High active and regioselective hydroformylation of 1-dodecene catalyzed by Rh-BISBIS in a two-phase system

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The hydroformylation of 1-dodecene under aqueous/organic two-phase reaction conditions with rhodium catalysts derived from BISBIS (sodium salt of sulfonated 2,2′-bis (diphenylphosphinomethyl)-1,1′-biphenyl) in the presence of cationic surfactants was studied; regioselectivities appear to be sensitive to pressure. In all cases, the activities and regioselectivities for linear aldehyde were higher.

KEY WORDS: aqueous/organic two-phase system; 1-dodecene hydroformylation; diphosphine; surfactants.

1. Introduction

Since the successful application of water-soluble rhodium-phosphine complexes in the industrial process of propene hydroformylation, much effort has been made to enhance the regioselectivity in the hydroformylation of long chain olefins for obtaining more desirable linear aldehyde and to facilitate the separation of catalyst from the products. Herrmann *et al.* [1] and Leeuwen and co-workers [2] had reported that rhodium complexes with ligand BISBIS (sodium salt of sulfonated 2,2′-bis (diphenylphosphinomethyl)-1,1′-biphenyl) or 2,7-bis (SO_3Na) Xantphos had high regioselectivities in the hydroformylation of long chain olefins, but their catalytic activities were low because of the limited solubility of the substrates in water. Hanson *et al.* [3] synthesized the amphiphilic diphosphines with surface-active groups that could form the micelle and improve the transfer of substrates from oil phase to micellar interface, thereby accelerate the reaction of long chain olefins, but the value of TOF was low. Our research results showed that rhodium complexes with ligand TPPTS [$P\text{-}(m\text{-}C_6H_4SO_3Na)_3$], and TPPDS [$Ph\text{-}P\text{-}(m\text{-}C_6H_4SO_3Na)_2$] [4,5], or BISBIS [6] in the presence of cationic surfactant CTAB as promoter exhibited high catalytic activities and high regioselectivities for linear aldehyde in the hydroformylation of long chain olefins.

In this paper, we report the effects of surfactants with different two long alkyl chain and different cation head on the 1-dodecene hydroformylation in the organic/aqueous biphasic system containing RhCI(CO)$(TPPTS)_2$ and BISBIS.

2. Experimental

The reactions were carried out in a 60 mL autoclave with magnetic stirring. The organic products were analyzed by a gas chromatograph HP1890II equipped with FID detector and a capillary column (30 m × 0.25 mm) SE-30. Both the hydrogenation product dodecane and isomeric dodecene were less than 3%. The rhodium complexes leaching into organic phase was determined by ICP and it was lower than 0.1 ppm.

3. Results and discussion

The results listed in table 1 showed that the high reaction rates and very high regioselectivities of 1-dodecene hydroformylation could achieve using the assembly catalyst system: RhCI(CO)$(TPPTS)_2$-BISBIS-Cationic surfactant.

The catalyst system containing surfactant with two long alkyl chains were more active than single long alkyl chain. The selectivity to form aldehyde was ≥96%, the content of linear aldehyde in the total aldehyde was 98–99%. The content of alkane and isomer of olefin in the products were about 3–4%. The catalyst system exhibited higher activities when the length of two alkyl chains was near that of substrate. The results suggested a relationship between the activity and critical micellar concentration (CMC) or critical vesiculation concentration (CVC) of surfactants. For example, $(C_{12}H_{25})_2N(CH_3)_2Br$ showed very excellent promotion for the reaction which was connected with its very low CMC (2.9×10^{-5} M) [7].

The effect of initial pressure on the hydroformylation showed that the activities and regioselectivities appear to be sensitive to the initial pressure of syngas. The increase of initial pressure could accelerate the reaction, but the content of linear aldehyde decreased gradually.

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Table 1
Effect of the different surfactants

Entry	Surfactant	Conversion (%)[a]	Linear aldehyde (%) (L/B)[b]	TOF (h^{-1})[c]
1	$C_{22}H_{45}N(CH_3)_2C_2H_5Br$	55.7	99.0 (99.0)	528
2	$C_{22}H_{45}N(CH_3)_2C_4H_9Br$	55.0	98.4 (62.6)	518
3	$C_{22}H_{45}N(CH_3)_2C_8H_{17}Br$	71.1	98.2 (53.4)	667
4	$C_{22}H_{45}N(CH_3)_2C_{12}H_{25}Br$	62.5	97.5 (39.4)	587
5	$(C_{12}H_{25})_2N(CH_3)_2Br$	72.2	98.6 (70.0)	678
6	$(C_{16}H_{33})_2N(CH_3)_2Br$	61.3	98.6 (68.3)	575
7	$C_{16}H_{33}N(CH_3)_2C_{12}H_{25}Br$	69.4	98.1 (52.3)	651
8	$C_{16}H_{33}N(C_2H_5)_3Br$	39.9	99.0 (103)	375
9	$C_{16}H_{33}N(CH_3)_3Br$	43.6	98.5 (67.8)	406

[a] Reaction conditions: [Rh] = 9.6×10^{-4} mol/L, [BISBIS]/[Rh] = 3, P = 1.0 MPa, surfactant concentration = 6.0×10^{-3} mol/L, H_2O: 5 mL, 1-dodecene = 2.0 mL, 120 °C, 120 min, the conversion of 1-dodecene.

[b] L/B: molar ratio of linear to branched aldehyde.

[c] TOF: aldehydes(mole)/Rh(mole) × time (h).

Table 2
Effect of the initial pressure

Entry	Initial pressure (MPa)	Conversion (%)		Linear aldehyde (%) (L/B)		TOF (h^{-1})	
		Surf. 1	Surf. 2	Surf. 1	Surf. 2	Surf. 1	Surf. 2
1	1.0	62.5	69.4	97.5 (39.4)	98.1 (52.3)	587	651
2	1.5	65.9	71.9	96.4 (27.4)	97.4 (36.8)	619	675
3	2.0	69.6	76.5	95.6 (21.9)	96.5 (28.0)	653	716
4	2.5	69.8	79.2	94.8 (18.3)	95.2 (19.1)	655	744
5	3.0	71.2	71.5	93.8 (15.1)	94.7 (18.0)	668	672

Reaction conditions: Surf. 1: $C_{22}H_{45}N(CH_3)_2C_{12}H_{25}Br$; surf. 2: $C_{16}H_{33}N(CH_3)_2C_{12}H_{25}Br$, surfactant concentration = 6.0×10^{-3} mol/L, others are the same as in table 1.

The structure of Rh-BISBIS-two long chain surfactant system and its promotion mechanism were progressively studied (table 2).

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References

[1] W.A. Herrmann, C.W. Kohlpaintner, H. Bahrmann and W. Knokol, J. Mol. Catal. 73 (1992) 191.

[2] M.S. Goedheijt, P.C.J. Kamer and P.W.N.M. van Leeuwen, J. Mol. Catal. A: Chem. 143 (1998) 243.

[3] B.E. Hanson, H. Ding and C.W. Kohlpaintner, Catal. Today 42 (1998) 421.

[4] H. Chen, Y. Li, J. Chen, P. Cheng, Y. He and X. Li, J. Mol. Catal. A: Chem. 149 (1999) 1.

[5] H. Chen, Y. Li, J. Chen, P. Cheng and X. Li, Catal. Today 74 (2002) 131.

[6] H. Chen, Y. Li, R. Li, P. Cheng and X. Li, J. Mol. Catal. A: Chem. 198(2002) 1.

[7] T. Matsumoto, Colloid Polym. Sci. 270 (1992) 492.