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Catalytic Properties of $RhCl_3 \cdot 3H_2O$ Immobilized on the Modified Poly(styrene–divinylbenzene) Copolymer in Aqueous Phase Hydroformylation of Propylene

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$RhCl_3 \cdot 3H_2O$ and $RhCl(CO)(PPh_3)_2$ were immobilized on the poly(styrene–divinylbenzene) copolymer (PS/DVB) containing $-CH_2P(C_6H_4SO_3H)_2$ (DPPDS: diphenylphosphine disulfonate) groups to give active and stable hydroformylation catalysts in an aqueous phase. Solid-state ^{31}P NMR spectra and FTIR analysis indicate that the structure of $RhCl_3 \cdot 3H_2O$ immobilized on the PS/DVB containing DPPDS groups (Rh(III)/SPPS) is similar to that of $RhCl(CO)(PPh_3)_2$ immobilized on the same polymer (Rh(I)/SPPS). The hydroformylation of propylene using these catalysts (Rh(III)/SPPS) has been investigated at 373 K and in the pressure range between 5 and 40 atm in an aqueous phase. The rate of hydroformylation was approximately first order with respect to catalyst concentration and increased with the increase of propylene concentration up to 0.45 mol/liter. The rate also increased with the increase of hydrogen pressure. However, the rate of hydroformylation passed through a maximum with the increase of partial pressure of carbon monoxide. The activation energy of propylene hydroformylation catalyzed over Rh(III)/SPPS between 353 and 393 K was found to be 12.1 kcal/mol. Kinetic study with Rh(III)/SPPS containing various amounts of SO_3H group indicates that SO_3H groups play an important role in improving the catalytic activity in the aqueous phase hydroformylation. © 1994 Academic Press, Inc.

INTRODUCTION

A homogeneous catalyst system containing triphenylphosphine *meta*-trisulfonate (TPPTS) has been recently commercialized for the oxo process (1). Kuntz (2) reported that the trisodium salt of tri(*m*-sulfophenyl)phosphine prepared by sulfonation of triphenylphosphine with oleum followed by neutralization was used as a ligand in the hydroformylation reaction catalyzed over rhodium complex. Rhodium complexes containing TPPTS are highly active and selective to *n*-butyraldehyde for the hydroformylation of propylene in an aqueous phase and can be reused without a significant loss in activity. Hence, we prepared a modified poly(styrene–divinylbenzene) copolymer support containing $-CH_2P(C_6H_4SO_3H)_2$ groups and immobilized rhodium complexes on this support. These catalysts can be used in a continuous fixed-bed reactor in an aqueous phase and have a high activity and stability (3, 4).

In this work, ^{31}P NMR and FTIR have been used to characterize the structures of polymer-immobilized catalysts. ^{31}P NMR spectroscopy is a highly sensitive technique to elucidate the structures of metal–phosphine complexes (5). High-resolution ^{31}P NMR of solvent-swollen polymers reported by Grubbs and Sweet (6) indicates that a signal observed for an uncoordinated immobilized phosphorus group subsequently disappeared upon coordination to a rhodium complex. They attributed this result to the increased relaxation time due to complexation of the phosphine to the metal center. The coordination of the metal center to phosphine compounds restricts the motion of the phosphorus so severely as to prevent its detection in a ^{31}P NMR high-resolution solution spectrum due to several line-broadening mechanisms.

To investigate the catalytic properties of these catalysts, the effects of the concentrations of catalyst and olefin, and the partial pressure of CO (P_{CO}) and $H_2(P_{H_2})$ on the rate of hydroformylation in an aqueous phase have been studied at 373 K. The effects of temperature, pH of solvent, and excess PPh_3 on the rate and selectivity were also investigated.

EXPERIMENTAL

Materials

$RhCl(CO)(PPh_3)_2$ and $RhCl_3 \cdot 3H_2O$ were purchased from Strem Chemical, Inc. (U.S.A.), and triphenylphosphine was procured from Aldrich Chemical Co. (U.S.A.). All other reagents are analytical grade and used without

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further purification. Carbon monoxide and hydrogen were purified with an oxy-trap, a gas drier, and a carbon dioxide adsorber (Alltech Assoc., Inc., U.S.A.). Propylene (CP grade, Matheson, U.S.A.) was purified with an oxy-trap and a gas drier.

Preparation of Catalysts

2%-Crosslinked gel-type phosphinated poly(styrene–divinylbenzene) copolymer(PS/DVB) containing $-CH_2PPh_2$ groups was prepared by the conventional method (7). SO_3H groups were incorporated to this phosphinated PS/DVB by sulfonation with concentrated sulfuric acid (7, 8). The phosphine content of this phosphinated PS/DVB (PPS) was 8.8 wt%. Phosphinated PS/DVB beads (5 g) were swollen in 20 ml of 1,2-dichloroethane at 353 K for 12 h and then sulfonated with 50 ml of concentrated sulfuric acid at 368 K for 32 h. These sulfonated beads were hydrated very slowly with deionized water to decrease the breakage of the beads. After slow hydration, these beads were washed with water and acetone repeatedly and dried at 353 K under high vacuum for 48 h. $RhCl_3 \cdot 3H_2O$ was immobilized on this sulfonated copolymer (SPPS) to form a polymer-bound catalyst (Rh(III)/SPPS). $RhCl_3 \cdot 3H_2O$ and a sulfonated copolymer were suspended in a deoxygenated mixture of distilled water (50 ml) and ethanol (50 ml). The mixture was refluxed for 6 h at 353 K, then cooled to room temperature. These catalyst beads were filtered, dried under vacuum at 353 K for 24 h, and stored in a desiccator. $RhCl(CO)(PPh_3)_2$ was immobilized on the same support (Rh(I)/SPPS) and on the 2%-crosslinked gel-type phosphinated PS/DVB (Rh(I)/PPS) to compare the structure of Rh(I)/SPPS with that of Rh(I)/PPS. The amount of SO_3H groups in Rh(III)/SPPS measured by NaOH titration was 1.5 meq H^+/g catalyst. In order to investigate the effect of SO_3H groups on the catalytic activity, commercial 2%-crosslinked phosphinated PS/DVB (Strem Chemical, Inc.; phosphine content = 1.92 wt%) was sulfonated with various concentration of sulfuric acid. All operations were carried out under a nitrogen atmosphere.

Reaction Procedure

Hydroformylation of propylene was conducted at a constant temperature and pressure in a 1000-ml autoclave (Parr, Model 4521). A detailed description of the reaction system was given in the previous paper (9). Constant reaction pressure was maintained by introducing a hydrogen–carbon monoxide gas mixture from a gas reservoir via a forward pressure regulator preset at the reaction pressure. The catalyst solution was transferred to the reactor, then reactants (propylene, carbon monoxide and hydrogen) were introduced at a desired reaction temperature. The reaction rate and selectivity were calculated from the product analysis with gas chromatography (Tracor 560).

Analytical Methods

The infrared spectra were obtained by FTIR (Bomem MB-102). The typical solution of IR spectra was 2 cm^{-1}. The FTIR spectra were obtained from a sample prepared as a KBr disk. Product analysis was done with gas chromatography using a column (10 ft. × 0.125 in. o.d.) packed with Carbowax 20 M on Chromosorb W (60–80 mesh). The rhodium contents of the solid catalysts were determined colorimetrically with a UV–VIS spectrophotometer (Beckman, Model 35). Phosphorus content was determined by atomic absorption spectroscopy according to the procedure described in the literature (10, 11). The amount of SO_3H groups in the resin catalyst was measured by titration with NaOH. Solid-state ^{31}P NMR employing high-power decoupling, cross-polarization, and magic-angle spinning was used to characterize polymer-immobilized rhodium complexes. The ^{31}P NMR spectra were recorded on Bruker AC 300 spectrometer at 121.5 MHz. All spectra were recorded in an N_2 atmosphere. Pulse-FT NMR and broadband noise decoupling techniques were used. The ^{31}P NMR spectra of the polymer-immobilized catalysts were recorded after averaging 18,000 pulses with a flip angle of 90° and a repetition rate of 3 Hz. Changing the flip angle or the repetition rate did not alter the spectra of the polymer complexes. Chemical shifts are expressed based on the chemical shift of aqueous H_3PO_4 solution (85 wt%). Negative shift values are upfield.

RESULTS AND DISCUSSION

1. Characterization of Polymer-Immobilized Rhodium Complexes by High-Resolution Solid-State ^{31}P NMR Using Magic-Angle-Spinning Techniques

In the present work, high-resolution solid-state CP/MAS ^{31}P NMR was used to study the structures of the polymer-immobilized catalysts. Fyfe *et al.* (12) reported an extensive study of tertiary phosphines, tertiary phosphine oxide transition-metal phosphine complexes, and their analogues immobilized on the surfaces of glass and silica using solid-state CP/MAS ^{31}P NMR high-resolution solution ^{31}P NMR. A number of spectra obtained in this study confirmed that the chemical shifts and coupling constants obtained with these techniques were directly comparable for each given compound. Table 1 and Fig. 1 indicate that Rh(I)/PPS($RhCl(CO)/(PPh_3)_2$ immobilized on PPS) has three signals at 63.6, 21.9, and −12.2 ppm. The resonance peak at 63.6 ppm is ascribed to the immobilized $RhCl(CO)(PPh_3)_2$. The resonance peak of immobilized tertiary phosphine oxide ligand and immobilized tertiary phosphine ligand appeared at approximately 21.9

TABLE 1

Summary of Solid-State CP/MAS ^{31}P NMR Chemical Shifts for Polymer-Immobilized Complexes

Sample	CP/MAS ^{31}P NMR δ (ppm)		
Commercial polymer-bound diphenylphosphine (polystyrene crosslinked with 2% divinylbenzene)		26.3	−6.2
SPPS		33.0	−12.3
Rh(III)(0.4)[a]/SPPS	67.4	31.7	−9.7
Rh(III)(3.7)/SPPS	65.3	25.8	−11.2
Rh(III)(11.8)/SPPS	63.8	27.3	−11.7
Rh(III)(3.9)/SPPS-Na	65.3	26.0	−10.6
Rh(I)(1.6)/SPPS-Na	64.5	31.6	−12.3
Rh(I)(2.2)/PPS	63.6	21.9	−12.2

[a] The numbers in parenthesis indicate the rhodium contents (wt%) in the catalysts.

and −12.2 ppm, respectively. Fyfe *et al.* (12) demonstrated that the solid-state ^{31}P NMR spectrum of (*p*-vinylphenyl)diphenylphosphine itself consists of a single resonance at −7.0 ppm (relative to phosphoric acid) and the spectra of commercial samples of polymer-immobilized diphenylphosphine has two resonances. They reported that the resonance peak at −6.2 ppm in 2%-crosslinked samples could be identified as immobilized binary phosphine and that the resonance at about 26 ppm could be assigned to phosphine oxide (12). However, Fig. 2A shows that SPPS has two signals at 33.0 and −12.3 ppm and has a shoulder between 60 and 70 ppm. The resonance peak at 33.0 ppm could be assigned to a sulfonated phosphine oxide ligand and the peak at −12.2 ppm could be assigned to a sulfonated phosphine ligand. The shoulder between 60 and 70 ppm could be assigned to an isomer of sulfonated phosphine ligand, to disulfonated phosphine or to disulfonated phosphine oxide. Arhancet *et al.* (13) reported that $P(O)(m\text{-}PhSO_3H)_3$ has a chemical shift of 34.7 ppm. This result indicates that SPPS has sulfonated triaryl phosphine oxide ligand. The presence of this oxide species arises from the oxidation of sulfonated triaryl phosphine ligands. Figures 2B and 2C show that Rh(III)/SPPS has a new resonance peak at about 63–67 ppm. The appearance of this peak could be due to the immobilized $RhCl_3 \cdot 3H_2O$ with two phosphine ligands, and the chemical shift of immobilized $RhCl_3 \cdot 3H_2O$ of Rh(III)/SPPS moves to downfield slightly with the increase of rhodium (III) contents. The resonance peak around 100 ppm in Figs. 2B and 2C is ascribed to the $RhCl_3 \cdot 3H_2O$ bonded with three phosphine ligands.

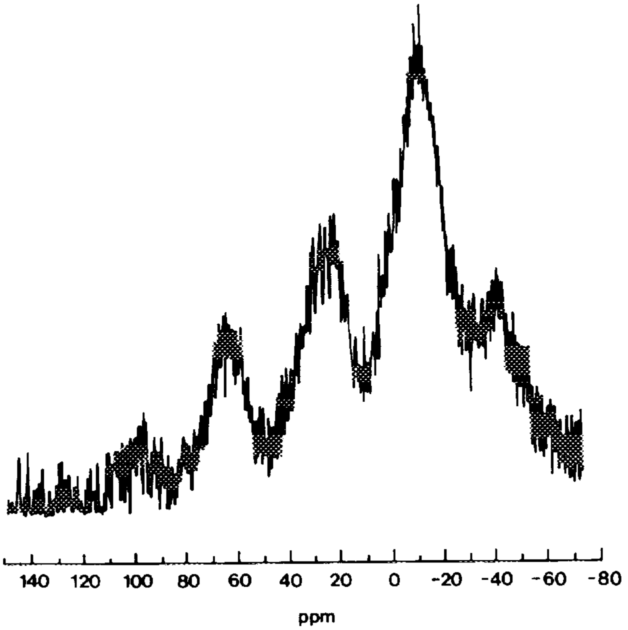


FIG. 1. Solid-state ^{31}P NMR spectrum of Rh(I)(2.2)/PPS.

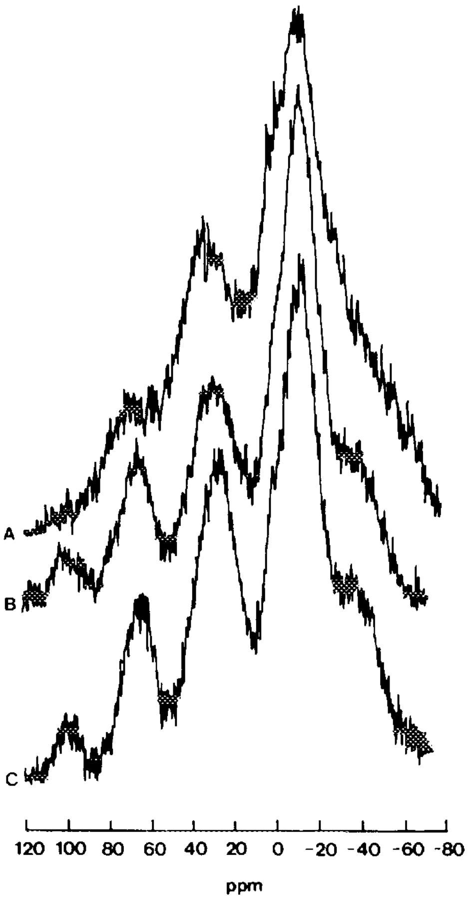


FIG. 2. Solid-state ^{31}P NMR spectra of (A) SPPS, (B) Rh(III)(0.4)/SPPS, and (C) Rh(III)(11.8)/SPPS.

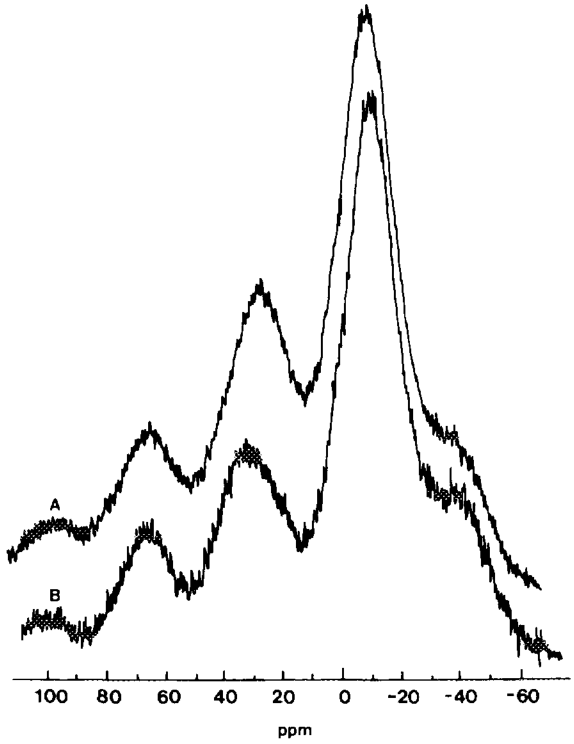


FIG. 3. Solid-state ^{31}P NMR spectra of (A) Rh(III)(3.9)/SPPS-Na and (B) Rh(I)(1.6)/SPPS-Na.

Rh(III)(3.9)/SPPS and Rh(III)(3.9)/SPPS-Na ($RhCl_3 \cdot 3H_2O$ immobilized on the PS/DVB containing neutralized DPPDS ligands) containing an equal amount of rhodium(III) have a similar chemical shift result. Table 1 and Figure 3 indicate that Rh(III)(3.9)/SPPS-Na and Rh(I)(1.6)/SPPS-Na have a similar peak at about 63–67 ppm. This result indicates that both $RhCl_3 \cdot 3H_2O$ and $RhCl(CO)(PPh_3)_2$ were immobilized on the polymer support in the similar manner.

2. *FTIR spectra of Rh(III)/PPS, SPS, and Rh(III)/SPPS*

FTIR was used to compare the structures of Rh(III)/PPS and SPS (sulfonated PS/DVB containing $-SO_3H$ groups) with that of Rh(III)/SPPS. Polystyrene has a skeleton stretching vibration of the benzene ring appeared at 1601, 1583 cm^{-1} and 1494, 1453 cm^{-1} as two doublets (14). The scissor vibration of the $-CH_2-$ group is masked by the skeleton vibration at 1453 cm^{-1}. Similar to polystyrene, SPS has skeleton stretching vibrations at 1600, 1583 (sh), 1492, and 1447 cm^{-1}, as shown in Fig. 4B. This result shows that a sulfonation of PS/DVB did not perturbate the skeleton stretching vibrations of polystyrene phenyl ring significantly.

The ring stretching bands of Rh(III)/SPPS (Fig. 4A) are different from those of Rh(III)/PPS (Fig. 4C), indicating that sulfonation of PPS significantly perturbate the stretching vibrations of the phenyl ring. Therefore it can be speculated that sulfonation of PPS did not occur at the phenyl groups of polystyrene but occurred at the phenyl ring of the phosphine. This result is in agreement with ^{31}P NMR study, as shown in Table 1, that the chemical shifts of ^{31}P in the SPPS are different from those of ^{31}P in PPS. However, IR data indicate the possibility of sulfonation on the phenyl rings of PS/DVB. Rh(III)/SPPS dehydrated completely shows three other bands at 1360, 1172, and 902 cm^{-1}. The band at 1360 cm^{-1} can be assigned to the asymmetric stretching vibration of S=O and the band at 1172 cm^{-1} to the symmetric stretching vibration of S=O. The band at 902 cm^{-1} can be assigned to the stretching vibration of S–O bond.

3. *Catalytic Properties of Rh(III)/SPPS*

The activity, selectivity, and stability of the Rh(III)/SPPS in the hydroformylation of propylene in an aqueous phase at 30 atm ($H_2 : CO = 1 : 1$) and 373 K were summarized in the previous paper (3). Under these reaction conditions, most of the product was aldehyde (>98 mol%). Rh(III)/SPPS was highly active and stable. The catalytic activity of Rh(III)/SPPS was maximized at the ratio of phosphine to Rh of 8.7. The activity and selectivity of the hydroformylation of propylene by Rh(III)/SPPS increased with the increase of the total pressure (3). Other

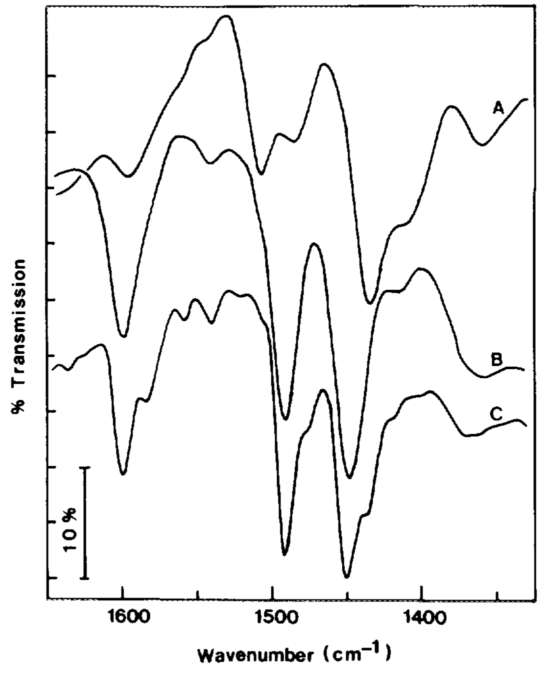


FIG. 4. FTIR spectra of (A) Rh(III)/SPPS, (B) SPS, and (C) Rh(III)/PPS.

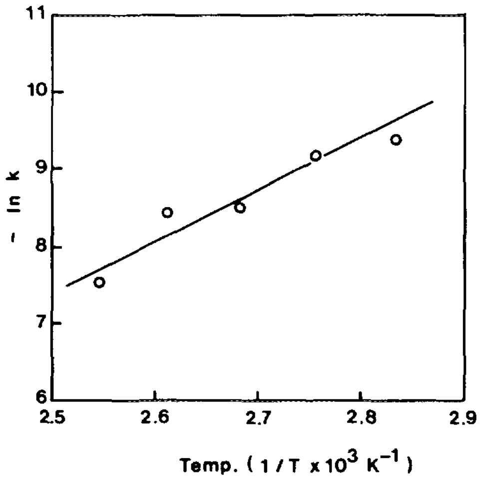


FIG. 5. Effect of reaction temperature on the rate of the hydroformylation of propylene catalyzed over Rh(III)/SPPS (Rh loading = 11.8 wt%, P/Rh = 2.5). Reaction conditions: C_3H_6 = 0.11 mol, solvent = 300 ml (water), P_{H_2}/P_{CO} = 15 atm/15 atm, and reaction time = 4 h.

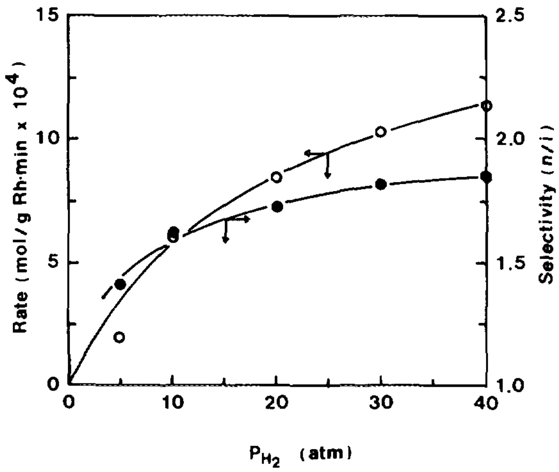
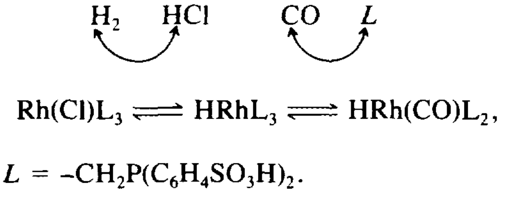


FIG. 6. Effect of H_2 partial pressure on the rate (○) and selectivity (●) catalyzed over Rh(III)/SPPS (Rh loading = 3.7 wt%, P/Rh = 7.9). Reaction conditions: C_3H_6 = 0.11 mol, solvent = 300 ml (water), P_{CO} = 5 atm, reaction temp. = 373 K, and reaction time = 4 h.

effects of reaction conditions on the catalytic properties of Rh(III)/SPPS are discussed in the following.

3.1. Effect of reaction temperature. Reaction rates were measured at 353–413 K. Above 413 K, severe decomposition of the catalyst was observed and the reaction rate was very low below 353 K. From the slope of the Arrhenius plot, as shown in Fig. 5, the activation energy of hydroformylation of propylene between 353–393 K was found to be 12.1 kcal/mol. The selectivity did not change much in this temperature range.

3.2. Effect of H_2 partial pressure. The effect of H_2 partial pressure (P_{H_2}) on the reaction rate and selectivity of the hydroformylation of propylene catalyzed over Rh(III)/SPPS was investigated at a constant partial pressure of carbon monoxide (5.0 atm). Figure 6 indicates that the activity and selectivity increased with the increase of H_2 pressure. No simple reaction order with respect to H_2 is observed. At low H_2 pressures, the active species, rhodium hydride, might be rapidly formed by addition of hydrogen to the Rh(III)/SPPS. Hence, the reaction rate increased rapidly with increase of this active species. FTIR analysis in the previous work (3) indicated that the catalyst might be converted to an active and stable Rh(I) carbonyl complex during the hydroformylation reaction as



$$Rh(Cl)L_3 \xrightleftharpoons{H_2 \quad HCl} HRhL_3 \xrightleftharpoons{CO \quad L} HRh(CO)L_2,$$

where $L = -CH_2P(C_6H_4SO_3H)_2$.

However, at high H_2 pressure, the formation of rhodium hydride was completed and the rate increased slightly with the increase of the pressure. This result indicates that this increase in the rate might be due to the increase of hydrogen solubility in the aqueous phase.

3.3. Effect of CO partial pressure (P_{CO}). The effect of P_{CO} on the rate of hydroformylation of propylene was studied at a constant partial pressure of H_2 (5.0 atm). Figure 7 indicates that the rate increased rapidly with the increase of P_{CO}, then passed through a maximum, and decreased with further increase in P_{CO}, which is similar to the case of hydroformylation of allyl alcohol using a

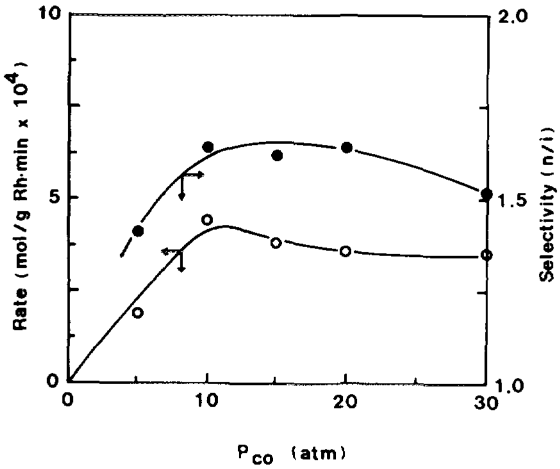


FIG. 7. Effect of CO partial pressure on the rate (○) and selectivity (●) catalyzed over Rh(III)/SPPS (Rh loading = 3.7 wt%, P/Rh = 7.9). Reaction conditions: C_3H_6 = 0.11 mol, solvent = 300 ml (water), P_{H_2} = 5 atm, reaction temp. = 373 K, and reaction time = 4 h.

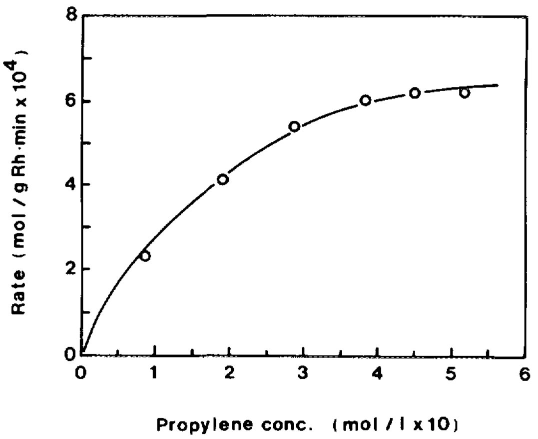


FIG. 8. Effect of propylene concentration on the rate catalyzed over Rh(III)/SPPS (Rh loading = 3.7 wt%, P/Rh = 7.9). Reaction conditions: solvent = 300 ml (water), P_{H_2}/P_{CO} = 15 atm/15 atm, reaction temp. = 373 K, and reaction time = 4 h.

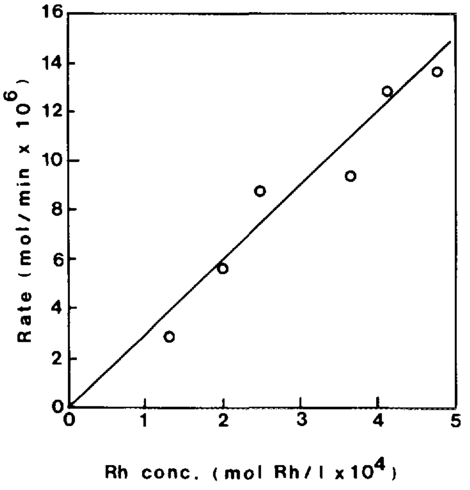


FIG. 9. Effect of catalyst concentration on the rate catalyzed over Rh(III)/SPPS (Rh loading = 3.7 wt%, P/Rh = 7.9). Reaction conditions: C_3H_6 = 0.11 mol, solvent = 300 ml (water), P_{H_2}/P_{CO} = 15 atm/15 atm, reaction temp. = 373 K, and reaction time = 4 h.

homogeneous $HRh(CO)(PPh_3)_3$ catalyst (15). Evans *et al.* observed that the rate of hydroformylation decreased with the increase of P_{CO} (16, 17). At the higher partial pressures of CO, the formation of inactive species was accelerated and the effective concentration of the active catalytic species was reduced due to the formation of dicarbonyl species and/or rhodium cluster.

Figure 7 also indicates that selectivity toward *n*-butyraldehyde (*n*-butyraldehyde/i-butyraldehyde) increased to 1.7 with the increase of P_{CO} and that a further increase of P_{CO} decreased the selectivity.

3.4. Effect of propylene concentration. Figure 8 shows the effect of propylene concentration on the rate of hydroformylation at a total pressure of 30 atm (CO : H_2=1 : 1) and 373 K. This result shows that the rate of reaction increased with the increase of the concentration of propylene (up to 0.45 mol/liter) and reached an asymptotic value. This increase may be due to the increase of the solubility of propylene in aqueous phase. The solubility of propylene increases to a certain extent with the increase of propylene pressure. This increase of solubility can enhance the accessibility of the catalyst to propylene in aqueous phase.

3.5. Effect of catalyst concentration. Figure 9 shows the effect of catalyst concentration on the rate of hydroformylation at a total pressure of 30 atm (CO : H_2=1 : 1) and 373 K. This result shows that the rate of reaction increases linearly with the catalyst concentration, indicating that the external mass transfer resistance is absent.

3.6. Effect of pH. In order to investigate the effect of pH of the reaction medium on the reaction rate and selectivity, the pH of reaction medium was changed by addition of NaOH. Table 2 shows that reaction rate has a maximum value when the pH of reaction medium is 7.3. The selectivity was not influenced by the pH of reaction medium.

Rh(III)/SPPS was activated with hydrogen to produce hydrogen chloride and catalytically active rhodium hydride complex. This hydride complex can be converted $HRh(CO)L_3$ and $HRh(CO)L_2$, subsequently which are assumed to be catalytically active species. Therefore, the removal of HCl with NaOH increased the formation of these catalytically active species. The pH of the reaction medium was acidic (pH = 5.9) without addition of NaOH due to the following reaction:

$$L_3RhCl_x \xrightleftharpoons{xH_2} L_3RhH_x + x\,HCl.$$

TABLE 2

Effect of pH on the Rate and Selectivity[a]

NaOH (mol/liter)	pH	Rate (mol/g Rh · min × 10^3)	Selectivity (*n*/i)
0	5.9	0.74	2.0
0.002	7.0	0.96	1.9
0.005	7.1	1.13	2.1
0.010	7.3	1.29	2.0
0.025	7.5	1.19	2.2
0.167	8.6	1.22	2.0

[a] Reaction conditions: Rh(III)/SPPS (Rh loading = 3.7 wt%, P/Rh = 7.9), C_3H_6 = 0.11 mol, solvent = 300 ml (water), P_{H_2} = 15 atm, P_{CO} = 15 atm, reaction temperature = 373 K, and reaction time = 4 h.

The low pH may also be due to the dissociation of SPPS-SO_3H into SPPS-SO_3^- and H^+.

During this reaction, Rh(III)/SPPS can be converted to the inactive species, L_3RhH_x, by reacting with excess hydrogen. The excess amount of sodium hydroxide reacted with HCl to produce sodium chloride. The removal of HCl makes the equilibrium reaction described above move from left to right. Hence, the formation of catalytically less active species, L_3RhH_x ($x \geq 2$), can be facilitated in alkaline medium, resulting in the decrease in the reaction rate, as shown in Table 2.

3.7. Effect of excess free PPh_3. The selectivity for linear aldehyde formation increased with the number of phosphine ligands of the complex and the increase in the concentration of PPh_3 during the reaction (18). The enhancement in the selectivity toward *n*-aldehyde was explained by the polarity of the rhodium hydride bond and by steric factors in the transition state leading to alkyl formation (17).

Figure 10 indicates that the activity decreased to the half of original activity by addition of PPh_3 to the aqueous reaction medium and remained constant with the further addition of PPh_3. The selectivity to linear aldehyde increased to 3.0 and a further increase was not observed with the more addition of PPh_3. Triphenylphosphine (PPh_3) is sparingly soluble in water and the melting point of PPh_3 is 373 K. Therefore, a small excess PPh_3 must be intact with catalytically active species and the rate and selectivity changes drastically. In this case PPh_3 enhances that steric effect because of the large size of the ligand and replacement of CO by weaker π-acid will make the Rh–H bond relatively more hydridic. This can promote anti-Markownikov addition, leading to higher selectivity toward linear aldehyde similar to the case of homogeneous catalysis by rhodium carbonyl complexes.

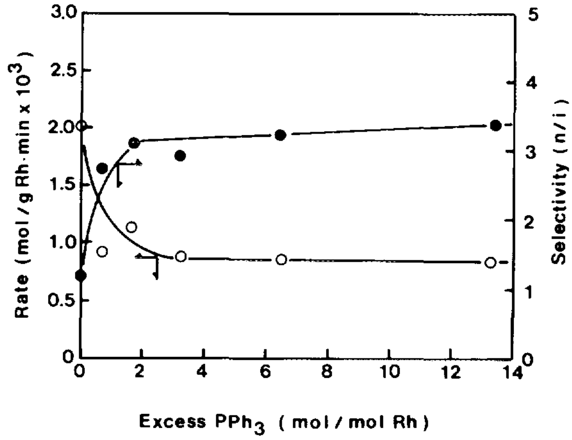


FIG. 10. Effect of excess PPh_3 on the rate (○) and selectivity (●) catalyzed over Rh(III)/SPSS (Rh loading = 3.7 wt%, P/Rh = 7.9). Reaction conditions: C_3H_6 = 0.11 mol, solvent = 300 ml (water), P_{H_2}/P_{CO} = 15 atm/15 atm, reaction temp. = 373 K, and reaction time = 4 h.

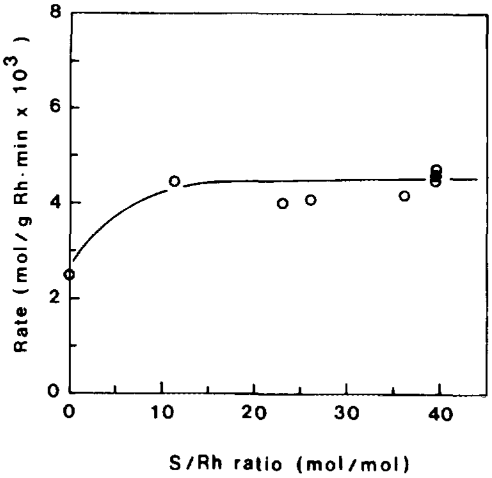


FIG. 11. Effect of S/Rh ratio on the rate catalyzed over Rh(III)/SPPS (Rh loading = 1.2 wt%, P/Rh = 5.3). Reaction conditions: C_3H_6 = 0.11 mol, solvent = 300 ml (water), P_{H_2}/P_{CO} = 15 atm/15 atm, reaction temp. = 373 K, and reaction time = 4 h.

3.8. Effect of the amount of SO_3H. In order to investigate the role of SO_3H groups on the catalytic properties, commercial phosphinated PS/DVB was sulfonated by the method outlined in the experimental section. Figure 11 indicates that the activity of Rh(III)/SPPS increased in the presence of SO_3H groups. The SO_3H groups attached to the polymer matrices play an important role in improving the activity and stability of polymer-immobilized catalyst. The SO_3H group on the phosphine ligand has an affinity for water. The hydroformylation in an aqueous phase must be a phase transfer catalysis reaction. The SO_3H groups provide the intimate contact of organic catalyst species with water at the interface of catalyst and aqueous reaction medium. The selectivity towards n-butyraldehyde was almost constant with respect to the S/Rh ratio, indicating that SO_3H groups do not participate in the catalytic cycle.

CONCLUSION

$RhCl_3 \cdot 3H_2O$ immobilized on the PS/DVB containing $-CH_2P(C_6H_4SO_3H)_2$ groups was an active and stable hydroformylation catalyst in an aqueous phase. ^{31}P NMR and FTIR study indicated that Rh(III)/SPPS and Rh(I)/SPPS have a similar structure and that rhodium complexes are covalently anchored on the polymer support. These immobilized rhodium complexes exhibited catalytic properties similar to those of the corresponding homogeneous counterpart in aqueous phase hydroformylation of propylene. The activity and selectivity increased with the increase of H_2 pressure. The rate increased rapidly with the increase of P_{CO} below 10 atm and decreased with CO pressure above 10 atm. The rate increased with the increase in the pressure of propylene. However, the rate did not change much at high propylene pressures. The rate increased linearly with the concentration of catalyst, indicating that there were no mass transfer limitations. The dependence of rate on the pH and the amount of SO_3H groups indicated that catalyst cycle is involved with phase-transfer catalysis.

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