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Using thermoregulated PEG biphase system to effect the hydroformylation of *p*-isobutylstyrene catalyzed by Rh/OPGPP complex

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Abstract

Thermoregulated poly(ethylene glycol) (PEG) biphase system, which is composed of PEG 4000 and the mixture of toluene and heptane, was developed and used in the hydroformylation of *p*-isobutylstyrene (IBS) catalyzed by Rh/OPGPP complex. Under the conditions of $P = 5.0$ MPa (H_2:CO = 1:1), P/Rh = 8 (molar ratio), reaction time = 5 h and temperature = 120 °C the conversion of IBS was 99% and the yield of aldehyde was 96%. The catalyst could be easily separated from the product by phase separation and reused for seven times without evident loss of activity.

Keywords: Thermoregulated PEG biphase system; IBS; Hydroformylation; Phosphite ligand; Rhodium

1. Introduction

To overcome the difficulty of separating the catalyst from the product in homogeneous catalysis, liquid/liquid biphase catalysis has been advanced [1]. The most commonly used process is the catalysis in aqueous/organic biphase systems, consisting of an aqueous phase containing water-soluble catalyst and another phase of either a hydrocarbon or any other solvent of low polarity [2]. However, this process was unsuitable for higher olefins due to their low water-solubility. In order to solve this problem, many improved aqueous/organic biphase systems have been proposed [3,4]. Based on the property of cloud point (Cp) of non-ionic phosphine ligands with PEG chains, Jin et al. proposed a novel idea of thermoregulated phase-transfer catalysis (TRPTC) [5,6]. But aqueous/organic biphase processes are not suitable for water-sensitive systems. This has stimulated the development of non-aqueous liquid/liquid biphase systems. Horvath and Rabai described a fluorous biphase system (FBS), which consists of a fluorous phase containing a phosphine ligand with fluorous ponytails and another organic phase. This thermoregulated non-aqueous liquild/liquild biphase system has been applied in the hydroformylation of higher olefins [7].

Being a non-toxic and inexpensive solvent of low volatility, PEG has drawn much attention of chemists recently as a recyclable solvent medium. One approach is that PEG was used as a reaction medium and after reaction is complete, products were extracted by other immiscible organic solvent. Chandrasekhar et al. studied Heck reaction in PEG and extracted the product with ether at the end of the reaction [8]. As an alternative method, a temperature-dependent biphase system, composed of PEG 1000, toluene and methyl linoleate (CML), was studied and used in the rhodium-catalyzed cooligomerization of CML with ethylene [9]. In addition, Loh and co-workers have described an organic biphase system containing PEG 3350, heptane and either CH_2Cl_2 or CH_3OH. This system has been tested in the hydrogenation of 1-hexene [10].

In our previous work, a phosphite ligand OPGPP has been synthesized and used in the Rh-catalyzed hydroformylation of IBS in the aqueous/organic biphase system. However, there was a considerable loss in activity after four successive reaction runs due to the hydrolysis of OPGPP in water [11].

In this paper, thermoregulated PEG 4000/toluene/heptane biphase catalytic system applied in the hydroformylation of IBS catalyzed by Rh/OPGPP complex (Scheme 1) is reported.

2. Experimental

2.1. Materials

Organic solvents were purified by distillation from an appropriate drying agent under inert atmosphere. IBS was prepared

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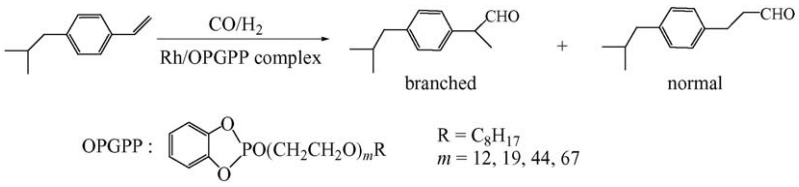

Scheme 1. Hydroformylation of IBS.

as previously described [11]. $RhCl_3{\cdot}3H_2O$ was used as received from Beijing Research Institute of Chemical Industry without any further purification. Phosphite ligand OPGPP was synthesized according to the literature [12] and the Rh/OPGPP complex catalyst was prepared in situ.

2.2. Instrumentation

Gas chromatographic analyses were performed by using a gas chromatograph "GC-8810" equipped with a flame ionization detector, a capillary column (OV-101, 30 m × 0.3 mm, carrier gas: 0.2 MPa N_2) and a Shimadzu C-R3A integrator. *n*-Decane was used as the internal standard. ICP-OES analyses were carried out on an Iris Interpid DUO ER/S (Thermo Elemental, USA).

2.3. Hydroformylation of IBS

All hydroformylation reactions were carried out in a 75 ml standard stainless-steel autoclave immersed in a thermostatic oil bath. The stirring rate was the same for all experiments performed. The autoclave was charged with PEG 4000, heptane, toluene, IBS, $RhCl_3{\cdot}3H_2O$, OPGPP and *n*-decane and flushed three times with 2.0 MPa CO. The reactor was pressurized with syngas (H_2:CO = 1:1) up to the required pressure and held at the scheduled temperature with magnetic stirring for a fixed length of time. Then the reactor was cooled to room temperature and depressurized. The upper organic phase was separated by phase separation from the lower PEG phase and immediately analyzed by GC.

3. Results and discussion

3.1. Thermoregulated PEG biphase system

The phase diagram for the system of PEG 4000/toluene/heptane is shown in Fig. 1. To get this phase diagram, miscibility tests were carried out in a glass autoclave at 80 and 110 °C. Given amounts of PEG 4000 and heptane were transferred into the autoclave, which was heated in an oil bath for 30 min. Toluene was then added to the autoclave stepwise till the mixture became homogeneous and remained stable as one phase. Through this investigation, the big miscibility gap of this solvent system (between 80 and 110 °C) facilitated a good operation range for the hydroformylation. Systems composed of many different compositions of PEG 4000/toluene/heptane may be changed from biphasic to homogeneous by increasing temperature. For example, when the ratio of PEG 4000/toluene/heptane = 2/3/1 (wt. ratio), the miscibility temperature (T_m) of the system is 110 °C.

The process of catalysis in thermoregulated PEG biphase system can be schematically depicted in Fig. 2. At room temperature ($T < T_m$), PEG phase containing the dissolved catalyst is immiscible with the upper organic phase that contains the substrate. On heating to the reaction temperature ($T > T_m$), the lower PEG phase becomes miscible with the upper phase. At this temperature a biphase system turns into a monophase system and the reaction proceeds homogeneously. After reaction, on cooling to room temperature ($T < T_m$), the PEG phase containing the dissolved catalyst becomes immiscible with the organic phase and the monophase system changes to a biphase system again. By simple phase separation, the lower PEG phase containing the catalyst can be reused in the next reaction runs.

3.2. Hydroformylation of IBS in PEG 4000/toluene/heptane system catalyzed by Rh/OPGPP complex

3.2.1. Effect of m in OPGPP

Table 1 illustrates the effect of *m* in OPGPP on the hydroformylation of IBS. The conversion of IBS and the aldehyde yield vary a little when *m* changes from 12 to 19. However, when *m* is increased from 19 to 44, the conversion of IBS and the aldehyde yield decrease evidently. This is probably due to the steric hindrance of OPGPP that causes the lower activity. In addition, considering the loss of OPGPP in the upper

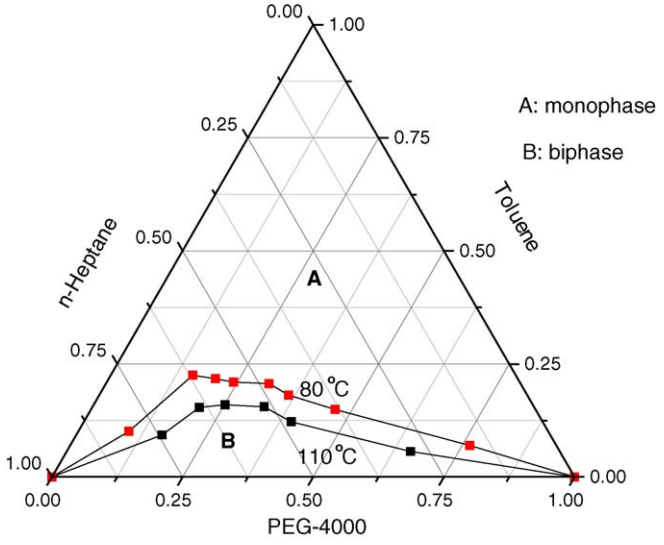

Fig. 1. Phase diagram of PEG 4000/toluene/heptane.

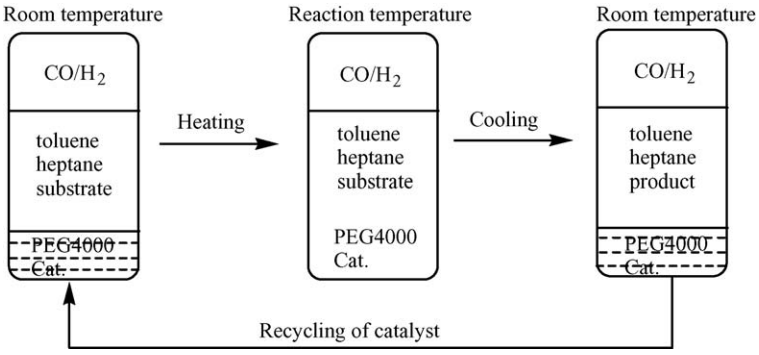

Fig. 2. Process of catalysis in thermoregulated PEG biphase system.

Table 1
Effect of *m* in OPGPP on the hydroformylation of IBS catalyzed by Rh/OPGPP complex[a]

Entry	*m*	Conversion (%)	Aldehyde yield (%)	b/n ratio[b]	TOF (h^{-1})[c]
1	12	99	97	1.4	388
2	19	99	96	1.3	384
3	44	69	67	0.9	268
4	67	63	62	0.8	248

[a] Reaction conditions: PEG 2.0 g, PEG 4000/toluene/heptane = 2/3/1(wt. ratio), $T = 120\,^{\circ}C$, $P = 5.0$ MPa (H_2:CO = 1:1), IBS/Rh = 2000 (molar ratio), P/Rh = 8 (molar ratio), $RhCl_3 \cdot 3H_2O$ 0.7 mg, *n*-decane 0.1 ml, reaction time 5 h.
[b] b denotes branched aldehyde and n denotes normal aldehyde.
[c] Turnover frequency (TOF) in mole of yield per mole of catalyst per hour.

toluene/heptane phase, *m* was chosen to be 19 because the loss of OPGPP decreases with the increase of the value of *m*.

3.2.2. Effect of reaction time

Data in Table 2 illustrate the effect of reaction time on the hydroformylation of IBS. The conversion of IBS and yield of aldehyde increases with the increase of reaction time. When the reaction time was over 5 h, only a slight increase of conversion and yield is observed. Therefore, the optimum reaction time is 5 h.

3.2.3. Effect of total pressure

Table 3 gives the effect of total pressure (H_2:CO = 1:1) on the hydroformylation of IBS. With the increase of total pressure, the conversion of IBS and yield of aldehyde all increase. However, when the total pressure is over 5.0 MPa, only a slight increase in conversion and yield are observed. Therefore, the optimum total pressure is 5.0 MPa.

Table 2
Effect of reaction time on the hydroformylation of IBS catalyzed by Rh/OPGPP complex[a]

Entry	Reaction time (h)	Conversion (%)	Aldehyde yield (%)	b/n ratio	TOF (h^{-1})
1	3	51	49	1.2	327
2	4	79	75	1.4	375
3	5	99	96	1.3	384
4	6	99	97	1.3	323

[a] Reaction conditions: $m = 19$, other conditions are the same as those in Table 1 except that the reaction time is varied.

Table 3
Effect of total pressure on the hydroformylation of IBS catalyzed by Rh/OPGPP complex[a]

Entry	Pressure (MPa)	Conversion (%)	Aldehyde yield (%)	b/n ratio	TOF (h^{-1})
1	3.0	64	62	1.2	248
2	4.0	84	81	1.2	324
3	5.0	99	96	1.3	384
4	6.0	99	97	1.4	388

[a] Reaction conditions: $m = 19$, other conditions are the same as those in Table 1 except that the total pressure is varied.

3.2.4. Effect of reaction temperature

The effect of temperature on the hydroformylation of IBS is shown in Table 4. Under experimental conditions, the conversion of IBS and yield of aldehyde all increase with the increase of temperature. When the temperature is increased from 100 to 120 °C, the conversion of IBS increases sharply. This may be due to the fact that the system changes from biphase to monophase. In order to prove the inference, hydroformylation of IBS was studied by using only toluene as the upper layer organic solvent (the system was homogeneous) at 110 °C (Entry 5, Table 4) and heptane as organic solvent (the system was biphasic) at 120 °C (Entry 6, Table 4). These results indicate that PEG biphase sys-

Table 4
Effect of reaction temperature on the hydroformylation of IBS catalyzed by Rh/OPGPP complex[a]

Entry	Temperature (°C)	Conversion (%)	Aldehyde yield (%)	b/n ratio	TOF (h^{-1})
1	100	48	45	1.7	180
2	110	68	66	1.5	264
3	120	99	96	1.3	384
4	130	99	97	1.1	388
5	110[b]	96	95	1.2	380
6	120[c]	71	68	1.3	272

[a] Reaction conditions: $m = 19$, other conditions are the same as those in Table 1 except that the reaction temperature is varied.
[b] Only toluene was used as the upper layer organic solvent.
[c] Only heptane was used as the lower layer organic solvent.

Table 5
Effect of P/Rh molar ratio on the hydroformylation of IBS catalyzed by Rh/OPGPP complex[a]

Entry	P/Rh (molar ratio)	Conversion (%)	Aldehyde yield (%)	b/n ratio	TOF (h^{-1})
1	3	98	96	1.4	384
2	8	99	96	1.3	384
3	13	98	96	1.3	384
4	20	90	87	0.7	348

[a] Reaction conditions: $m = 19$, other conditions are the same as those in Table 1 except that P/Rh molar ratio is varied.

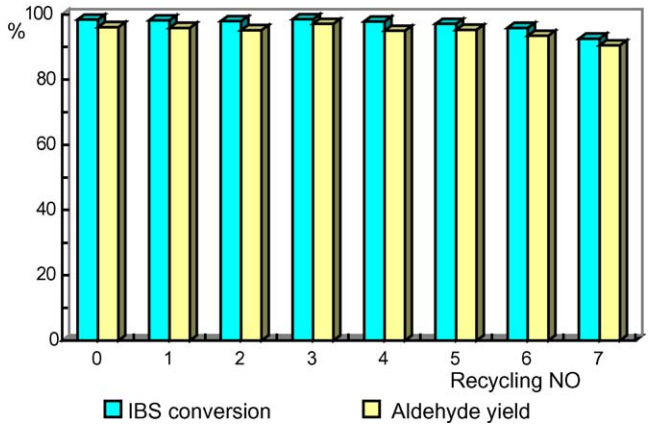

Fig. 3. The recovery efficiency of Rh/OPGPP complex catalyst on the hydroformylation of IBS.

tem changes from two-phase to monophase between 110 and 120 °C.

3.2.5. *Effect of P/Rh molar ratio*

Generally, reactions using metal complex as catalyst requires excessive ligands in order to increase the stability of catalyst. However, large amounts of ligands will decrease the reaction activity. The effect of P/Rh molar ratio on the hydroformylation of IBS is shown in Table 5. It can be seen that the conversion of IBS and yield of aldehyde increase slightly when the P/Rh molar ratio is changed from 3 to 8. However, further increasing of P/Rh molar ratio will decrease the conversion of IBS and yield of aldehyde. Thus, the optimum P/Rh molar ratio is chosen to be 8.

3.2.6. *Recovery efficiency of the Rh/OPGPP complex catalyst*

When the reaction was complete, the upper organic phase was separated from the lower catalyst-containing PEG phase by decantation. Then by adding fresh solvent and substrate, the catalyst can be directly recycled. Fig. 3 illustrates the results of catalyst recovery efficiency on the hydroformylation of IBS. Under the conditions of $T = 120$ °C, $P = 5.0$ MPa, IBS/Rh = 2000, P/Rh = 8, the Rh/OPGPP ($m = 19$) complex catalyst could be recycled for seven times without evident loss of activity. Though the catalyst can be simply recycled,

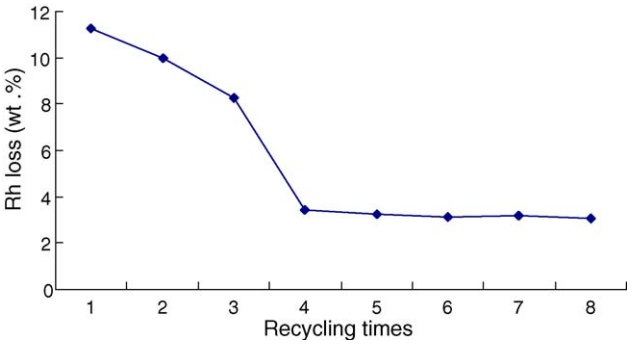

Fig. 4. Loss of rhodium in the upper product-containing phase.

small amounts of Rh were still detected in the upper product-containing phase. From results of the ICP-OES analysis shown in Fig. 4, it can be seen that the loss of Rh decreases with the increase of recycle times.

4. Conclusions

Thermoregulated PEG biphase system composed of PEG 4000, toluene and heptane was developed. By using this system, hydroformylation of IBS catalyzed by Rh/OPGPP complex was systematically investigated. Under optimum conditions, the conversion of IBS and yield of aldehyde are 99% and 96%, respectively. In addition, the catalyst could be easily separated from products and efficiently recovered.

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