

Hydroformylation of diisobutylene using thermoregulated phase-separable phosphine rhodium complex catalyst

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Abstract

Based on the critical solution temperature (CST) of non-ionic phosphine ligand, a thermoregulated phase-separable catalyst formed in situ from $P[p\text{-C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}]_3$ (PETPP, $n = 10$) and $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was applied for the first time in the hydroformylation of diisobutylene. It was found that the reaction temperature, total pressure and reaction time, as well as the P/Rh molar ratio had great influence on the reactivity of the catalyst. Under the optimum conditions, the conversion of diisobutylene and yield of aldehyde are 93.1 and 82.5%, respectively. Recycling of the PETPP/Rh complex catalyst up to three times without loss of activity has been observed.

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1. Introduction

The great problem of homogeneous catalysis is the difficulty to separate the catalyst from the reaction mixture. So far, intensive work has been focused on developing efficient catalytic system for heterogenization of homogeneous catalysts [1].

In 1984, the aqueous–organic biphasic hydroformylation of propene to butanal was industrialized at Ruhrchemie in Germany [2]. But for higher olefins the mentioned two phase catalytic process often suffers from low reaction rates caused by the poor solubility of higher olefins in water. To deal with this problem, a variety of approaches have been attempted, such

as “fluorous biphasic system (FBS)” [3], “supported aqueous phase catalysis (SAPC)” [4] and ionic liquid [5].

Recently, a concept of “thermoregulated phase-transfer catalysis (TRPTC)” based on the cloud point of non-ionic phosphine ligand has been successfully applied in the aqueous/organic two phase hydroformylation of higher olefins [6,7]. By means of this catalytic system, the application scope of biphasic catalysis was greatly widened.

In the present paper, based on the critical solution temperature (CST) of non-ionic phosphine ligand, a novel catalytic system termed as “thermoregulated phase-separable catalysis” (TPSC) is applied for the first time in the Rh-catalyzed hydroformylation of diisobutylene. In detail, we describe the general principle of TPSC and effects of various parameters on the reaction.

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2. Experimental

2.1. Materials and product analysis

Organic solvent was purified by distillation from appropriate drying agent under inert atmosphere. Diisobutylene (three parts 2,4,4-trimethyl-1-pentene and one part 2,4,4-trimethyl-2-pentene) was obtained from Fluka. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was purchased from the Beijing Research Institute of Chemical Industry. The catalyst was prepared in situ with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ as a catalyst precursor and PETPP as a ligand.

The reaction products were analyzed by a gas chromatograph (GC-8810) equipped with a flame ionization detector, a capillary column (OV-101, 30 m \times 0.3 mm, carrier gas: 0.2 MPa N_2) and a Shimadzu C-R3A integrator.

2.2. Preparation of $P[p\text{-C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}]_3$ (PETPP)

The non-ionic 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 solvent. After the autoclave was completely purged with N_2 , the reaction system was heated to 130 °C. Ethylene oxide was then added to maintain a pressure of 0.4 MPa. The gradual reduction of pressure indicated that 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 ligand without further purification. ^1H NMR (CDCl_3 , δ): 6.8–7.8 (m, 12H, arom.); 3.6 (br, s, 123H, $\text{C}_2\text{H}_4\text{O}$, OH); ^{13}C NMR (CDCl_3 , δ): 60.5, 67.6, 69.0, 70.0, 72.5, 114.6, 124.3, 127.2, 133.8, 137.2, 161.2; FT-IR (neat, cm^{-1}): 3425, 2882, 1592, 1463, 1120, 836. Solubilities of PETPP in toluene ($\mu\text{mol/g}$ solution) depending on the temperature: $T = 15^\circ\text{C}$, 1.19; $T = 22^\circ\text{C}$, 1.81; $T = 31^\circ\text{C}$, 2.14; $T = 40^\circ\text{C}$, 2.17; $T = 45^\circ\text{C}$, 2.18; $T = 50^\circ\text{C}$, 2.42; $T = 55^\circ\text{C}$, 3.75; $T = 60^\circ\text{C}$, 5.05.

2.3. Hydroformylation of diisobutylene

All hydroformylation reactions were carried out in a 75 ml standard stainless steel autoclave immersed in a thermostatic oil bath. The stirring rate was kept constant for all experiments performed. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, PETPP, toluene, diisobutylene and the internal standard *n*-decane were placed in the autoclave and were flushed three times with 2.0 MPa of CO. The reactor was pressurized with syngas ($\text{CO}/\text{H}_2 = 1:1$) up to the required pressure and held at the designated temperature with magnetic stirring for a fixed time. Then the reactor was cooled to room temperature and depressurized. The organic phase was separated by decantation from the catalyst.

3. Results and discussion

3.1. General principle of thermoregulated phase-separable catalysis (TPSC)

There have been many studies on the solubility property of non-aqueous solution of ionic surfactants. On the other hand, information on non-ionic surfactant solutions is still scarce. Kon-no et al. [8] studied the effect of temperature on the solubility of α -monoglycerol esters of C_{11} – C_{17} fatty acids in benzene. Such a solubility behavior has also been observed for zinc soaps in various organic solvents by Martin et al. [9]. The solubility increases slowly as the temperature is raised. Then within a narrow temperature range, the solubility begins to increase very rapidly. The temperature at which the abrupt change in the solubility occurs is called the CST.

Recently, we have discovered that non-ionic phosphine ligand PETPP firstly synthesized by our research group also exists the property of CST in toluene. Based on the CST of non-ionic phosphine ligand, a novel catalytic process named as “thermoregulated phase-separable catalysis (TPSC)” was suggested [10].

The general principle of TPSC can be described as follows: before reaction, at room temperature ($T < \text{CST}$), the catalyst is insoluble in organic solvent and the organic phase is colorless. When heated to $T > \text{CST}$, the catalyst was soluble in organic solvent and the whole system turned to be

homogeneous with a brown color. At the reaction temperature ($T > \text{CST}$), the reaction proceeds homogeneously. After reaction, on cooling to room temperature ($T < \text{CST}$), the catalyst precipitates from the organic phase, which contains the products. Thus, by decantation, products could be easily separated from the catalyst. So the process of TPSC combines the advantages of homogeneous and heterogeneous catalysis.

3.2. Catalytic hydroformylation of diisobutylene

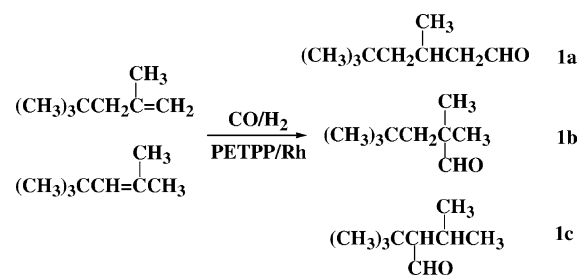
In our previous study, we have shown that thermoregulated phase-separable Rh/PETPP complex catalyst are active and recyclable for hydroformylation of higher terminal olefins [11]. Encouraged by this good results, we decide to adopt this new catalytic process to the hydroformylation of more inert higher branched olefins, and diisobutylene is chosen as a model substrate (see Scheme 1).

3.2.1. Effect of the reaction temperature

Hydroformylation of diisobutylene catalyzed by PETPP/Rh complex was performed between 85 and 130 °C. As shown in Table 1, when the reaction temperature increases, the conversion of diisobutylene and yield of aldehyde all increase. At $T = 130$ °C, the conversion of diisobutylene and yield of aldehyde could reach up to 93.1 and 82.5%, respectively.

3.2.2. Effect of the total pressure

Table 2 lists the effect of total pressure ($\text{CO}/\text{H}_2 = 1:1$) on the hydroformylation of diisobutylene. With increasing of total pressure, the conversion of diisobutylene and yield of aldehyde increase. Therefore, the optimum total pressure would be 6.0 MPa.



Scheme 1.

Table 1

Effect of temperature on the hydroformylation of diisobutylene catalyzed by PETPP/Rh complex

Entry	Temperature (°C)	Conversion (%)	Yield of aldehyde ^a (%)	TOF (h ⁻¹) ^b
1	85	40.0	37.3	40
2	100	59.0	52.5	59
3	115	84.1	77.3	84
4	130	93.1	82.5	93

Reaction conditions: diisobutylene: 6.7 mmol, substrate/Rh = 1000, $P = 6.0$ MPa ($\text{CO}/\text{H}_2 = 1$), solvent: toluene, P/Rh = 9, internal standard: 1-decane, reaction time: 10 h.

^a Among the aldehyde, yield of 1a is more than 90%.

^b Turnover frequency (TOF) in moles of diisobutylene converted per mole of Rh per hour.

Table 2

Effect of total pressure on the hydroformylation of diisobutylene catalyzed by PETPP/Rh complex

Entry	Total pressure (Mpa)	Conversion (%)	Yield of aldehyde (%)	TOF (h ⁻¹)
1	3.0	48.1	43.1	48
2	4.0	68.4	61.4	68
3	5.0	80.3	72.3	80
4	6.0	93.1	82.5	93

Temperature: 130 °C, the other conditions are the same as in Table 1 except that the pressure is varied.

3.2.3. Effect of the reaction time

The data in Table 3 indicate the effect of reaction time on the hydroformylation of diisobutylene. When the reaction time is over 4 h, the conversion of diisobutylene and yield of aldehyde increase significantly. But with prolonged reaction time, only slightly increase of conversion and yield of aldehyde were obtained.

Table 3

Effect of reaction time on the hydroformylation of diisobutylene catalyzed by PETPP/Rh complex

Entry	Reaction Time (h)	Conversion (%)	Yield of aldehyde (%)	TOF (h ⁻¹)
1	4	32.9	32.9	82
2	6	75.1	73.3	125
3	8	82.8	75.3	104
4	10	93.1	82.5	93

Temperature: 130 °C, the other conditions are the same as in Table 1 except that the reaction time is varied.

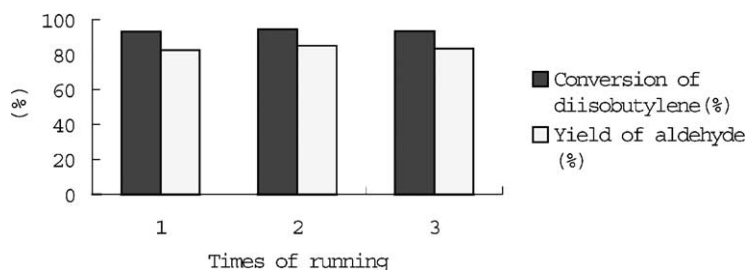


Fig. 1. The recycling efficiency of thermoregulated phase-separable catalyst.

3.2.4. Effect of the P/Rh molar ratio

The effect of PETPP/Rh ratio on the hydroformylation of diisobutylene is shown in Table 4 (entries 1–5). It can be seen that the conversion of diisobutylene increases slightly with increasing of PETPP/Rh ratio, then decreases when the PETPP/Rh ratio reaches 9. Thus, the optimum PETPP/Rh ratio is found to be 9. In the reaction with Rh(acac)(CO)₂/PPh₃ complex, good conversion and yield of aldehyde is obtained when the P/Rh molar ratio equals 3. By comparing the results summarized in Table 4 (entries 2 and 7), one can observe that PETPP/Rh complex catalyst has the same activity as the lipophilic PPh₃/Rh complex.

3.3. Recycling efficiency of the PETPP/Rh complex catalyst

When the reaction completed, the organic phase was separated from catalyst by decantation and the thermoregulated phase-separable catalyst would stay

Table 4
Effect of P/Rh ratio on the hydroformylation of diisobutylene catalyzed by P/Rh complex

Entry	P/Rh (molar ratio)	Conversion (%)	Aldehyde Yield (%)	TOF (h ⁻¹)
1	3	88.8	84.9	89
2	9	93.1	82.5	93
3	11	65.6	65.6	66
4	13	47.5	47.5	48
5	18	33.7	33.7	34
6 ^a	9	46.0	46.0	46
7 ^a	3	92.8	85.3	93

Temperature: 130 °C, the other conditions are the same as in Table 1 except that the P/Rh ratio is varied.

^a The catalyst is Rh(acac)(CO)₂/PPh₃ complex.

at the bottom of autoclave. Thus, by adding fresh solvent and substrate the catalyst could be directly recycled. Fig. 1 gives the results of catalyst recycling efficiency in the hydroformylation of diisobutylene. The PETPP/Rh complex catalyst could be used for three times and no loss in activity has been observed.

4. Conclusion

Thermoregulated phase-separable PETPP/Rh complex catalyst has been employed in the hydroformylation of diisobutylene for the first time. Under the optimum conditions, the conversion of diisobutylene and yield of aldehyde are 93.1 and 82.5%, respectively. In addition, the catalyst could be efficiently recycled. The concept of TPSC may, therefore, be of interest not only for hydroformylation of linear or branched higher olefins but also for many other catalytic reactions. Especially for the reaction in which substrate or catalyst is sensitive to water, because no water has been involved in the TPSC system. Thus, TPSC provides a novel approach for dealing with the separation of catalyst from products in homogeneous catalysis.

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References

- [1] J.M. Thomas, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 3588.
- [2] E.G. Kuntz, *Chem. Tech.* 17 (1987) 570.
- [3] I.T. Horvath, J. Rabai, *Science* 266 (1994) 72.
- [4] J.P. Arhancet, M.E. Davis, J.S. Merola, B.E. Hanson, *Nature* 339 (1989) 454.
- [5] P. Wasserscheid, H. Waffenschmidt, P. Machnitzki, K.W. Kottsieper, O. Stelzer, *Chem. Commun.* (2001) 451
- [6] Z.L. Jin, X.L. Zheng, B. Fell, *J. Mol. Catal. A: Chem.* 116 (1997) 55.
- [7] J.Y. Jiang, Y.H. Wang, C. Liu, F.S. Han, Z.L. Jin, *J. Mol. Catal. A: Chem.* 147 (1999) 131.
- [8] K. Kon-no, T. Jin-no, A. Kitahara, *J. Coll. Interf. Sci.* 49 (1974) 383.
- [9] E.R. Martin, R.C. Pink, *J. Chem. Soc.* (1948) 1750.
- [10] Y.H. Wang, J.Y. Jiang, X.W. Wu, F. Cheng, Z.L. Jin, *Catal. Lett.* 79 (2002) 55.
- [11] Y.H. Wang, J.Y. Jiang, R. Zhang, X.H. Liu, Z.L. Jin, *J. Mol. Catal. A: Chem.* 157 (2000) 111.