

A Novel Water-Soluble Rhodium–Poly(enolate-*co*-vinyl alcohol-*co*-vinyl acetate) Catalyst for the Hydroformylation of Olefins

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Abstract: The water-soluble polymer, poly(enolate-*co*-vinyl alcohol-*co*-vinyl acetate) (PEVV), prepared by controlled oxidation of poly(vinyl alcohol-*co*-vinyl acetate), is a valuable ligand for the rhodium biphasic catalytic hydroformylation of olefins. The average turnover frequency for the catalytic hydroformylation of 1-octene was 5.46×10^{-5} kmol (kg(Rh)s)⁻¹ at 90 °C, and that of 1-dodecene was 2.36×10^{-4} kmol (kg(Rh) s)⁻¹ at 60 °C. Selective hydroformylation of styrene and its derivatives gave up to 97% of branched-chain aldehyde using Rh–PEVV under biphasic reaction conditions but at low conversions.

Homogeneous catalysis has many advantages over heterogeneous catalysis.¹ However, the recovery of homogeneous catalysts from high-boiling products is difficult. The idea of biphasic catalysis, which simplifies the separation of catalysts from products by decantation, has attracted great attention in recent years.^{2–6} Biphasic catalysis relies on the transfer of organic substrates into the aqueous phase containing the catalyst. The reaction rate could be reduced to such an extent that it becomes unacceptable when the solubility of the substrates in the aqueous phase is low, preventing adequate transfer of organic substrates into the aqueous catalytic phase or at the phase boundary.³ Therefore, studies have focused on improving the affinities between the two phases.^{2,3} The addition of cosolvents, such as alcoholic solvents, surfactants, and modified cyclodextrins, to enhance mutual solubility or mobility of the components across the phase boundary can increase the reaction rate by more than 10 times.^{2–5} Addition of water-soluble organic ligands, such as P(Ph(SO₃))₃, and inorganic salts to increase the concentration of the catalyst to the interface enhances the catalytic reactivity as well.^{2–5} Extensive studies have been undertaken to improve the ligands for these reactions. One example is the use of a catalyst bearing partially fluorinated “ponytail” ligands bound via phosphorus in a fluorous biphasic system.⁷ The fluorous biphasic system becomes a one-phase system by increasing the temperature.⁷ A similar idea for “smart ligands” has been reported for biphasic hydrogenation.⁸ Recently, ligands with surfactant structures, such as Ph₂P(CH₂)₂-C(O)NHC(CH₃)₂CH₂SO₃Li, P[(CH₂)_nC₆H₄SO₃Na]₃, P[C₆H₄-(CH₂)_nC₆H₄SO₃Na]₃, (menthyl)P[(CH₂)₈C₆H₄-*p*-SO₃Na]₂, and Ph₂P(CH₂)_nSO₃Na, have been used in catalytic hydroformylation.⁹ These ligands are superior to P(C₆H₄-*p*-SO₃Na)₃ (TPPTS)

for the catalytic hydroformylation of olefins.⁹ As the structure of the surfactant ligands implies, the lipophilic phosphine ligand coordinated to the catalytic active center is concentrated close to the interface while the hydrophilic part of the component aids in the solubilization of the catalyst into the aqueous solution. This concept encouraged us to develop a water-soluble, polymer-anchored, rhodium catalyst having a structure of a lipophilic rhodium center and a hydrophilic long chain for the catalytic hydroformylation of olefins. Such a catalyst, with the noted features, could offer significant advantages over conventional ligands in terms of regioselectivity, reactivity, and separation of reaction mixtures. The chemical modifications of polymers have been used to prepare polymers with various functional groups.¹⁰ Therefore, a polymer composed of both lipophilic and hydrophilic structures, such as lipophilic functionality grafted polyvinyl alcohol (PVA), may be ideal for such a purpose.

The controlled oxidation of PVA using sodium hypochlorite has been reported to afford lipophilic poly(methylene ketone) (PMK).¹¹ Under basic conditions, tautomerization of PMK gave the enolate which chelated metal ions such as nickel.¹¹ Thus, oxidation of PVA affords poly(vinyl alcohol-*co*-methylene ketone) composed of both lipophilic and hydrophilic components of methylene ketone and vinyl alcohol. The strong chelating ability of the PMK enolate results in a rhodium complex which can serve as a biphasic hydroformylation catalyst precursor, while the unoxidized hydroxyl groups promote the dissolution of the catalyst in aqueous solution.

Results and Discussion

(1) Preparation of Rhodium–Poly(enolate-*co*-vinyl alcohol-*co*-vinyl acetate) (Rh–PEVV) Complexes. Oxidation of secondary alcohols with NaOCl affords ketones in high yields.¹²

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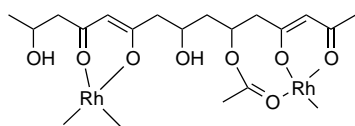
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Table 1. ^{13}C NMR Chemical Shifts for P(VA-*co*-VAc), Its Oxidized Product, PEVV, and Rh-PEVV (DMSO- d_6 , ppm)

P(VA- <i>co</i> -VAc)	P(MK- <i>co</i> -VA- <i>co</i> -VAc)	PEVV	Rh-PEVV
	206.9; 204.9	207.2, 204.9, 193.2	207.9, 204.2, 174.4, 173.9
169.7	169.7	169.9, 159.5	169.7, 165.8
	100.4	100.6, 98.2	98.4
66.7	66.7	69–62	69–62
45.8	51–44	51–46	51–46
20.7	20.7	20.7	21.6; 20.8

Table 2. Molecular Weight Data for P(MK-*co*-VA-*co*-VAc) at Different Conversions

polymer	conversion (%)	M_w	M_n	M_w/M_n
1	20	7380	3120	2.37
2	31	7353	3145	2.34
3	48	7255	2961	2.45

Scheme 1. Complex of Rh-PEVV

This reaction has been applied to the oxidation of PVA to give PMK.¹¹ Controlled oxidation of poly(vinyl alcohol-*co*-vinyl acetate) (P(VA-*co*-VAc)) with NaOCl affords poly(methylene ketone-*co*-vinyl alcohol-*co*-vinyl acetate) (P(MK-*co*-VA-*co*-VAc)). The ^{13}C NMR spectrum (Table 1) of P(MK-*co*-VA-*co*-VAc) showed ketone signals at 206.9 and 204.9 ppm. This is in agreement with an intense band in the infrared spectrum at 1704 cm^{-1} , overlapped with the absorption of the acetyl group at 1724 cm^{-1} , and the intensity of the C–O stretching band at 1043 cm^{-1} decreased significantly compared to that of P(VA-*co*-VAc). The infrared spectrum of poly(enolate-*co*-vinyl alcohol-*co*-vinyl acetate) (PEVV), formed by treatment of P(MK-*co*-VA-*co*-VAc) with Et_3N , showed a broad absorption at 1581 cm^{-1} with the disappearance of the band of 1704 cm^{-1} compared to that of P(MK-*co*-VA-*co*-VAc). The ^{13}C NMR spectrum of PEVV gave signals at 193.2, 159.5, 100.6, and 98.2 ppm for the α,β -unsaturated carbonyl and the $\text{C}=\text{C}-\text{O}^-$ carbons, respectively. These spectroscopic data clearly indicate the formation of PEVV (Table 1). The ^{13}C NMR integration ratio of carbonyl groups between ketone and acetyl in P(MK-*co*-VA-*co*-VAc) gave the percentage conversion of alcohol to ketone listed in Table 2. It is seen that no chain degradation and cross-linking took place, as implied by the weight average molecular weight data and number average molecular weight for the conversion of the alcohol (Table 2).

Reaction of PEVV with RhCl_3 in aqueous solution afforded Rh-PEVV. The ^{13}C NMR spectrum (Table 1) of Rh-PEVV gave new signals at 174.4, 173.9, and 98.4 ppm assigned to the rhodium-chelated enolate. The signals for the acetyl groups shifted from 169.7 to 165.8 ppm for the carbonyl carbons and from 20.8 to 21.6 ppm for the methyl group. These signals suggest the coordination of rhodium to both enolate and acetyl groups in PEVV. Therefore, the complex of Rh-PEVV can be represented as in Scheme 1.

(2) Catalytic Hydroformylation of Olefins Using Rh-PEVV. Treatment of neat 1-octene (10 mmol) with 1:1 CO/H_2 (41.4 bar, $40\text{ }^\circ\text{C}$, 22 h) and an aqueous solution of RhCl_3 (0.02 mmol), with and without P(VA-*co*-VAc) as the catalyst precursor, gave less than 1% conversion and poor selectivity for the hydroformylation of 1-octene (entries 1 and 2, Table 3).

Table 3. Catalytic Hydroformylation of 1-Octene Using Different Catalyst Precursors Under the Same Reaction Conditions^a

entry	catalyst	conversion (%) (CHO selectivity)	L/B ^b
1	RhCl_3	<1	1.00
2	$\text{RhCl}_3 + \text{P(VA-}i>co-VAc)$	<1	1.00
3	Rh-PEVV ^c	49 (98)	1.14

^a Reaction conditions: H_2/CO , 1:1, 41.4 bar, $40\text{ }^\circ\text{C}$, 22 h, $[\text{Rh}]/n$ -1-octene = 0.2 mol %. ^b 1-Nonanal/2-methyloctanal ratio (L/B = linear to branched) determined by NMR spectroscopy. ^c Reaction time of 28 h.

Table 4. Catalytic Hydroformylation of Aliphatic Olefins Using Rh-PEVV as the Catalyst Precursor^a

entry	substrate	t (h)	conversion (%)	aldehyde selectivity (%)	L/B
1	1-octene ^b	22	89	67 ^s	2.45
2	1-dodecene ^c	4	70	70 ^b	1.95
3	1-octene	1.5	38	44 ^s	2.69
4	1-octene ^d	1.5	25	28 ^s	2.96
5	1-octene ^e	1.5	43	28 ^s	2.50
6	1-octene ^c	4	14	85 ^s	1.61
7	4-vinyl cyclohexene ^f	2	24	100	5.65
8	methyl 3,3-dimethyl-4-pentenoate	2	23	93	L only
9	<i>n</i> -butyl vinyl ether	2	5	100	0.35
10	<i>n</i> -butyl vinyl ether	8	12	92	0.41

^a Reaction conditions: substrate (10 mmol)/Rh = 500:1 in 3 mL of H_2O ; temperature = $100\text{ }^\circ\text{C}$; H_2/CO = 1:1, 41.4 bar, L/B ratio was determined by ^1H NMR. ^b $T = 90\text{ }^\circ\text{C}$. ^c $T = 60\text{ }^\circ\text{C}$. ^d H_2/CO = 1:3, 27.6 bar. ^e H_2/CO = 3:1, 27.6 bar. ^f No hydroformylation of the internal double bond occurred here. ^s The other product was 2-octene. ^b The other product was 2-dodecene.

In contrast, treatment of 1-octene with Rh-PEVV under the same conditions for 28 h resulted in 49% conversion and 98% selectivity for hydroformylation with a small preference for *n*-nonanal (Table 3). The organic phase, upon reuse, did not show any catalytic activity. Reuse of the aqueous phase (three times) did not diminish the activity and selectivity for the hydroformylation reaction, indicating no rhodium leaching to the organic phase. The average turnover frequency (TOF) is $2.36 \times 10^{-5}\text{ kmol (kg(Rh) s)}^{-1}$ (entry 3, Table 3) for the catalytic hydroformylation of 1-octene at $40\text{ }^\circ\text{C}$, and the value increased to 5.46×10^{-5} (entry 1, Table 4) at $90\text{ }^\circ\text{C}$. The catalytic hydroformylation of 1-dodecene proceeded at $60\text{ }^\circ\text{C}$ at an excellent TOF of 2.36×10^{-4} (entry 2, Table 4). Comparing these results with the TOF values of 8.6×10^{-6} and 7.8×10^{-5} for the catalytic hydroformylation of 1-octene using $[\text{Rh}(m\text{-S}^i\text{Bu})(\text{CO})(\text{TPPTS})]_2$ with and without ethanol as the cosolvent, respectively,⁴ one can conclude that Rh-PEVV is a very reactive biphasic catalyst. The TOF was 7.85×10^{-6} when $\text{HRh}(\text{CO})(\text{TPPTS})_3$ was used as the catalyst precursor for the hydroformylation of 1-octene at $100\text{ }^\circ\text{C}$.² The reactivity of Rh-PEVV compares well with the best TOF of 5.11×10^{-4} using the PPh_3 ligand promoted $\text{HRh}(\text{CO})(\text{TPPTS})_3$ biphasic catalytic system for 1-octene at $100\text{ }^\circ\text{C}$.² The selectivity for the linear aldehyde improved as the temperature was raised to $90\text{ }^\circ\text{C}$ (entry 3, Table 3; entry 1, Table 4). However, the rate of isomerization of 1-octene to 2-octene was greater than the hydroformylation reaction rate at higher temperature (entries 3–5, Table 4). Changing the H_2/CO ratio affected the rates of linear/branched aldehydes with a 1:3 ratio of H_2/CO being the most selective for the linear product (entries 3–5, Table 4). These excellent results led us to apply the Rh-PEVV catalyst to the selective catalytic hydroformylation of other olefins. Substitution at the allylic position markedly increases the selectivity for the linear aldehyde product (entries 7 and 8, Table

4). The catalytic hydroformylation of methyl 3,3-dimethylpenten-4-onate gives only the linear product (entry 8, Table 4). While the conversion was low, the vinyl ether *n*-butyl vinyl ether afforded the branched chain aldehyde as the major product (entries 9 and 10, Table 4).

Although the hydroformylation of styrene gave poor selectivity at 90 °C using Rh-PEVV as the catalyst precursor, excellent selectivity (up to a 36.7 ratio of B/L) for the catalytic hydroformylation of styrene and its derivatives was achieved at 40 °C (Table 5). These results can be compared with the homogeneous system using a zwitterionic rhodium complex¹³ and the rhodium complex of electron deficient phosphine ligands as catalyst precursors.¹⁴ Change of the H₂/CO ratio or addition of PPh₃, did not improve the B/L selectivity and reactivity (entries 2–5, Table 5) as was found in the hydroformylation of aliphatic olefins. Unfortunately the conversion of styrenes is low after reaction times of 22–24 h.

Conclusion

In conclusion, Rh-PEVV is a novel, highly active, water-soluble catalyst for the hydroformylation of olefins, especially for aliphatic olefins. Excellent selectivity for the preparation of branched-chain aldehydes was found for styrene and its derivatives, albeit at low conversion.

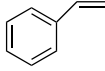
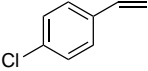
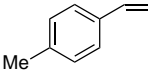
Experimental Section

General Considerations. All chemicals were purchased from Aldrich and were used as received. P(VA-*co*-VAc) has the microstructure of 80% vinyl alcohol and 20% vinyl acetate. P(MK-*co*-VA-*co*-VAc) was prepared according to the literature procedure by the controlled oxidation of P(VA-*co*-VAc).¹² All ¹H and ¹³C NMR spectra were recorded on either a Gemini-200 or AMX-500 NMR spectrometer using CDCl₃ or DMSO-*d*₆ as the solvent and TMS as the internal standard. The ¹H NMR spectra of the hydroformylation products were analyzed by comparison with authentic samples. The yield of hydroformylation products was calculated using either anisole or *tert*-butylbenzene as the internal standard by ¹H NMR integration. Infrared spectra were recorded on a Bomem-100 FT-IR spectrometer. Gel permeation chromatography (GPC) was run using a Waters 510 HPLC pump operating on 1 mL/min flow rate with three consecutive Styragel HT columns effective from 5 × 10² to 4 × 10⁶ and detected using a Waters 410 differential refractometer detector. HPLC grade THF was used as eluant. The molecular weights of the polymers are based on calibration with polybutadiene standards.

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Table 5. Catalytic Hydroformylation of Olefins Using Rh-PEVV as the Catalyst Precursor^a

entry	substrate	<i>t</i> (h)	conversion (%)	selectivity (%)	B/L ^b
1		22	13	>99	17.3
2	c	24	12	>99	17.9
3	d	22	7	>99	9
4	e	22	4	>99	9
5	f	22	10	>99	9
6		24	12	>99	15.3
7		22	14	>99	9
8	g	24	4	>99	36.7

^a Reaction conditions: substrate 10 mmol, Rh 0.2 mol %, H₂/CO = 1:1, 41.4 bar, 40 °C. ^b L = 1-phenylpropanal; B = 2-phenylpropanal. Ratio is based on ¹H NMR data. ^c Rh/PPh₃ = 1:10. ^d Rh/PPh₃ = 1:57. ^e H₂/CO = 1:3, 27.6 bar. ^f H₂/CO = 3:1, 27.6 bar. ^g Reaction temperature = 28 °C.

General Procedures for the Preparation of Rh-PEVV. To a solution of P(MK-*co*-VA-*co*-VAc) (4.55 g) in methanol (30 mL) was added Et₃N (4.0 mL) at room temperature under N₂ to give a red-brown solution of PEVV which was immediately treated with an aqueous solution of RhCl₃·3H₂O (320.5 mg, 40 mL). The reaction mixture was stirred for 5 h at room temperature under N₂. The resulting solution was dried in vacuum to afford 4.88 g of Rh-PEVV. The concentration of Rh in Rh-PEVV is 2.56 mg/100 mg.

General Procedure for the Hydroformylation Reactions. A glass liner containing an aqueous solution of Rh-PEVV (84.0 mg, 3 mL, 0.02 mmol of Rh) and olefin (10 mol) was placed in a 45 mL autoclave equipped with a magnetic stirring bar. The autoclave was flushed three times with CO and then pressurized to the desired level. The hydrogen line was attached to the autoclave, the autoclave was flushed three times with H₂, and then the pressure was gradually increased to the desired level. The autoclave was placed in an oil bath on a heater/stirrer preset to the reaction temperature. After the appropriate reaction time, the autoclave was cooled to room temperature, the excess H₂/CO gas was released, and the resulting solution was separated and immediately analyzed by ¹H NMR spectroscopy.

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