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Nonaqueous Biphasic Hydroformylation of Long Chain Alkenes Catalyzed by Water Soluble Phosphine Rhodium Catalyst with Polyethylene Glycol Instead of Water

Yuanjiang Zhao[1] · Yanli Liu[1] · Jianzhang Wei[1] · Haiyan Fu[1] · Xueli Zheng[1] · Maolin Yuan[1] · Ruixiang Li[1] · Hua Chen[1]

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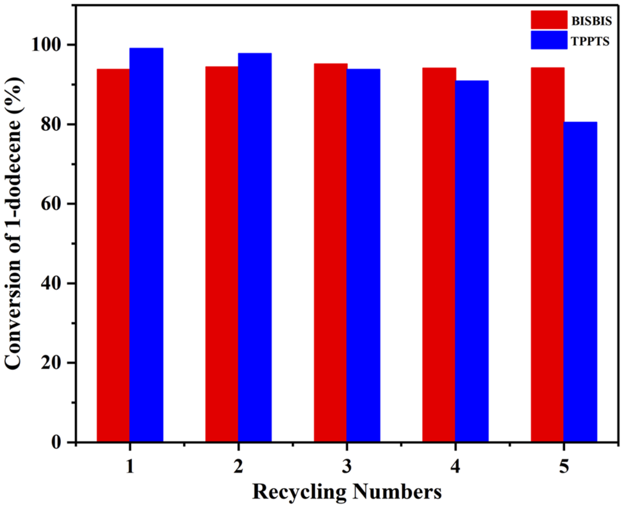
Abstract

The application of polyethylene glycol (donated as PEG), as an environmentally benign solvent instead of water, in rhodium catalyzed hydroformylation of long chain alkenes by using water soluble phosphine BISBIS or TPPTS (TPPTS: sodium salt of sulfonated triphenylphosphine, BISBIS: sodium salt of sulfonated 2,2′-bis(diphenylphosphinomethyl)-1,1′-biphenyl) is herein reported. The conversion of long chain alkenes in PEG-200 could reach above 95.0% after a short reaction time (15 min). In addition, an efficient phase separation and recycling of PEG-200 and catalyst were achieved. The leaching of rhodium into product phase detected by ICP-AES was less than 0.06 wt% of the initial amount.

Graphical Abstract



Keywords Polyethylene glycol · Hydroformylation · Long chain alkene · Water soluble phosphine · Rhodium

1 Introduction

Hydroformylation is a reaction route for olefins toward aldehydes with 100% atom economy and has been developed into one of the most important homogeneous catalytic processes [1–3]. The global production capacity of aldehydes is beyond 10 million tons per year [4], which can be typically processed into valuable consumer products in cosmetics, bulk and fine

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✉ Maolin Yuan
cdscyml@sina.com

[1] Key Lab of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, China

chemicals industries [5–9]. Rhodium complexes have been examined as the most effective homogenous catalysts for hydroformylation as they display high activity and selectivity under milder reaction conditions [10]. However, a serious shortcoming of homogeneous catalysis is the cumbersome separation by distillation of reaction products from catalyst.

Aqueous media are now viewed as excellent means to effect nearly complete catalyst separation and recovery [11–16], but the poor solubility of long chain alkenes ($> C_6$) in water is of potential limitation. In addition, this process is not suitable for water-sensitive substrates.

Recently, as a nontoxic, biodegradable and inexpensive solvent of low volatility, polyethylene glycol (PEG) has attracted much interest as a recycling solvent [17, 18].

Among rhodium catalyzed hydroformylation of long chain alkenes in PEG, the tested catalysts are commonly rhodium complexes with phosphines containing PEG chain or rhodium polyethylene glycolate complex, so as to increase the solubility and affinity of the catalyst to PEG. Results obtained show that the regioselectivity for linear aldehyde is low, alongside, the rhodium leaching into product phase is high (up to 10 wt% of the initial amount). To the best of our knowledge, the hydroformylation of long chain alkenes catalyzed by rhodium catalyst with water soluble phosphine BISBIS or TPPTS (TPPTS: sodium salt of sulfonated triphenylphosphine, BISBIS: sodium salt of sulfonated 2,2′-bis(diphenylphosphinomethyl)-1,1′-biphenyl) in PEG has not been described yet.

Herein, water soluble phosphine rhodium catalyzed the hydroformylation of long chain alkenes in PEG (Scheme 1) is chosen to investigate the reaction performance, phase behavior and catalyst recycling.

2 Experimental

2.1 Materials

Ligands TPPTS, BISBIS (Fig. 1) and rhodium precursor $HRh(CO)(TPPTS)_3$ were prepared according to literatures [19, 20]; DEG (Diethylene glycol), PEG-200, PEG-400 and PEG-600 (the number refers to the average molecular weight) were purchased from Kelong Chemical Co. of Chengdu. All chemicals were used without any additional purification; 1-octene, 1-decene and 1-dodecene were purchased from Sigma-Aldrich; hydrogen (H_2, 99.99%) and carbon monoxide (CO, 99.9%) were obtained from Southwest Institute. The composition of reaction mixture was determined by means of gas chromatography (PANNA A91, KB-1: 30 m × 0.25 mm × 0.50 μm, FID).

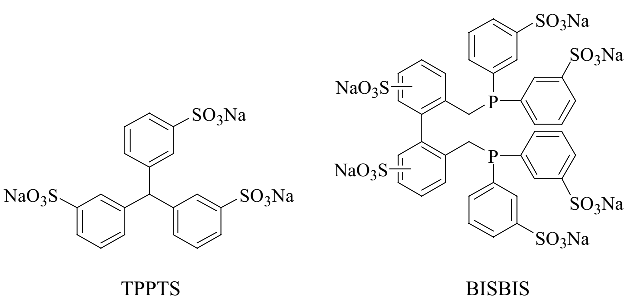


Fig. 1 Structure of TPPTS and BISBIS

The content of rhodium in products mixture was detected by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

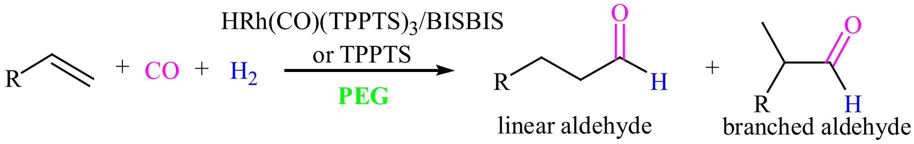
2.2 Hydroformylation and Catalyst Recycling

All hydroformylation was carried out in a 60 mL stainless steel autoclave equipped with a magnetic stirrer. $HRh(CO)(TPPTS)_3$, TPPTS or BISBIS, PEG and long chain alkene were introduced to the autoclave under a nitrogen atmosphere. The autoclave was closed, flushed with syngas three times, and then pressurized with syngas (H_2:CO = 1:1) to desired pressure and heated to needed temperature for a specified time. After the reaction was finished, the autoclave was cooled to room temperature and carefully depressurized. The product phase was separated from the PEG phase containing water soluble rhodium catalyst by simple phase separation. The products were analyzed by GC (PANNA A91, KB-1, 30 m × 0.25 mm × 0.50 μm, FID). In catalyst recycling experiments, the PEG phase and new portion of long chain alkene were introduced to the autoclave under a nitrogen atmosphere. The other operations were the same as the former hydroformylation.

3 Results and Discussion

As well known, bidentate phosphine ligands are crucial for regioselectivity control toward linear aldehyde, because their specific bite angle can improve the regioselectivity [21, 22]. In this report, 1-dodecene was chosen as a probe substrate, BISBIS as a water soluble bidentate phosphine ligand to investigate the reaction performance in PEG. Based on our previous research on rhodium catalyzed hydroformylation with BISBIS [23, 24], 3.0 MPa of syngas and 120 °C were

Scheme 1 Hydroformylation of long chain alkenes



selected as reaction parameters. According to the mechanism in literature [25], the catalytically active specie HRh(CO)(BISBIS) is formed in situ by the ligand exchange reaction between HRh(CO)(TPPTS)$_3$ and BISBIS. The side reactions include isomerization and hydrogenation of 1-dodecene. Table 1 indicates that the average molecular weight of PEG and the volume of PEG-200 have a significant influence on 1-dodecene hydroformylation. The conversion of 1-dodecene increased significantly with the decrease in the average molecular weight of PEG. The order of 1-dodecene conversion is PEG-200 > DEG > PEG-400 > PEG-600. Although the solubility of 1-dodecene in different PEGs increases with the increase in the average molecular weight of PEG at 120 °C (0.7 g/100 g PEG-200, 3.5 g/100 g PEG-400, 5.9 g/100 g PEG-600), the solubility of catalyst precursor HRh(CO)(TPPTS)$_3$ and ligand BISBIS decreases greatly. For example, the solubility of HRh(CO)(TPPTS)$_3$ in PEG-200 is about 130 g/100 g PEG-200 at 120 °C while the solubility of that in PEG-400 and PEG-600 is only 0.8 g/100 g PEG-400 and 0.6 g/100 g PEG-600, which results into much lower conversions of 1-dodecene in PEG-400 and in PEG-600. 1-dodecene conversion could reach above 95.0% (entry 2) after a short reaction time (15 min) in PEG-200. As the similar explanation in literature [26], the reason may be that catalyst precursor HRh(CO)(TPPTS)$_3$, ligand BISBIS and 1-dodecene have a good solubility in PEG-200 under the reaction conditions. However, the conversion is only 0.8% when water was used as a solvent in 1-dodecene hydroformylation due to the much lower solubility of 1-dodecene in water. In tested experiments, the regioselectivity for linear aldehyde remained almost about 95.0%, which is attributed to the bidentate ligand BISBIS with e.e. Configuration [27]. Results in Table 1 also show that the volume of PEG-200 has a obvious effect on activity of 1-dodecene hydroformylation. The rate of 1-dodecene hydroformylation increased with increasing the volume of PEG-200, however, when it further increased, the 1-dodecene conversion dropped to 85.5% due to the decrease in concentration of rhodium in PEG-200. The optimum dosage of PEG-200 was 4.0 mL under the reaction conditions. It can be seen from Table 1 that the selectivity for aldehydes achieved 90.0%, accompanied by about 10.0% isomerized dodecenes and dodecane as the main byproducts and the regioselectivity for linear aldehyde around 95.0%. These results were similar to that obtained in aqueous biphasic 1-dodecene hydroformylation catalyzed by Rh/BISBIS in the presence of a surfactant [24].

Encouraged by the catalytic performance of the above studied system, the hydroformylation of other long chain alkenes catalyzed by water soluble phosphine rhodium catalyst HRh(CO)(TPPTS)$_3$ and BISBIS in PEG-200 was also investigated. Results presented in Fig. 2 indicate that the conversion of long chain alkenes decreased slightly with increase in carbon number of them. For example, the conversion of 1-octene was 97.6%, but that of 1-dodecene was 95.1%. The reason might be attributed to the different reaction activity of long chain alkenes. After hydroformylation finished, the interphase boundary of two phases was very obvious. The upper phase was colorless, while the lower phase containing catalyst and BISBIS was golden yellow (see Fig. 3). Results in Fig. 2 further show that the hydroformylation of other long chain alkenes was also successfully performed in PEG-200.

Table 2 firstly summarizes the recycling experimental results in 1-dodecene hydroformylation catalyzed by the catalytic system derived from HRh(CO)(TPPTS)$_3$, BISBIS and PEG-200, exhibiting high catalytic efficiency and long service life with no significant loss in activity, selectivity or Rh loss for more than five cycles. TPPTS is one of the most widely used water soluble monodentate phosphines,

Table 1 Hydroformylation of 1-dodecene with HRh(CO)(TPPTS)$_3$/BISBIS system in PEG

Entry	Solvent	Volume (mL)	Conv. (%)^a	$S_{Ald.}$ (%)^b	$S_{Linear\ ald.}$ (%)^c	TOF (h^{-1})^d
1	DEG	4.0	78.2	89.4	96.9	1408
2	PEG-200	4.0	95.1	90.1	96.5	1712
3	PEG-400	4.0	25.3	88.6	95.8	455
4	PEG-600	4.0	1.7	53.8	98.2	31
5	H_2O	4.0	0.8	89.8	93.8	14
6	PEG-200	1.0	63.1	90.6	96.8	1136
7	PEG-200	2.0	89.1	91.0	96.7	1604
8	PEG-200	4.0	95.1	90.1	96.5	1712
9	PEG-200	5.0	85.5	88.3	96.4	1539

Reaction conditions Rh = 2.0×10^{-2} mmol, [BISBIS]/[Rh] = 17.5, S/C = 450, 1-dodecene = 2.0 mL, P = 3.0 MPa (CO:H_2 = 1.0:1.0), T = 120 °C, t = 15 min

[a] Conversion of 1-dodecene

[b] Selectivity for aldehydes

[c] Linear aldehyde content in total aldehydes

[d] Turnover frequency defined as the moles of converted alkene per mole of Rh per hour

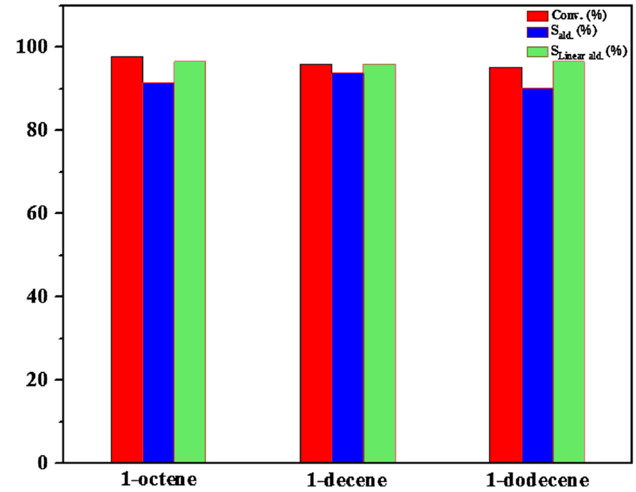
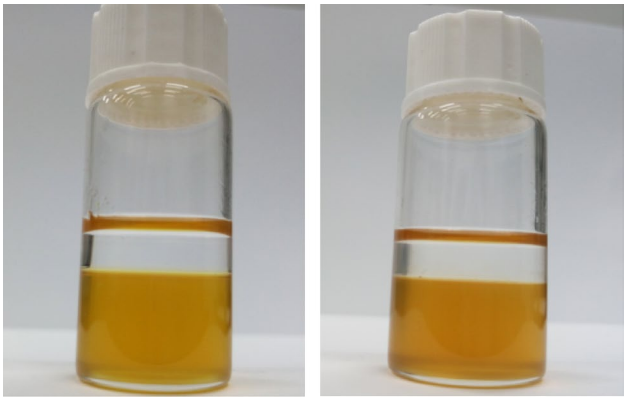


Fig. 2 Hydroformylation of long chain alkenes with HRh(CO)$(TPPTS)_3$/BISBIS in PEG-200 Reaction conditions: Long chain alkene = 2.0 mL, PEG-200 = 4.0 mL, others are the same as in Table 1



before reaction after reaction

Fig. 3 Picture of before and after reaction

Table 2 Catalyst recycling with HRh(CO)$(TPPTS)_3$/BISBIS or TPPTS in PEG-200

Run	Ligand	Conv. (%)	S_{Ald}. (%)	$S_{Linear\ ald}$. (%)	TOF(h^{-1})
1	BISBIS	93.8	89.6	96.2	1688
2		94.4	91.5	95.0	1699
3		95.2	91.8	94.7	1714
4		94.1	92.1	94.4	1694
5		94.2	90.9	94.4	1696
1	TPPTS	99.1	92.9	73.3	1784
2		97.8	91.7	74.3	1760
3		93.8	90.0	74.3	1688
4		90.9	90.1	75.8	1636
5		80.5	89.9	75.9	1449

Reaction conditions 1-dodecene = 2.0 mL, [P]/[Rh] = 35.0, PEG-200 = 4.0 mL, others are the same as in Table 1

however, the activity decreased slightly after five catalytic cycles when BISBIS was replaced with TPPTS. The main reason may be that TPPTS was partly oxidized owing to contact with air during the separation. In contrast, the chelating complex Rh/BISBIS formed with HRh(CO)$(TPPTS)_3$ and bidentate ligand BISBIS is more stable during the separation. Therefore the catalyst recycling is significantly improved. As far as the two catalytic systems, the content of rhodium leaching into product phase was less than 0.06 wt% because of their own strong charge of BISBIS and TPPTS. It could be seen that the catalytic systems consisting of HRh(CO)$(TPPTS)_3$, TPPTS or BISBIS and PEG-200 show a good catalyst recycling performance.

4 Conclusions

In conclusion, a simple, highly effective and recyclable hydroformylation catalytic system for long chain alkenes has been established based on water soluble phosphine BISBIS or TPPTS, HRh(CO)$(TPPTS)_3$ and PEG-200, which showed an excellent hydroformylation efficiency for 1-octene, 1-decene and 1-dodecene. The analysis of Rh loss and catalyst recycling experiments indicated that the water soluble phosphine rhodium catalysts can be effectively immobilized in PEG-200 due to the strong charge of BISBIS or TPPTS, which significantly improved the stability and reusability of catalytic system during the catalytic cycle. No significant loss of catalytic efficiency or Rh was observed for more than five cycles. Nowadays, the application of the catalytic systems in functional olefin hydroformylation and other reactions was under the way.

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References

1. Agbossou F, Carpentier JF, Mortreux A (1995) Asymmetric hydroformylation. Chem Rev 95:2485
2. Brezny AC, Landis CR (2017) Unexpected CO dependencies, catalyst speciation, and single turnover hydrogenolysis studies of hydroformylation via high pressure NMR spectroscopy. J Am Chem Soc 139:2778
3. van Leeuwen PWNM, Claver C (eds) (2000) Rhodium catalyzed hydroformylation. Kluwer Academic Publishers, Dordrecht
4. Franke R, Selent D, Börner A (2012) Applied hydroformylation. Chem Rev 112:5675
5. Wang YY, Chen JH, Luo MM, Chen H, Li XJ (2006) Highly regioselective hydroaminomethylation of long chain alkenes catalyzed by Rh-BISB6IS in a two-phase system. Catal Commun 7:979
6. Eilbracht P, Bärfacker L, Buss C, Hollmann C, Kitsos-Rzychon BE, Kranemann CL, Rische T, Roggenbuck R, Schmidt A (1999)

Tandem reaction sequences under hydroformylation conditions: new synthetic applications of transition metal catalysis. Chem Rev 99:3329

7. Liu Y, Li ZH, Wang B, Zhang Y (2016) A fine dispersed cobalt catalyst with macro-pore for hydroformylation of 1-hexene. Catal Lett 146:2252
8. Jin X, Zhao K, Kong FF, Cui FF, Liu QQ, Zhang YW (2014) The mechanism of acetal formation in acid-free Rh-catalyzed tandem hydroformylation-acetalization of olefins in MeOH. Catal Lett 144:192
9. Zhang L, Li C, Zheng XL, Fu HY, Chen H, Li RX (2014) Synthesis, characterization of *N*-pyrrolylphosphanes based on heterocyclic amine backbones and their application in hydroformylation of 1-octene. Catal Lett 144:1074
10. Behr A, Neubert P (2013) Applied homogeneous catalysis. Angew Chem Int Ed 52:1627
11. Kuntz EG (1987) Homogeneous catalysis in water. Chem Tech 17:570
12. Cornils B, Wiebus E (1995) Aqueous catalysts for organic reactions. Chem Tech 23:33
13. Cornils B, Kuntz EG (1995) Introducing TPPTS and related ligands for industrial biphasic processes. J Organomet Chem 502:177
14. Cornils B, Herrmann WA, Eckl RW (1997) Industrial aspects of aqueous catalysis. J Mol Catal A 116:27
15. Cornils B (1999) Bulk and fine chemicals via aqueous biphasic catalysis. J Mol Catal A 143:1
16. Siangwata S, Baartzes N, Makhubela BCE, Smith GS (2015) Synthesis, characterisation and reactivity of water-soluble ferrocenylimine-Rh(I) complexes as aqueous-biphasic hydroformylation catalyst precursors. J Organomet Chem 796:26
17. Feng CL, Wang YH, Jiang JY, Yang YC, Yu FL, Jin ZL (2006) Using thermoregulated PEG biphase system to effect the hydroformylation of *p*-isobutylstyrene catalyzed by Rh/OPGPP complex. J Mol Catal A 248:159
18. Borrmann T, Roesky HW, Ritter U (2000) Biphasic hydroformylation of olefins using a novel water soluble rhodium polyethylene glycolate catalyst. J Mol Catal A 153:31
19. Herrmann WA, Kohlpaintner CW, Bahrmann H, Knokol W (1992) Water-soluble metal complexes and catalysts Part 6. A new, efficient water-soluble catalyst for two-phase hydroformylation of olelins. J Mol Catal 73:191
20. Chen H, Liu HC, Li YZ, Cheng FM, Li XJ (1994) J Mol Catal 8:124
21. Kamer PCJ, vanLeeuwen PWNM., Reek JNH (2001) Wide bite angle diphosphines: xantphos ligands in transition metal complexes and catalysis. Acc Chem Res 34:895
22. van Leeuwen PWNM., Kamer PCJ, Reek JNH, Dierkes P (2000) Ligand bite angle effects in metal-catalyzed C–C bond formation. Chem Rev 100:2741
23. Yuan ML, Chen H, Li RX, Li YZ, Li XJ (2004) High active and regioselective hydroformylation of 1-dodecene catalyzed by Rh-BISBIS in a two-phase system. Cat Lett 94:15
24. Yuan ML, Chen H, Li RX, Li YZ, Li XJ (2003) Hydroformylation of 1-butene catalyzed by water-soluble Rh–BISBIS complex in aqueous two-phase catalytic system. Appl Cat A 251:181
25. Walter S, Spohr H, Franke R, Hieringer W, Wasserscheid P, Haumann M (2017) Detailed investigation of the mechanism of Rh-Diphosphite supported ionic liquid phase (SILP)-catalyzed 1-butene hydroformylation in the gas phase via combined kinetic and density functional theory (DFT) modeling studies. ACS Catal 7:1035
26. Fu HY, Li M, Chen J, Zhang RM, Jiang WD, Yuan ML, Chen H, Li XJ (2008) Application of a new amphiphilic phosphine in the aqueous biphasic catalytic hydroformylation of long chain olefins. J Mol Catal A: Chem 292:21
27. Casey CP, Whiteker GT, Melville MG, Petrovich LM, Gavney JA Jr, Powell DR (1992) Diphosphines with natural bite angles near 120° increase selectivity for n-aldehyde formation in rhodium-catalyzed hydroformylation. J Am Chem Soc 114:5535