INTERACTIONS OF RHODIUM CARBONYL COMPOUNDS SUPPORTED ON INORGANIC OXIDES WITH CO, H$_2$ AND PROPYLENE

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Abstract — RhCl(CO)(PPh$_3$)$_2$, RhH(CO)(PPh$_3$)$_3$, and [RhCl(CO)$_2$]$_2$ were supported on silica gel, γ-alumina, titania, and magensia in 3 to 5 wt % to study the interactions of rhodium carbonyl with the surface of inorganic oxides When trans-RhCl(CO)(PPh$_3$)$_2$ was supported on the surface of silica gel, cis-RhCl(CO)(PPh$_3$)$_2$ species was detected via the splitting of the CO infra red stretching band of trans-RhCl (CO)(PPh$_3$)$_2$. With other supports, same phenomenon was observed but with the different pattern of intensities of the splitted CO stretching bands. RhH(CO)(PPh$_3$)$_3$ was easily decarbonylated, after interacting with the surface of silica gel, γ-alumina, and titania. However, [RhCl(CO)$_2$]$_2$ was decarbonylated on the surface of inorganic oxides mentioned above and most of supported [RhCl(CO)$_2$]$_2$ converted to a stable surface carbonyl species [M-OH-RhCl(CO)$_2$; M = Si, Al, Ti]. Diffuse reflectance infrared spectroscopy (DRS) was used to study the interactions of 5 wt % RhCl(CO)(PPh$_3$)$_2$ supported on silica gel with H$_2$, CO and/or propylene at various temperatures. The result indicated that the surface intermediates formed from the interaction of RhCl(CO)(PPh$_3$)$_2$ with CO, H$_2$ and C$_3$H$_6$ were not identical to the corresponding liquid-phase intermediates of RhCl(CO)(PPh$_3$)$_2$ in the presence of solvent.

INTRODUCTION

Most reactions catalyzed by homogeneous catalysts occur at relatively low temperatures with higher activities and selectivities than their heterogeneous counterparts. However, they have such disadvantages as the need to separate and recover them from the reaction products. This recovery step can be both complex and expensive. Many studies of the immobilization of soluble homogeneous catalysts have been carried out in attempts to retain those advantages of homogeneous catalysts while removing the associated disadvantages [1-13]. However, these attempts have not been successful in finding any commercial applications so far. Homogeneous catalytic components immobilized on the solid support were often easily removed during the prolonged use in the reaction. Sometimes, immobilized homogeneous catalysts have catalytic activities far less than their homogeneous counterparts. Previous *in situ* high pressure Raman studies of the catalytic gas-phase hydroformylation of propylene catalyzed by Co$_2$(CO)$_6$(PPh$_3$)$_2$ supported on γ-alumina and on silica have indicated that the surface reaction intermediates differed from those for the homogeneous liquid-phase hydroformylation reaction catalyzed by Co$_2$(CO)$_6$(PPh$_3$)$_2$ [14]. The catalytically ac-

tive species for the liquid-phase hydroformylation reaction was HCo(CO)$_3$(PPh$_3$), while HCo(CO)$_3$(PPh$_3$) was not observed in the gas phase hydroformylation, which is a plausible explanation for the reason why Co$_2$(CO)$_6$(PPh$_3$)$_2$ supported on alumina has less catalytic activity in the gas-phase hydroformylation reaction than in the liquid-phase hydroformylation reaction [15]. The Raman study of Co$_2$(CO)$_8$ covalently attached to a phosphinated silica indicated that the stoichiometric hydroformylation of propylene occured in a manner similar to that for the liquid-phase stoichiometric hydroformylation with Co$_2$(CO)$_6$(PPh$_3$)$_2$ [16]. When physically supported on γ-alumina without any anchoring ligand tethered on the surface of γ-alumina, Co$_2$(CO)$_6$(PPh$_3$)$_2$ directly interacted with hydroxyl groups or Lewis acid sites of γ-alumina either to form hydrogen bonding between the oxygen atoms of the carbonyl ligands and the hydrogen atoms of the hydroxyl groups or to form a Lewis acid-base adduct [17]. These species can interact with simple molecules such as H$_2$, CO and C$_3$H$_6$ in the absence of a solvent. The mode of interactions in the gas phase was not always identical to that of interactions in the liquid phase.

With these results reported from our laboratory, we have a particular interest in the gas phase hydroformylation reaction catalyzed by the supported

homogeneous catalytic components. Gerritsen et al. [18] have reported the preparation and characterization of a supported liquid-phase rhodium catalyst which was active for the gas phase hydroformylation of propylene. Rony and Roth [19] prepared Co$_2$(CO)$_6$(PBu$_3$)$_2$ supported on activated carbon by impregnating with Co$_2$(CO)$_6$(PBu$_3$)$_2$ dissolved in chloroform. This supported catalyst was found to be less active for the hydroformylation reaction than was the homogeneous counterpart dissolved in the liquid phase. Spek and Scholten [20] prepared Rh (π-C$_3$H$_5$)CO(PPh$_3$)$_2$ adsorbed on γ-alumina and found that it has catalytic activity for the gas-phase hydrogenation and hydroformylation of ethylene and propylene at atmospheric pressure and 60-90°C. The allyl ligand in Rh(π-C$_3$H$_5$) CO(PPh$_3$)$_2$ was readily split off under process conditions to produce a coordinatively unsaturated compound. In the present study, diffuse reflectance IR spectroscopy was used to study the interaction of rhodium carbonyl compounds with CO, H$_2$ and propylene in the absence of solvent. In order to compare the surface intermediates of rhodium carbonyls supported on inorganic oxides with the intermediates in the liquid-phase hydroformylation reaction, a high pressure in situ Raman study in the liquid phase was also performed. The catalytic activity of RhCl(CO)(PPh$_3$)$_2$ supported on γ-alumina was also measured in gas-phase hydroformylation of propylene to evaluated the potential use in industrial applications.

EXPERIMENTAL

Materials

RhCl(CO)(PPh$_3$)$_2$, RhH(CO)(PPh$_3$)$_3$ and [RhCl(CO)$_2$]$_2$ were purchased from Strem Chemicals (Newburyport, MA, U.S.A.) and used without further purification. Silica gel (BDH Chemical Ltd., England), γ-alumina (BDH Chemical Ltd., England), magnesia (Fischer) Chemical Co., U.S.A.) titania (Fischer Chemical Co., U.S.A.) titania (Fischer Chemical Co., U.S.A.) were evacuated under about 10^{-3} torr at 200°C to remove physisorbed water. The analytical grade solvents, benzene, and hexene-1, purchased from Aldrich Chemical Co. were used without further purification. Carbon monoxide (99.99% pure), hydrogen (99.95% pure) and propylene (CP grade) were obtained from Matheson (Chicago, U.S.A.) and used without further purification. A conventional vacuum-line and globe box equipped with cartridges for removal of H$_2$O and O$_2$ were used for handling of RhH(CO)(PPh$_3$)$_3$ and [RhCl(CO)$_2$]$_2$.

Apparatus

The Raman spectrometer was a Spex Ramalog 5

(Model 14018) equipped with a third monochromator and coupled to a PDP 11/03 minicomputer. The excitation source was a Spectra Physics Model 164 argon ion laser powered by a Spectra Physics model 265 exciter. Rated power output of all laser lines was 2 W. The green (514.5 nm) and blue (488.0 nm) lines had outputs of 800 and 700 mW, respectively.

The in situ high pressure Raman cell useable up to 2000 psig at 200°C and the hydroformylation reactor system were described elsewhere in detail [14].

A Nicolet 7199 FTIR instrument was used for the diffuse reflectance studies. For the diffuse reflectance study, a vacuum chamber (Model KKK, Harrick Scientific Corporation, Ossining, NY) was used with a Model DRA-PMN (Harrick) diffuse reflectance attachment.

A conventional vacuum system was used for sample pretreatment and evacuation and for introduction of adsorbates.

RESULTS AND DISCUSSIONS

Sample Preparation

Table 1 provides a summary of the preparations of rhodium carbonyls supported on inorganic oxides which were studied in this work. Experiences with the RhCl(CO)(PPh$_3$)$_2$ catalysts indicated that they were air and moisture stable. Therefore, catalysts prepared from RhCl(CO)(PPh$_3$)$_2$ were prepared in air under a ventilation hood. All other aspects of the synthesis were identical as described below.

0.15g of RhCl(CO)(PPh$_3$)$_2$ was added to a clean dry 100 ml round-bottom flask. Enough benzene was added to cover the catalyst and the mixture was stirred with a magnetic stirrer. 4.85 g of silica gel (partially dehydroxylated at 300°C under 10^{-5} torr of vacuum for 12 hrs) was added to the flask and the resulting slurry was diluted with benzene. The mixture was stirred for 20 hours before the benzene solvent was removed by a vacuum pump.

This procedure was repeated for the other supported catalysts. The amount of the carbonyl used was varied as needed to obtain the desired loading. When triphenyl phosphine was used, triphenyl phosphine was dissolved in the benzene before the support materials was added.

In order to obtain samples from which FTIR spectra could be obtained 5 mg of the supported catalyst was mixed with 60 mg of KBr. This mixture was ground by a mechanical pulverizer to give a fine homogeneous powder which was then poured into a KBr pelletizer. The mixture inside the pelletizer chamber was evacuated for two minutes to remove moisture.

The pelletizer was placed in a mechanical press

Table 1. Summary of rhodium carbonyl catalysts supported on inorganic oxides.

Catalysts/wt %	Support material	Other/wt%	Monolayer coverage loading[c] (wt%)
RhCl(CO) (PPh$_3$)$_2$/3	Silica gel (300)[b]	—	16.5
RhCl(CO) (PPh$_3$)$_2$/5	Silica gel (300)	—	16.5
RhCl(CO) (PPh$_3$)$_2$/5	γ-alumina (200)	—	10.7
RhCl(CO) (PPh$_3$)$_2$/5	Magnesia (45)	—	2.4
RhCl(CO) (PPh$_3$)$_2$/5	Titania (50)	—	2.7
RhCl(CO) (PPh$_3$)$_2$/5	Silica gel (300)	TPP/5[a]	—
RhCl(CO) (PPh$_3$)$_2$/5	Silica gel (300)	TPP/10	—
RhH(CO) (PPh$_3$)$_3$/5	Silica gel (300)	—	16.5
RhH(CO) (PPh$_3$)$_3$/5	γ-alumina (200)	—	10.7
RhH(CO) (PPh$_3$)$_3$/5	Titania (50)	—	2.7
[RhCl(CO)$_2$]$_2$/5	Silica gel (300)	—	—
[RhCl(CO)$_2$]$_2$/5	γ-alumina (200)	—	—
[RhCl(CO)$_2$]$_2$/5	Titania (50)	—	—

a: TPP = triphenyl phosphine

b: The value in parenthesis indicates the specific surface area (m^2/g).

c: These values were calculated on the assumption that RhCl(CO)(PPh$_3$)$_2$ and RhH(CO)(PPh$_3$)$_2$ occupy 213Å^2 per molecule.

and compressed to 8 tons/cm^2. Two minutes were allowed for stress relaxation before the pelletizer was again compressed to 8 tons/cm^2 and allowed to stand for ten minutes. The pelletizer was then slowly depressurized and the pellet was carefully removed and stored in a vacuum desiccator to avoid contact with moisture.

In order to study the interactions of 5 wt % RhCl(CO)(PPh$_3$)$_2$ supported on silica gel with CO, H$_2$, and propylene, DRS spectra of this catalyst were obtained under various conditions.

FTIR Spectra of RhCl(CO)(PPh$_3$)$_2$ Supported on Inorganic Oxides

FTIR spectra of RhCl(CO)(PPh$_3$)$_2$ supported on various inorganic oxides are presented in Figure 1. The band locations are summarized in Table 2. The CO stretching band of RhCl(CO)(PPh$_3$)$_2$ at 1969 cm^{-1} became a doublet and was shifted to 1966 and 1984 cm^{-1} when 3 wt % RhCl(CO)(PPh$_3$)$_2$ was supported on silica gel [Figures 1 (A) and (B)]. The band at 1966 cm^{-1} is attributed to trans-RhCl(CO)(PPh$_3$)$_2$ supported on silica gel, because trans-RhCl(CO)(PPh$_3$)$_2$ has a CO stretching band at 1969 cm^{-1}. The band at 1984 cm^{-1} is attributed to cis-RhCl(CO)(PPh$_3$)$_2$, because this compound has a CO stretching band at 1980 cm^{-1} (21, 22). The plausible equilibrium reactions involved in formation of cis-RhCl(CO)(PPh$_3$)$_2$ are indicated below.
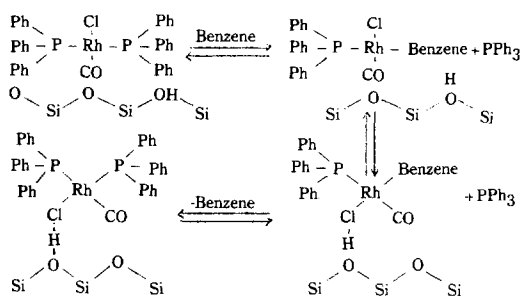
There are two reasons why formation of the cis-compound is favored on the surface of silica gel. First, the cis-RhCl(CO)(PPh$_3$)$_2$ is less sterically hindered on the surface of the silica gel than is the transform. In this case the bulky PPh$_3$ groups are located far above the surface of the silica gel. Second, the chlorine in RhCl(CO)(PPh$_3$)$_2$ can be hydrogen bonded to hydrogen atoms in the hydroxyl groups on the surface of the silica gel.

This explanation is further supported by the pattern of CO stretching bands of 5 wt % RhCl(CO)(PPh$_3$)$_2$ supported on silica gel [1965 cm^{-1} and 1975 cm^{-1} (sh), Figure 1 (C)]. The band at 1965 cm^{-1} arises from the bulky species, trans-RhCl(CO)(PPh$_3$)$_2$, and the shoulder at 1975 cm^{-1} arises from the monolayer surface species, cis-RhCl(CO)(PPh$_3$)$_2$. The intensity of the band
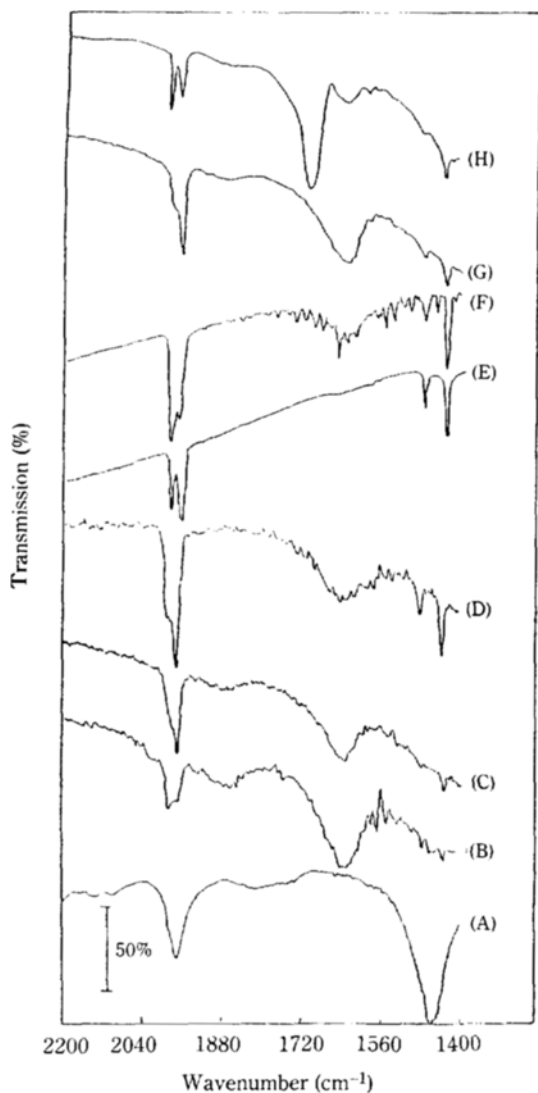
Fig. 1. FTIR spectra of RhCl(CO)(PPh₃)₂ supported on various inorganic oxides.

(A) : RhCl(CO)(PPh₃)₂ in THF solution.
(B) : 3 wt % on silica gel.
(C) : 5 wt % on silica gel.
(D) : 5 wt % on γ-alumina.
(E) : 5 wt % on MgO.
(F) : 5 wt % on TiO₂.
(G) : 5 wt % on silica gel [5 wt % PPh₃ was preadsorbed before the sample was impregnated with RhCl(CO)(PPh₃)₂].
(H) : 5 wt % on silica gel [10 wt % PPh₃ was preadsorbed before the sample was impregnated with RhCl(CO)(PPh₃)₂].

at 1965 cm⁻¹ is stronger than that of the band at 1975 cm⁻¹, because the concentration of the bulky species at 5 wt % loading of RhCl(CO)(PPh₃)₂ is higher than that of the bulky species at 3 wt % loading. Monolayer coverage of RhCl(CO)(PPh₃)₂ on the silica gel calculated from the molecule size of RhCl(CO)(PPh₃)₂ occurs at 16.5 wt % loading of RhCl(CO)(PPh₃)₂. However, bulk phase of RhCl(CO)(PPh₃)₂ was identified even at 3 wt % loading with infrared spectroscopy, indicating that when RhCl(CO)(PPh₃)₂ was recrystallized on the surface of silica gel, rhodium compound forms particles or multilayers as well as the surface monolayer. In other words, identical coverages of RhCl(CO)(PPh₃)₂ cannot be guaranteed merely by the normalization of loading of rhodium compound with the surface area of support materials. Hence we intended to study the support effect qualitatively with the constant loading of rhodium carbonyl compounds (5 wt %).

In order to investigate the support effect, 5 wt % of trans-RhCl(CO)(PPh₃)₂ was supported on γ-alumina. Its FTIR spectrum and band locations are presented in Figure 1 (D) and in Table 2, respectively. No evidence was found for the formation of a Lewis acid-base adduct on the surface of γ-alumina via interaction of a carbonyl ligand and an Al³⁺ site on the surface of γ-alumina. Such species were observed when Co₂(CO)₆(PPh₃)₂ was supported on γ-alumina [17]. Formation of this adduct shifts the CO stretching band to lower wavenumbers. However, the CO stretching bands of 5 wt % RhCl(CO)(PPh₃)₂ supported on the γ-alumina appeared at 1965 and at 1981 cm⁻¹ (as a shoulder). The absence of the Lewis acid-base adduct suggests that hydrogen bonding between Cl and H atoms in the hydroxyl groups occurs more readily than formation of a Lewis acid-base adduct between CO and Al³⁺. The distance between the Cl atom and a hydroxyl group is less than that between CO and Al³⁺ sites on the surface of γ-alumina. Hence, the species present on the surface of γ-alumina are similar to those present in the case of 5 wt % RhCl(CO)(PPh₃)₂ on the silica gel, i.e., both a bulky species, trans-RhCl(CO)(PPh₃)₂, and a less sterically hindered species, cis-RhCl(CO)(PPh₃)₂ will be present.

When 5 wt % of RhCl(CO)(PPh₃)₂ was supported on magnesia, CO stretching bands appeared at 1966 and 1985 cm⁻¹ [Figure 1 (E) and Table 2]. The band at 1985 cm⁻¹ is a shoulder as observed previously. The intensity of the band at 1966 cm⁻¹ [attributed to the trans-RhCl(CO)(PPh₃)₂] is stronger than that of the band at 1985 cm⁻¹ attributed to cis-RhCl (CO) (PPh₃)₂.

When 5 wt % of RhCl (CO) (PPh₃)₂ was supported on titania, CO stretching bands appeared at 1967 and

Table 2. FTIR band locations for RhCl(CO)(PPh$_3$)$_2$ supported on inorganic oxides (1400-2200 cm^{-1}).

Pure compound in THF solution	3 wt% on silica gel	5 wt% on γ-alumina	5 wt% on silica gel	5 wt% on magnesia	5 wt% on titania	5 wt% + 5 wt% TPP on silica gel	5 wt% + 10 wt% TPP on silica gel
	1435 sw	1435 ss	1435 sw	1435 ss	1435 sm	1438 sm	1422 sh
1460 ss	1456 sw						1439 sm
	1465 sw						
	1480 sw	1481 ss	1479 sw	1480 ss	1480 sm	1480 sw	1483 mw
					1616 sm		
					1624 sm		
	1633 bs	1629 bm			1636 sm	1637 bs	1635 bm
					1653 sm		1709 ms
1800 bw	1862 bw					1868 bw	1852 bw
1969 ss	1966 ss	1965 ss	1965 sm	1966 ss	1967 ss	1965 ss	1967 ss
	1984 ss	1981 sh	1975 sh	1985 ss	1984 ss	1981 sh	1985 ss

TPP = Tri-phenyl phosphine   s = strong, sharp
m = medium   w = weak
b = broad   sh = shoulder

1984 cm^{-1} [Figure 1 (F) and Table 2]. The intensity of the band at 1967 cm^{-1} [attributed to the trans-RhCl (CO) (PPh$_3$)$_2$] is weaker than that of the band at 1984 cm^{-1} attributed to the cis compound. This situation is the reverse of that of 5 wt % RhCl (CO) (PPh$_3$)$_2$ supported on magnesia.

In order to study the effects of PPh$_3$ adsorbed on the surface of silica gel on the structure of the surface species, 5 wt % trans-RhCl (CO) (PPh$_3$)$_2$ was supported on silica gel on which PPh$_3$ had been preadsorbed at levels of 5 and 10 wt %. The FTIR spectra are presented in Figures 1 (G) and (H) and band locations are summarized in Table 2. The CO stretching bands of RhCl (CO)(PPh$_3$)$_2$ supported on silica gel on which PPh$_3$ had been preadsorbed at 5 wt % appeared at 1965 and at 1981 cm^{-1} (sh). This pattern is similar to that of 5 wt % RhCl (CO) (PPh$_3$)$_2$ supported on silica gel [compare Figures 1 (C) and (G)]. Hence, at the 5 wt % level PPh$_3$ preadsorbed on silica gel does not significantly affect the structure of the surface species. However, when 10 wt % PPh$_3$ preadsorbed on silica gel, the structure of the surface species of RhCl(CO) (PPh$_3$)$_2$ was affected as indicated by the facts that the intensity of the band at 1967 cm^{-1} [arising from trans-RhCl (CO) (PPh$_3$)$_2$] is less than that of the band at 1985 cm^{-1} arising from the cis compound. Moreover it is also readily evident that a new strong CO stretching band appeared at 1709 cm^{-1} in the case of the higher loading of PPh$_3$. This band can not be assigned on the basis of available information.

The amount of cis-compound was calculated from the integration of the CO stretching infrared band of cis-RhCl (CO) (PPh$_3$)$_2$ normalized with the band area of ring deformation band of phenyl groups in PPh$_3$ ligand. The amount of cis-compound supported on silica gel, γ-alumina, magnesia and titania is roughly proportional to the surface area of each support materials (Ratio of surface area; silica gel: γ-alumina: magnesia: titania = 1:0.66:0.15:0.17, and Ratio of the amount of the cis-compount; silica gel: γ-alumina: magnesia: titania = 1:0.47:0.09:0.17). This result also suggests that cis-compound formed on the surface of support materials.

RhH(CO)(PPh$_3$)$_3$ Supported on Inorganic Oxides

Several 5 wt % RhH (CO) (PPh$_3$)$_3$ samples were prepared using silica gel, γ-alumina, and titania as supports. Their FTIR spectra can be compared with that of RhH (CO) (PPh$_3$)$_3$ dissolved in THF (See Fugure 2). The CO stretching bands of RhH (CO) (PPh$_3$)$_3$ supported on silica gel appeared with low intensities at locations similar to those of unsupported RhH (CO) (PPh$_3$)$_3$. The spectrum of 5 wt % RhH (CO) (PPh$_3$)$_3$ supported on γ-alumina does not exhibit any apparent CO stretching bands. This observation indicates that RhH(CO) (PPh$_3$)$_3$ were decarbonylated easily on the surface of silica gel and γ-alumina. The bands at 1865 cm^{-1} and at 1868 cm^{-1} in Figure 2 (B) and (D) are attributed to benzene adsorbed on the support. When 5 wt % of RhH(CO)(PPh$_3$)$_3$ as supported on titania, a new
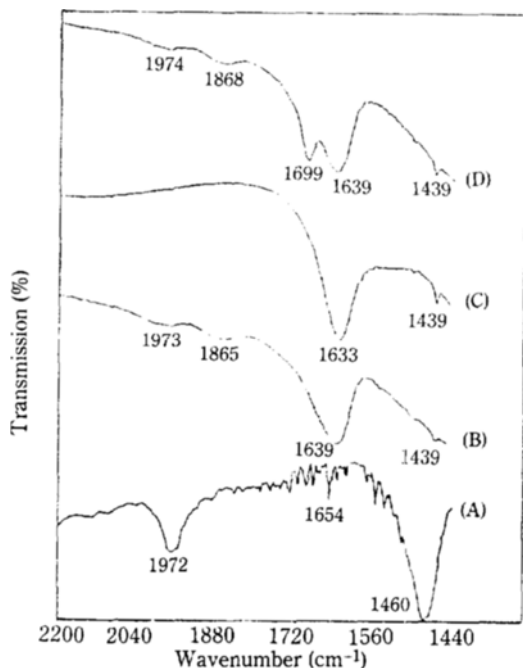
Fig. 2. FTIR spectra of RhH(CO)(PPh$_3$)$_3$ supported on various inorganic oxides.

(A) : FTIR spectrum of RhH(CO)(PPh$_3$)$_3$ dissolved in THF.

(B) : FTIR spectrum of 5 wt % RhH(CO)(PPh$_3$)$_3$ supported on silica gel.

(C) : FTIR spectrum of 5 wt % RhH(CO)(PPh$_3$)$_3$ supported on γ-alumina.

(D) : FTIR spectrum of 5 wt % RhH(CO)(PPh$_3$)$_3$ supported on titania.

strong band appeared at 1699 cm^{-1}, indicating formation of a new surface species. However, a definite assignment of this band can not be made.

[RhCl(CO)$_2$]$_2$ Supported on Inorganic Oxides

Samples containing 5 wt % [RhCl(CO)$_2$]$_2$ supported on silica gel, γ-alumina, and titania were prepared in a glove box under N$_2$. Drastic evolution of CO was observed during preparation of the catalyst supported on a fully hydroxylated titania. This sample had the FTIR spectrum shown in Figure 3 (C). It has only a weak CO stretching band at 1991 cm^{-1}. However, a new strong band at 1699 cm^{-1} was observed. This band was not observed when [RhCl(CO)$_2$]$_2$ was supported on either silica gel [Fugure 3 (B)] or γ-alumina [Figure 3 (D)].

When [RhCl(CO)$_2$]$_2$ was supported on partially dehydroxylated silica gel, three CO stretching bands were observed at 2086, 2017, and 1842 cm^{-1}. The band at 1842 cm^{-1} is attributed to a bridged CO species in a partially decarbonylated species or adsorbed on rhodium crystallites. At higher loadings of

[RhCl(CO)$_2$]$_2$, all of the [RhCl(CO)$_2$]$_2$ can not be stabilized by formation of surface species. The stabilized surface species are indicated by CO stretching bands at 2086 and 2017 cm^{-1}. These bands can be assigned to symmetric and asymmetric CO stretching bands of dicarbonyl species. When RhCl$_3$·3H$_2$O was supported on the fully hydroxylated silica gel and treated with CH$_3$I and CO at 120°C, Krzywicki et al. [23] observed two CO stretching bands at 2091 and 2018 cm^{-1}. They concluded that these bands can be attributed to the following species:

$$\begin{array}{cc} \text{H} & | \\ \text{Si} - \text{O} - \text{Rh} - \text{CO} & \quad (I) \\ | \\ \text{CO} \end{array}$$
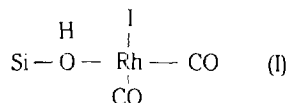
This previous result permits us to propose that the surface species of [RhCl(CO)$_2$]$_2$ supported on silica gel is similar to species (I) and that it has the structure shown below because of the similar locations of CO stretching
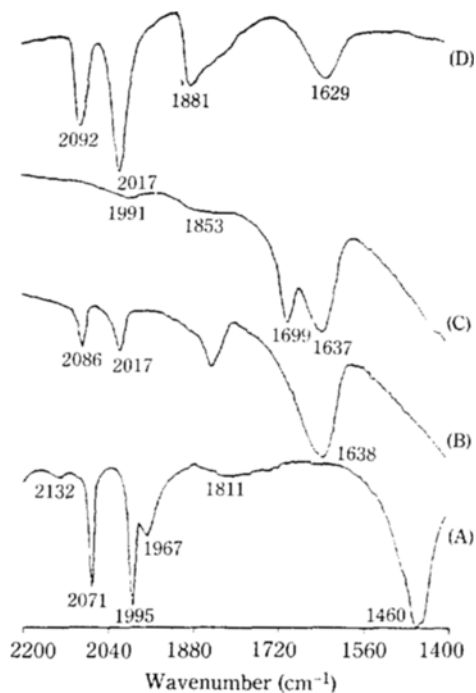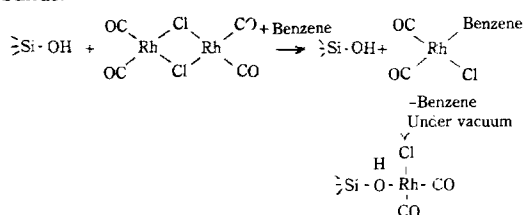

Fig. 3. FTIR spectra of [RhCl(CO)$_2$]$_2$ supported on various inorganic oxides.

(A) : FTIR spectrum of [RhCl(CO)$_2$]$_2$ dissolved in THF.

(B) : FTIR spectrum of 5 wt % [RhCl(CO)$_2$]$_2$ supported on silica gel.

(C) : FTIR spectrum of 5 wt % [RhCl(CO)$_2$]$_2$ supported on titania.

(D) : FTIR spectrum of 5 wt % [RhCl(CO)$_2$]$_2$ supported on γ-alumina.

bands.

When 5 wt % $[RhCl(CO)_2]_2$ was supported on γ-alumina, two CO stretching bands attributed to linear CO species appeared at 2092 and 2017 cm^{-1}. An unresolved broad bridged CO stretching band with an absorption maximum at 1881 cm^{-1} was also observed [Figure 3 (D)]. Krzywicki et al. [23] observed similar CO stretching bands at 2096 and 2024 cm^{-1} when $[RhCl(CO)_2]_2$ was supported on fully hydroxylated γ-alumina. Hence, the surface species of $[RhCl(CO)_2]_2$ supported on partially dehydroxylated γ-alumina is very similar to that of $[RhCl(CO)_2]_2$ supported on silica gel. Possible interactions between CO ligands and Al^{3+} Lewis acid sites are indicated by the facts that the intensities of the bands at 2092 and 2017 cm^{-1} are not equal each other and that several bridged CO stretching bands are present. The possibility of hydrogen bonding between CO and OH group is slim. When hydrogen bonding occurs, the electron transfer from the oxygen atom of CO to the hydrogen atom of OH group reduces the electron density at oxygen atom. This will shift the CO stretching bands of surface rhodium car-

bonyl compound to the higher wavenumber region. This kind of shifts in CO stretching bands was not observed.

Interactions of $RhCl(CO)(PPh_3)_2$ Supported on Silica Gel with CO, H_2, and Propylene

Diffuse reflectance infrared spectroscopy (DRS) was used to study the interactions of 5 wt % $RhCl(CO)$ $(PPh_3)_2$ supported on silica gel with H_2. This sample was equilibrated with 800 torr of H_2 at 20°C, 60°C, and 121°C (See Table 3). These spectra are identical with the diffuse reflectance spectrum of $RhCl(CO)$ $(PPh_3)_2$ supported on the silica gel. This result indicates that at one atmosphere hydrogen does not react with supported $RhCl(CO)(PPh_3)_2$ at temperatures up to 121°C. However, under 20 atmospheres each of CO and H_2, $RhCl(CO)(PPh_3)_2$ is known to react with H_2 to produce $RhH(CO)(PPh_3)_2$ and HCl [24].

Subsequently, the aforementioned $RhCl(CO)$ $(PPh_3)_2$ supported on silica gel was equilibrated with 400 torr of CO and H_2 at 66°C for 4 hours. The DRS spectrum of the sample under this equilibrium condition is almost the same as that of $RhCl(CO)(PPh_3)_2$ supported on silica gel. No new species were found at 66°C. However, at 121°C a new CO stretching band appeared at 2086 cm^{-1}. This band suggests the formation of a dicarbonyl species [25].

$$RhCl(CO)(PPh_3)_2 \underset{121°C}{\overset{CO/H_2}{\rightleftharpoons}} RhCl(CO)_2(PPh_3) + PPh_3$$
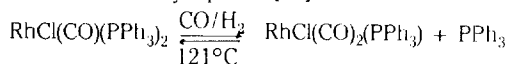
Subsequently, these surface species were equilibr-

Table 3. Diffuse reflectance infrared bands of 5 wt% $RhCl(CO)(PPh_3)_2$ supported on silica gel under various reactants (1400-2200 cm^{-1}).

Reactants	Temperature (°C)	Band locations (cm^{-1})
None	20	1435, 1479, 1631, 1966, 1975 sh
800 torr of H_2	20	1437, 1480, 1626, 1697, 1863, 1963
	66	1436, 1481, 1630, 1882, 1960, 1981
	121	1437, 1480, 1630, 1962, 1979
400 torr of H_2 and CO	66	1436, 1481, 1630, 1877, 1965, 1981
	121	1436, 1480, 1628, 1872, 1966, 2086
	170	1630, 1875, 2083
125.5 torr of H_2, 125.5 torr	20	1630, 1884, 1973, 2082
of CO, and 434 torr of	66	1630, 1884, 1978, 2078
propylene[a]	190	1612, 1861
250 torr of CO, 250 torr	20	1441, 1481, 1640, 1664, 1840, 1963, 1984
of H_2, and 265 torr of	66	1441, 1481, 1640, 1666, 1837, 1966, 2094
propylene[b]	121	1441, 1479, 1640, 1664, 1838, 1957, 1978, 2086
	170	1439, 1479, 1630, 1665, 1830, 1972, 1980, 2080

a: Subsequent to the equilibrium under 400 torr of CO and H_2 at 170°C.

b: Fresh $RhCl(CO)(PPh_3)_2$ supported on silica gel.

ated with CO and H₂ at 170°C for 11 hours. The bands at 1436 and 1480 cm⁻¹ (assigned to the CH deformation and the C-C stretching band of phenyl group, respectively) disappeared. This observation suggests that PPh₃ is not coordinated to the rhodium atom, and that rhodium crystallites are produced on the surface of silica gel. Because the uncoordinated PPh₃ has a melting points of 80.5°C and would desorb from the surface of silica gel due to the high vapor pressure of PPh₃ at 170°C. Hence, it can be concluded that the remaining CO stretching band at 2083 cm⁻¹ is attributed to a linear CO species adsorbed on rhodium crystallites.

Subsequently, the system was cooled to 20°C and then equilibrated with 125.5 torr of H₂, 125.5 torr of CO, and 434 torr of C₃H₆ for 1 hour. This treatment restored the CO stretching band at 1973 cm⁻¹ (See Table 3), but did not restore any bands arising from coordinated PPh₃. Equilibration at 66°C for 1.5 hours did not restore any bands associated with coordinated PPh₃. Equilibration at 170°C for 2.5 hours caused the CO stretching band at 2078 cm⁻¹ to disappear, indicating that linear CO species was not present under this condition.

Virgin RhCl(CO)(PPh₃)₂ supported on silica gel was equilibrated with a hydroformylation gas mixture (250 torr each of CO, H₂, and propylene at 20°C for 1.5 hours). The pattern of the DRS bands under this equilibrium condition is almost the same as that of RhCl(CO)(PPh₃)₂ supported on silica gel without reactants except for the band at 1660 cm⁻¹. This band is attributed to the C=C stretching band of propylene physisorbed on the surface of silica gel. However, a new CO stretching band appeared at 2094 cm⁻¹ when the system was equilibrated with CO, H₂, and propylene at 66°C for 10 hours. This band is attributed to a dicarbonyl species, Rh(CO)₂Cl(PPh₃)₂, which has a strong CO stretching band at 2088 cm⁻¹ [26]. Subsequently the system was equilibrated at 121°C for 1.5 hours. Three CO stretching bands appeared at 1957, 1978, and 2086 cm⁻¹. The CO stretching band at 1978 cm⁻¹ can arise from a dimeric species, [Rh(CO)(PPh₃)Cl]₂, which has a broad CO stretching band at 1980 cm⁻¹. In the liquid phase reaction in the presence of CO the Rh(CO)₂(PPh₃)Cl is in equilibrium with [Rh(CO)(PPh₃)Cl]₂ [27]. At this equilibrium condition, the hydroformylation reaction occurred to a small extent as indicated by the presence of aldehydic CH stretching bands at 2858 and 2881 cm⁻¹.

Subsequently, the system was equilibrated at 170°C for 1 hour. The features of the spectrum did not change significantly from those of the DRS spectrum equilibrated at 121°C. It is interesting to observe that when RhCl(CO)(PPh₃)₂ supported on the silica gel was
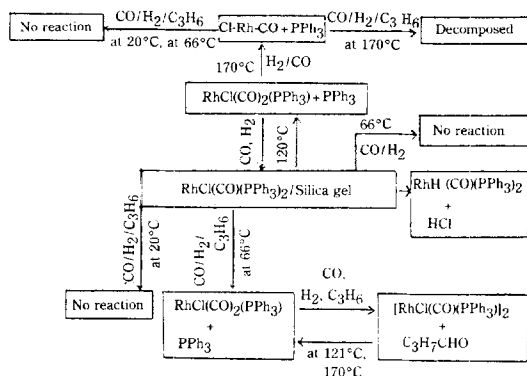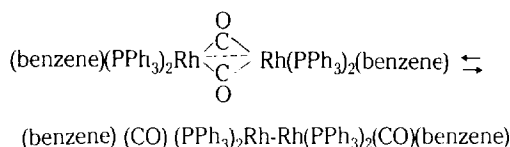

Fig. 4. Surface species of RhCl(CO)(PPh₃)₂/silica gel interacted with CO, H₂ and C₃H₆.

equilibrated with CO and H₂ at the same temperature, 170°C, RhCl(CO)(PPh₃)₂ was no longer stable and decomposed into rhodium crystallites. However, when RhCl(CO)(PPh₃)₂ supported on silica gel was equilibrated with CO, H₂, and propylene at 170°C, RhCl(CO)(PPh₃)₂ did not decompose into rhodium crystallites. This observation suggests that complicated equilibria exist between RhCl(CO)(PPh₃)₂ and the hydroformylation gas mixture.

The surface species formed when RhCl(CO)(PPh₃)₂ supported on silica gel interacts with CO, H₂, and C₃H₆ are illustrated in Figure 4.

In situ Raman study of RhCl(CO)(PPh₃)₂ Dissolved in Benzene Interacting with CO, H₂, and Hexene-1 at High Pressures

0.27 g of RhCl(CO)(PPh₃)₂ was dissolved in 5 cc of benzene. Then the system was pressurized with 260 psig each of CO and H₂ at 25°C. As soon as the system was pressurized, the color of solution changed from yellow to orange-yellow. The Raman spectrum of this system is presented in Figure 5(A). A strong CO stretching band is present at 1743 cm⁻¹. The bands at 1602 and 1584 cm⁻¹ are assigned to Fermi resonance of benzene. The band at 1543 cm⁻¹ can not be assigned adequately. The rhodium carbonyl dimer, [Rh(CO)(solvent)(PPh₃)₂]₂, involved in the equilibria of RhCl (CO) (PPh₃)₂ with CO and H₂ has an infrared CO stretching band at 1740 cm⁻¹ [28]. This compound is in equilibrium with its tautomer in benzene.

$$(benzene)(PPh_3)_2Rh \overset{\overset{O}{\underset{\parallel}{C}}}{\underset{\underset{\parallel}{C}}{\underset{O}{}}} Rh(PPh_3)_2(benzene) \rightleftarrows$$

(benzene) (CO) (PPh₃)₂Rh-Rh(PPh₃)₂(CO)(benzene)

The linear CO stretching band attributed to the tautomer was not observed because of its weak inten-

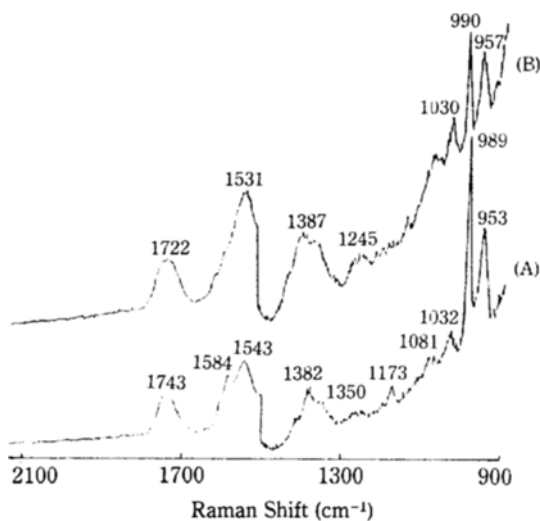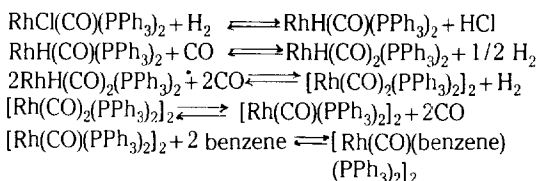Fig. 5.

(A) : Raman spectrum of RhCl(CO)(PPh$_3$)$_2$ dissolved in benzene equilibrated at 25°C with 260 psig each of CO and H$_2$.

(B) : Raman spectrum of RhCl(CO)(PPh$_3$)$_2$ dissolved in benzene equilibrated at 80°C with 310 psig each of CO and H$_2$.

sities. Formation of [Rh(CO)(solvent)(PPh$_3$)$_2$]$_2$ can be explained by the following equilibria.

$$RhCl(CO)(PPh_3)_2 + H_2 \rightleftharpoons RhH(CO)(PPh_3)_2 + HCl$$
$$RhH(CO)(PPh_3)_2 + CO \rightleftharpoons RhH(CO)_2(PPh_3)_2 + 1/2\ H_2$$
$$2RhH(CO)_2(PPh_3)_2 + 2CO \rightleftharpoons [Rh(CO)_2(PPh_3)_2]_2 + H_2$$
$$[Rh(CO)_2(PPh_3)_2]_2 \rightleftharpoons [Rh(CO)(PPh_3)_2]_2 + 2CO$$
$$[Rh(CO)(PPh_3)_2]_2 + 2\ benzene \rightleftharpoons [Rh(CO)(benzene)(PPh_3)_2]_2$$

If [Rh(CO)(benzene)(PPh$_3$)$_2$]$_2$ has a Raman CO stretching band around 1740 cm^{-1} (This compound has an infrared CO stretching band at 1740 cm^{-1}.), the predominant species of RhCl(CO)(PPh$_3$)$_2$ equilibrated with CO and H$_2$ at 25°C would be the rhodium carbonyl dimer. Although [Rh(CO)$_2$(PPh$_3$)$_2$]$_2$ has a CO stretching band below 1800 cm^{-1}, this compound has a strong CO stretching band at 1992 cm^{-1} indicating that this compound is not the predominant species when RhCl (CO) (PPh$_3$)$_2$ was equilibrated with CO and H$_2$ at 25°C.

Subsequently, the equilibrium temperature was raised to 80°C. The resultant Raman spectrum is presented in Figure 5(B). The Raman bands of RhCl (CO) (PPh$_3$)$_2$ equilibrated under this condition are almost the same as those of RhCl(CO)(PPh$_3$)$_2$ equilibrated with CO and H$_2$ at 25°C. The strong CO stretching band at 1722 cm^{-1} is attributed to [Rh(CO) (solvent) (PPh$_3$)$_2$]$_2$. An FTIR spectrum of the sample drawn from the reaction mixture after it was cooled to 25°C and
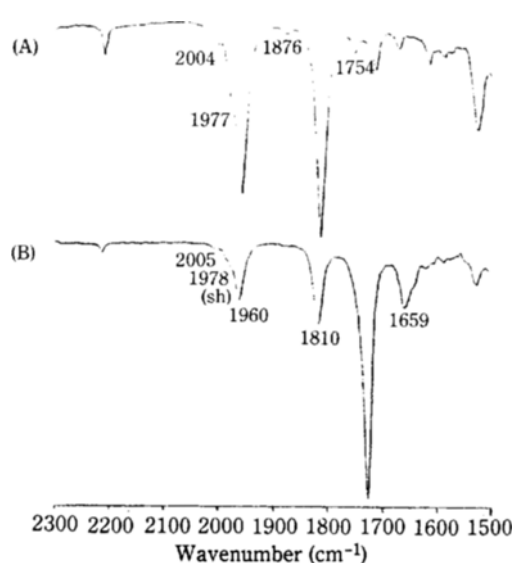

Fig. 6.

(A) : FTIR spectrum of RhCl(CO)(PPh$_3$)$_2$ dissolved in benzene at 25°C after previous exposure at 80°C to 310 psig of CO and H$_2$ for 7 hours and after release of CO and H$_2$ pressure.

(B) : FTIR spectrum of RhCl(CO)(PPh$_3$)$_2$ dissolved in benzene at 25°C after previous exposure at 80°C to 290 psig each of CO and H$_2$ and hexene-1 and after release of CO and H$_2$ pressure.

the pressure of CO and H$_2$ decreased to atmospheric has CO stretching bands at 2004 (m), 1977 (sh, s), 1876 (w), and 1754 (m) cm^{-1} [Figure 6(A)]. This pattern of CO stretching bands is similar to that of [Rh(CO)$_2$(PPh$_3$)$_2$]$_2$ having CO stretching bands at 2005 (sh, w), 1985 (s), 1790 (sh), and 1765 (s) cm^{-1}. This result indicates that [Rh(CO)$_2$(PPh$_3$)$_2$]$_2$ is involved in the equilibria of RhCl(CO)(PPh$_3$)$_2$ at high pressures of CO and H$_2$ at 80°C.

In order to identify intermediate species formed under *in situ* hydroformylation reaction conditions, 0.1 g of RhCl(CO)(PPh$_3$)$_2$ was dissolved in 3 m*l* of benzene and 2 m*l* of hexene–1.This system was then pressurized with 250 psig each of CO and H$_2$ at 25°C. The Raman spectrum of this system is presented in Figure 7. A strong broad band appeared at 1705 cm^{-1}. This band location is in the region of wavenumbers characteristic of [Rh(CO)(benzene)(PPh$_3$)$_2$]$_2$, and aldehyde species. Another band indicating the presence of the aldehyde species is observed at 1407 cm^{-1}. The band at 1705 cm^{-1} can be assigned to the CO stretching band of a rhodium carbonyl dimer and the aldehyde species. A new weak band appeared at 1623 cm^{-1}. The

location of this band is characteristic of the acylcarbonyl species [28]. In homogeneous catalysis by RhCl $(CO)(PPh_3)_2$, the oxidative addition of H_2 and the reductive elimination of aldehyde is believed to be the rate determining step at low temperatures. If this is true, the characteristic of acylcarbonyl species or the π-complexed hexene-1 rhodium carbonyl compound would be the predominant species when $RhCl(CO)$ $(PPh_3)_2$ is equilibrated at 25°C with CO, H_2, and hexene-1. The absence of the strong $C=C$ stretching band in the *in situ* Raman spectrum suggests that most of the hexene-1 is coordinated via the formation of either a π-complex or a σ-complex. The bands at 1548 cm^{-1} and 1518 cm^{-1} in Figure 7 can be attributed to these π-or σ-complexes. Hence, the intermediate species formed when $RhCl(CO)(PPh_3)_2$ is equilibrated with CO, H_2, and hexene-1 at 25°C are believed to be $[Rh(CO)(benzene)(PPh_3)_2]_2$ and $RCORh(CO)(PPh_3)_2$ (R = alkyl).

Subsequently, the equilibrium temperature was raised to 80°C. After the hydroformylation reaction was allowed to proceed for three hours the system pressure was dropped from 590 psig to 200 psig. The Raman spectrum of the resultant product mixture is presented in Figure 8. The pattern of Raman bands between 1500 and 2100 cm^{-1} is similar to that of the Raman bands of $RhCl(CO)(PPh_3)_2$ equilibrated with CO, H_2, and hexene-1 at 25°C (See Figure 7). The strong doublet at 1716 and 1700 cm^{-1} is attributed to $[Rh(CO)(benzene)(PPh_3)_2]_2$ and the product species, normal and iso-heptaldehyde. The increase in the concentration of the aldehyde species is reflected in the increase in the intensity of the bands at 1716 and 1700 cm^{-1}. The bands characteristic of acylcarbonyl species and of π-or σ-complexed hexene-1 rhodium carbonyls are still present, indicating that the rate determining
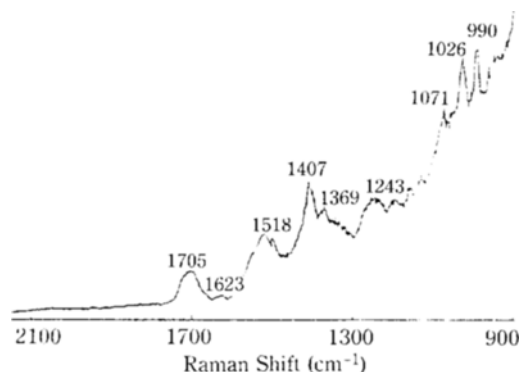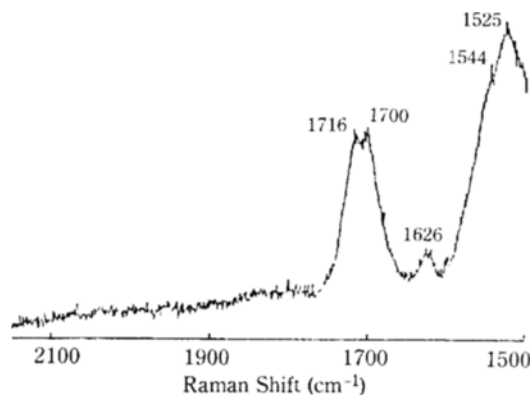

Fig. 8. Raman spectrum of $RhCl(CO)(PPh_3)_2$ dissolved in benzene equilibrated at 80°C with 250 psig each of CO and H_2 and hexene-1.

step for the hydroformylation of hexene-1 is the oxidative addition of hydrogen and the reductive elimination of the aldehyde species. The presence of the acylcarbonyl species is indicated by the CO stretching band at 1659 cm^{-1} in the FTIR spectrum of the sample drawn from the *in situ* high pressure Raman cell after 5 hours of reaction and depressurized [Figure 6(B)]. Other linear CO stretching bands characteristic of acylcarbonyl species (1990 and 1943 cm^{-1}) are not observed because these bands overlap with the strong band of benzene at 1960 cm^{-1}. However, the acylcarbonyl species must be present in the sample because the band at 1659 cm^{-1} is characteristic only of acylcarbonyl species. The presence of $[Rh(CO)_3(PPh_3)_2]_2$ when $RhCl(CO)(PPh_3)_2$ was equilibrated with CO, H_2, and hexene-1 at 80°C is indicated by the CO stretching band at 2005 and 1978 (sh) cm^{-1} in Figure 6(B). [Rh $(CO)_2(PPh_3)_2]_2$ dissolved in CH_2Cl_2 has CO stretching bands at 2005 (sh), 1985 (s), 1790 (sh), and 1765 (s) cm^{-1}. Unfortunately, the bands at 1790 and 1765 cm^{-1} overlap the strong bands of benzene and aldehyde species respectively.

Measurement of Catalytic Activity of RhCl (CO) $(PPh_3)_2$ Supported on γ-Alumina in the Gas Phase Hydroformylation

5 wt % of $RhCl(CO)(PPh_3)_2$ was supported on γ-alumina by an impregnation method. 2 g of RhCl (CO) $(PPh_3)_2/\gamma$-alumina and 18 g of propylene (0.429 mol) were charged into the autoclave reactor in the absence of any solvent. This reaction mixture was pressurized with 125 psig each of CO and H_2 at 24°C. The reaction proceeded at 100°C under a constant total pressure of 620 psig. The CO/H_2 up-take rate was 3 psig per minute of initial 80 minutes. The ratio of the normal aldehyde to the isoaldehyde formed was 1.60 at the time of 78 % conversion of propylene. The turnover number

Fig. 7. Raman spectrum of $RhCl(CO)(PPh_3)_2$ and hexene-1 dissolved in benzene equilibrated at 25°C with 250 psig each of CO and H_2.

was calculated to be 28.9 min^{-1}. The catalytic activity of RhCl(CO)(PPh$_3$)$_2$ is much larger than that of Co$_2$(CO)$_6$(PPh$_3$)$_2$ supported either on γ-alumina or on silica gel [14]. The catalytic properties of [RhCl(CO)$_2$]$_2$ covalently anchored to the phosphinated silica gel [LRh(CO)$_2$Cl; L = SIL-(CH$_2$)$_8$PPh$_2$]. The normalized uptake rate of CO/H$_2$ for RhCl(CO)(PPh$_3$)$_2$ supported on γ-alumina in the gas phase is 1.2 times as great as that for catalysis by LRh(CO)$_2$Cl in liquid phase. The selectivity (ratio of normal aldehyde to isoaldehyde = 1.6) in the gas-phase hydro-formylation of propylene catalyzed by supported RhCl(CO)(PPh$_3$)$_2$ was found to be larger than that in the liquid-phase hydroformylation of propylene catalyzed by LRh(CO)$_2$Cl (Selectivity = 1.41)

CONCLUSION

Infrared studies of RhCl(CO)(PPh$_3$)$_2$ supported on silica gel, γ-alumina, titania and magnesia showed that some of the trans-RhCl(CO)(PPh$_3$)$_2$ was converted to the cis-RhCl(CO)(PPh$_3$)$_2$ on the surface of inorganic oxides due to the steric hindrance and the hydrogen bonding between the chlorine atom and hydroxyl groups on the surface of inorganic oxides. The differences in the physicochemical properties of the inorganic oxides used as support materials perturbed the splitting of the CO stretching band in RhCl(CO)(PPh$_3$)$_2$ in a different manner to show the different pattern of intensities of the CO stretching bands.

When RhH(CO)(PPh$_3$)$_3$ was supported on silica gel, γ-alumina and titania, RhH(CO)(PPh$_3$)$_3$ was easily decarbonylated not to show any strong CO stretching bands in the infrared spectrum, indicating the surface hydroxyl groups or surface acidic and/or basic sites facilitated the decarbonylation of RhH(CO)(PPh$_3$)$_3$.

The surface species of [RhCl(CO)$_2$]$_2$ when supported on silica gel, γ-alumina and titania was found to be M-OH-RhCl(CO)$_2$ (M = Si, Ti, Al) which was identified with the pattern of CO stretching bands of infrared spectrum of [RhCl(CO)$_2$]$_2$ supported on various inorganic oxides.

DRS study of the interaction of RhCl(CO)(PPh$_3$)$_2$ supported on silica gel with CO, H$_2$, and/or C$_3$H$_6$ indicated that the surface intermediates in the gas phase was not always indentical with the liquid phase intermediates of RhCl(CO)(PPh$_3$)$_2$ with CO, H$_2$ and/or C$_3$H$_6$.

The high pressure in situ Raman study of RhCl (CO) (PPh$_3$)$_2$ dissolved in benzene interacting with CO, H$_2$, and hexene-1 and the infrared spectra of the reaction mixture after equilibration of RhCl(CO)(PPh$_3$)$_2$ with high pressures of CO, H$_2$, and hexene-1 indicated the presence of Rh(CO)(benzene)(PPh$_3$)$_2$, acylcarbonyl, and [Rh(CO)$_3$(PPh$_3$)$_2$]$_2$. This study also confirmed that

the rate determining step in the hydroformylation reaction catalyzed by RhCl(CO)(PPh$_3$)$_2$ in the liquid phase was the oxidative addition of H$_2$ and reductive elimination of aldehyde in the catalytic cycle involved with rhodium carbonyls.

Turn-over number of RhCl(CO)(PPh$_3$)$_2$ supported on the silica gel and the selectivity towards n-aldehyde in the gas-phase hydroformylation reaction were reasonably large. Hence, it can be concluded that RhCl (CO) (PPh$_3$)$_2$ supported on the silica can have a potential for the industrial application in the gas-phase hydroformylation reaction.

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