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STUDIES ON THE SYNTHESIS OF SULFUR-CONTAINING POLYMER–RHODIUM COMPLEXES AND THEIR USE AS CATALYSTS FOR HYDROFORMYLATION

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ABSTRACT

A kind of nonphosphine polymer catalyst has been synthesized by partial substitution of the chlorine atoms of poly(vinyl chloride) with –SR groups (*n*-propyl, *n*-hexyl, benzyl, and *p*-tolyl). Rhodium complexes of these sulfur-containing polymer ligands are highly active catalysts for the hydroformylation of α-olefins. At 60°C and 60 kg/cm^2, conversion of 1-hexene was nearly complete within 4-6 h. The rhodium to 1-hexene mole ratio was 1/800 to 1/1 000, and the catalyst could be reused once again without losing activity. The effects of reaction temperature, pressure, H_2/CO ratio, S/Rh ratio, concentration of catalyst, and reaction time on the catalyst's activity were examined. The possible mechanism of hydroformylation is discussed. A copolymer of butyl vinyl sulfide

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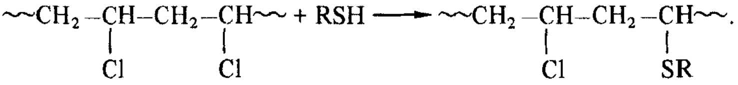
and acrylonitrile was synthesized and its rhodium complex was prepared. The catalytic acitvities of this complex for the hydroformylation of 1-hexene was also investigated.

INTRODUCTION

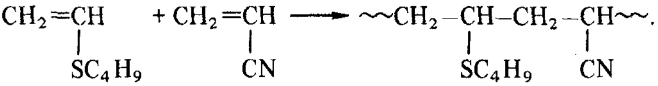
In recent years, in the study of hydroformylation, polymer-metal catalysts have attracted great attention by virtue of their high activity and selectivity as well as the convenience of separation and recovery. At present, polymers with phosphine ligands are commonly used as catalysts for hydroformylation of olefins [1]. Although such polymer catalysts are inconvenient owing to the difficulty of preparation and their toxicity, other kinds of ligands are rarely reported. Moreover, polymer ligands with thioether groups have received little attention to date.

We have prepared poly(vinyl chloride) with –SR groups (R = *n*-propyl, *n*-hexyl, benzyl, and *p*-tolyl) by reaction of silica-supported poly(vinyl chloride) with RSH in ethylene diamine [2].



$$\sim\!\!\sim CH_2-\underset{\overset{|}{Cl}}{CH}-CH_2-\underset{\overset{|}{Cl}}{CH}\sim\!\!\sim + RSH \longrightarrow \sim\!\!\sim CH_2-\underset{\overset{|}{Cl}}{CH}-CH_2-\underset{\overset{|}{SR}}{CH}\sim\!\!\sim.$$

Another type of ligand is copolymer containing sulfur and nitrogen. This was synthesized by copolymerization of butyl vinyl sulfide and acrylonitrile [3].



$$\underset{\overset{|}{SC_4H_9}}{CH_2=CH} + \underset{\overset{|}{CN}}{CH_2=CH} \longrightarrow \sim\!\!\sim CH_2-\underset{\overset{|}{SC_4H_9}}{CH}-CH_2-\underset{\overset{|}{CN}}{CH}\sim\!\!\sim.$$

(PBVS-AN)

Rhodium complexes of these polymer ligands are highly active catalysts for the hydroformylation of olefins, and their catalytic properties are here investigated in detail.

EXPERIMENTAL

Preparation of Silica-Supported Poly(Vinyl Chloride)

Poly(vinyl chloride) was extracted with ethanol for 30 h to remove low molecular weight substances. Dried PVC (15 g) was dissolved in 700 mL

TABLE 1. Condition of Synthesis and Analytical Data of PVC-SR

Ligand	Mercaptan, g	Temperature, °C	Time, h	Sulfur content, %
PVC-SC_3H_7	C_3H_7SH, 8.4	30	2	3.52
PVC-SC_6H_{13}	$C_6H_{13}SH$, 13.5	30	2	1.66
PVC-SCH_2Ph	$PhCH_2SH$, 10.5	30	2	2.43
PVC-$SPhCH_3$	CH_3PhSH, 15	50	4	7.34

tetrahydrofuran with stirring at room temperature, 12.5 g SiO_2 was added, and stirring was continued until the reaction mixture turned to a transparent colloid. The mixture was poured into 1 400 mL of ethanol for precipitation of the product. Silica-supported PVC (27.0 g) was obtained.

Reaction of Mercaptans with Silica-Supported PVC

To 180 mL ethylene diamine was added 12.5 g silica-supported PVC and the calculated amount of mercaptan (Cl/S gram atomic ratio 1). The mixture was stirred at the appropriate temperature for several hours, as shown in Table 1. The product was filtered and extracted with ethanol. IR, 570-705 cm^{-1} (C–S–C), 700-750 cm^{-1} (C–Cl).

Copolymerization of Butyl Vinyl Sulfide and Acrylonitrile

Butyl vinyl sulfide (5 g), acrylonitrile (10 g), divinylbenzene (1.5 g), and AIBN (190 mg) were polymerized in the presence of 15 g SiO_2 in 100 mL absolute ethanol at 60°C for 8-10 h. The copolymer was extracted with ethanol for more than 24 h to remove unreacted monomers. Analysis: C, 35.91; H, 4.48; N, 5.88; S, 5.74. IR, 695 cm^{-1} (C–S–C), 2 200 cm^{-1} (CN).

Preparation of Rhodium Complex

Polymer ligand and dirhodium tetracarbonyl dichloride were reacted in benzene in various S/Rh gram-atomic ratios. The mixture was magnetically stirred for several hours at room temperature. After that, the upper layer of solvent became colorless, the complex was filtered out, and it was dried under vacuum.

The complexes are fine powder, of light yellow to yellow color. The evi-

TABLE 2. X-ray Photoelectron Spectra of PVC-SR-Rh, PVC-SR, and $Rh_2(CO)_4Cl_2$

	Binding energy, eV				
Compound	Si_{2p}	O_{1s}	Cl_{2p}	S_{2p}	$Rh_{3d\ 5/2}$
$Rh_2(CO)_4Cl_2$			199.5		310.2
PVC-SR[a]	103.6	532.7	199.6	162.9	
PVC-SR-Rh	103.9	532.4	199.9	163.8	308.6

[a] R = n-C_3H_7.

dence of complex formation can be provided by x-ray photoelectron spectroscopy (XPS) data, as shown in Table 2.

Hydroformylation of Olefins

To a stainless steel autoclave were added 1-hexene (or 1-heptene), catalyst, and benzene, the autoclave was pressurized with carbon monoxide and hydrogen, then it was placed in a preequilibrated oil bath, heated, and magnetically stirred for several hours. Upon completion the autoclave was cooled (ice-salt bath) and the gases were vented slowly. The reaction mixture was filtered to separate catalyst, and the products were quantitatively analyzed by gas chromatography. The catalyst could be recovered and reused.

RESULTS AND DISCUSSION

Comparison of Catalytic Activities of PVC-SR-Rh Complexes

Four PVC-SR-Rh complexes mentioned above were used as catalysts for the hydroformylation of 1-hexene. It can be seen from Table 3 that under the conditions illustrated, the activities of all these catalysts are very high, but their selectivities are not satisfactory. In order to compare the effect of R groups on the activities of PVC-SR-Rh, hydroformylations were carried out under milder conditions, as shown in Table 4. Table 4 shows that the activity and selectivity of PVC-SPh-CH_3-Rh are the best among these four catalysts.

TABLE 3. Activity and Selectivity of PVC-SR-Rh for the Hydroformylation of 1-Hexene[a]

Catalyst	Conversion of 1-hexene, %	n/b[b]	Selectivity of n-heptanal, %
R = C_3H_7	95.7	0.80	44.6
R = C_6H_{13}	97.4	0.84	45.6
R = CH_2Ph	100	0.98	49.4
R = $PhCH_3$	99.1	0.80	44.4

[a] Conditions. 1-Hexene, 7.8 mmol (1 mL); catalyst: S/Rh, 10; Rh/1-hexene, 1/400; 100°C; total pressure, 60 atm; H_2/CO, 1; reaction time, 8 h; Solvent, benzene.

[b] *n/b* = normal/branched aldehyde ratio.

TABLE 4. Activity and Selectivity of PVC-SR-Rh for the Hydroformylation of 1-Hexene[a]

Catalyst	Conversion of 1-hexene, %	n/b	Selectivity of n-heptanal, %
R = C_3H_7	28.0	–	–
R = C_6H_{13}[b]	68.8	1.47	59.5
R = CH_2Ph	53.6	1.45	59.1
R = $PhCH_3$	86.9	1.80	64.3

[a] Conditions. 1-Hexene, 7.8 mmol (1 mL); catalyst: S/Rh, 10; Rh/1-hexene, 1/1 000; 60°C; total pressure, 60 atm; H_2/CO, 1; reaction time, 4 h; Solvent, benzene.

[b] S/Rh, 5.

Hydroformylation of 1-Hexene Catalyzed by PVC-SC_6H_{13}-Rh

(1) Effect of Temperature

It can be seen from Table 5 that, as the temperature is raised from 40 to 100°C, conversion of 1-hexene increased, but it decreased slightly above

TABLE 5. Effect of Temperature on the Activity of PVC-SC_6H_{13}-Rh for the Hydroformylation of 1-Hexene[a,b]

Temperature, °C	Conversion of 1-hexene, %	n/b	Selectivity of n-heptanal, %
40	6.2	1.34	57.2
(60)	(81.2)	(1.62)	(61.8)
70	42.9 (99.0)	1.66 (1.14)	62.5 (53.2)
(80)	(99.2)	(1.06)	(51.5)
(90)	(100)	(1.03)	(50.7)
100	98.8 (99.7)	0.85 (0.93)	46.0 (48.3)
(120)	(96.6)	(0.75)	(42.9)
130	94.2	0.89	47.0
150	95.4	0.49	32.8

[a] Conditions. PVC-SC_6H_{13}-Rh: S/Rh, 10; Rh/1-hexene, 1/800; total pressure, 50 kg/cm^2; other conditions as given in Table 3.

[b] Values in parentheses are for identical conditions, except S/Rh = 5.

100°C. This is probably due to the contraction of the surface area of the catalyst beyond T_g of PVC and, to a small extent, to degradation of polymer ligand at the higher temperatures. The n/b (normal to branched aldehyde ratio) decreased with increasing temperature, which indicated that the activation energy for isoheptanal is higher than that of n-heptanal. Thus, the higher temperature favors the formation of isoheptanal.

(2) Effect of Pressure

Conversion of 1-hexene increased as the total pressure increased, but the n/b ratio decreased at the same time, as summarized in Table 6.

(3) Effect of H_2/CO Ratio

Conversion of 1-hexene has its optimum value at H_2/CO 1, but the selectivity is not significantly affected by it, as shown in Table 7.

TABLE 6. Effect of Pressure on the Activity of PVC-SC_6H_{13}-Rh for the Hydroformylation of 1-Hexene[a]

Pressure, kg/cm^2	Conversion of 1-hexene, %	*n/b*	Selectivity of *n*-heptanal, %
30	18.6	–	–
40	65.6	1.92	65.8
60	82.0	1.63	61.9
70	88.0	1.37	57.8
80	97.9	0.94	48.8
90	100	0.97	49.3

[a] Conditions. 1-Hexene, 3.9 mmol; temperature, 60°C. Other conditions as given in Table 5.

TABLE 7. Effect of H_2/CO Ratio on the Activity of PVC-SC_6H_{13}-Rh for the Hydroformylation of 1-Hexene[a]

H_2/CO ratio	Conversion of 1-hexene, %	*n/b*	Selectivity of *n*-heptanal, %
1/2	52.4	1.38	58.0
1	79.8	1.63	61.9
2	53.7	1.63	61.9
4	38.3	1.67	62.5

[a] Conditions. Temperature, 60°C; time, 4 h; other conditions as given in Table 5.

(4) Effect of Concentration of Catalyst

At a very low concentration of catalyst (Rh/1-hexene = 1/2 000, mole ratio), conversion of 1-hexene was 31.3%. When this ratio was in the range 1/500-1/1 500, conversion and selectivity were constant, as shown in Table 8.

TABLE 8. Effect of Concentration of PVC-SC_6H_{13}-Rh on its Activity for the Hydroformylation of 1-Hexene[a]

Rh/1-hexene, mole ratio	Conversion of 1-hexene, %	*n/b*	Selectivity of *n*-heptanal, %
1/2 000	31.3	0.82	45.2
1/1 500	98.4	1.17	53.9
1/1 000	98.9	1.15	53.4
1/800	98.8	1.17	54.0
1/500	97.8	1.20	54.4

[a] Conditions. $H_2/CO = 1$; other conditions as given in Table 6.

(5) Effect of Reaction Time

It can be seen from Table 9 that conversion of 1-hexene was nearly complete and that the *n/b* ratio decreased from 2 to 6 h and remained unchanged after 6 h.

Hydroformylation of 1-Heptene Catalyzed by PVC-SC_3H_7-Rh

The activity of PVC-SC_3H_7-Rh for the hydroformylation of 1-heptene is of the same order of magnitude as with of PVC-SC_6H_{13}-Rh for 1-hexene. Conversion of 1-heptene was complete at 100°C and a total pressure of 50 kg/cm^2. The activity and selectivity of the catalyst were greatly affected by the partial pressure of hydrogen, as shown in Table 10.

For the hydroformylation of 1-heptene, the activity of PVC-SC_3H_7-Rh was the same with or without benzene as solvent, but for hydroformylation of cyclohexene, the conversion was very low (20%) in the absence of solvent. Benzene is a better solvent than ether, ethanol, and dioxane.

PVC-SC_3H_7-Rh is an active and stable catalyst. It has been reused for the hydroformylation of 1-heptene; the turnover number was up to 80 000. Its x-ray photoelectron spectroscopy remain unchanged after standing in the open air for 10 months.

TABLE 9. Effect of Reaction Time on the Activity of PVC-SC_6H_{13}-Rh for the Hydroformylation of 1-Hexene[a]

Reaction time, h	Conversion of 1-hexene, %	*n*/*b*	Selectivity of *n*-heptanal, %
2	46.2	1.79	64.2
4	79.8	1.63	61.9
6	97.6	1.13	53.1
8	98.8	1.17	54.0
10	98.4	1.20	54.4

[a] Conditions as given in Table 7.

TABLE 10. Effect of CO/H_2 Ratio on the Activity of PVC-SC_3H_7-Rh for the Hydroformylation of 1-Heptene[a]

CO/H_2 ratio	Conversion of 1-heptene, %	*n*/*b*	Selectivity of *n*-heptanal, %
1.0	95.0	1.64	62.1
1.5	96	3.84	79.3
2.0	79	4.64	82.3

[a] Conditions. 1-Heptene, 7 mmol; catalyst: Rh, 0.02 mmol, Rh/1-heptene, 1/350; S/Rh, 4; 100°C, total pressure, 50 kg/cm^2 ; time, 8 h; solvent, benzene.

Hydroformylation of 1-Hexene Catalyzed by PBVS-AN-Rh

Addition of polar solvents altered the conversion and the selectivity in the hydroformylation of 1-hexene catalyzed by PBVS-AN-Rh, as shown in Table 11. This could be attributed to the effect on the coordinating situation by polar solvents.

TABLE 11. Effect of Polar Solvent on the Activity of PBVS-AN-Rh for the Hydroformylation of 1-Hexene[a]

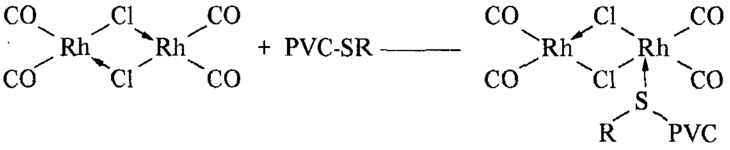
Solvent, mL	Conversion of 1-hexene, %	*n*/*b*
Benzene, 2	97.2	1.07
Benzene, 1.5; EtOH, 0.5	94.0	1.27
Benzene, 1; EtOH, 1	86.4	1.33
Benzene, 0.5; EtOH, 1.5	61.6	1.49
Benzene, 1; dioxane, 1	51.0	1.44
Benzene, 1; DMSO, 1	0	0

[a] Conditions. 1-Hexene, 1 mL (7.8 mmol); catalyst: S/Rh, 5; Rh/1-hexene, 1/1 000; 60°C; total pressure, 60 kg/cm^2; H_2/CO, 1; 8 h.

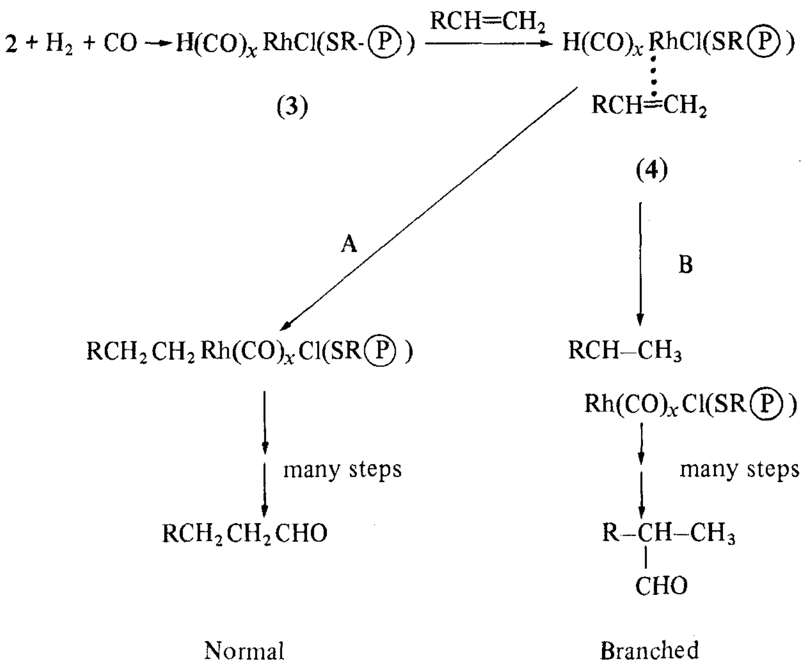
Discussion of Possible Mechanisms of Hydroformylation

Extensive mechanism studies on the hydroformylation of olefins catalyzed by polymer phosphine-rhodium complexes have been published [4] and the mechanism was well established, but no work has been reported with regard to sulfur-containing polymer-metal complexes. Referring to the related literature and the results of our experiments, we suggest the reaction mechanism shown in Scheme 1.

From the x-ray photoelectron spectroscopy of $Rh_2(CO)_4Cl_2$, its structure is as shown as **1** [5]. The sulfur atoms of polymer ligands of the type PVC-SR can displace one of the chlorine atoms of this low molecular weight complex to form a more stable polymer comples (**2**) by reason of the stronger coordinating power of sulfur compared to the chlorine atom.



(1) (2)



SCHEME 1. Suggested mechanism of hydroformylation.

Under conditions of hydroformylation, **2** will be activated to form an active intermediate like **3**; the latter coordinates with the olefin double bond to give **4**. Then addition of hydrogen to the carbon atom of the double bond occurs by two pathway, A and B, to yield normal and branched aldehyde, respectively.

The steric hindrance of Pathway A (anti-Markownikoff addition) is smaller than that of Pathway B, and the activation energy is lower, so that formation of normal aldehyde is less sensitive to the influence of reaction conditions, which is consistent with the results of our experiments.

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