Thermoregulated phase-transfer ligands and catalysis. Part VI. Two-phase hydroformylation of styrene catalyzed by the thermoregulated phase-transfer catalyst OPGPP/Rh

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Abstract

A novel nonionic water-soluble octylpolyglycol-phenylene-phosphite (OPGPP) was synthesized and the two-phase hydroformylation of styrene catalyzed by an OPGPP/Rh catalyst was investigated fully. The catalyst displayed excellent catalytic activity; high styrene conversion and high aldehyde yield (99.6 and 99.3%, respectively) were obtained at 80°C and 5.0 MPa, and the molar ratio of branched/normal aldehyde was 4.8. The experimental results revealed that there was a 'thermoregulated phase-transfer catalysis (TRPTC)' process present in the reactions. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Water-soluble phosphine; Two-phase hydroformylation; Styrene; TRPTC

1. Introduction

It is well known that 2-arylpropionaldehyde is an important starting material for cosmetics, polymers and pharmaceuticals [1]. A great deal of research interest has been focused on the homogenous hydroformylation of styrene catalyzed by Rh carbonyl complexes using various phosphine ligands [2–6], whilst water-soluble catalysts in a biphasic system has received little attention so far [7–9]. In a previous report [10], we reported the synthesis of a series of water-soluble polyether-substituted triphenylphosphines (PETPPs) which exhibit thermoregulated phase-transfer function, and successfully applied them to the biphasic hydroformylation of higher olefins [11].

In this paper, two-phase hydroformylation of styrene catalyzed by a new rhodium catalyst with octylpolyglycol-phenylene-phosphite (OPGPP) as the ligand is studied.

$$P(OCH_2CH_2)_{13}OC_8H_{17}$$
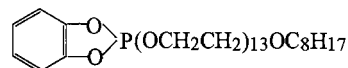
Comparing the anion water-soluble ligand TPPTS (trisodium salt of trisulfonated triphenylphosphine) and TPPMS (sodium salt of mono-sulfonated triphenylphosphine), the polyoxyethylene-modified nonionic water-soluble phosphine OPGPP has a critical solution temperature—'cloud point (T_p)'—and manifests a special property of inverse temperature-dependent water-solubility similar to that of the nonionic surfactants. As a result, the OPGPP/Rh catalyst is soluble in the aqueous phase at lower temperatures and it can transfer into the organic phase to catalyze the hydroformylation reaction at temperatures higher than T_p and return to the aqueous phase to be separated from the production at temperatures lower than T_p. The OPGPP/Rh catalyst also exhibits desirable catalytic reactivity in the two-phase (water/organic) hydroformylation of styrene, with the conversion up to 99.6% and the yield of aldehyde 99.3%.

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2. Experimental

All solvents and styrene are distilled prior to use. Distilled deionized water was used and the $Rh(acac)(CO)_2$ was purchased from the Beijing Research Institute of Chemical Industry.

2.1. Hydroformylation experiments

Hydroformylation of styrene was carried out in a stainless steel autoclave of 75 ml capacity, which was placed in an oil bath containing a thermostat. $Rh(acac)(CO)_2$, OPGPP, water, organic solvent, styrene and the internal standard decane were placed in the autoclave and were flushed four times with 2.0 MPa of CO. The reactor was pressurized with synthesis gas $(CO/H_2 = 1/1)$ up to the reaction pressure and held at the designated temperature with magnetic stirring for a fixed time. After cooling, the reactor was discharged and the reaction solution was siphoned into a separatory funnel. After phase separation, the organic layer was washed with distilled water and dried over anhydrous magnesium sulfate and subjected to GC analysis.

2.2. Preparation of polyether-substituted 1-octanol $[C_8H_{17}(OCH_2CH_2)_{13}OH]$

Ethoxylation was carried out in a 100 ml glass autoclave equipped with an apparatus for continuous ethoxylation. 1-Octanol (7 g, 0.054 mol) together with a catalytic amount of anhydrous sodium acetate (0.056 g, 0.8%) was charged in the autoclave. The system was purged with nitrogen and heated to 130°C. Then the desired amount of ethylene oxide (EO) was added to maintain a pressure of 0.4 MPa $(EO/N_2 = 3/1)$ for the required period of time. After ethoxylation was complete, $C_8H_{17}(OCH_2CH_2)_nOH$ was obtained, and could be used without further purification. The average length of polyether chain $(n = 13)$ was determine by ^{1}H-NMR spectroscopy.

2.3. Preparation of o-phenylene chlorophosphite $(o\text{-}C_6H_4O_2PCl)$

A total of 65 ml (0.75 mol) of PCl_3 was added to a 250-ml, round-bottom flask which contained 55 g (0.5 mol) catechol over a 30 min period. After the addition, the mixture was stirred at refluxing for 2 h. Distillation of the reaction mixture afforded 74.2 g (85%) of o-phenylene chlorophosphite, b.p. 98°C/25 mmHg.

2.4. Preparation of octylpolyglycol-phenylene-phosphite (OPGPP)

A solution of o-phenylene chlorophosphite (7 g, 0.04 mol) in 5 ml toluene was added over a 30 min period to a stirred solution of polyether-substituted 1-octanol (14 g, 0.02 mol) in 10 ml toluene. After the addition, the mixture was stirred at refluxing for 4 h. Toluene was drawn out under vacuum. The crude product OPGPP 14.9 g (85%) was dissolved in 20 ml diethylether to further purification. ^{1}H-NMR/CDCl$_3$: δ(ppm) 0.9(3H, CH$_3$), 1.3(12H, CH$_2$), 3.5(52H, C$_2$H$_4$O,), 4.4(2H, OCH$_2$), 6.8–8.1(4H, Ph). FT-IR (cm^{-1}): ν(C–O–C) 1116, ν(P–O–C(alkyl)) 1035, ν(P–O–C(aromatic)) 975.

2.5. Preparation of OPGPP/Rh(acac)(CO)$_2$

The catalyst was generated in situ with $Rh(acac)(CO)_2$ as a catalyst precursor and OPGPP as a ligand.

3. Results and discussion

3.1. Styrene hydroformylation

The hydroformylation of styrene was carried out using Rh/OPGPP as a catalyst. The influences of ligand OPGPP to rhodium molar ratio, temperature, total pressure and organic solvents were assessed concerning this reaction.

The effect of OPGPP/Rh molar ratio on the styrene conversion and the yield of aldehyde are shown in Table 1. The conversion and yield of aldehyde increase remarkably when OPGPP/Rh ratio varies from 2 to 13. At P/Rh = 13, the styrene conversion reaches 99.6%, the yield of aldehyde is 99.3%. If P/Rh ratio is above 13, the yield of aldehyde does not change greatly. Therefore, the ratio of 13 seems to be an optimum result at these hydroformylation conditions. In addition, the branched/normal (i.e. b/n) ratio of aldehyde slightly decreases with an increase in the P/Rh ratio.

The influence of reaction temperature has been investigated (Table 2). Under the experimental conditions, the conversion of styrene and the yield of aldehyde increase with temperature. In addition, the b/n ratio

Table 1
Effect of P/Rh mol ratio on the two-phase hydroformylation of styrene

P/Rh	Conversion (%)	Yield of aldehyde (%)	b/n[a]
2	52.1	51.4	5.6
8	91.3	88.9	4.9
13	99.6	99.3	4.8
20	99.8	98.9	4.7

Reaction conditions: $T = 80°C$, $P = 5.0$ MPa (CO/H$_2$ = 1), styrene 1 ml, styrene/Rh = 1000 (molar ratio), H$_2$O 2 ml, organic solvent n-heptane 2 ml, reaction time $t = 6$ h.
[a] b/n, branched/normal aldehyde ratio.

Table 2
Effect of reaction temperature on the two-phase hydroformylation of styrene

T (°C)	Conversion (%)	Yield of aldehyde (%)	b/n
40	22.5	22.0	14.6
60	78.4	77.6	7.7
80	99.6	99.3	4.8
100	99.8	98.4	1.6

P/Rh = 13; all other conditions are the same as in Table 1.

Table 4
Effect of organic solvent on the two-phase hydroformylation of styrene

Organic solvent	Conversion (%)	Yield of aldehyde (%)	b/n
Toluene	99.8	99.7	4.9
n-hexane	99.4	99.1	4.7
n-heptane	99.6	99.3	4.8
Cyclohexane	98.9	98.4	4.6

P/Rh = 13; all other conditions are the same as in Table 1.

depends largely on temperature, decreasing sharply as temperature increased. The optimum temperature for the reaction is 80°C.

The data in Table 3 indicates that the rate of hydroformylation increases with the total pressure ($CO/H_2 = 1/1$) whilst the aldehyde b/n ratio remains constant. Only minor changes in the styrene conversion and the aldehyde yield are observed above 5.0MPa. Therefore, a pressure of 5.0 MPa is chosen for this hydroformylation reaction.

Table 4 shows the results of hydroformylation with various organic solvents. Little effect on the catalytic results is observed with different non-polar solvents. However, after hydroformylation the color of organic layer, which indicates the loss of Rh, had changed. Using toluene as solvent, the organic layer after reaction was yellow ash; whilst it was almost colorless if n-heptane used as solvent, thus n-heptane is chosen in order to reduce the Rh loss.

Four water-soluble catalysts for the two-phase hydroformylation of styrene are tested in Table 5. Poor catalytic activity was obtained when the anion water soluble phosphine ligand TPPTS was used and TPPMS exhibits better activity because it is more soluble in the organic phase than TPPTS. The noninic water-soluble phosphine ligands polyether-substituted triphenylphosphine PETPPs ($Ph_2P[p$-C_6H_4 ($OCH_2CH_2)_{25}OH]$) and OPGPP gave the best results. This attributed to the thermoregulated phase-transfer function, i.e. the OPGPP/Rh catalyst would transfer into organic phase above its T_p temperature and, therefore, the hydroformylation of styrene occurs in the organic phase.

3.2. Investigation of thermoregulated phase-transfer function of OPGPP/Rh

OPGPP has a distinct cloud point ($T_p = 56.5$°C) which indicated that it possessed a property termed as 'inverse temperature-dependent water-solubility'. In order to further investigate the thermoregulated phase-transfer function of OPGPP/Rh catalyst, atmospheric pressure hydrogenation experiments of allyl alcohol with OPGPP/Rh were carried out in an aqueous medium. As outlined in Fig. 1, an unusual inversely temperature-dependent catalytic behavior was observed. At 30°C, which is $< T_p$, the hydrogenation reaction proceeds (A region), since the uptake of hydrogen appeared; on heating of the sample to 70°C ($T > T_p$), the reaction ceases (B region). Such an anti-Arrhenius kinetic behavior could only be attributed to the loss of catalytic activity of the Rh/OPGPP catalyst when it precipitates from the aqueous phase at the reaction temperature above its T_p. Moreover, the reactivity of the catalyst could be restored since the phase separation process is reversible on cooling to 30°C (C region) lower than the T_p. Obviously, the existence of such an anti-Arrhenius phenomenon provides fundamental support for the TRPTC of the OPGPP/Rh catalyst.

In addition, the effects of $V_{water}/V_{styrene}$ ratio on the two-phase hydroformylation of styrene have been investigated (Table 6). Table 6 shows that the $V_{water}/V_{styrene}$ ratio has no effect on the styrene conversion and the yield of aldehyde. Conversely, the results would be varied with the $V_{water}/V_{styrene}$ ratio if TPPTS/Rh or

Table 3
Effect of total pressure on the two-phase hydroformylation of styrene

P (MPa)	Conversion (%)	Yield of Aldehyde (%)	b/n
3.0	50.3	48.7	3.1
4.0	82.1	80.3	4.6
5.0	99.6	99.3	4.8
6.0	99.9	99.5	5.2

P/Rh = 13; all other conditions are the same as in Table 1.

Table 5
Catalytic reactivity of different water-soluble catalysts in the two-phase hydroformylation of styrene

Ligand	Conversion (%)	Yield of aldehyde(%)	b/n
TPPTS	37.8	36.9	2.8
TPPMS	87	83	1.5
PETPPs	95.7	92.8	2.2
OPGPP	99.2	99.0	4.9

Reaction conditions: $Rh(acac)(CO)_2$ 0.01 mmol, P/Rh = 12, styrene/Rh = 1000 (molar ratio), heptane 2.0 ml, H_2O 3 ml, P = 5.0 MPa ($CO/H_2 = 1/1$), T = 80°C, t = 5 h.
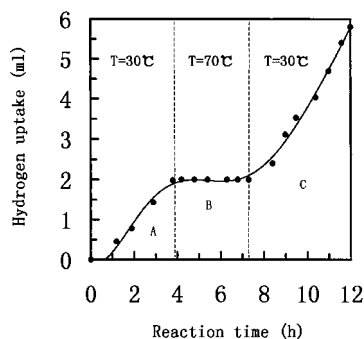
Fig. 1. Atmospheric-pressure hydrogenation of allyl alcohol using OPGPP/Rh as the catalyst in water at different temperatures. Reaction conditions: OPGPP 0.5 mmol, RhCl$_3$·H$_2$O 10.5 mg (0.04 mmol), ally alcohol 0.58 g (10 mmol), H$_2$O 25 ml.

TPPMS/Rh is employed as a catalyst under the same conditions [12]. The usually two-phase (aqueous/organic) hydroformylation occurs in the aqueous phase or at the aqueous/organic interface [13,14], and thus the $V_{water}/V_{styrene}$ ratio has obvious effects on the reaction results; whilst the biphasic hydroformylation catalyzed by OPGPP/Rh occurs in the organic phase when $T > T_p$, so the $V_{water}/V_{styrene}$ ratio has no influence on the reaction results. This experimental result provides an additional proof for the TRPTC process in the two-phase hydroformylation of styrene catalyzed by OPGPP/Rh catalyst.

4. Conclusion

The water-soluble catalyst formed in situ from OPGPP and Rh(acac)(CO)$_2$ exhibits a thermoregulated phase-transfer function, and a catalytic process named TRPTC in the two-phase hydroformylation of styrene is observed.

Table 6
Effect of $V_{water}/V_{styrene}$ (v/v) ratio on the two-phase hydroformylation of styrene catalyzed by OPGPP/Rh

$V_{water}/V_{styrene}$	Conversion (%)	Yield of aldehyde (%)	b/n
0	99.4	99.2	4.8
1	99.2	99.0	4.8
2	99.6	99.3	4.8
4	99.4	99.2	4.8

P/Rh = 13; all other conditions are the same as in Table 1.

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