should be realized, however, that the observation of diffraction phenomena in this way gives evidence only of the *presence* of crystalline material in the sample and says nothing about the presence or relative amount of any

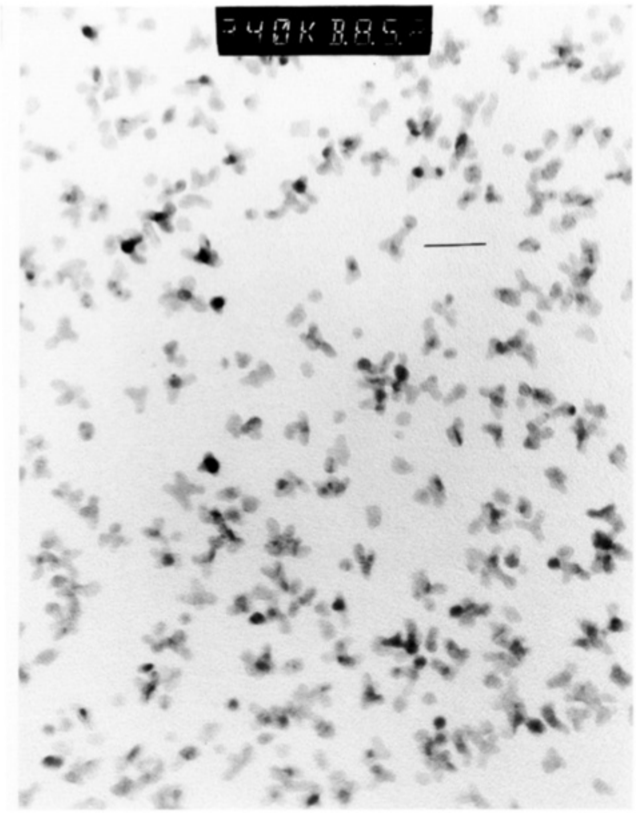

Figure 2. Transmission electron micrograph of PVP-stabilized palladium colloid II, prepared from $Pd(dba)_2$ in CH_2Cl_2 by hydrogen reduction (3 bar, 25 °C; scale bar = 180 Å).

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(18) This observation raised the possibility that once a small initial quantity of palladium metal had formed, an autocatalytic hydrogenation of the remaining $Pd(dba)_2$ occurred. However, addition of a small amount of a preformed colloidal palladium solution to the reaction mixture had no noticeable effect on the course of the reduction or its erratic kinetics.

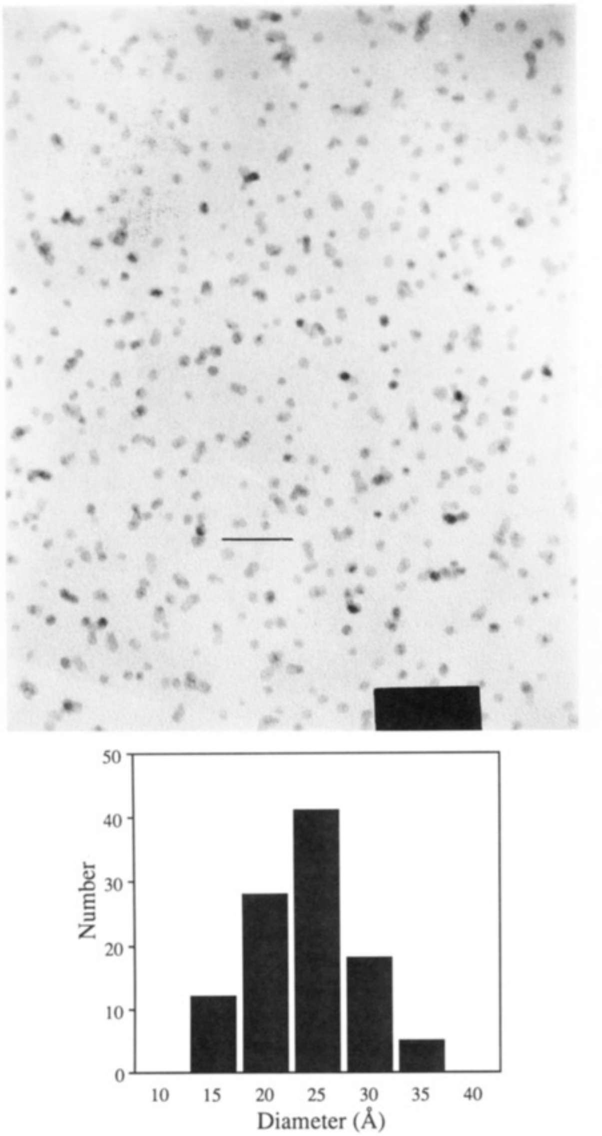

Figure 3. (a) Transmission electron micrograph of PVP-stabilized palladium colloid III, prepared from $Pd(dba)_2$ in CH_2Cl_2 by hydrogen reduction (1 bar, 25 °C; scale bar = 180 Å). (b) Particle size distribution.

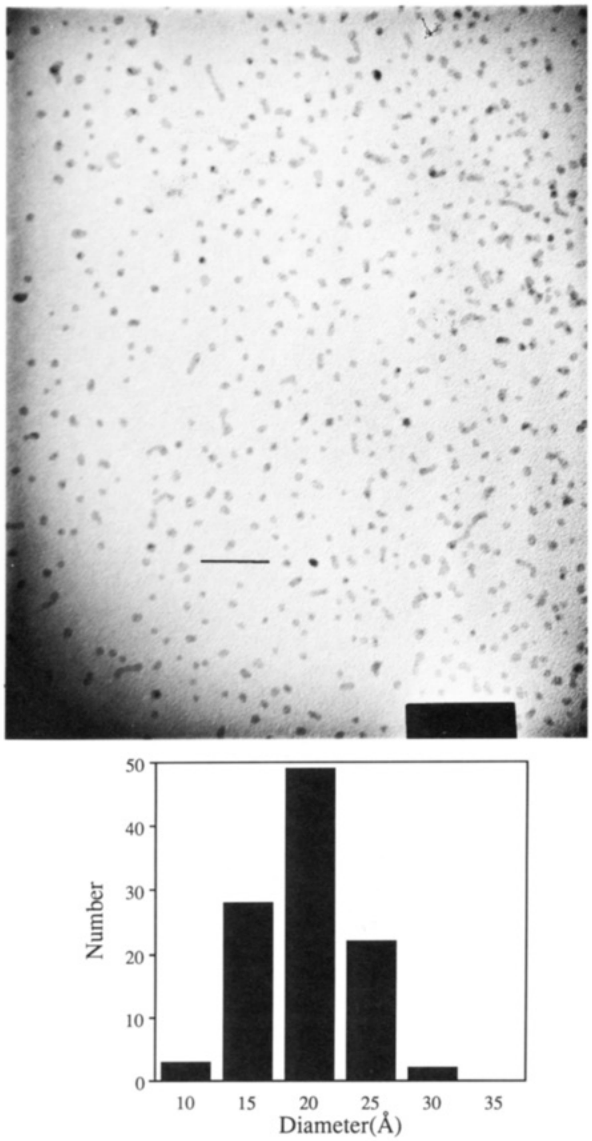

Figure 4. (a) Transmission electron micrograph of PVP-stabilized palladium colloid IV, prepared from $Pd(dba)_2$ in CH_2Cl_2 by carbon monoxide reduction (1 bar, 25 °C; scale bar = 180 Å). (b) Particle size distribution.

amorphous or poorly diffracting component.

Reduction of the same reaction mixture ($Pd(dba)_2$/PVP (40 000 MW)/CH_2Cl_2) with carbon monoxide at 1 atm and 25 °C results in a rapid color change, with completion of colloid formation occurring in a few seconds. The colloids produced by this method (IV) are of slightly smaller size (ca. 20 Å) than those prepared by hydrogen reduction of $Pd(dba)_2$ at 1 atm (III), as shown in Figure 4. Attempts to detect crystallinity by electron diffraction in colloids prepared by this method were less successful than in the case of the colloids prepared by hydrogen reduction of $Pd(dba)_2$. Very weak diffraction rings are observed in some preparations but not in others. It is possible that the formation of palladium metal in the reaction of CO with $Pd(dba)_2$ is sufficiently rapid that either amorphous particles or poorly crystalline particles are produced in which crystallinity is present on a length scale which would result in significant broadening of the diffraction rings. The slower hydrogen reduction of $Pd(dba)_2$ may allow for the formation of a more ordered lattice. It is tempting to draw parallels between this process and the crystallization from solution of molecular compounds, a process which if induced rapidly by thermal or chemical means often yields poorly crystalline materials, while slower crystallization results in the formation of well ordered crystals. From these observations it is clear that colloidal particles of similar sizes can posess varying degrees of crystallinity, especially in the low size range. The additional complexity caused by such irregular or amorphous structures in the context of a study such as this has caused us to seek means of standardizing the structures of these clusters, and we are in the process of evaluating methods of annealing colloidal metal particles in solution.

In refining our preparative technique for these materials, we investigated the effect of varying two synthesis parameters, metal-to-polymer ratio and polymer molecular weight.

(*i*) *Metal Loading.* The effect on particle size of metal-to-polymer ratio (loading) was investigated by reducing $Pd(dba)_2$ under 3 atm of hydrogen in dichloromethane containing concentrations of PVP necessary for the formation of Pd/PVP colloids of 2%, 5%, and 8% metal loading (system II). Particles of ca. 40 Å were produced in all cases. The effect of higher metal loading is simply to allow more effective interparticle contact, and at the higher loadings some coalescence into elongated poly-

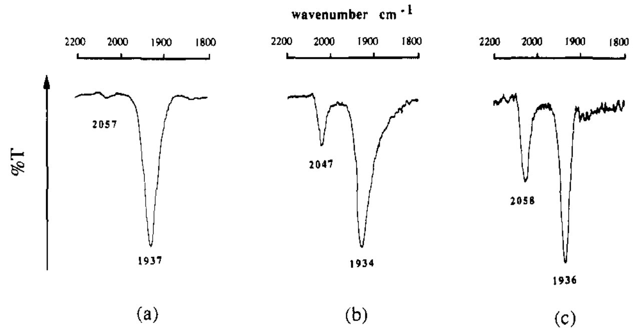

Figure 5. Infrared spectra of carbon monoxide adsorbed on PVP-stabilized palladium colloids: (a) I; (b) IIc, and (c) III in dichloromethane solution. Spectra are in percent transmittance, after subtraction of absorptions due to colloid solution prior to CO addition.

crystalline particles is apparent (Figure 2). The resulting particles seem to be aggregates of the 40-Å crystallites which are the predominant product under the preparation conditions used. For each of these colloids the particles are beginning to have recognizably facetted shapes, and this, together with the observation of well-developed electron diffraction rings, makes it clear that the sample is crystalline.

(*ii*) *Polymer Molecular Weight.* In a study of the effect of polymer molecular weight on colloid particle size, Pd(dba)$_2$ was treated with carbon monoxide in the presence of PVP with molecular weights of 10 000, 24 000, 40 000, and 90 000 (system IV). In all cases, particles of ca. 20-Å diameter were produced, and no significant effect of polymer molecular weight on particle size was observed.

Adsorption of Carbon Monoxide—Particle Size and Structural Effects on CO Binding Geometry. One of the themes of our research into the chemistry of nanoscale transition-metal clusters is the development of the surface chemistry of these aggregates in the liquid phase. In this we make use of comparisons between the chemistry of molecular carbonyl clusters, of supported metal crystallites and of single crystal surfaces, with the properties of colloidal metal nanoclusters in solution. Carbon monoxide is exceptionally useful as an adsorbate/ligand due to its infrared absorption characteristics, and we[4-7] and others[8-10] have reported infrared absorption spectroscopic studies of adsorbed CO on colloidal transition metals in studies of their surface chemistry. The adsorption (or coordination) of carbon monoxide onto metal surfaces or metal cluster complexes has been extensively studied[19,20] and provides a rich source of data with which to compare these colloidal systems.

The addition of carbon monoxide at 1 atm to solutions of the palladium colloids I–IV results in rapid CO adsorption, as shown by the appearance of infrared absorbances in the frequency range between 1800 and 2100 cm^{-1}, the region associated with C–O vibrational transitions for adsorbed CO, as shown in Figure 5. The growth of these absorbances is complete in seconds, and all the spectra reported here are at what we presume to be saturation coverage. In stipulating saturation coverage, we imply only that the maximum possible amount of CO is present on the surface, given the constraints imposed by the polymer and solvent molecules. Thus the effects of partial coverage and island formation, which result in frequency shifts for CO on metal surfaces[20] are not accounted for in this study. In this context it should also be pointed out that small changes in the frequencies of the CO vibrational bands would be difficult to interpret with meaning in a complex system such as this, with solvent, polymer, and CO competing for surface sites on the colloidal metal particles. Gross and systematic changes demand interpretation, but we frequently observe random shifts of several wavenumbers and make no suggestion at this point to explain their source other than the inherent complexity of the system.

The infrared spectrum of CO adsorbed on palladium colloid I, prepared from Pd(OAc)$_2$ in methanol (60-Å mean diameter) is shown in Figure 5a. An absorption band at 1940 cm^{-1} showed the presence of doubly bridging carbon monoxide (μ^2-CO), with a weak absorption at 2050 cm^{-1} in the frequency range expected for terminal CO on palladium.[19]

Carbon monoxide occupies both terminal and bridging sites to significant degrees on the smaller particles II and III and comparisons between different colloids in this lower size range reveal the relative increase of terminal CO over bridging CO with decreasing particle size. For example, a comparison of can be made between IIc (40 Å) and III (25 Å), as shown in Figure 5b,c, both of which exhibit crystallinity by electron diffraction. III shows a greater relative concentration of terminal CO than does IIc. For the colloidal palladium particles in the three size ranges represented by I–III, the ratio of bridging CO to terminal CO decreases with decreasing particle size from 60 Å to 25 Å.[21] Mucalo and Cooney[9], in a detailed analysis of the IR absorptions of CO on ca. 90-Å palladium hydrosol particles, report a predominance of bridged CO at this particle size, the intensity of the linear CO stretching absorption being too low to quantify.

The variation of relative abundances of linear and bridged CO could be the result of a number of factors. Comparison with molecular cluster chemistry would suggest that bridged CO would be preferred as the metal surface becomes more electron rich, but it seems unlikely that the electronic properties of the palladium particles would change dramatically over this size range. The particles do however undergo an important geometric change as the size increases, in that for crystallites of the same geometry the ratio of edge sites to face sites increases with decreasing particle size. This intuitive relationship was given some 20 years ago in analytical form by van Hardeveld and Hartog,[22] who also identified the particle size range between 20 and 40 Å as the region in which the changes in the relative abundance of these two types of surface site would be the most marked. We propose that the variation of the relative intensities of bridged and terminal CO absorptions with particle size for the colloidal palladium particles is a consequence of this fact. A similar dependence of the relative populations of bridging and terminal CO on particle size for a number of silica supported palladium catalysts has been reported by Sachtler and co-workers.[23] They concluded that linear CO is more stable on the low coordination number palladium atoms at the edges and vertices of crystallites, which are relatively more abundant in smaller crystallites, and bridged CO is preferred at higher coordination number face atoms.[24]

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(19) Sheppard, N.; Nguyen, T. T. In *Advances in Infrared and Raman Spectroscopy*; Clarke, R. J., Hester, R. E., Eds.; Heyden, London, 1978; pp 106.

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(21) We have previously reported[5,6] the infrared characterization of carbon monoxide on even smaller colloidal palladium particles prepared from the metal vapors. It was found that for an 18-Å colloid both bridging and terminal CO were observed, with the latter predominating, while with a particle size of ca. 10 Å, exclusively terminal CO was present. The lack of structural data on these last two examples precludes their inclusion in the present analysis.

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Support for this analysis in the case of colloidal palladium comes from our recent observation[6] of the effect of particle size on the NMR characteristics of ^{13}CO adsorbed on I and III. CO bound to PVP-stabilized colloidal palladium (25 Å) has a resonance intensity much greater in the higher field (lower Knight shift) range (650–300 ppm) than that seen for CO on an analogous 75-Å colloid, and we interpreted this as due to the higher proportion of edge and vertex sites on the smaller crystallites. CO on these low coordination number metal atoms is expected to be less Knight shifted than that bound to higher coordination number metal atoms on the faces of the crystallites.[25] This observations when coupled to the observation of the greater relative intensity of terminal to bridged CO on I than on II and on II than on III adds weight to our and Sachtler's conclusion that bridged CO occupies sites on the higher coordination number metal atoms on the faces of palladium crystallites and linear CO those on the edges. The size dependence of the infrared spectrum then follows.

These purely geometric arguments require, of course, that particles in the three size ranges under comparison in our study have the same structure and the same morphology. The former requirement is demonstrably met, since I–III all have the face-centered cubic structure of bulk palladium. Although the TEM images of I–III suggest reasonably equidimensional crystallites, the morphologies of the particles are not known. However, over the size range 25–60 Å the effects of small differences in morphology are probably outweighed by gross changes in site abundance.

This correlation does not survive our attempt to compare particles with sizes which differ only slightly. As described above, we carried out a series of experiments designed to reveal the effect of various synthesis parameters on particle size. Despite the fact that we found no reproducible effects, these experiments generated a large number of PVP-stabilized colloidal palladium solutions, and CO adsorption and infrared spectroscopy were performed on all of them. For example we found in the series IVa–d relatively minor but uncorrelatable changes in both size distribution and relative intensities of terminal and bridging C–O stretching absorptions. Even when comparisons are made in a series of quite reproducible samples (IIa–c) over a range of metal-to-polymer ratios, under conditions which produced crystalline colloidal particles of similar diameters, terminal to bridged CO absorbance ratios varied from 2.0–3.5. Thus, while infrared spectroscopy provided a guide to particle size in comparisons between palladium colloids with significantly different sizes (I–III), the technique was not useful in itself as a measure of particle size for more similarly sized particles (IIa–c and IVa–d). Presumably the particles are not ideal close packed crystallites with uniform planar surfaces and straight edges but are more irregular and possibly polycrystalline aggregates with surfaces of varying geometry. We noted above that electron diffraction suggests that the particles produced by this method were poorly crystalline. However, the presumably uneven surfaces of even amorphous metal particles would adsorb CO and thus contribute to the infrared spectrum of the sample, quite probably by enhancing the linear CO stretching absorption, since an irregular surface presents a greater proportion of low coordination number metal atoms.

Infrared spectra at partial coverage of CO, ^{12}CO/^{13}CO exchange studies, and adsorption of ^{12}CO/^{13}CO mixtures will shed light on the surface chemistry and structure of these metal particles, and these are underway and will be reported separately. Preliminary results indicate a great similarity in CO adsorption characteristics between the colloidal palladium particles in this study and the supported palladium crystallites which have been thoroughly studied over a period of many years by a number of research groups.[13] It seems that neither the stabilizing polymer nor the solvent matrix has a drastic effect on the structure and surface chemistry of the palladium particles in comparison with their supported counterparts. It should be pointed out that the study of metal crystallites in oxide-supported metal catalysts is often complicated by the effects of the oxide itself. Interfacial phenomena such as partial oxidation can lead to corrosive chemisorption, and more complex effects such as the strong metal support interaction can also occur, which while they have yielded to detailed analysis of the interaction of metal particles with oxide surfaces, are nevertheless perturbations on the intrinsic chemistry of metal crystallites. The study of well-characterized metal nanoclusters in the liquid phase allows the mitigation of these complications.

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Registry No. PVP (homopolymer), 9003-39-8; Pd(dba)$_2$, 32005-36-0; Pd(OAc)$_2$, 3375-31-3; CO, 630-08-0.

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(24) Detailed analysis of CO adsorption on the extended faces of single crystals reveals a more complex situation. It has been reported recently (Tüshaus, M.; Berndt, W.; Conrad, H.; Bradshaw, A. M.; Persson, B. *Appl. Phys. A* **1990**, *51*, 91) that on Pd{111} alone, some 18 ordered overlayers of CO have been identified at various coverages including structures in which on top sites (linear CO) are occupied.

(25) Zilm, K. W.; Bonneviot, L.; Haller, G. L.; Han, O. H.; Kermarec, M. *J. Phys. Chem.* **1990**, *94*, 8495.