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# Thermoregulated phase-separable phosphine rhodium complex catalyst for hydroformylation of cyclohexene

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Based on the critical solution temperature of nonionic tensioactive phosphine ligand, a novel process termed as thermoregulated phase-separable catalysis has been applied for the first time in the hydroformylation of cyclohexene. The catalyst is formed *in situ* from $P[p\text{-}C_6H_4O(CH_2CH_2O)_nH]_3$ (PETPP) and $RhCl_3{\cdot}3H_2O$. Under the conditions of $T = 130\,^\circ C$, $P = 5.0$ Mpa, the conversion of cyclohexene and yield of aldehyde are 98.4%. The catalyst was reused four times and no loss in activity has been observed.

**KEY WORDS:** nonionic phosphine; critical solution temperature; hydroformylation; thermoregulated phase-separable catalyst; rhodium.

## 1. Introduction

The great problem of homogeneous catalysis is the difficulty of separating 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 above mentioned two-phase catalytic process often suffers from low reaction rates caused by the poor solubility of higher olefins in water. To deal with problem, a variety of approaches have been attempted, such as fluorous biphase system (FBS) [3] and supported aqueous phase catalysis (SAPC) [4].

Recently, a concept of thermoregulated phase-transfer catalysis (TRPTC) based on the cloud point of nonionic phosphine ligand has been successfully applied in the aqueous/organic two-phase hydroformylation of higher olefins [5,6]. By means of this catalytic system, the application scope of biphasic catalysis was greatly widened.

In this paper, based on the critical solution temperature (CST) of nonionic phosphine ligand, a novel catalytic system termed thermoregulated phase-separable catalysis (TPSC) is proposed and applied for the first time in the hydroformylation of cyclohexene.

## 2. Experimental

### 2.1. Materials

All organic solvents were purified by distillation from appropriate drying agents under inert atmosphere. Cyclohexene was distilled prior to use. $RhCl_3{\cdot}3H_2O$ was purchased from the Beijing Reseach Institute of Chemical Industry. Nonionic phosphine ligand PETPP was prepared by literature procedures [7]. The catalyst was prepared *in situ* with $RhCl_3{\cdot}3H_2O$ as a catalyst precursor and PETPP as a ligand.

### 2.2. Hydroformylation experiment and product analysis

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, cyclohexene 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 ($CO/H_2 = 1:1$) 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.

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 thermoregulated phase-separable catalysis

The critical solution temperature (CST) is the temperature from which the solubility increases markedly.

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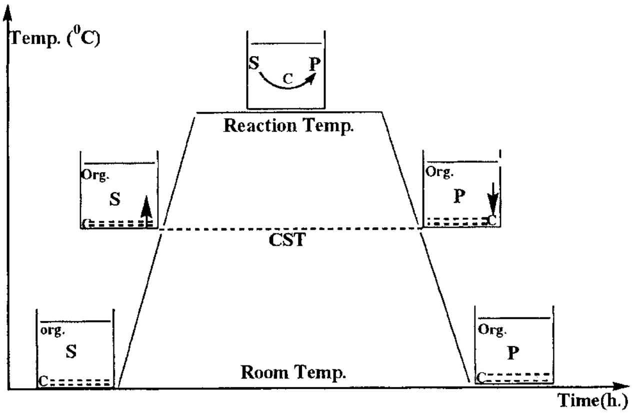


**C**: catalyst, **CST**: critical solution temperature, **Org.**: organic solvent, **P**: product, **S**: substrate, **Temp.**: temperature

Figure 1. The general principle of the thermoregulated phase-separable catalysis.

Table 1
Effects of temperature and pressure on the hydroformylation of cyclohexene catalyzed by PETPP/Rh complex [a]

| Entry | Temperature (°C) | Pressure (MPa) [b] | Conversion and yield (%) [c] | TOF ($h^{-1}$) [d] |
|---|---|---|---|---|
| 1 | 80 | 5.0 | 48.5 | 75 |
| 2 | 100 | 5.0 | 63.8 | 99 |
| 3 | 110 | 5.0 | 87.3 | 135 |
| 4 | 130 | 5.0 | 98.4 | 153 |
| 5 | 130 | 4.0 | 86.0 | 133 |
| 6 | 130 | 3.0 | 70.0 | 109 |
| 7 | 130 | 2.0 | 40.9 | 63 |

[a] Reaction conditions: Cyclohexene : P : Rh = 1000 : 13 : 1 (molar ratio), cyclohexene = 10 mmol, $V_{\text{toluene}} = 2$ ml, $t = 7$ h.

[b] Pressure means total pressure of syngas ($CO/H_2 = 1:1$).

[c] Conversion means the conversion of cyclohexene; yield means yield of aldehyde.

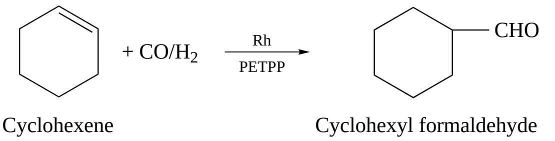
[d] Turnover frequency : mol aldehyde/(mol rhodium × h).

The property of CST in organic solvent of ionic surfactants has been reported [8]. Recently, we have discovered that nonionic phosphine ligand PETPP, first synthesized by our research group, also exists at the CST in toluene [9]. Based on the CST of nonionic phosphine ligand, a novel catalytic process named as thermoregulated phase-separable catalysis (TPSC) was suggested.

The general principle of TPSC is illustrated in figure 1. Before reaction, 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 whole system became homogeneous with a brown color. At the reaction temperature ($T >$ CST), the reaction proceeds homogeneously. After reaction, on cooling to room temperature ($T <$ 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 has combined the advantages of a one-phase homogeneous catalysis with an easy way of catalyst separation.

### *3.2. Hydroformylation of cyclohexene*

Hydroformylation of cyclohexene to cyclohexyl formaldehyde catalyzed by PETPP/Rh complex is shown in equation (1).



(1)

The effects of temperature and pressure on the hydroformylation of cyclohexene are listed in table 1. When the reaction temperature and pressure increase, the conversion and yield of aldehyde all increase. Under the conditions of $T = 130\,^{\circ}C$, $P = 5.0$ Mpa, the conversion of cyclohexene and yield of aldehyde could reach 98.4%. Analysis results indicate that no other byproducts have been observed. The catalytic activity of PETPP/Rh complex is higher than that of the reported $Co_2(CO)_6(PBu_3)_2$ complex [10] and is comparable with that of the Wilkinson catalyst [11].

### *3.3. Recycling efficiency of the PETPP/Rh complex catalyst*

When the reaction was complete, the organic phase was separated from catalyst by decantation and the thermoregulated phase-separable catalyst stayed at the bottom of autoclave. Thus, by adding fresh solvent and substrate the catalyst could be directly recycled. Figure 2 gives the results of catalyst recycling in the hydroformylation of cyclohexene. After recycling four times the conversion of cyclohexene and yield of aldehyde are still as high as 97.3%. The analysis experiments indicated that leaching of rhodium was

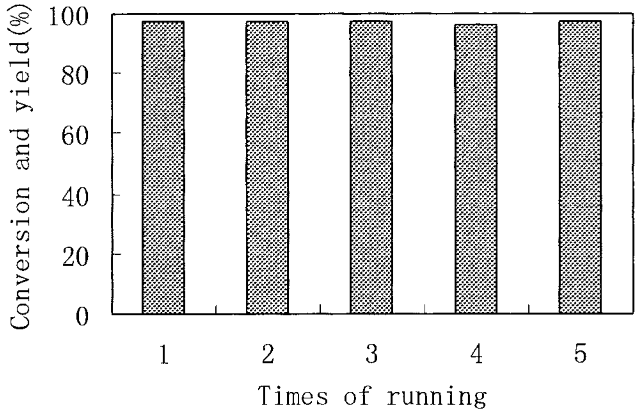


Figure 2. Recycling efficiency of the PETPP/Rh complex catalyst.

less than 1% (wt%). Moreover, to further investigate the efficiency of the catalyst recovery procedure, the decanted organic solutions have been checked for residual activity by adding some extra substrate and carrying out a second catalytic experiment. The GC analysis results showed that no activity has been detected for the decanted solutions.

## 4. Conclusions

Based on the critical solution temperature of nonionic phosphine ligand, a new catalytic system termed as thermoregulated phase-separable catalysis (TPSC) has been proposed. Thermoregulated phase-separable catalyst PETPP/Rh complex has been employed successfully to catalyze the hydroformylation of cyclohexene. Under the optimum conditions, the conversion of cyclohexene and yield of aldehyde are 98.4%. In addition, the catalyst could be directly recycled four times and no loss in activity has been observed.

## Acknowledgments

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