Thermoregulated Phase Transfer Ligands and Catalysis IX. Hydroformylation of higher olefins in organic monophase catalytic system based on the concept of critical solution temperature of the nonionic tensioactive phosphine ligand

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Abstract

Application of the concept of critical solution temperature (CST) of nonionic tensioactive phosphine ligand $P[p\text{-}C_6H_4O(CH_2CH_2O)_nH]_3$ (PETPP) in the hydroformylation of higher olefins in organic monophase system is presented for the first time. The PETPP/Rh complex catalyst is insoluble in organic solvent at room temperature ($T < \text{CST}$), on heating to the temperature $T > \text{CST}$, the catalyst would be soluble in organic solvent. Thus, the catalytic reaction would have taken place homogeneously at the reaction temperature ($T > \text{CST}$). When the reaction is completed, on cooling to the room temperature ($T < \text{CST}$), the catalyst would precipitate out from the organic solvent, and could be easily separated from the product and recycled efficiently. Hydroformylation of higher olefins catalyzed by PETPP/Rh complex in organic monophase system is investigated. Under the conditions of $T = 130°C$, $P = 4.0$ MPa, the conversion of 1-dodecene and yield of the aldehyde are 95.8% and 93.7%, respectively.] © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Critical solution temperature; Nonionic tensioactive phosphine ligand; Organic monophase system; Higher olefins; Rhodium; Hydroformylation

1. Introduction

The most severe drawback in homogeneous catalysis is the separation of catalyst from the reaction mixture. So far, two main techniques have been developed to deal with this problem. One of them is to immobilize solid homogeneous complex catalyst on solid ("stationary") supports [1,2]. Although it has been practiced

for many years, the continuous loss of the metal and low reaction rates have still existed. The other technique, generally described as aqueous/organic two-phase system, is the immobilization of a catalyst in a "mobile phase", that is, the aqueous solution immiscible with the product [3,4]. It is generally accepted that the reaction takes place in the aqueous phase or at the interface. After completion of reaction, a simple phase-separating operation could lead the catalyst and product to be separated. With the aid of this strategy, the aqueous/organic

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two-phase hydroformylation of propene to butanal was realized and industrialized at Ruhrchemie in Germany [5,6].

Aqueous/organic biphase catalysis often suffers from low reaction rates caused by slow phase transfer and becomes a serious problem in the hydroformylation of the higher olefins of even very slight solubility in water. To solve this problem, a variety of approaches have been attempted. Addition of co-solvents [7] or surfactants [8,9] to the system would increase the rate of phase transfer yet would render difficult phase-separability. Application of amphiphilic phosphines is also a way to increase the reaction rates [10,11]. Apart from the methods already mentioned, other approaches such as ''promoter ligands'' [12], ''fluorous biphase system'' (FBS) [13] and ''supported aqueous phase catalysis'' (SAPC) [14] have also been developed to deal with this problem.

Recently a concept of ''thermoregulated phase-transfer catalysis'' (TRPTC) based on the cloud point (Cp) of nonionic surface active phosphine ligand, which has been successfully applied to the aqueous-organic biphasic hydroformylation of higher olefins, was reported by Jin [15–17]. The scope of application of biphasic catalysis was greatly widened.

In this paper, a novel approach based on the critical solution temperature (CST) of the nonionic tensioactive phosphine ligand for separating a catalyst from the reaction mixture is presented. The concept of CST is introduced in the hydroformylation of higher olefins catalyzed by PETPP/Rh complex in organic monophase system for the first time. The PETPP/Rh complex catalyst used in such a reaction has been shown to be efficient and easy to separate from the product.

2. Experimental

All solvents and olefins were distilled prior to use. $RhCl_3 \cdot 3H_2O$ was purchased from the Beijing Research Institute of Chemical Industry.

2.1. Preparation of $P[p\text{-}C_6H_4O(CH_2CH_2\text{-}O)_nH]_3$ (PETPP)

The nonionic phosphine ligand PETPP was prepared by the ethoxylation of tri(p-hydroxyphenyl)phosphine. The reaction was carried out in a 100-ml glass autoclave equipped with an apparatus for ethoxylation. Tri(p-hydroxyphenyl)phosphine (3.2 mmol) together with 0.37 mmol (0.03 g) of anhydrous sodium acetate were introduced into the autoclave, and 10.0 ml of toluene was added as the solvent. After the autoclave was completely rinsed with N_2, the reaction system was heated to 130°C. Ethylene oxide was then added to maintain a pressure of 4.0 atm. The gradual reduction of pressure indicated the ethoxylation proceeded smoothly. After the desired amount of ethylene oxide has been added, the reaction was kept for 30 min. Toluene was then drawn out under vacuum. The residue PETPP could be used as ligands without further purification.

2.2. Preparation of $PETPP / RhCl_3 \cdot 3H_2O$ complex catalyst

The catalyst was prepared in situ with $RhCl_3 \cdot 3H_2O$ as a catalyst precursor and PETPP as a ligand.

2.3. Organic monophase hydroformylation experiments

All hydroformylation reactions were carried out in a 75-ml standard stainless-steel autoclave immersed in a thermostatic oil bath. The stirring rates were kept constant for all experiments performed. $RhCl_3 \cdot 3H_2O$, PETPP, organic solvent, olefins and the internal standard n-heptane were placed in the autoclave and were flushed three times with 2.5 MPa of CO. The reactor was pressurized with syn-gas $(CO/H_2 = 1:1)$ up to the required pressure and held at the designated temperature with magnetic stirring
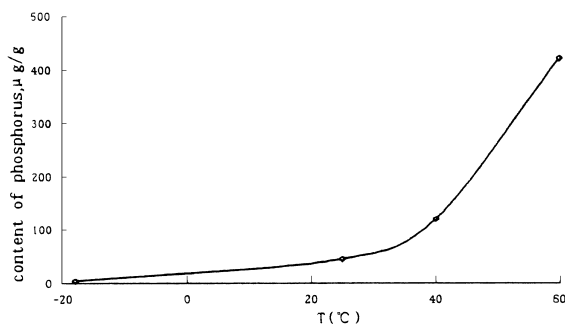
Fig. 1. The relationship between the solubility of PETPP in toluene and temperature.

for a fixed time. Then the reactor was cooled to room temperature and depressurized. The organic phase was separated by decantation from the catalyst and analyzed with GC immediately.

2.4. Analysis

Hydroformylation products were identified by GC-mass spectrometry and compared with the standard spectra. Gas chromatography analyses were run on an SP-09 instrument (OV-101, 50 m $\times$ 0.3 mm capillary column, carrier gas: 2.0 atm N_2, FID detector) equipped with a Shimadzu C-R3A integrator. Mass spectra were measured on a Finnigan 312/ss 200 GC-mass spectrometer.

3. Results and discussion

3.1. General principle of the hydroformylation catalyzed by PETPP / Rh complex in organic monophase system

The CST is the temperature from which the solubility increases markedly. The property of CST in organic solvent of ionic surfactants has been reported [18]. In order to investigate whether the nonionic phosphine ligand PETPP provides the characteristic of CST, the solubility of PETPP ($n = 6$) in toluene was measured. The results are shown in Fig. 1. The curve in Fig. 1 indicates that there appears an inflection point from which the solubility of PETPP in toluene increases sharply. However, the increase of solubility with the increase of temperature in contrast with ionic surfactants is much less for the system under study. This may probably be due to the distribution in n number of the PETPP, which was prepared by ethoxylation.

The general principle of the hydroformylation catalyzed by PETPP/Rh complex in organic monophase system is illustrated in Fig. 2. It differs from aqueous/organic two-phase system. The organic monophase system involves only the organic phase; no water has been added. At room temperature ($T <$ CST), the catalyst is insoluble in organic solvent and the organic phase is colorless. When heated to $T >$ CST, the catalyst was soluble in organic solvent and the

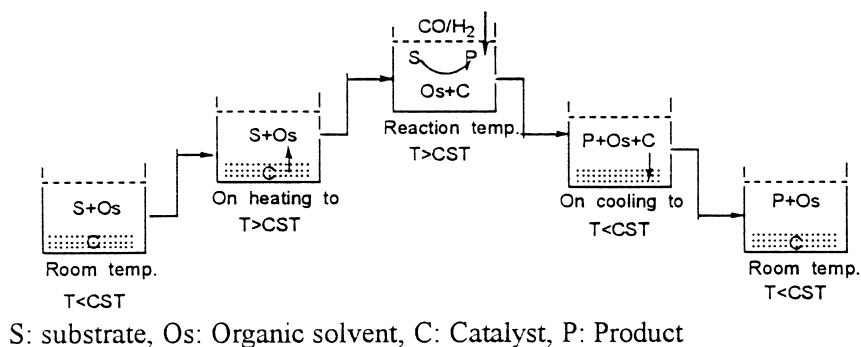S: substrate, Os: Organic solvent, C: Catalyst, P: Product

Fig. 2. The general principle of the hydroformylation of higher olefins catalyzed by PETPP/Rh complex in organic monophase system.

Table 1
Effect of reaction temperature on the organic monophase hydroformylation of dodecene

Reaction conditions: $P = 4.0$ MPa $(CO/H_2 = 1:1)$, 1-dodecene 1 ml, P/Rh = 13, [Rh] = 4.73×10^{-6} mol/ml, PETPP $(n = 6)$, reaction time $t = 6$ h, organic solvent: toluene 2 ml.

Entry	Temperature (°C)	Conversion (%)	Yield of aldehyde (%)
1	60	16.5	13.9
2	100	62.8	58.0
3	120	90.5	84.4
4	130	95.8	93.7

Table 3
Effect of P/Rh ratio on the organic monophase hydroformylation of 1-dodecene

$T = 130$°C, all the other conditions are the same as in Table 1.

Entry	P/Rh ratio	Conversion (%)	Yield of aldehyde (%)
1	9	79.1	74.3
2	13	95.8	93.7
3	20	70.8	67.6
4	30	47.3	45.3

whole system turned to be homogeneous with a brown yellow color. At the reaction temperature $(T > CST)$, the reaction proceeds homogeneously. After completion of the reaction, on cooling to room temperature $(T < CST)$, the catalyst precipitates from the organic phase, which contains the products and is colorless. Thus, by decantation, products could be easily separated from the catalyst. The organic monophase system described above gives a combination of the advantages of homogeneous and heterogeneous catalysis: high activity and simple catalyst/product separation.

3.2. Hydroformylation of higher olefins

The hydroformylation of higher olefins are carried out in the organic monophase system using PETPP/Rh complex as a catalyst. The effects of temperature, total pressure, molar ratio of PETPP to rhodium and recycling of catalyst on the hydroformylation of 1-dodecene are

investigated. In addition, hydroformylation of various higher olefins are also examined.

The effect of reaction temperature has been investigated and is shown in Table 1. Under the reaction conditions, the conversion of 1-dodecene and the yield of aldehyde increase with the increase of temperature. At $T = 130$°C, the conversion and yield of aldehyde reach up to 95.8% and 93.7%, respectively.

The data in Table 2 indicate that the rate of hydroformylation increases with the total pressure $(CO/H_2 = 1:1)$. Only slight differences in the 1-dodecene conversion and the yield of aldehyde are observed above 4.0 MPa. Therefore, the optimum total pressure would be 4.0 MPa.

The effect of PETPP/Rh ratio on the 1-dodecene conversion and the yield of aldehyde are shown in Table 3. The optimum P/Rh ratio is 13. If the P/Rh ratio is higher or lower than

Table 2
Effect of total pressure on the organic monophase hydroformylation of 1-dodecene

$T = 130$°C, all the other conditions are the same as in Table 1.

Entry	Total pressure (MPa)	Conversion (%)	Yield of aldehyde (%)
1	2.0	8.1	7.6
2	3.0	59.2	57.7
3	4.0	95.8	93.7
4	5.0	96.0	93.8

Table 4
The recycle efficiency of the PETPP/Rh complex catalyst in the organic monophase hydroformylation of 1-dodecene

$T = 130$°C, all the other conditions are the same as in Table 1.

No. of recycle	Conversion (%)	Yield of aldehyde (%)
1	95.8	93.7
2	95.0	92.4
3	95.6	94.6
4	95.2	93.5
5	95.7	94.3
6	95.8	92.6
7	95.8	94.0
8	95.6	93.2

Table 5
Organic monophase hydroformylation of various higher olefins catalyzed by PETPP/Rh complex
V_{olefin} = 1 ml, other conditions are the same as in Table 1.

Entry	Olefins	Reaction temperature (°C)	Conversion (%)	Yield of aldehyde (%)
1	1-Hexene	100	95.5	95.5
2	1-Octene	100	96.5	92.6
3	1-Dodecene	130	95.8	93.7

13, the conversion and the yield of aldehyde would decrease correspondingly.

Table 4 shows the recycling efficiency of PETPP/Rh complex in the organic monophase hydroformylation of 1-dodecene. After separation, the catalyst PETPP/Rh complex was recycled eight times in the hydroformylation of 1-dodecene. Almost no loss in reactivity was observed.

The results of organic monophase hydroformylation of various higher olefins catalyzed by PETPP/Rh complex are shown in Table 5. Under the optimum reaction conditions, higher conversion of olefins and yield of aldehyde have been obtained.

4. Conclusion

The concept of CST of nonionic tensioactive phosphine ligand PETPP has been primarily applied to the hydroformylation of higher olefins in organic monophase catalytic system. It has been found that the hydroformylation of higher olefins catalyzed by PETPP/Rh complex proceeds rather efficiently, and high conversion of olefins and yield of aldehyde are obtained under the optimum reaction conditions. The PETPP/Rh complex catalyst could be recycled up to eight times and nearly no loss in activity was observed. The organic monophase strategy we developed based on the concept of CST of nonionic tensioactive phosphine ligand provides not only a method for the water-sensitive reactions but also a novel approach for the hydroformylation of higher olefins. Credit goes to efficient separation, recovery, and recycling of the catalyst in homogeneous catalysis.

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