Aqueous biphasic olefin hydroformylation catalyzed by water-soluble rhodium complexes

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Abstract

Catalysis with water-soluble rhodium complexes, $RhCl(CO)(TPPMS)_2$, [TPPMS = $P(C_6H_5)_2(C_6H_4SO_3)$] *(1)*, $RhCl(CO)(TPPDS)_2$, [TPPDS = $P(C_6H_5)(C_6H_4SO_3)_2$] *(2)* and $RhCl(CO)(TPPTS)_2$, [TPPTS = $P(C_6H_4SO_3)_3$] *(3)* in hydroformylation of 1-hexene, 2-pentene, 2,3-dimethyl-1-butene, cyclohexene and several mixtures of these olefins have been studied, under moderate reaction conditions (*T*: 50–150 °C; pCO/pH_2 = 1; total p: 14–68 bar; Substrate/Catalyst: 600/1) in biphasic toluene/water media. The catalytic system shows high activity but low selectivity. The linear and branched oxygenated products obtained are equally useful in naphtha upgrading, as observed in the real El Palito naphtha tried. The catalysts can be recycled several times without significant activity loss.

Introduction

Since the Ruhrchemie–Rhone–Poulenc propene hydroformylation process in 1984 [1, 2] the use of water-soluble metal complex catalysts has been recognized as an effective method for catalyst, product separation, and catalyst recycling [3–8]. A new hydroformylation application is the treatment of C4–C7 alkene mixtures from refinery cuts, converting some of the alkenes into valuable oxygenates (aldehydes or alcohols), that improves the combustion properties of the fuel. In our laboratory we have been studying the catalytic activity of water-soluble rhodium complexes with sulphonated phosphines in a biphasic medium [9]. In the present paper we describe alkenes and alkene mixtures hydroformylation in aqueous biphasic (toluene/water) media, using water-soluble rhodium complexes with TPPMS, TPPDS, and TPPTS ligands.

Experimental

Materials and methods

$RhCl_3 \cdot 3H_2O$ (Strem), PPh_3 (Aldrich), H_2, CO and Ar (Gases Industriales de Venezuela) were obtained commercially and used directly. Liquid substrates employed in catalysis were distilled before use; all solvents were purified as described in the literature [10]. A naphtha cut used was from El Palito, Venezuela,

refinery. The TPPMS, TPPDS and TPPTS ligands were synthesized by reported methods [11–13]. The complexes *(1)*, *(2)* and *(3)* were synthesized by Wilkinson's method for neutral ligands [14]; thus for complex *(1)* [$RhCl(CO)(TPPMS)_2$]: to a TPPMS refluxing solution (2.0 g, 4.2 mmoles) in EtOH (25 ml) was slowly added a $RhCl_3 \times 3H_2O$ (0.50 g, 2.1 mmol) in EtOH (20 ml) solution; after 30 min with CO bubbling, a 37% formaldehyde (3 cm³) solution was added and the mixture was refluxed for 10 more minutes. The solution was then allowed to cool, filtered, and the solid was washed twice with cold EtOH. Complexes *(2)* and *(3)* were synthesized the same way, but using the correct Ru/ligand stoichiometric relationship. The resulting complexes are soluble in H_2O and MeOH, and decompose above 250 °C. Complex *(1)* is red, and shows the following FT-IR bands (cm⁻¹): 3684 [ν(O–H), broad hydroxyl band], 3037 [ν(C–H), aromatic], 2080 [ν(C≡O), terminal] 1670 [ν(C=C)], 1483 [ν_a(P–C)], 1198 [ν_a(C–SO₃)], 1089 [ν_s(P–C)]; ³¹P-NMR [δ(ppm)]: 35 (doublet), J_{P-Rh}: 124 Hz. Complex *(2)* is dark yellow, and shows the following FT-IR bands (cm⁻¹): 3459 [ν(O–H), broad hydroxyl band], 3061 [ν(C–H), aromatic], 1981 [ν(C≡O), terminal] 1653 [ν(C=C)], 1469 [ν_a(P–C)], 1196 [ν_a(C–SO₃)], 1038 [ν_s(P–C); ³¹P-NMR [δ(ppm)]: 32(doublet), J_{P-Rh}: 113 Hz. Complex *(3)* is light yellow, and shows the following FT-IR bands (cm⁻¹): 3446 [ν(O–H), broad hydroxyl band], 3057 [ν(C–H), aromatic], 1979 [ν(C≡O), terminal] 1633 [ν(C=C)], 1466 [ν_a(P–C)], 1197 [ν_a(C–SO₃)], 1036 [ν_s(P–C); ³¹P-NMR [δ(ppm)]: 23 (doublet), J_{P-Rh}: 144 Hz.

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Catalytic trials

Catalytic trials were carried out in a Parr reactor (600 cm^3) with internal stirring. Conditions for a typical trial: Toluene (30 cm^3), 1-hexene, olefin or olefin mixtures (0.5 cm^3, 4 mmol), or the "synthetic naphtha" (32% 1-hexene, 28.3% 2,3-dimethyl-1-butene, 28.3% 2-pentene and 11.4% cyclohexene; 0.5 cm^3) were used for catalytic studies; complexes *(1)*, *(2)* and *(3)*, (4 mg); H$_2$/CO pressure: 14–68 bar range, temperature: 50–150 °C, 1200 rpm stirring rate. Reaction products were analyzed in a PE, Autosystem GC, using a 30 m. capillary column of methyl-silicone, with H$_2$ carrying gas and FID detector.

Results and discussion

Temperature effect

1-Hexene was used to optimize the variables for the hydroformylation reactions. The temperature effect is shown in Table 1. At ambient temperatures the reaction is slow; only after 50 °C the percent conversion is high and increases at 100 °C, but lower conversion at 150 °C, probably due to slow complex decomposition, similar to biphasic systems with Ru complexes [15–18]. The three Rh complexes show similar conversion and the oxygenated products are mainly aldehydes with a slightly higher selectivity to linear product and a lesser amount of alcohols.

Pressure effect

The pressure effects are shown in Table 2. The percent conversion increases with increasing total pressure (P$_{CO/H2}$ = 68 bar), the main products are from the hydroformylation reaction with a slightly higher selectivity to linear products and lesser amounts of alcohols. At lower pressures (14–17 bar, not shown) hydrogenation and isomerization of 1-hexene are the main products. The hydroformyla-

Table 1. 1-Hexene hydroformylation with complexes *(1)*, *(2)* and *(3)*. Temperature effect

Complexes	Temperature (°C)	Total conversion (%)	Selectivity (%)		
			L	B	Al
(1)	50	82	36	33	13
	100	95	42	35	18
	150	89	41	38	10
(2)	50	79	37	29	13
	100	96	44	33	19
	150	88	39	34	15
(3)	50	75	35	28	12
	100	94	42	37	15
	150	82	38	31	13

Total pressure: 68 bar; P$_{CO/H2}$ = 1/1; t = 3 h.; stirring rate: 1200 rpm. L = linear aldehyde, B = branched aldehyde, Al. = alcohol.

Table 2. 1-Hexene hydroformylation with complexes *(1)*, *(2)* and *(3)*. Gas pressure effect

Complexes	P (bar)	Total conversion (%)	Selectivity (%)		
			L	B	Al
(1)	14	29	15	10	4
	34	62	27	21	14
	68	95	42	35	18
(2)	14	40	18	14	8
	34	75	38	25	12
	68	96	44	33	19
(3)	14	45	20	14	11
	34	82	45	35	12
	68	94	42	37	15

T: 100 °C; P$_{CO/H2}$ = 1/1; t = 3 h.; stirring rate: 1200 rpm. L = linear aldehyde, B = branched aldehyde, Al = alcohol.

tion reaction has a critical pressure as shown for other systems [19].

CO/H$_2$ relation effect

The results are shown in Table 3. When the hydrogen pressure is double, the percent conversion is still high, but the hydrogenation and isomerization products are now important. The oxygenated products come mainly from hydroformylation with a slight selectivity toward linear aldehyde and more alcohols as the hydrogenation product of the carbonyl groups.

Hydroformylation of other substrates

For the hydroformylation of other substrates the selected conditions were P = 34 bar and T = 100 °C, where the percent conversions were high. The results are shown in Table 4. The three chosen olefins are representative of C$_6$ alkenes present in naphtha, and the three Rh complexes gave similar total conversion with them. Cyclohexene and 2-pentene gave only oxygenated products, while 2,3-dimethyl-1-butene gave a considerable percentage of hydrogenated product besides the expected oxygenated compounds. At the end of each catalytic run with the three Rh complexes, the separated water layer containing the Rh complex (UV–vis spectra monitored, under Ar) could be recycled at least four times without apparent catalytic activity loss. Test reactions in the presence of liquid mercury do not show any significant activity changes, indicating that metallic rhodium is not the catalytic phase.

Hydroformylation of olefins mixtures

A mixture containing 32% 1-hexene, 28.3% 2,3-dimethyl-1-butene, 28.3% 2-pentene and 11.4% cyclohexene, that is representative of the olefins in naphtha, was studied under two different conditions. At P = 17 bar and T = 100 °C, a greater amount of oxygenated products were obtained for complexes *(1)* and *(2)* and a reasonable amount of hydrogenated

Table 3. 1-Hexene hydroformylation with complexes *(1)*, *(2)* and *(3)*. CO/H$_2$ relation effect

Complexes	CO/H$_2$ relation	Total conversion (%)	*n*-Hexane (%)	1-Hexene isomers (%)	Selectivity (%)		
					L	B	Al
(1)	2/1	97	–	–	42	37	18
	1/2	96	14	5	34	27	16
(2)	2/1	98	–	–	40	36	22
	1/2	96	12	8	30	26	20
(3)	2/1	97	4	–	39	34	20
	1/2	98	18	6	31	25	18

T = 100 °C, P$_T$ CO/H$_2$ = 68 bar; 4 mg of complex; substrate/catalyst: 600/1, t = 3 h.; stirring rate: 1200 rpm. L = linear aldehyde, B = branched aldehyde, Al = alcohol.

Table 4. Olefins hydroformylation with complexes *(1)*, *(2)* and *(3)*

Complex	Substrate	Total conversion (%)	Hydrogenated products (%)	Oxygenated products (%)
(1)	Ciclohexene	76.5	–	76.5
	2,3-Dimethyl-1-butene	80.5	49	31.5
	2-Pentene	65	–	65
(2)	Ciclohexene	75	–	75
	2,3 Dimethyl-1-butene	65	40	25
	2-Pentene	47	–	47
(3)	Ciclohexene	68	–	68
	2,3 Dimethyl-1-butene	76	46	30
	2-Pentene	40	–	40

P: 34 bar, Temperature: 100 °C, P$_{CO/H2}$ = 1/1, t = 3 h. Stirring rate: 1200 rpm. Oxygenated products include aldehydes and alcohols.

products. For complex *(3)*, a greater amount of hydrogenated products than oxygenated compounds was observed. At 34 bar, for the three complexes, the oxygenated products predominate with very little amount of hydrogenated compounds. Using this last hydroformylation condition, a real naphtha sample, from El Palito (Carabobo, Venezuela) refinery, was studied, giving conversions near 15% to oxygenated products for the three Rh complexes; the results show potential application in fuel upgrading.

Conclusions

Rh complexes *(1)*, *(2)* and *(3)* can be used in catalytic hydroformylation reactions of linear, branched and cyclic olefins, in biphasic (toluene/water) media; the oxygenated compounds are produced in greater proportion, with some hydrogenation and isomerization products obtained at higher hydrogen pressures.

Acknowledgement

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