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Thermoregulated phase transfer ligands and catalysis
Part XIII. Use of nonionic water-soluble phosphine ligands to effect homogeneous catalyst separation and recycling

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Abstract

Nonionic tensioactive water-soluble phosphines that act as ligands for rhodium-catalyzed hydroformylation of higher olefins under aqueous-organic biphasic conditions are described with emphasis on the recycling efficiency of homogeneous catalyst. Phosphines discussed are $P\text{-}[p\text{-}C_6H_4(OCH_2CH_2)_nOH]_3$ (1a: $N = 3n = 18$, 1b: $N = 3n = 25$) and $Ph_2P\text{-}[p\text{-}C_6H_4(OCH_2CH_2)_nOH]$ (2a: $N = n = 16$, 2b: $N = n = 25$) (PEO-TPPs). The rhodium catalyst combined with these ligands gave an average turnover frequency (TOF) of $182\,h^{-1}$ for 1-hexene. More importantly, recovery and reuse of catalyst is possible because of the inverse temperature-dependent water solubility of the phosphines. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nonionic phosphine; Homogeneous catalyst; Environmentally benign catalysis; Separation; Hydroformylation

1. Introduction

Though the basic problems of homogeneous catalysis are separation and recycling of the catalyst, they can be elegantly solved by using biphasic catalysis [1]. The trisodium triphenylphosphine trisulfonate (TPPTS) served as the first for the development of new water-soluble ligands. Nowadays, they are produced on a ton-scale. The examples of the technical application to biphasic catalysis are the hydroformylation of propene to butyraldehyde [2], butadiene telomerization [3] and allyl substitution [4]. Usually ligands using in biphasic catalysis are phosphines with ionic substituents (sulfonic and carboxylic acids, quaternary aminoalkyl/aryl groups) [5]. However, nonionic ligands, such as phosphino alcohols [6], and polyether [7,8], crown ether [9],ethylene oxide–propylene oxide–ethylene oxide triblock copolymer (PEO–PPO–PEO) [10] and carbohydrate-substituted phosphines [11], have been the subject of attention in connection with biphasic catalysis for many years.

Recently, we have proposed a novel catalytic system based on the nonionic water-soluble phosphine bearing polyoxyethylene moieties [12,13]. Due to the polyoxyethylene chains as the hydrophilic group in the molecules, the ligands demonstrate inverse temperature-dependent solubility in water similar to that of the nonionic surfactants. As a result, their metal complexes are soluble in the aqueous phase at a lower temperature and, on the contrary, are soluble in the organic phase on heating above the cloud point (CP). The successful application of this so-called "thermoregulated phase transfer catalysis (TRPTC)" in the hydroformylation of higher olefins under aqueous-organic biphasic conditions not only

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provides a meaningful solution to the problem of catalyst–product separation, but also extricates itself from the limitation of low reaction rates of water-immiscible substrates. Thus, the scope of application of biphasic catalysis could be greatly broadened. In this paper, the hydroformylation of higher olefins catalyzed by Rh-ethoxylated hydroxytriphenyl phosphine complex under aqueous-organic biphasic conditions was chosen as a model reaction to investigate the recycling efficiency of the catalyst. The effects of several parameters on the catalyst recovery have also been examined.

2. Experimental

2.1. General comments

All solvents and olefins were dried and distilled prior to use. Distilled deionized water was used. Complex Rh(acac)$(CO)_2$ was purchased from the Beijing Research Institute of Chemical Industry. GC analyses were performed on a SP-09 instrument equipped with a Shimadzu C-R3A integrator with 50m capillary column packed with OV-101 and FID detector. MS spectra were recorded on a Finnigan 312/SS 200 instrument. UV-240 spectrophotometer and 72 spectrophotometer were employed to measure the distribution coefficient and phosphorus content, respectively.

2.2. Hydroformylation

All reactions were carried out in a 75 ml stainless steel autoclave. In a typical reaction, Rh(acac)$(CO)_2$ (2.6 mg, 0.01 mmol), PEO-TPP (0.12 mmol), 3.0 ml of water and 2.0 ml of heptane were placed into the autoclave. To this mixture, 10 mmol of olefins and 0.3 ml of decane (internal standard) were added. The reactor was sealed, flushed five times with 10 atm of carbon monoxide, and checked for leaks. Then the autoclave was pressurized with CO:H_2 (1:1) to the designated pressure and placed in the preheated oil bath with magnetic stirring for a fixed time. After cooling, the reactor was discharged and the organic layer was dried over anhydrous magnesium sulfate. The products were analyzed by GC–MS and compared with the standard spectra.

3. Results and discussion

3.1. Synthesis of nonionic tensioactive phosphine and its thermoregulated phase transfer property

It is well known that the water solubility of nonionic surfactants with the hydrophilic polyoxyethylene moieties is based on the hydrogen bonds formed between the polyoxyethylene chain and water (Fig. 1). However, the nonionic surfactant would lose its water solubility and precipitate from aqueous phase on account of the disruption of hydrogen bonds at a certain higher temperature, which is called CP.

Based on the concept of CP of nonionic surfactants, we have designed and synthesized a series of phosphine ligands possessing polyoxyethylene chain as the hydrophilic group. The general formulae

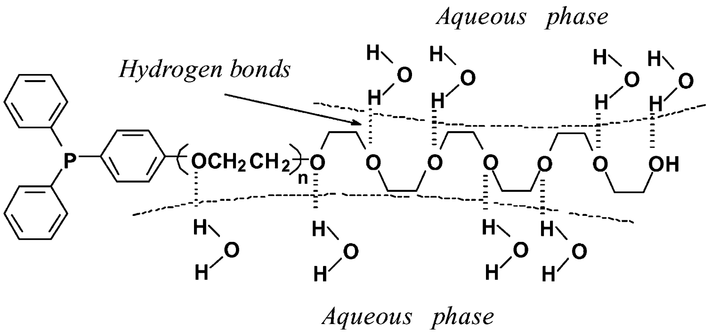


Fig. 1. Hydrogen bonds between polyoxyethylene chain and water.

Table 1
The CP of nonionic tensioactive phosphine ligands

Type	Phosphine ligands			CP (°C)
	m	*N*	R	
PEO-TPP[a]	1	16	–	52
	1	25	–	75
	2	15	–	55
	3	18	–	95
AEOPP[b]	2	8	C_{12}	40
	2	10	C_{12}	59
	2	13	C_{12}	66
	2	16	C_{12}	71
	2	16	C_{18}	52
PEO-DPPSA[c]	–	17	–	49
	–	25	–	57
	–	34	–	68
OPGPP[c]	–	13	*n*-C_8H_{17}	57

[a] Determined in 3.0% aqueous solutions of ligands.
[b] Determined in 0.5% aqueous solutions of ligands.
[c] Determined in 2.0% aqueous solutions of ligands.

are as follows:

$Ph_{3-m}P[p\text{-}C_6H_4(OCH_2CH_2)_nOH]_m$

(m=1,2,3;N=n×m=8-25)

1a; m=3, N=18; 1b; m=3, N=25;

2a; m=1, N=16; 2b; m=1, N=25;

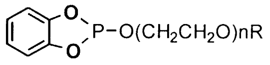
PEO-TPP

$Ph_{3-m}P[(OCH_2CH_2)_nOR]_m$

(m=1,2;N=n=7,8,10,13,16;

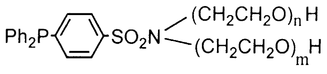
R=C_4,C_5,C_8,C_{12},C_{18} straight chain alkyls)

AEOPP



(N=n=13-55;R=n-C_8H_{17},Ph)

OPGPP



N = n + m = 17, 25, 34

PEO - DPPSA

The data in Table 1 indicate that these phosphines possess the property of nonionic surfactants. Their water solubility is greatly dependent on the length of polyoxyethylene chain. Take PEO-TPP ($m = 3$) as an example, the water solubility is much better when the value of $n \times m$ is greater than 9. They all exhibit the property of inverse temperature-dependent water solubility, namely CP. It is noteworthy that the value of CP is influenced by *N* and R. The CP increases with the increase of *N*, while it decreases with the increase of the carbon number of R.

3.2. Biphasic hydroformylation of higher olefins catalyzed by Rh-PEO-TPP complex

Based on the CP of nonionic tensioactive phosphine ligands, a new concept of TRPTC is proposed, which is outlined in Fig. 2.

The characteristic feature of TRPTC is that at a temperature higher than the CP the catalyst is transferred into the organic phase, where the reaction occurs. Thus, the water solubility of the substrate is no longer a control factor of the reaction rates. It should be emphasized that the catalyst can be easily separated from products at lower temperature by means of simple phase separation and recycled. The results using PEO-TPP-Rh complex as catalyst for the biphasic hydroformylation of higher olefins are described in Table 2. It was observed that PEO-TPP showed increasing turnover frequencies (TOFs) in the following order, **1a** < **2a** = **2b**. Use of **2b** as the ligand achieved a TOF of 180 h^{-1}. It is well known that a major drawback associated with such an aqueous-organic biphasic reaction lies in the limited solubility of higher olefins in water, where the reaction takes place [14]. For example, Rh-TPPTS complex is a perfect catalyst used in the biphasic hydroformylation of propene in the Ruhrchemie/Rhône-Poulenc process. However, if it was applied to higher olefins, the conversions were only about 20% [15].

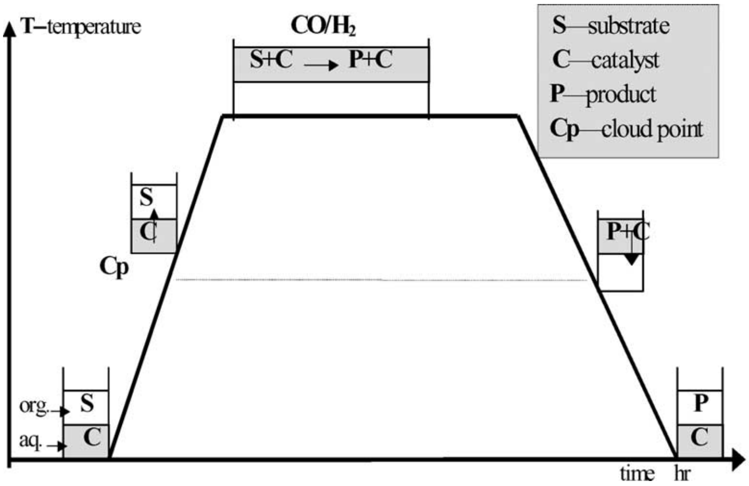


Fig. 2. General principle of TRPTC.

3.3. Recycling of Rh-PEO-TPP complex catalyst

In order to investigate the recycling efficiency of the catalyst, the biphasic hydroformylation of 1-hexene catalyzed by Rh-**2b** was examined. To the aqueous phase, which was separated from the organic phase after the reaction, was added a fresh heptane solution of 1-hexene and the hydroformylation was carried out again. This procedure was repeated five times. In Fig. 3 the conversion and yield of aldehyde are depicted for the six runs. It can be seen that the catalytic activity is retained for the first four recycles. The lose of rhodium is 1.5–2% by measurement of ICP-AES. These recycling experiments (four times) demonstrate that the nonionic tensioactive phosphine works well for the catalyst–product separation. However, for more than four times, the catalytic activity began to decrease. To overcome this problem, the effects of organic solvent, the amount of aldehyde in the organic phase and the length (n) of polyoxyethylene chain on the recycling efficiency of catalyst were investigated. The distribution coefficients (D) of PEO-TPP in aqueous-organic biphasic media are shown in Table 3. It clearly shows that the use of non-polar aprotic solvents, such as n-heptane, results in a higher value of D, namely most of the PEO-TPP resides in the aqueous phase ($D > 98\%$), only <2% of PEO-TPP lies in the organic phase. On the contrary, the use of polar solvents results in a lower value of D (<40%). Thus, in order to recycle the catalyst efficiently it needs to select a non-polar aprotogenic solvent as the organic phase.

Considering that the hydroformylation product aldehyde may affect the solubility of PEO-TPP in the organic solvent, we investigated the relation between

Table 2
Aqueous-organic biphasic hydroformylation of higher olefins catalyzed by Rh-PEO-TPP catalysts[a]

Entry	Ligand	Olefin	Temperature (°C)	Conversion (%)	Yield of aldehyde (%)	TOF (h^{-1})[b]
1	**1a**	1-Hexene	100	82	80	160
2	**2a**	1-Hexene	100	95	91	182
3	**2b**	1-Hexene	100	96	91	182
4	**2b**	1-Octene	100	97	91	182
5	**2b**	1-Decene	100	93	90	180
6	**2b**	1-Dodecene	100	96	90	180

[a] Reaction conditions: $Rh(acac)(CO)_2$ 0.01 mmol; olefin 10 mmol; $P/Rh = 12$; heptane 2.0 ml; H_2O 3.0 ml; $P = 5.0$ MPa ($CO/H_2 = 1{:}1$); time 5 h.

[b] Average $TOF(h^{-1}) = mol(aldehyde)/mol(Rh)$.

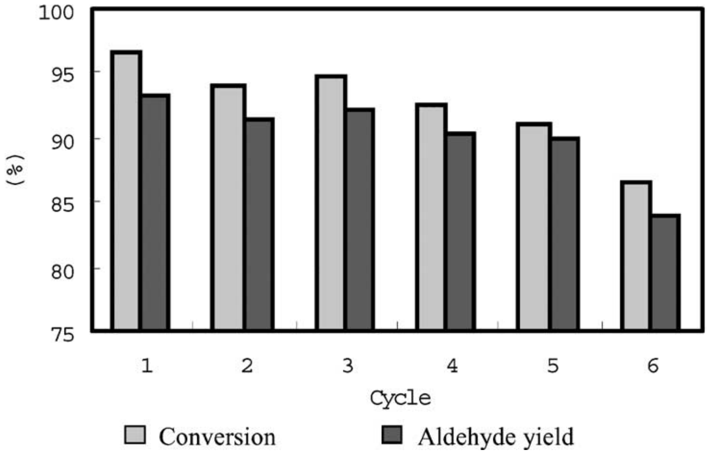


Fig. 3. The recycling of Rh-PEO-TPP catalyst in the biphasic hydroformylation.

the solubility of PEO-TPP (**1b**) in toluene and the content of 1-hexanal. Fig. 4 indicates that the solubility of PEO-TPP (**1b**) in the toluene solution increases remarkably with the aldehyde content. When the content of 1-hexanal is about 20%, the concentration of PEO-TPP (**1b**, 48 μmol) reaches the maximum and remains constant above this concentration. Therefore, to recycle the catalyst efficiently, the content of aldehyde should be reduced.

Last but not least, the effect of distribution of *n* number of PEO-TPP (**1b**) on the recycling efficiency of the catalyst must be discussed. Since the phosphine ligand PEO-TPP was prepared by ethoxylation of corresponding hydroxy-substituted triphenylphosphine [12,13], the product exists as a mixture with different chain number (*n*). The solubility of PEO-TPP in organic solvent varies with the value of *n*. The solubility of PEO-TPP (**1b**) in toluene decreases with *n* number. Fig. 5 illustrates the changes of the solubility of PEO-TPP (**1b**) in toluene with the extraction times. Since PEO-TPP with smaller value of *n* shows lipophilic property, the phosphine ligand with smaller *n* value would be transferred into toluene after extraction with toluene several times. Therefore, the residue would be hardly soluble in toluene. Based on this result, narrowing the distribution of *n* number by repeated extraction with toluene would be a new

Table 3
Distribution coefficients of PEO-TPP in aqueous-organic biphasic media[a]

Entry	PEO-TPP	Biphasic media	D (%)[b]
1	**2a**	H_2O–n–C_7H_{16}	98.6
2	**2a**	H_2O–$(n$–$C_4H_9)_2O$	94.3
3	**2a**	H_2O–$CHCl_3$	31.2
4	**2b**	H_2O–n–C_7H_{16}	99.1
5	**2b**	H_2O–$(n$–$C_4H_9)_2O$	95.0
6	**2b**	H_2O–$C_6H_5CH_3$	92.4
7	**2b**	H_2O–$CHCl_3$	36.7
8	**1a**	H_2O–n–C_7H_{16}	99.8
9	**1a**	H_2O–$(n$–$C_4H_9)_2O$	99.1
10	**1a**	H_2O–$C_6H_5CH_3$	98.9
11	**1a**	H_2O–$CHCl_3$	10.2

[a] Temperature of measurement 25 °C.

[b] $D(\%) = C_{aq}/(C_{aq} + C_{org}) \times 100$, C_{aq} and C_{org} stand for the equilibrium concentrations of PEO-TPP in aqueous and organic phases, respectively.

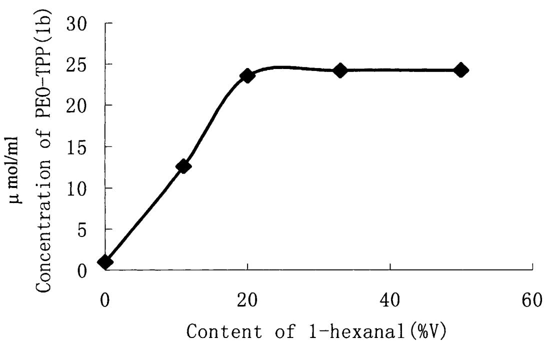


Fig. 4. The relationship between the solubility of PEO-TPP (**1b**) in toluene and 1-hexanal content.

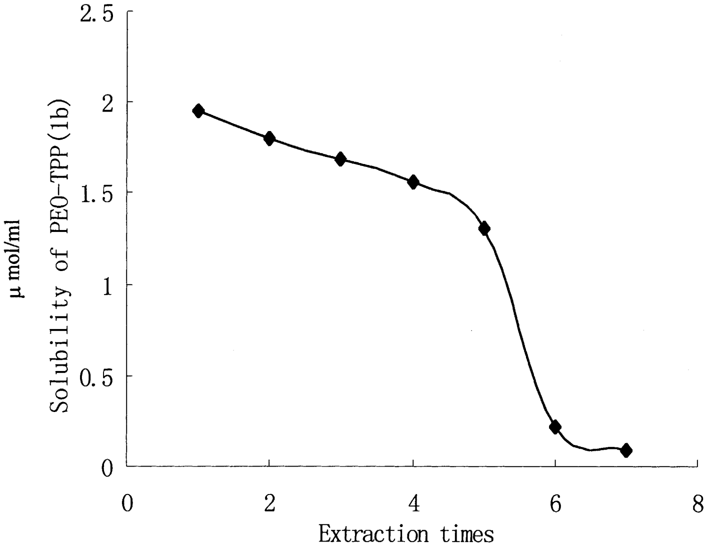


Fig. 5. Relationship between the solubility of PEO-TPP (**1b**)in toluene and the extraction times.

approach to address the recovery and reuse of the catalyst containing this kind of phosphine ligands.

4. Conclusion

The use of nonionic water-soluble phosphine PEO-TPP as ligands for the rhodium catalyzed hydroformylation of higher olefins under aqueous-organic biphasic conditions allows the reaction to be conducted in the organic phase at 100 °C and also allows the convenient separation and recovery of the catalyst at the room temperature. It is proposed here that this new strategy is named TRPTC, which combines the advantages of homogeneous and heterogeneous catalysis. The strategy of TRPTC can be applied to either water-soluble or water-insoluble substrate in biphasic reactions and provide a novel approach for separation and recycling of the homogeneous catalyst. At present, our efforts focus on narrowing the distribution of the chain number (*n*) of polyoxyethylene moieties of the phosphine, in order to further improve the recycling efficiency of the catalyst.

Acknowledgements

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