

Preparation of Rh-Containing Cellulose Acetate Films and the Chemistry of Rh in Cellulose Acetate

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SYNOPSIS

RhCl [P(C₆H₅)₃]₃ complexes have been incorporated in cellulose acetate as a dispersion medium using cosolvent (tetrahydrofuran). The interactions between Rh(I) complexes and cellulose acetate (CA) are examined by infrared spectroscopy and thermal analysis. The chemical reactivities of Rh-CA films have been investigated by reacting Rh sites with CO, H₂, O₂, and C₂H₄ in the temperature range 90–150°C and at a pressure of less than 1 atm. Three different Rh-carbonyls and a Rh-hydride species formed in CA are characterized by their infrared spectra. Treatment of 10 or 20 wt % Rh-CA films with hydrogen (600 torr) at 150°C produces small Rh metal particles of ca. 10 Å or less in diameter in CA, which show catalytic activities under mild conditions in various reactions such as hydrogenation of C₂H₄, oxidation of CO, and Fischer-Tropsch type reactions.

INTRODUCTION

Metal-containing polymeric materials have been an active research area in recent years because of their potential applications as versatile materials and for the purpose of modifying polymer properties such as increasing the glass transition temperature (T_g), decreasing the melting temperature (T_m), enhancing adhesive properties, or increasing the electrical conductivity.^{1–6}

In these materials, central metal complex or metal ions, surrounded by giant polymer chains, show interesting physical properties and chemical reactivities different from those of the corresponding ordinary metal complex or polymer itself. Also, these have been an excellent model for the metalloenzymes, leading to the developments of highly efficient catalytic systems.⁷

In addition, it had been reported that when cobalt complexes that selectively coordinate O₂ were incorporated into polymer membrane, the transport of O₂ was facilitated and the permeate was enriched in O₂, suggesting that the permeation selectivities

of organic polymers could be changed by incorporation of metal species.⁸

However, there have been, to the best of our knowledge, only a few reports about the study of the metal site interactions and the chemistry of metal complexes in the polymer matrix. Against this background, RhCl[P(C₆H₅)₃]₃ complexes have been incorporated into cellulose acetate (CA), which is well characterized and known to have good membrane properties. The resulting Rh-containing polymeric material has been investigated to understand the interactions between the Rh complex and CA, the effect of the metal complex on the thermal property of CA, and the reactivities of Rh complex in the polymer matrix. The results are reported in this paper.

EXPERIMENTAL

Ten weight percent Rh-containing cellulose acetate films were prepared by following procedure: 3.6 g of cellulose acetate and 0.4 g of RhCl[P(C₆H₅)₃]₃ (Aldrich Co.) were dissolved in 90 mL tetrahydrofuran (Hayashi Pure Chem. Ind. Ltd.) and the resulting mixture was boiled gently in the open for 10 min. After filtration of the solution to remove insoluble material, the filtrate was warmed to about

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60°C and the solvent evaporated until the concentration of the solution reaches about 12% by weight. After cooling to room temperature, the polymer solution was cast on a glass plate using a doctor knife (Gardner Co.). The thickness of the films was controlled in the range from 10 to 20 μm , which is convenient for study by transmission infrared spectroscopy. After 3 h in air at room temperature, the yellow-colored transparent films were annealed at 110°C overnight. Other cellulose acetate films containing 20, 30, 40, and 50 wt % of $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ were made similarly. These films decompose at about 200°C, but are stable below 150°C even when they are heated for a long period at the temperature.

Elemental analysis indicates that there is no loss of the phosphine ligand upon the incorporation of Rh metal complex into cellulose acetate.

ANAL: Calcd for 10 wt % Rh-CA film: Rh, 1.11%; P, 1.00%. Found: Rh, 1.06%; P, 0.96%.

Infrared spectra in the 4000–600 cm^{-1} were recorded on Nicolet MX-S spectrometer and Hitachi 260-10 IR spectrometer. The transmission electron microscopy analyses were performed on a JEM-200CX microscope at 100 kV by direct observation to investigate the Rh-CA films after reduction reactions with H_2 , as described under the Results and Discussion. The samples were prepared by embedding the metal containing films in epoxy resin and microtoming them.

A series of measurements of the glass transition temperature (T_g) were carried out using a 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 and automatically cooling to 30°C.

The gases used in this work, carbon monoxide, hydrogen, oxygen, and ethylene (Dong Jin Trade Co. high purity > 99.9%), were dried by passing them through Drierite gas-drying units before they were added for the reactions.

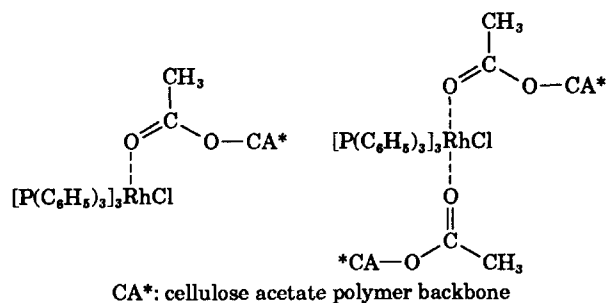
RESULTS AND DISCUSSION

Interactions between Rh Complex and CA

It was reported that when solutions composed of CA and an equal weight of $\text{Cu}(\text{NO}_3)_2$ were cast into membranes, the Cu(II) ion became coordinated to the acyl carbonyl oxygen of the CA.^{8,9} This presumed coordination of the Cu(II) to the CA was evidenced

from infrared spectral studies. The IR spectra of the membranes showed a shift to lower frequencies of the acyl carbonyl stretching band from 1750 cm^{-1} to about 1727 cm^{-1} and a high frequency shift of the ether carbon-oxygen band from 1230 cm^{-1} to about 1255 cm^{-1} .

In a typical infrared spectra of 10 wt % Rh-CA films, the characteristic bands due to phosphine ligands at 690, 720, 745, 1120, 1435, 1585, and 3060 cm^{-1} are observed in addition to the bands from CA, and the intensities of these bands increase as the Rh metal complex concentration increases. 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 Rh complex into CA. This result is quite analogous to the aforementioned case of CA and Cu(II) and can be explained by the complete or at least partial coordination of Rh metal, to oxygen atom of the carbonyl group of CA. Accordingly, the coordination numbers around the Rh metal are believed to be 5 or 6 as described below:



But it should be mentioned that some of the Rh complexes may exist without direct interactions with CA like additives. These changes in infrared spectra are noticeable in the cases of 10 and 20 wt % Rh-CA films, but weak in the cases of 30 and 40 wt % Rh-CA films as expected since the intensities of the bands arising from the CA decrease due to the relatively decreased concentration of CA itself.

T_g of Rh-Containing Cellulose Acetate

As described above, the oxygen atoms of acyl groups of CA become the primary coordinating ligands toward Rh metal atoms, and accordingly the CA polymer molecules could be crosslinked through their coordination to Rh metal complexes, resulting in the increase of T_g .^{10,11}

As expected, the glass transition temperature of 10 and 20 wt % Rh-CA increases by 10 and 18°C,

respectively in comparison to that of pure CA (94°C). In the cases of 30 and 40 wt % Rh-CA films, however, they are decreased to 108 and 96°C, respectively. These results can be explained by the fact that at these relatively high metal concentrations the Rh complexes do not act as crosslinking agents any more but rather cause an increase in the mobility of CA molecules, resulting in the decrease of T_g .

Thus, in this study, we investigate the 10 and 20 wt % Rh-CA films, and these films are dried at 150°C in vacuum for 12 h to remove any adsorbed solvents or water molecules.

Phosphine Ligand Loss of Rh-CA Film in Benzene

When 10 or 20 wt % Rh-CA films are immersed in benzene or methanol at room temperature for 1 day, and then dried to remove adsorbed solvent molecules at 150°C in vacuum for 12 h, the yellow color of the films remains unchanged, but surprisingly the characteristic bands due to the phosphine ligands disappear completely in their infrared spectra (see Fig. 1). When these films are reacted with CO (600 torr) at 150°C for 1 day, two bands at 2010 and 2085 cm^{-1} with equal intensities are observed in their infrared spectra and these are believed to arise from the typical *cis*-Rh(I)(CO)₂ species (see later section). Their band intensities are exactly same as those of corresponding Rh-CA films without the treatment

in benzene solution, indicating that the Rh complex itself in cellulose acetate is not eluted in benzene solution.

Thus, in benzene solution, the $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ complexes in cellulose acetate are thought to lose only phosphine ligands. In this case, acyl carbonyl groups of CA are believed to replace the phosphine ligands and accordingly the interactions between CA and Rh complexes increase, resulting in the increase of T_g of the films by about 3°C in addition to the relatively greater changes of the bands at 1750 and 1230 cm^{-1} as discussed in the previous section. It is quite interesting to note that such easy loss or substitution of all three phosphine ligands around Rh metal atom in CA is unusual in comparison to the chemistry of unsupported $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ complex.

When these Rh-CA films are treated with free phosphine $[\text{P}(\text{C}_6\text{H}_5)_3]$ in benzene solution, recoordination of the phosphine ligands to Rh atoms are observed in the infrared spectra.

Reaction of Rh in CA with CO

When 10 wt % Rh-CA films, dried at 150°C in vacuum for 12 h, are treated with CO (600 torr) at 150°C for 12 h, three strong $\nu(\text{CO})$ bands at 2085, 2010, and 1980(sh) cm^{-1} are observed in their infrared spectra. The band at 1980(sh) cm^{-1} is quite weak in its intensity when the thickness of the film

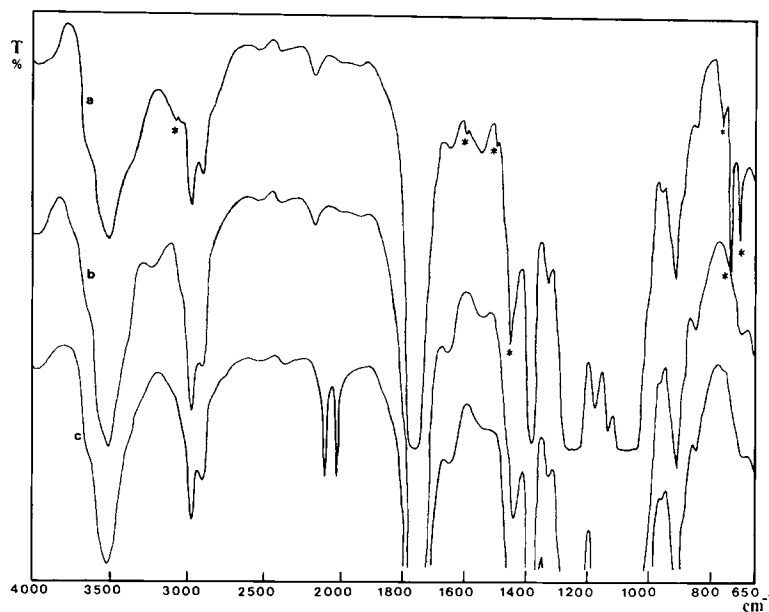


Figure 1 IR spectra for the loss of phosphine ligands of Rh complex in benzene solution: (a) 10 wt % Rh-CA film (neat, * due to phosphine); (b) the same film after 1 day in benzene solution; (c) after treatment with CO (600 torr) at 150°C for 1 day.

is less than about $12\ \mu\text{m}$, but it is strong when the film is thick (over about $12\ \mu\text{m}$) or the Rh metal complex concentration is over 20 wt %. The band at $1980\ \text{cm}^{-1}$ remains unchanged upon reaction with H_2 or upon desorption at 150°C under vacuum for 12 h, whereas the band intensities of the other two bands are reduced significantly by the reactions under the same conditions. Also, the band does not reappear when the film is reexposed to CO after the reactions with H_2 and O_2 . Therefore, these results

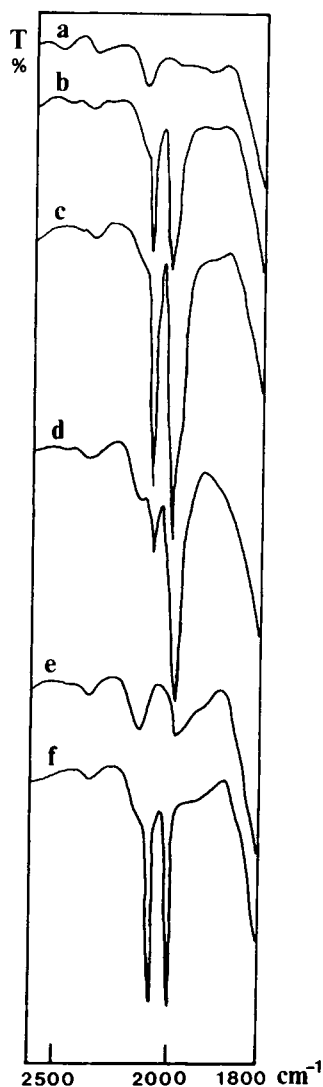


Figure 2 IR spectra for the formation of Rh-carbonyl species in CA: (a) 20 wt % Rh-CA film (neat); (b) 10 wt % Rh-CA film, reacted with CO (600 torr), 150°C , 12 h; (c) 20 wt % Rh-CA, reacted with CO (same conditions); (d) from (c), after reaction with H_2 (600 torr), 100°C , 12 h; (e) after reaction with O_2 (600 torr), 150°C , 12 h; (f) after reaction with CO (600 torr), 150°C , 12 h.

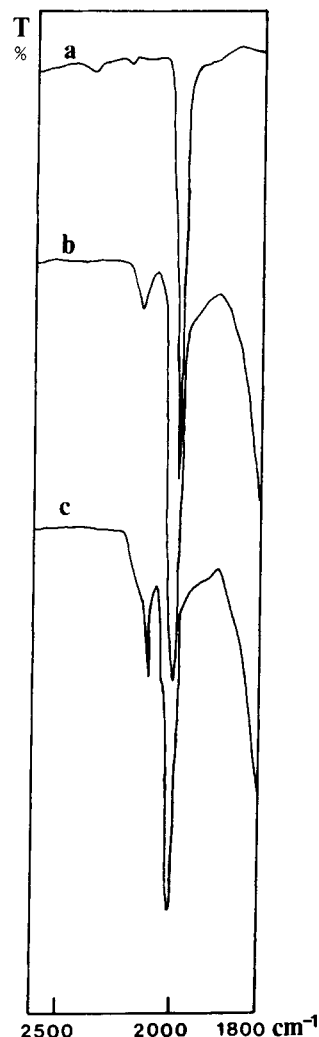


Figure 3 IR spectra for the formations of $\text{RhCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$ in CA: (a) products $\text{RhCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$ and unreacted $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ from the reaction between CO and $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ in KBr disc; $\nu(\text{CO})$, $1970\ \text{cm}^{-1}$; (b) same products in CA; $\nu(\text{CO})$, $1980\ \text{cm}^{-1}$; (c) from (b), after reaction with CO (600 torr), 150°C , 12 h; $\nu(\text{CO})$, 2085 , $2100\ \text{cm}^{-1}$; due to CA-*cis* $\text{Rh}(\text{I})(\text{CO})_2$, $1980\ \text{cm}^{-1}$; due to $\text{RhCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$.

reveal that the three bands have two different origins, as illustrated in Figure 2.

In order to ascertain the origin of the band at $1980\ \text{cm}^{-1}$, pure $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ in solid state is exposed to CO (600 torr) at 150°C for 12 h, and the resulting product is identified to be $\text{RhCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$, as already reported.¹² It shows a strong $\nu(\text{CO})$ band at $1970\ \text{cm}^{-1}$ in IR spectrum (KBr Disc), and there is no appreciable change of the band upon reactions with H_2 or O_2 at 150°C . When this

Table I Summary of CO Species on Polymer or Silica Supported Rh

Assignment	$\nu(\text{CO})$ (cm^{-1})	Reference
<i>Cis</i> -Rh(CO) ₂ (A21) ^a Cl	2083, 2002	13
<i>Cis</i> -Rh(CO) ₂ (PVPy) ^b Cl	2085, 2010	13
<i>Cis</i> -Rh(CO) ₂ (PBCN) ^c Cl	2088, 2018	13
<i>Cis</i> -Rh(CO) ₂ (SiI) ^d Cl	2085, 2015	14
<i>Cis</i> -Rh(CO) ₂ PSSA ^e Cl	2095, 2023	15

^a A21 = poly(*N,N*-dimethylvinylbenzylamine).

^b PVPy = poly-2-vinyl pyridine.

^c PBCN = polyvinylbenzylcyanide.

^d SiI = phosphine ligand bound on the surface of silica.

^e PSSA = sulfonated linear polystyrene.

complex is incorporated into CA, the band shifts to 1980 cm^{-1} (see Fig. 3).

Accordingly, the band at 1980 cm^{-1} can be assigned to $\nu(\text{CO})$ of RhCl(CO)[P(C₆H₅)₃]₂, which is formed by the reaction between CO and RhCl[P(C₆H₅)₃]₃ in CA. Considering the effects of film thickness and metal concentration on the intensity of the band at 1980 cm^{-1} as discussed in previous section, some of the RhCl[P(C₆H₅)₃]₃ in CA is believed to exist as only additive without direct interactions with CA polymer matrix and to form RhCl(CO)[P(C₆H₅)₃]₂ by the reaction with CO. At this stage, it is not clear why the band in question does not reappear after reactions with H₂ or O₂, or consecutive thermal heating, but it is thought that its interactions with CA are increased after such treatments. Consequently, it does not reappear in the infrared spectra.

The bands at 2085 and 2010 cm^{-1} with equal intensities are quite similar in shape to those of other polymer or silicone supported Rh-carbonyl species which are characteristically assigned to *cis*-Rh(I)(CO)₂. Examples are shown in Table I.

When the films containing the *cis*-Rh(I)(CO)₂ species are immersed in methanol or benzene solution at room temperature for 12 h and then dried in vacuum at 110°C overnight, the two bands disappear completely, and reappear after the reaction of the films with CO (600 torr) at 150°C for 12 h. But their intensities reduce by about 80%, indicating that some of the Rh-carbonyl complexes in CA is eluted in methanol solution (see Fig. 4).

This can be explained by that, upon the reaction with CO, the Rh metal atoms are saturated by six ligands [Cl, 3P(C₆H₅)₃, 2CO] and the interactions between acyl carbonyls of CA and Rh complexes decrease, causing easy separation of the complexes

from CA polymer matrix. Thus, RhCl[P(C₆H₅)₃]₃ complexes in CA produce *cis*-Rh(CO)₂ species upon the reaction with CO, and the coordinated carbonyls are found to be active in reaction with H₂ or O₂. These results are quite interesting in contrast with the reactivities of the same Rh complex without polymer support, in which only RhCl(CO)[P(C₆H₅)₃]₂ is formed and its Rh-carbonyl is not active to H₂ or O₂ under the same conditions.¹²

Reactions of Rh in CA with H₂ and CO

When 10 wt % (or 20 wt %) Rh-CA films are exposed to H₂ (600 torr), the light yellow color of the

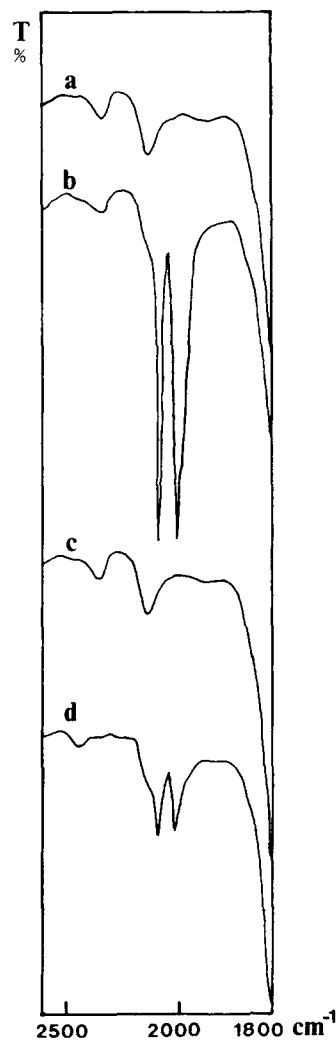


Figure 4 IR spectra showing the elution of Rh-carbonyl species formed in CA in methanol solution: (a) 20 wt % Rh-CA film in CH₃OH at RT for 12 h; (b) after reaction with CO (600 torr), 150°C, 12 h; (c) after 12 h in CH₃OH at RT; (d) after reaction with CO (same conditions as above).

film changes to dark brown at around 90°C. This color change is frequently observed in metal particle formation, especially, in polymer or inorganic oxide-supported systems.^{14,15}

In infrared spectra of the resulting Rh-CA films, a weak band at 1990 cm^{-1} is observed, and it can be attributed to rhodium monohydride. After 30 min in air, the band disappears in the spectra, and this result is consistently observed in repeated experiments. Compared to the known Rh(I) and Rh(III) hydride complexes,¹⁶⁻²⁰ usually stable in air at room temperature, the Rh-hydride species formed in CA are thought to be Rh(0)-monohydride, which is quite active in air at the ambient temperature (see Fig. 5).

After exposure to H_2 (600 torr) at 110°C for 12 h, the Rh-CA films are subsequently treated with CO at the same conditions and three $\nu(\text{CO})$ bands at 2085, 2035, and 2010 cm^{-1} appear in their infrared spectra. The two bands at 2085 and 2010 cm^{-1} correspond to the aforementioned *cis*-Rh(I)(CO)₂ species, indicating that the reduction reaction of Rh(I) to Rh(0) by H_2 is not complete at the described conditions. The new band at 2035 cm^{-1} disappears after about 30 min in air but reappears after readmission of CO. It seems reasonable to relate this band to Rh(0)-monocarbonyl (linear) since the $\nu(\text{CO})$ bands due to Rh(0) linear carbonyl, obtained by adsorption of CO on metallic Rh films²¹ or inorganic oxide-supported Rh samples, have been characteristically observed in 2010-2058 cm^{-1} region.²²⁻²⁵ But it should be mentioned that in the case of inorganic oxide-supported Rh complexes the reduction reaction under hydrogen are carried out at above 300°C in higher H_2 pressure. Thus, Rh(I) in CA is found to be reduced at relatively milder conditions, though the reduction is incomplete. Also, it is interesting to note that there was no Rh metal particle formation in case of silica-supported $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ under hydrogen for 1 month.¹⁴

In transmission electron microscopy study, very small Rh metal particles ca. 10 Å in diameter (about 1.86×10^{10} particles per cm^2) are observed. This result means that there is very weak Brownian motion-type behavior of the produced Rh metal atoms in CA, giving small particles by collision,²⁶ and explains why there is no formation of bridged Rh(0) carbonyls in Rh-CA films after reduction under hydrogen.

Reaction of Rh in CA with O_2

When the Rh-CA films are exposed to O_2 (600 torr) at 150°C for 3 days, there are no appreciable changes

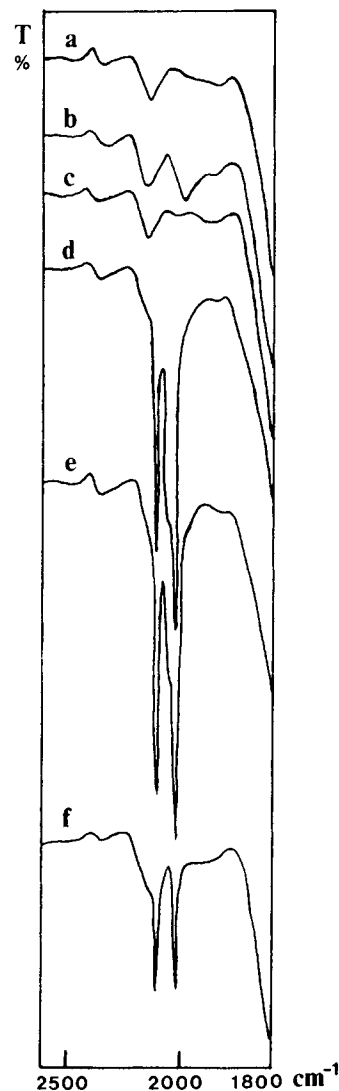


Figure 5 IR spectra showing the formations of CA-Rh(0)-H and CA-Rh(0)-CO species: (a) 20 wt % Rh-CA film; (b) after reaction with H_2 (600 torr), 150°C, 12 h; (c) spectrum taken after 20 min in air; (d) after reaction with CO (same conditions as above); (e) spectrum taken after 5 min in air; (f) after reaction with O_2 (600 torr), 100°C, 4 h.

in color of the films and in their infrared spectra except the effect of dehydration. When the same films are treated with CO at the same conditions, only two strong bands at 2085 and 2010 cm^{-1} appear in their infrared spectra, indicating that there is no oxidation of Rh(I) to Rh(III) at all. It is known that Rh species in inorganic oxide supports such as Al_2O_3 , SiO_2 , MgO , and TiO_2 are usually oxidized by oxygen above 300°C.²¹⁻²⁵

The carbonyl groups formed in Rh(I)-CA are removed completely when reacted with O_2 (600 torr)

at 150°C for 24 h, and the same result is consistently observed when the Rh-CA films are consecutively reacted with CO, O₂, CO, and O₂. The product of these reactions is easily identified as CO₂ by infrared spectroscopy. In addition, when the Rh-CA films partially reduced by hydrogen are reacted with O₂ at the described conditions as above, no appreciable oxidation of the Rh(0) atom to Rh(I) or Rh(III) takes place, but the Rh(0)-CO species are found to be active to O₂ as above.

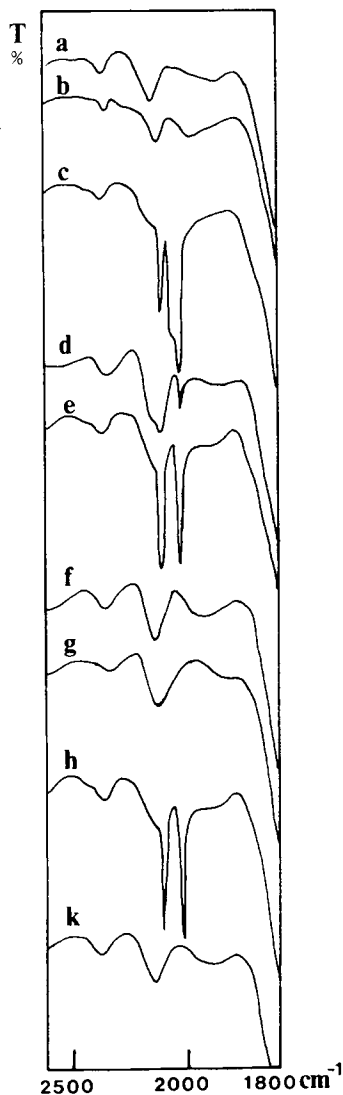


Figure 6 IR spectra for the cyclic reactions of Rh in CA with H₂, CO, O₂, CO, H₂, O₂, and CO consecutively: (a) 10 wt % Rh-CA film (neat); (b) after reaction with H₂ (600 torr), 150°C, 12 h; (c) after reaction with CO; (d) after reaction with O₂; (e) after reaction with CO; (f) after reaction with H₂; (g) after reaction with O₂; (h) after reaction with CO under the same conditions as above; (k) after 30 days in air at RT.

Table II Summary of Rh-Carboxyl and Rh-Hydride Species Formed in Cellulose Acetate

ν (cm ⁻¹)	Assignment
1980	CA ^a -L ^b ₂ RhCl(CO)
2085, 2010	CA-L ₃ RhCl(CO) ₂ (<i>cis</i>)
2035	CA-Rh(O)(CO)
1990	CA-Rh(O)H

^a CA = cellulose acetate matrix.

^b L = P(C₆H₅)₃.

Finally, several cyclic reactions of Rh-CA films with hydrogen, carbon monoxide, and oxygen give rise to the same results consistently as above without any decrease in rhodium reactivities (see Fig. 6). The types of CA-Rh carbonyls and hydride discussed and their frequencies are listed in Table II.

Catalytic Reactivities of Rh in CA

In the cellulose acetate matrix, the rhodium species are found to be quite reactive toward carbon monoxide, hydrogen, and oxygen at relatively mild conditions. Also, small rhodium metal particles are observed to be formed in CA upon the reduction reaction with hydrogen, which are expected to be active catalysts or catalytic precursors.^{14,27} Therefore, a few catalytic reactions in simple static state are carried out using the CA-Rh films after reduction by hydrogen at 150°C for 24 h to test the catalytic potentials in a preliminary way.

Hydrogenation of Ethylene

When a 1 : 1 mixture of ethylene and hydrogen (total pressure: 1 atm) in about 720 mL flask is reacted at 110°C with 0.08 g of Rh-CA films (metal contents: 2.2 wt %), complete conversion of ethylene to ethane is observed in the infrared spectra of the reaction mixture. There is no noticeable decrease of catalytic activity of the Rh-CA films after repeated hydrogenation reactions (five or six times). The turnover numbers given in substrate molecules transformed per Rh metal particle per second is estimated about 1.5×10^6 .

Oxidation of CO by O₂

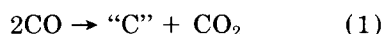
A 2 : 1 mixture of CO and O₂ is reacted at the same conditions as above and complete conversion of CO to CO₂ is observed in the same manner, i.e., after reaction, the $\nu(\text{CO})$ band disappears, while the bands due to CO₂ at 667, 2343, 3640, and 3740 cm⁻¹ appear in the infrared spectrum of the product in gas phase.

Water-Gas Shift Reaction

CO (1 atm) and slight excess of equivalent H₂O are reacted in the same flask at 140°C; but in this case the reacting flask is insulated to avoid condensation of water, and the reaction mixture is frequently monitored by infrared spectroscopy. During the reaction, the intensity of the band due to $\nu(\text{CO})$ at 2143 cm⁻¹ gradually decreases and those of the bands due to CO₂ increase correspondingly. After 5 days, the conversion is completed.

Fischer-Tropsch Type Reaction

A 1 : 3 mixture of CO and H₂ (total pressure: 1 atm) is reacted at 130°C for 5 days and surprisingly the products are found to be CO₂ and mixture of hydrocarbons such as methane and ethane. This result is evidenced by their infrared spectra.²⁸ This result is quite interesting since there are no alcohols or aldehyde, which are typical products of F-T type reaction.²⁹ At this stage, the function of CA polymer matrix and the mechanism of this F-T type reaction is unknown. However, it is believed that the "active carbon" or "surface carbide"^{30,31} is involved in reaction mechanism as below:



where $n = 1$ or 2 , $m = 2$ or 3 , and C = "active carbon" or "surface carbide."

Hydroformylation Type Reaction

In connection with the above F-T type reaction, a mixture of C₂H₄ (100 torr), CO (200 torr), and H₂ (460 torr) is reacted with 0.1 g of 20 wt % Rh-CA films at 130°C for 5 days, and the products are identified as CO₂ and mixture of hydrocarbons (propane, propene, isobutane, and small amount of ethane), on the basis of infrared spectral analysis.²⁸ This result is similar to those of the F-T type reaction. Accordingly, the mechanism of this reaction is supposed as above. But when only CO is reacted in the same conditions, there is no reaction like eq. (1) at all. Therefore, the active carbon species in Rh-CA films are thought to be formed from carbon monoxide under hydrogen.

Further investigation of the catalytic use of Rh-CA films is underway to determine actual product yields under controlled static and dynamic conditions.

CONCLUSIONS

RhCl[P(C₆H₅)₃]₃ complexes have been incorporated, using tetrahydrofuran as cosolvent, into cellulose acetate which has no typically known ligand groups such as phosphine, amine, and ionic functional groups. The resulting yellow colored Rh-CA films of 10–20 wt % Rh complex concentration are found to be thermally stable up to 150°C. The interactions between Rh metal atoms and acyl oxygen atoms of CA are assumed on the basis of infrared spectral and thermal analysis data. The reactions of 10 or 20 wt % Rh-CA films with CO in the temperature range of 90–150°C result in two different Rh-carbonyl species, which are assigned to CA-*cis*-Rh(I)(CO)₂ [$\nu(\text{CO})$: 2085 and 2010 cm⁻¹] and CA-RhCl(CO)[P(C₆H₅)₃]₂ [$\nu(\text{CO})$: 1980 cm⁻¹]. Treatment of the Rh-CA films with hydrogen at 150°C produces small Rh metal particles and active rhodium hydride species [$\nu(\text{Rh-H})$: 1990 cm⁻¹], of which oxidation state is assumed to be zero. When these partially reduced Rh-CA films are exposed to CO at 150°C, new Rh(0) monocarbonyls [$\nu(\text{CO})$: 2035 cm⁻¹] are observed. These carbonyls coordinated to Rh in CA are found to be quite reactive to H₂ and O₂ under relatively mild conditions. Finally, the Rh(I) complex supported by cellulose acetate shows catalytic reactivities in the temperature range of 100–150°C in the hydrogenation of ethylene, oxidation of carbon monoxide, water-gas shift reaction, and F-T type reactions. These catalytic activities under mild conditions are believed to arise from the small Rh metal particles in CA polymer matrix, resulting in large metallic surface area. Further studies involving cellulose acetate supported transition metals are in progress.

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REFERENCES

1. M. Kaneko and E. Tsuchida, *J. Polym. Sci. Macromol. Rev.*, **16**, 397–522 (1981).
2. C. E. Carraher, Jr., J. E. Sheats, and C. U. Pittman, Jr. (Ed.), *Organometallic Polymer*, Academic, New York, 1978.
3. A. K. St. Clair and L. T. Taylor, *J. Macromol. Sci. Chem.*, **A16**(1), 95–137 (1981).
4. R. E. Wetton, D. B. James, and W. Whiting, *J. Polym. Sci. Polym. Lett. Ed.*, **14**, 577–583 (1976).

5. A. K. St. Clair, V. C. Carrar, L. T. Taylor, and T. A. Furtch, *J. Am. Chem. Soc.*, **102**(2), 876 (1980).
6. O. Sumita, A. Fukuda, and E. Kuze, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 877-890 (1980).
7. (a) D. W. Macomber, W. P. Hart, and M. D. Rausch, *Adv. Organomet. Chem.*, **21**, 1-55 (1982); (b) R. S. Drago and K. J. Balkus, Jr., *Inorg. Chem.*, **25**, 718-719 (1986).
8. K. F. Wissbrun and M. J. Hannon, *J. Polym. Sci. Polym. Phys. Ed.*, **13**, 223 (1975).
9. J. Feldman, I. W. Shim, and Milton Orchin, *J. Appl. Polym. Sci.*, **34**, 969-976 (1987).
10. I. W. Shim and W. M. Risen, Jr., *Bull. Korean Chem. Soc.*, **9**(6), 368-376 (1988).
11. A. Eisenberg and M. King, *Ion Containing Polymers: Physical Properties and Structures*, Academic, New York, 1977; A. L. Andrady and M. O. Sefcik, *J. Appl. Polym. Sci.*, **29**, 3561 (1984).
12. G. Wilkinson (Ed.), *Comprehensive Organometallic Chemistry*, Pergamon, New York, 1982, Vol. 5, pp. 277-540.
13. L. D. Rollmann, *Inorg. Chem. Acta*, **6**, 137-140 (1972).
14. M. Bartholin, C. H. Graillat, A. Guyot, G. Condurier, J. Bandiera, and C. Nacache, *J. Mol. Catal.*, **3**, 17-32 (1977/78).
15. V. D. Mattera, Jr., P. J. Squatrito, and W. M. Risen, Jr., *Inorg. Chem.*, **23**, 3587 (1984).
16. K. Thomas, J. A. Osborn, A. R. Powell, and G. Wilkinson, *J. Chem. Soc. A*, **1968**, 1801.
17. W. Keim, *J. Organomet. Chem.*, **8**, 25 (1967).
18. T. Ito, S. Kitazume, A. Yamamoto, and S. Ikeda, *J. Am. Chem. Soc.*, **1970**, 3011.
19. D. Evans, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc. A*, **1968**, 2660.
20. J. V. Kingston and G. R. Scollary, *J. Chem. Soc. Chem. Commun.*, **1970**, 670.
21. C. W. Garland, R. C. Lord, and P. F. Troiano, *J. Phys. Chem.*, **69**, 1188 (1965).
22. I. W. Shim, V. D. Mattera, Jr., and W. M. Risen, Jr., *J. Catal.*, **94**, 531 (1985).
23. M. F. Brown and R. D. Gonzalez, *J. Phys. Chem.*, **80**, 1731 (1976).
24. Dela Betta, *J. Phys. Chem.*, **79**, 2519 (1975).
25. A. T. Bell, V. L. Kuznetsov, and Y. I. Yermakov, *J. Catal.*, **65**, 374 (1980).
26. A. Masson, J. J. Metois, and R. Kern, *Surf. Sci.*, **27**, 463-483 (1971).
27. D. Farin and D. Avnir, in *Proceedings 9th International Congress on Catalysis*, 1988, Vol. 3, p. 998; E. J. Braunschweig, A. D. Logan, S. Chakraborti, and A. K. Datye, *ibid*, p. 1122.
28. L. J. Bellamy, *The Infra-Red Spectra of Complex Molecules* Chapman and Hall, 1975.
29. M. Ichikawa, *J. Catal.*, **56**, 127 (1979); P. C. Ellgen et al., *Am. Chem. Soc. Adv. Chem. Ser.*, **178**, 147 (1979).
30. G. L. Geoffroy et al., *J. Am. Chem. Soc.*, **108**, 1315 (1986).
31. R. G. Copperthwaite et al., *J. Chem. Soc. Chem. Commun.*, **1987**, 541.

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