

The Chemistry of Pd in Cellulose Acetate

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SYNOPSIS

Pd(OAc)₂ complex has been incorporated in cellulose acetate (CA) as a dispersion medium using cosolvent (THF). The interactions Pd(II) complexes and cellulose acetate are examined by infrared spectroscopy and thermal analysis (DSC). The chemical reactivities of Pd-CA films have been investigated by reacting Pd sites with CO, H₂, O₂, and C₂H₄ in the temperature range 25–150°C and at the pressure of less than 1 atm. Two different Pd-carbonyls and a Pd(O)-hydride species formed in CA are characterized by their infrared spectra. Treatment of 10 wt % Pd-CA films with hydrogen (600 torr) at 70°C produces small Pd metal particles of ca. 30–60 Å in diameter in CA, which show catalytic activities under mild conditions in the reactions such as hydrogenation of C₂H₄ and oxidation of CO.

INTRODUCTION

The field of metal-containing polymeric materials has received much attention during the past decade because of the burgeoning interests in the search for new high-performance materials.^{1–6}

In addition, these materials have been studied for the development of highly efficient catalytic systems modeled after the metalloenzyme, and for their application as a separation medium.^{7–9}

Recently, we have reported that Ru and Rh complexes can be easily incorporated into ion-exchange resins or neutral cellulose acetate (CA) and that the metal complexes in the polymer matrix show interesting chemical reactivities toward small gaseous molecules at relatively mild conditions that are different from those of the corresponding ordinary metal complex or polymer itself.^{10,11} Also, surprisingly, it was found that essentially pure H₂ gas could be recovered from a 1 : 1 mixture of H₂ and CO gases using ruthenium-containing cellulose acetate membrane. In this case relatively stable ruthenium carbonyl species formed in cellulose acetate are believed to function as a blocking barrier for CO permeation through the CA membrane, resulting in such separation.¹²

This shows that the chemical alteration of permselectivity of organic polymer membrane^{12,13} or the so-called active membrane¹⁴ could be realized by incorporation of transition metal complexes into them. However, there have been only a few reports about fundamental reaction chemistry of transition metal complexes in organic polymers.

In an effort to extend this study, palladium acetate complexes have been incorporated into cellulose acetate (CA) and the resulting Pd-containing polymeric material has been investigated to understand the interactions between the Pd complex and CA, the effect of metal complex on the thermal property of CA, and the reaction chemistry of Pd complex in the polymer matrix. The results are reported in this study.

EXPERIMENTAL

Pure cellulose acetate and palladium-containing cellulose acetate films (metal complex concentration; 10–30 wt %) were prepared as previously reported by using cellulose acetate (CA), Pd(OOCCH₃)₂ (Aldrich Co.), and tetrahydrofuran (THF) as a cosolvent.^{11,12} The thickness of the films was controlled in the range of 10–25 μm, which is convenient for the study by transmission infrared spectroscopy. After 3 h in air at room temperature, the light-brown-colored transparent films were annealed at 110°C overnight. These films shrink at about 160°C

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and decompose at over 200°C, but they are stable below 150°C even when they are heated for a long period at the temperature.

Infrared spectra in the 4000–600 cm^{-1} were recorded on Nicolet MX-5 spectrometer and Hitachi 260-10 IR spectrometer. The transmission electron microscopy (TEM) analyses were performed on a JEM-200 CX microscope at 100 kV by direct observation to investigate the Pd-CA films after reduction with CO and/or H_2 as described under the results and discussion section. The samples were prepared by embedding the metal-containing films in epoxy resin and microtoming them. In all cases direct magnification was 4.1×10^4 and photographic enlargement was up to 8.2×10^4 . A series of measurements of the glass transition temperature (T_g) were carried out using DuPont Model 910 thermal analyzer. In a typical DSC scan sequence, dq/dT was measured on heating 20°C/min from 30 to 170°C with 2 mV/cm range. Several DSC scans were made on the cycles of heating at the above conditions to remove the effect of thermal history for each sample.

The gases used in this work—carbon monoxide, hydrogen, oxygen, ethylene (Dong Jin Trade Co., high purity > 99.99%)—were dried by passing them through Drierite gas-drying units before they were added for the reactions.

RESULTS AND DISCUSSION

Interaction between Pd Complex and CA

The interactions between Pd-acetate complexes and CA can be considered as electrostatic in nature, namely, ion-dipole interactions. Accordingly, the electron-rich oxygen atoms of polar hydroxyl and/or acetate groups of CA are expected to interact with electrophilic transition metal cations, and this interaction is believed to be the most important attractive force between Pd complexes and CA. This presumption was evidenced in the infrared spectroscopic studies of Be (II) and Mg (II) containing cellulose acetate.¹⁵

In these cases both the hydroxyl and the acyl carbonyl absorption bands (3500 and 1750 cm^{-1} , respectively) undergo the red shifts indicative of bond weakening due to the competition of the metal cations for the electrons of which the bonds are composed. But the IR spectra of the Cu (II)¹⁶ and Rh (I)-containing CA films¹¹ showed a red shift of the acyl carbonyl stretching band at 1750 cm^{-1} and a corresponding high-frequency shift of the ether carbon-oxygen band at 1230 cm^{-1} , indicating that there is

no appreciable interaction between hydroxyl group of CA and transition metal complexes. This dependence of metal cations are thought to arise from the differences in charge densities of metal cations.

In a typical infrared spectra of 10 wt % Pd-containing CA films, the characteristic bands¹⁷ due to acetate ligands of Pd complex are observed at 690, 1425, 1520(b), and 1580(sh) cm^{-1} in addition to the bands from CA, and the intensities of these bands increase as the Pd complex concentration increases. This result suggests that the acetate ligands in CA function as bridging bidentates,¹⁸ and agrees with the well-known trimeric structure of Pd acetate complex in liquid or in solid.¹⁹

Besides, the band at 1750 cm^{-1} due to $\nu(\text{C}=\text{O})$ of CA broadens to about 1700 cm^{-1} and the band at 1230 cm^{-1} due to $\nu(\text{C}-\text{O})$ of CA broadens to higher frequency of about 1280 cm^{-1} upon incorporation of Pd complex into CA. This result is quite analogous to the reported cases of Cu (II) and Rh (I), denoting that there are some interactions between Pd complexes and acyl carbonyl groups rather than hydroxyl groups of CA.^{11,16} But, at this stage, it is not clear whether there is complete coordination of Pd metal ions to oxygen atoms of acyl groups leading to the coordination number 6.

T_g of Pd-Containing Cellulose Acetate

As discussed earlier, the oxygen atoms of acyl groups of CA are believed to coordinate at least partially to Pd metal atoms. Accordingly, the CA polymer molecules are expected to be crosslinked through their coordinations and to decrease their mobility, resulting in the increase of T_g .^{5,11,20}

As predicted, the glass transition temperature of 10 wt % Pd-CA films increases by 7°C in comparison to that of pure CA (94°C). But in case of 20 wt % Pd-CA films, it rather decreases to 90°C. This result reveals that the degree of crosslinking of CA membranes via coordination to Pd metal atoms is relatively weaker than that of Rh (I)-containing CA and that at 20 wt % Pd complex concentration the metal complexes do not act as crosslinking agents any more but exist like impurities, resulting in the decrease of T_g .¹¹

Thus, in this study, we investigate the 10 wt % Pd-CA films, and these films are dried at 110°C in vacuum for 12 h to remove adsorbed solvents or water molecules.

Behavior of Pd-CA Films in Solution

When 10 wt % Pd-CA films are immersed in methanol at room temperature for 24 h and then dried

to remove adsorbed solvent molecules at 110°C in vacuum for 24 h, the light brown color of the films becomes much darker and also, interestingly, the characteristic bands due to acetate ligands disappear in their infrared spectra. When these films are treated with CO (600 torr) at 110°C for 24 h, there are two $\nu(\text{CO})$ bands at 1945 and 2060 cm^{-1} , which can be assigned to bridged and terminal carbonyls coordinated to palladium(0) metal atoms (see later section). Their band intensities are exactly the same as those of corresponding Pd-CA films without the dip in methanol solution as above, indicating that the Pd metal cation in CA are not eluted from CA matrix in the solution, although Pd acetate complex itself is completely soluble in methanol. Also, the infrared spectra of the Pd-CA films after elution test in methanol are quite similar to that of pure cellulose acetate film or that of the reduced Pd-CA films by H_2 as described in a later section. Of course, there is no evidence of other possible ligands such as OH^- or CH_3O^- . Therefore, from these results with the color change from light brown to dark brown of the films, which usually indicates the metal particle formation in the films,^{21,22} we believe that there is some reduction reaction in the Pd-CA films in methanol solution, and that such reduction reaction might include the already reported unstable Pd-methoxide²³ intermediate leading to alcohol oxidation or decarboxylation of ester. Similar reduction reaction of palladium acetate was reported to occur in butanol at 60–70°C in the presence of PPh_3 .²⁴

When the Pd-CA films are immersed in aqueous KCN solution (0.1M), all of the Pd complexes are found to be removed from CA, and the resulting $\text{Pd}(\text{CN})_4^{2-}$ complexes, which are well-characterized stable species,²⁴ are identified in aqueous solution. This can be easily interpreted by assuming that the soft CN^- ligands coordinated strongly to Pd metal cation, resulting in separation of the palladium complex from CA polymer matrix.

Reaction of Pd in CA with CO

When 10 wt % Pd-CA films, dried at 110°C in vacuum for 12 h, are treated with CO (600 torr) at room temperature for 12 h, two $\nu(\text{CO})$ bands at 2090 and 1950 cm^{-1} in medium intensities are observed in their infrared spectra, which are quite similar to those of palladium carbonyls supported on silica²⁵ (Pd particle size, 150 Å; $\nu(\text{CO})$, 2074, 1914 cm^{-1}). As the reaction temperature increases to 110°C, the intensities of the bands increase and they shift to 2060 and 1945 cm^{-1} , respectively (Fig. 1). During the reaction with CO, the color of the Pd-CA films

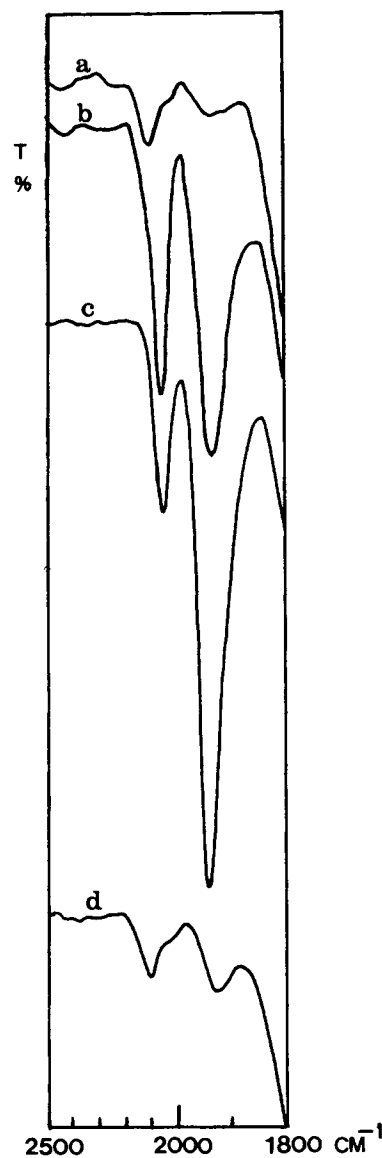
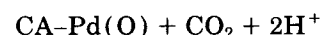
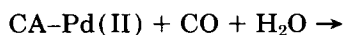


Figure 1 IR spectra for Pd-carbonyl species formed in CA. (a) 10 wt % (Pd-CA) film; (b) after reaction with CO (600 torr), 110°C; (c) 20 wt % (Pd-CA) film after reaction with CO (600 torr), 110°C; (d), from (c), after 40 min in air at room temperature.

changed to dark brown at about 70°C, and the bands due to acetate ligands gradually disappear from their infrared spectra. When these dark-brown-colored films are examined by TEM, Pd metal particles of about 15–30 Å in diameter are observed.

As a result, it is concluded that during the reaction with CO, the Pd(II) metal cations are reduced by CO with adventitiously contained water molecules as below:



In the infrared spectral studies of various Pd(O)-carbonyls, the bands above 2000 cm^{-1} were usually assigned to a linear metal carbonyl and the bands below 2000 cm^{-1} were attributed to bridged metal-carbonyl.^{25,26} Also, the band intensities were reported to depend on the metal particle size, i.e., the major absorbance peak above 2000 cm^{-1} increases in its intensity relative to the peak below 2000 cm^{-1} when the metal particle size decreases. In the 10 wt % Pd-CA films, the lower-frequency band at 1945 cm^{-1} is a little bit higher in intensity than that of the band at 2060 cm^{-1} . But in the case of 20 wt % Pd films as shown in Figure 1, the lower band intensity is about 4 or 5 times bigger than that of high-frequency band, indicating that most of the chemisorbed carbonyls are bridged species and that the palladium metal particles have much larger size relative to that of the 10 wt % Pd-CA case (see later section for the size of the palladium particles formed in 20 wt % Pd-CA films).

Also Eischens et al.²⁷ suggested that the relatively high frequency for a bridged Pd-CO group around 1930 cm^{-1} region could be rationalized by the relatively smaller M-C-M bond angle than usual. Therefore, the bands at 2060 and 1945 cm^{-1} are assigned to linear Pd(O)CO and bridged Pd(O)-CO species, respectively.

These Pd(O) carbonyls formed in CA films disappear within a few hours in air at room temperature or in vacuum. It is interesting to note that the intensity of the linear Pd-CO band reduces more rapidly than that of the bridged CO band at 1945 cm^{-1} . Same result was obtained when the Pd-carbonyls were treated with H_2 or O_2 , indicating that the terminal (linear) Pd-carbonyl in CA is quite reactive. This result is rather surprising since the unsupported palladium acetate complexes were reported to form $\text{Pd}_4(\text{CO})_4(\text{OAc})_4 \cdot 2\text{AcOH}$ upon reaction with CO in acetic acid.²⁸ This tetrameric Pd metal carbonyl $\nu(\text{CO})$'s were found at 1934 and 1975 cm^{-1} . In order to compare the reaction chemistry of palladium acetate complex with that contained in CA, pure Pd acetate complex is treated with CO (600 torr) at 110°C for 12 h in solid state, but no Pd-carbonyl species is obtained. In addition, it should be mentioned that, when the Pd-CA films are treated with CO at the described conditions, only a very small amount of CO_2 is observed, suggesting that there is no appreciable CO disproportionation reaction ($2\text{CO} = \text{C} + \text{CO}_2$).²⁵ This result does not agree with that of silica-supported palladium cases although the palladium particle is relatively very small in size.²⁵

Reaction of Pd in CA with H_2

When 10 wt % Pd-CA films are reacted with H_2 (600 torr), the color of Pd-CA films change to dark brown at 50°C and a band at 1915 cm^{-1} is observed in medium intensity (Fig. 2). But this band disappears after 15 min in air, and this result is quite reproducible. In TEM study of these films, Pd metal particles of ca. $30\text{--}60\text{ \AA}$ in diameter are observed (Fig. 3).

This metal particle size range is relatively larger in comparison with that of the Rh-CA case, and the reason is thought to be due mainly to the trimeric structure¹⁹ of palladium acetate like $\text{Pd}_3(\text{OAc})_6$ as

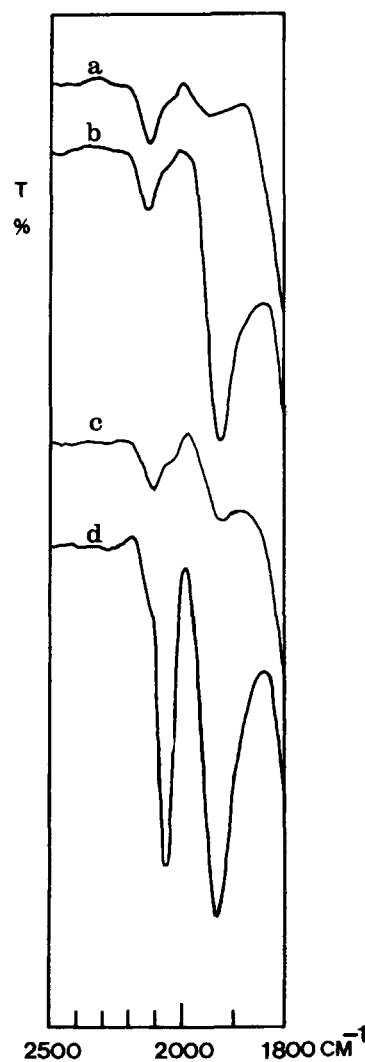


Figure 2 IR spectra for Pd(O)-hydride species formed in CA and its reactivity. (a) 10 wt % (Pd-CA) film; (b) after reaction with H_2 (600 torr), 110°C ; (c), from (b), after 15 min in air at room temperature; (d), from (c), after reaction with CO (600 torr), 110°C .

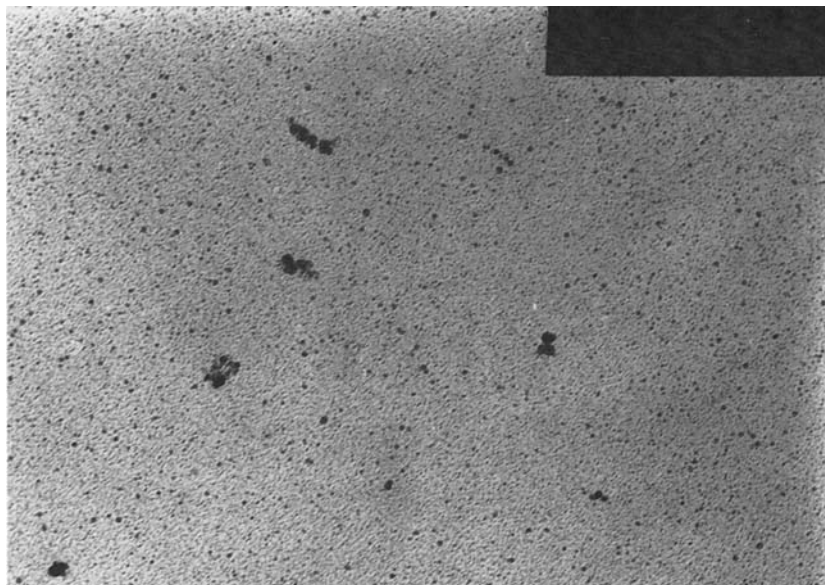


Figure 3 Electron micrograph of 10 wt % (Pd-CA) film after reduction reaction with H_2 (600 torr, $110^\circ C$) (magnification, $\times 82,000$).

well as the relatively larger Brownian motions²⁹ of the metal particles in CA. Besides, various known Pd(II) hydride complexes³⁰⁻³² usually showed $\nu(\text{Pd-H})$ bands above 2000 cm^{-1} in infrared spectra.

On the bases of these results, the observed Pd-hydride species is assigned to Pd(O)-hydride. In addition, when these reduced Pd-CA films by H_2 are treated with CO at $110^\circ C$ for 12 h, two $\nu(\text{CO})$ bands at 2060 and 1945 cm^{-1} are observed and this agrees well with previous discussion (Fig. 2). When 20 wt % Pd-CA films are exposed to H_2 (600 torr) at $110^\circ C$ for 12 h, the color of the films are much darker than that of the 10 wt % Pd-CA films and the large palladium particles in ca. $60\text{--}500\text{ \AA}$ in diameter are identified on their electron micrographs. This result gives good explanation for the strong absorbance band at 1945 cm^{-1} , which arises from the bridged palladium carbonyls since the relative concentration of bridged carbonyls is predicted to increase as the particle size increases.

Reaction of Pd in CA with O_2

When 10 wt % Pd-CA films are exposed to O_2 (600 torr) at $110^\circ C$, there is no change in the color of the films and in their infrared spectra except dehydration effect. When these films are treated with CO (600 torr) at $110^\circ C$, the aforementioned two bands at 2060 and 1945 cm^{-1} appear in infrared

spectra, indicating that there is no oxidation of Pd(II) complexes.

However, when these films are consecutively treated with O_2 at the same condition, the coordinated carbonyls completely disappear and the resulting gaseous product is found to be CO_2 (Fig. 4).

Catalytic Reactivities of Pd in CA

As discussed in previous sections, the palladium complexes in CA are found to be quite reactive toward carbon monoxide, hydrogen, and oxygen at relatively mild conditions. Also small palladium metal particles are observed to be formed in CA upon various reduction reactions, and these are expected to be catalytic precursors.

In order to test the catalytic potentials in a preliminary way, a 1 : 1 mixture of ethylene and hydrogen (total pressure, 1 atm) reacted in a 720-mL Pyrex glass flask at $130^\circ C$ for 4 days in simple static state, and complete conversion of ethylene to ethane is identified in the infrared spectra of the reaction mixture. But the efforts to find palladium-ethylene adducts in CA during the reaction was unsuccessful. There is no noticeable decrease of catalytic activity of the Pd-CA films after repeated reactions. The turnover number in substrate molecules transformed per Pd metal particle per second is estimated about 1×10^4 .

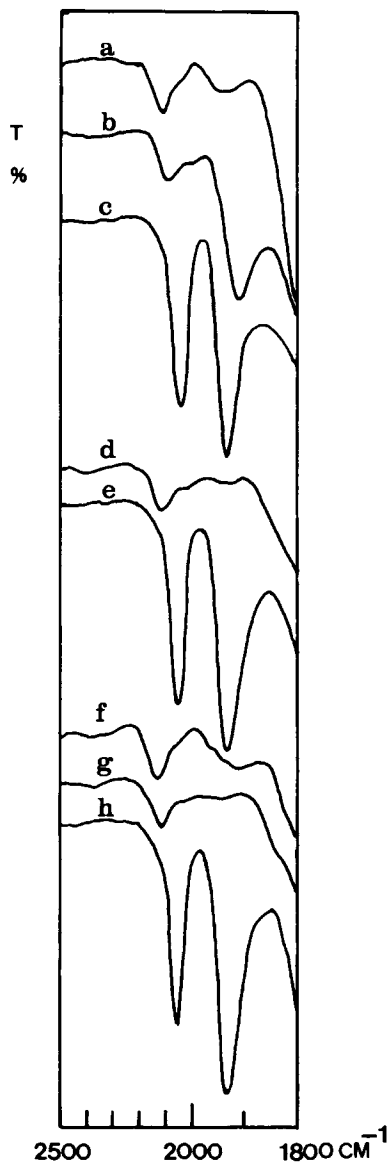


Figure 4 IR spectra for the consecutive reactions of (Pd-CA) films: (a) 10 wt % (Pd-CA) film; (b) after reaction with H_2 ; (c) with CO; (d) with H_2 ; (e) with CO; (f) with H_2 ; (g) with O_2 ; (h) with CO (gas pressure: 600 torr, temperature: $110^\circ C$).

Also, when a 2 : 1 mixture of CO and O_2 is reacted at the same condition as above, the conversion of CO to CO_2 is identified by the infrared spectral observation of appearance of the bands due to CO_2 and corresponding disappearance of the band due to CO.

Further investigation of the catalytic applications of Pd-CA films such as Fisher-Tropsch type reaction or NO reduction by CO and H_2 is in progress in this laboratory.

CONCLUSION

Palladium acetate complexes have been incorporated, using tetrahydrofuran as a cosolvent, into cellulose acetate, which has no typical ligands such as phosphine, amine, and ionic functional groups. The resulting light-brown-colored Pd-CA films of 10–20 wt % Pd complex concentration are found to be thermally stable up to $150^\circ C$. The interactions between Pd metal cations and acyl oxygen atoms of cellulose acetate are proposed on the basis of infrared spectral and thermal analysis data. The reactions of the Pd-CA films with CO at the described conditions result in two different Pd(O) metal carbonyl species, which are assigned to the linear [$\nu(CO)$; 2060 cm^{-1}] and the bridged [$\nu(CO)$; 1945 cm^{-1}] carbonyl species. These palladium carbonyls are found to be active to H_2 and O_2 . Also, very active palladium hydride species [$\nu(Pd-H)$; 1915 cm^{-1}] is observed by the reaction of the Pd-CA films with H_2 (600 torr) at $110^\circ C$. It is noteworthy that palladium metal particles are easily formed in CA at relatively mild conditions and that their sizes can be controlled from 10 to about 500 Å by various reaction conditions. Finally, the Pd complexes in cellulose acetate show catalytic activities in the temperature range of $100\text{--}130^\circ C$ in hydrogenation of ethylene and oxidation of carbon monoxide to carbon dioxide.

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