

# Thermoregulated phase-separable phosphine ruthenium complex for hydrogenation catalysis

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## Abstract

Thermoregulated phase-separable  $\text{Ru}_3(\text{CO})_{12}/\text{PETPP}$  ( $\text{P}-[p\text{-C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}]_3$ ,  $n = 6$ ) complex was applied in the hydrogenation catalysis for the first time. With styrene as the model substrate, under the optimum conditions of  $\text{P}(\text{H}_2) = 2.0 \text{ MPa}$ ,  $T = 90^\circ\text{C}$ , the conversion of styrene and yield of ethylbenzene were 100 and 99.5%, respectively. After reaction, the catalyst could be easily separated from reaction mixture and reused for ten times without loss of activity has been observed. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Nonionic phosphine ligand;  $\text{Ru}_3(\text{CO})_{12}$ ; Styrene; Thermoregulated phase-separable catalysis (TPSC); Hydrogenation

## 1. Introduction

Although homogeneous catalysts show remarkable performance for a large variety of reactions, technical problems such as separation, recovery, and recyclization of the soluble catalysts create the demand for heterogenization of homogeneous catalysts.

In 1984, the aqueous/organic biphasic hydroformylation of propene to *n*-butanal was industrialized at Ruhrchemie in Germany [1]. 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 this problem, a variety of approaches have been attempted, such as “fluorous biphasic system (FBS)” [2], “supported aqueous phase catalysis (SAPC)” [3] and ionic liquid [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. Meanwhile, other efforts have been focused on using soluble polymers to phase-isolate a catalyst by Bergbreiter et al. [7,8].

Several papers involving the synthesis of polyether-bound phosphines have been published previously. Okano et al. prepared tertiary phosphines by Grignard reactions [9], and Harris et al. synthesized high-molecular-weight phosphines through the functionalization of poly(ethylene glycols) [10]. In our previous papers the synthesis of polyether-bound nonionic phosphine ligand PETPP ( $\text{P}-[p\text{-C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}]_3$ ) and its property of critical solution temperature (CST) in organic solvent toluene have been reported. Based on the CST of nonionic phosphine ligand, a novel biphasic catalytic process termed as “thermoregulated phase-separable catalysis (TPSC)” has been proposed and applied in the hydroformylation

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of higher olefins [11,12]. The general principle of TPSC can be described as follows: before reaction, at room temperature ( $T < CST$ ), the catalyst is insoluble in toluene and the organic phase is colorless. When heated to  $T > CST$ , the catalyst was soluble in toluene and the whole system turned to be 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 would precipitate from the organic phase as a viscous membrane located at the bottom of the autoclave. Thus, products could be easily separated with a syringe from the catalyst. So the process of TPSC combines the advantages of homogeneous and heterogeneous catalysis—one phase reaction coupled with two-phase separation.

Till now, application of TPSC in other reactions except for the hydroformylation has not been reported. Therefore, this study seeks to address the activity and recycling efficiency of thermoregulated phase-separable  $Ru_3(CO)_{12}/PETPP$  complex catalyst on the hydrogenation of styrene with the aim to enlarge the application scope of TPSC.

## 2. Experimental

### 2.1. Materials

Styrene and toluene were purified by distillation from appropriate drying agent under inert atmosphere. The nonionic phosphine ligand PETPP and  $Ru_3(CO)_{12}$  were prepared according to the literatures [11,13]. The  $Ru_3(CO)_{12}/PETPP$  complex was synthesized as follows: a 100-ml three-neck flask equipped with a reflux condenser was charged with  $Ru_3(CO)_{12}$  (0.192 g, 0.3 mmol) and PETPP (1.058 g, 0.96 mmol). The mixture was heated to reflux for 12 h. under a nitrogen atmosphere and then cooled and evaporated to dryness in vacuo. The residue obtained was used directly without further purification.

### 2.2. Instrumentation

Gas chromatographic analyses were performed using a gas chromatograph “GC-8810” equipped with a flame ionization detector, a capillary column (OV-101, 30 mm  $\times$  0.3 mm, carrier gas: 0.2 MPa  $N_2$ ) and a Shimadzu C-R3A integrator.

### 2.3. Catalysis tests

All hydrogenation 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.  $Ru_3(CO)_{12}/PETPP$  complex, toluene, styrene and the internal standard were placed in the autoclave and were flushed three times with 2.0 MPa  $H_2$ . The reactor was pressured with  $H_2$  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 with a syringe from the catalyst and immediately analyzed by GC. The recovery procedure of the catalyst is shown below. When the reaction completed, the organic phase was moved away from catalyst with a syringe and the thermoregulated phase-separable catalyst would stay at the bottom of autoclave. Thus, by adding fresh solvent and substrate the catalyst could be directly reused.

## 3. Results and discussion

Our earlier work has emphasized the utility of TPSC on the hydroformylation reactions using Rh as the central metal atom. With the aim to enlarge the application scope of TPSC, we decided to adopt this new catalytic process to the hydrogenation reaction and styrene was chosen as the substrate (see Fig. 1). Meanwhile, the central atom is changed from Rh to Ru.

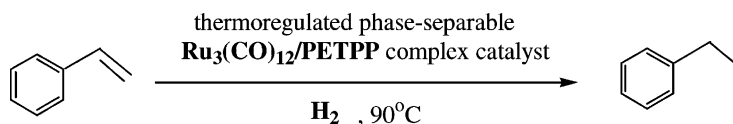


Fig. 1. Hydrogenation of styrene catalyzed by thermoregulated phase-separable catalyst.

Table 1

Effect of reaction temperature on hydrogenation of styrene catalyzed by thermoregulated phase-separable  $\text{Ru}_3(\text{CO})_{12}/\text{PETPP}$  complex<sup>a</sup>

Entry	Temperature (°C)	Conversion (%) <sup>b</sup>	Yield (%) <sup>c</sup>	TOF ( $\text{h}^{-1}$ ) <sup>d</sup>
1	50	28.5	28.3	94
2	60	40.1	40.0	133
3	70	60.4	60.1	200
4	80	93.7	93.1	310
5	90	100.0	99.5	332

<sup>a</sup> Reaction conditions:  $\text{P}(\text{H}_2) = 2.0 \text{ MPa}$ , substrate/catalyst = 1000 (molar ratio), styrene 2.0 ml, toluene 4.0 ml,  $t = 3 \text{ h}$ .

<sup>b</sup> Conversion means the conversion of styrene and is based on GC analysis.

<sup>c</sup> Yield refers to the yield of ethylbenzene and is determined by GC.

<sup>d</sup> Turnover frequency (TOF) in mol of yield per mol of catalyst per hour.

### 3.1. Effects of reaction conditions on the hydrogenation of styrene

Hydrogenation of styrene catalyzed by  $\text{Ru}_3(\text{CO})_{12}/\text{PETPP}$  complex was performed between 50 and 90 °C. As shown in Table 1, when the reaction temperature increases, the conversion of styrene and yield of ethylbenzene all increase. At  $T = 90 \text{ °C}$ , the conversion and yield of ethylbenzene could reach up to 100 and 99.5%, respectively.

Table 2 lists the effect of hydrogen pressure on the hydrogenation of styrene. With increasing of pressure, the conversion of styrene and yield of ethylbenzene increases. When the pressure is over 1.5 MPa, only slight increase in the conversion and yield are observed.

The data in Table 3 indicate the effect of reaction time on the hydrogenation of styrene. When the reaction time is 1 h, the maximum value of TOF is ac-

Table 2

Effect of hydrogen pressure on hydrogenation of styrene catalyzed by thermoregulated phase-separable  $\text{Ru}_3(\text{CO})_{12}/\text{PETPP}$  complex<sup>a</sup>

Entry	Pressure (MPa)	Conversion (%)	Yield (%)	TOF ( $\text{h}^{-1}$ )
1	0.5	58.2	57.9	193
2	1.0	80.7	80.4	268
3	1.5	99.3	98.8	329
4	2.0	100.0	99.5	332

<sup>a</sup> Reaction conditions: temperature = 90 °C, the other conditions are the same as in Table 1 except that the pressure is varied.

Table 3

Effect of reaction time on hydrogenation of styrene catalyzed by thermoregulated phase-separable  $\text{Ru}_3(\text{CO})_{12}/\text{PETPP}$  complex<sup>a</sup>

Entry	Time (h)	Conversion (%)	Yield (%)	TOF ( $\text{h}^{-1}$ )
1	0.5	23.1	23.0	460
2	1.0	56.4	56.1	561
3	2.0	80.1	79.5	398
4	3.0	100.0	99.5	332

<sup>a</sup> Reaction conditions: temperature = 90 °C, the other conditions are the same as in Table 1 except that the reaction time is varied.

quired. However, the conversion and yield are comparatively lower. When prolonging the reaction time to 3 h, 100% conversion and 99.5% yield of ethylbenzene are achieved.

The effect of substrate/catalyst molar ratio on the hydrogenation of styrene is shown in Table 4. It can be seen that the conversion and yield decreases with increasing of substrate/catalyst molar ratio. However, the TOF increases from 332 to 648  $\text{h}^{-1}$  when the molar ratio of substrate/catalyst changes from 1000 to 2500.

### 3.2. Hydrogenation of styrene catalyzed by different phosphine ruthenium complex

Table 5 shows the effects of different phosphine ruthenium complex catalysts on the hydrogenation of styrene. It is well known that TPP is a typical lipophilic phosphine ligand. In contrast, phosphine ligand TPPTS is water-soluble. Among phosphine ligands, which are selected to compare with PETPP, the water-solubilities are in the order of TPPTS > TPPMS > TPP. But the catalytic activity decreases with increasing of the water-solubility of phosphine ligands. From

Table 4

Effect of substrate/catalyst molar ratio on hydrogenation of styrene catalyzed by thermoregulated phase-separable  $\text{Ru}_3(\text{CO})_{12}/\text{PETPP}$  complex<sup>a</sup>

Entry	Substrate/catalyst (molar ratio)	Conversion (%)	Yield (%)	TOF ( $\text{h}^{-1}$ )
1	1000	100.0	99.5	332
2	1500	95.6	94.9	477
3	2000	86.8	86.0	574
4	2500	78.5	78.2	648

<sup>a</sup> Reaction conditions: temperature = 90 °C, the other conditions are the same as in Table 1 except that the molar ratio of substrate/catalyst is varied.

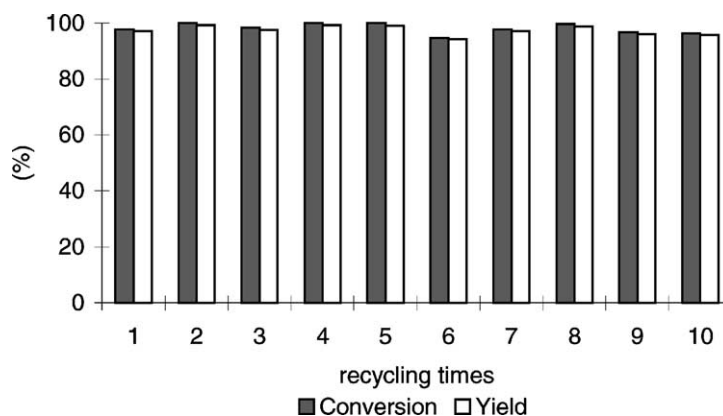


Fig. 2. Recycling efficiency of thermoregulated phase-separable Ru<sub>3</sub>(CO)<sub>12</sub>/PETPP complex catalyst.

the experimental data we can also see that the catalytic activity of Ru<sub>3</sub>(CO)<sub>12</sub>/PETPP complex (TOF = 332 h<sup>-1</sup>) is comparable to that of the lipophilic Ru<sub>3</sub>(CO)<sub>12</sub>/TPP complex (TOF = 319 h<sup>-1</sup>). This phenomenon can be easily explained by TPSC. As we have known that TPP is soluble in toluene, the reaction system is homogeneous. For PETPP, at room temperature it is insoluble in toluene. However, it turns to be soluble in toluene at the reaction temperature that is higher than the CST of the catalyst. Therefore, at the reaction temperature, the catalytic system is also homogeneous. Such a designed experimental result provides an additional experimental support for the process of TPSC.

### 3.3. Recycling efficiency of the Ru<sub>3</sub>(CO)<sub>12</sub>/PETPP complex catalyst

The process of TPSC offered advantages in product isolation and catalyst recycling. Fig. 2 displays the re-

sults of catalyst recycling efficiency on hydrogenation of styrene. The Ru<sub>3</sub>(CO)<sub>12</sub>/PETPP complex catalyst could be reused for ten times and no loss in activity has been observed. Moreover, no formation of ethylbenzene has been detected when using the organic phase, which was separated from catalyst in the first reaction run, as the catalyst for hydrogenation of styrene.

## 4. Conclusions

The work presented in this paper has demonstrated again the potentiality of the novel TPSC process through a new application—hydrogenation catalysis. High activity, selectivity and easy separation and recycling of the thermoregulated phase-separable Ru<sub>3</sub>(CO)<sub>12</sub>/PETPP complex catalyst are the important features described here. In addition to the advantages discussed above, it is envisaged that TPSC will find more application especially in reactions where aqueous systems are not possible or show serious drawbacks.

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Table 5

Hydrogenation of styrene catalyzed by different phosphine ruthenium complexes<sup>a</sup>

Entry	Catalyst	Conversion (%)	Yield (%)	TOF (h <sup>-1</sup> )
1	Ru <sub>3</sub> (CO) <sub>12</sub> /TPP	96.6	95.8	319
2	Ru <sub>3</sub> (CO) <sub>12</sub> /TPPMS	76.8	76.4	255
3	Ru <sub>3</sub> (CO) <sub>12</sub> /TPPTS	48.2	48.0	160
4	Ru <sub>3</sub> (CO) <sub>12</sub> /PETPP	100.0	99.5	332

<sup>a</sup> Reaction conditions: temperature = 90 °C, the other conditions are the same as in Table 1 except that the phosphine ligand is varied.

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