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Thermoregulated phase transfer ligands and catalysis. III. Aqueous/organic two-phase hydroformylation of higher olefins by thermoregulated phase-transfer catalysis

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Abstract

A series of poly(ethylene oxide)-substituted triphenylphosphines, $Ph_{3-m}P[C_6H_4\text{-}p\text{-}(OCH_2CH_2)_nOH]_m$ (PEO-TPPs; **1a** $m=1$, **1b** $m=2$, **1c** $m=3$; $N=m\times n=8$–25), have been prepared by the ethoxylation of mono-, di-, and tri-*p*-hydroxytriphenylphosphines. PEO-TPPs demonstrate an inverse temperature-dependent solubility in water, and possess distinct cloud points range from 26°C to 90°C.

Based on the clouding property of PEO-TPPs, a new line of aqueous/organic two-phase catalysis termed the thermoregulated phase-transfer catalysis (TRPTC) has been described. That is, the catalyst transfers into the organic phase to catalyze a reaction at a higher temperature, and returns to the aqueous phase to be separated from the products at a lower temperature. Application of this novel strategy to the rhodium-catalyzed two-phase hydroformylation of higher olefins gave desirable results with an average turnover frequency of $180\,h^{-1}$ for 1-dodecene. The TRPTC is suitable for carrying out a reaction with extremely water-immiscible substrate in the aqueous/organic two-phase system. Thus, the application scope of the classical two-phase catalysis has been widened. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Water-soluble ligand; Two-phase catalysis; Thermoregulated phase-transfer catalysis; Poly(ethylene oxide)-substituted triphenylphosphine; Hydroformylation; Higher olefin

1. Introduction

It has been long recognized that homogeneous catalytic processes suffer from the difficulty of separating the catalyst from the product. Up to now, mainly two strategies have been developed to solve this problem. One is to immobilize complex catalysts on solids supports [1,2]. Although it has been practiced for a long period of time, no commercially viable immobilized homogeneous catalyst has been put into effect so far, simply due to the restriction of the leaching of metals and relatively low reaction rates. The other strategy involves the use of water-soluble catalysts so as to carry out a homogeneously catalyzed reaction in the immiscible aqueous/organic two-phase media [3,4]. It is generally accepted that the reaction takes place in the aqueous phase or at the phase boundary. After the reaction is complete, facile catalyst/product separation could be realized by a simple phase-separating operation. Introduction of this methodology to the rhodium-catalyzed hydroformylation of propene has been developed industrially to generate

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butanal with a capacity of 300 000 tons a year in the Ruhrchemie/Rhône–Poulenc process (RCH/RP process) [5,6].

The use of water as the second phase, however, has its drawbacks, especially when the water solubility of the organic substrate proves too low. Propene has sufficient water solubility to allow the hydroformylation to take place at a commercially acceptable rate in the aqueous phase, whereas the reaction of water-immiscible higher olefins is far less effective as a result of mass transfer control [7–9]. A variety of approaches have been attempted to deal with this problem. Surfactants or cosolvents were employed to increase the mutual solubility and mobility of two-phase media [10,11]. The modification of water-soluble ligands with long alkyl chains or quaternized aminoalkyl groups could grant them with certain surface-active properties, which played an important role in enhancing the reaction rates [12,13]. Other alternatives including "promoter ligands" [14], "supported aqueous phase catalysts" (SAPC) [15], and "fluorous biphase system" (FBS) [16] have also been developed.

We are interested in the special catalytic behaviors of nonionic water-soluble phosphines bearing polyoxyethylene moieties [17]. In this work, we report in detail the thermoregulated phase-transfer property of poly(ethylene oxide)-substituted triphenylphosphines $Ph_{3-m}P[C_6H_4\text{-}p\text{-}(OCH_2CH_2)_nOH]_m$ (PEO-TPPs; **1a** $m=1$, **1b** $m=2$, **1c** $m=3$; $N=m\times n=8$–25), and its application to the hydroformylation of higher olefins in the aqueous/organic two-phase system. PEO-TPPs demonstrate an inverse temperature-dependent solubility in water and possess distinct cloud point (C_p) pertaining to typical nonionic surfactants. Therefore, their transition-metal complexes can transfer into the organic phase to catalyze the reaction at a temperature higher than the C_p, and return to the aqueous phase to be separated from the product at a temperature lower than the C_p. A two-phase catalytic process in which the catalyst is capable of transferring between the aqueous phase and the organic phase is termed the thermoregulated phase transfer catalysis (TRPTC). Since the TRPTC ensures the catalyst and substrates to stay in the same phase at the reaction temperature, even the catalytic reaction of extremely water-immiscible substrate could be carried out in the aqueous/organic two-phase system.

2. Experimental

2.1. *General*

All solvents and olefins were dried and distilled prior to use. The preparation of phosphines were carried out under the protection of nitrogen gas. Diphenyl(*p*-hydroxyphenyl)phosphine (**2a**), phenylbis(*p*-hydroxyphenyl)phosphine (**2b**), and tri(*p*-hydroxyphenyl)phosphine (**2c**) were prepared by published procedures [26,27]. Gas chromatographic analyzes were run on a SP-09 instrument (OV-101, 50 m capillary column, carrier gas: 2.0 atm N_2, FID detector) equipped with a Shimadzu C-R3A integrator. *n*-decane was used as an internal standard. Mass spectra were measured on a Finnagan 312/SS 200 GC–mass spectrometer.

2.2. *Ethoxylation of* **2a**–**2c**

The ethoxylation of hydroxy-substituted triphenylphosphines **2a**–**2c** was carried out in a 100 ml glass autoclave equipped with an ethylene oxide dispenser and a magnetic stirrer. 7.0 mmol of **2a**–**2c** together with 20 mg (0.24 mmol) of anhydrous sodium acetate were introduced into the autoclave, and 5.0 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 the pressure meant the ethoxylation was carried out smoothly. After the desired amount of ethylene oxide was added, the reaction was continued for 30 min. Toluene was then drawn out under vacuum. The residues were PEO-TPPs, and could be used as ligands without further purification.

2.3. *Hydrogenation of allyl alcohol*

The hydrogenation was carried out in a 100 ml two-necked flask fitted with a reflux condenser and a thermometer. On the top of the condenser was connected with a hydrogen dispenser sealed by water. $RhCl_3\cdot 3H_2O$ (10.5 mg, 0.04 mmol), PEO-TPP (**1b**, $N=15$, 0.48 g, 0.50 mmol) and 15 ml of water were added to the reactor under an atmosphere of N_2. The system was thoroughly purged with H_2, and checked for leaks. Then the reactor was heated to the reaction temperature and 0.58 g (10 mmol) of allyl alcohol was injected into the reaction mixture. The uptake of H_2 was monitored till all necessary experimental data were collected. After the reaction, the aqueous solution was extracted with ether (3×30 ml). The ether extract was dried over $MgSO_4$, and concentrated to 2 ml. GC analysis was applied to quantify the amount of *n*-propyl alcohol formed. The value was identical with the amount of H_2 consumed.

2.4. General procedure for hydroformylation

All hydroformylation reactions were carried out in a 75 ml standard stainless-steel autoclave immersed in a thermostatic oil bath. The stirring rates were constant for all the experiments. Into the autoclave were placed with $Rh(acac)(CO)_2$ (2.6 mg, 0.01 mmol), PEO-TPPs (0.12 mmol), 3.0 ml of H_2O and 2.0 ml of heptane. 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 CO, and checked for leaks. Then the autoclave was pressurized with CO/H_2 (1/1), and placed in the oil bath preheated to the reaction temperature. After the appropriate reaction time, the reactor was cooled to room temperature and depressurized. The organic phase was dried over $MgSO_4$ and analyzed by gas chromatography immediately. The products were identified by GC–mass spectrography and compared with the standard spectra.

3. Results and discussion

3.1. Thermoregulated phase-transfer property of PEO-TPPs

The addition of ethylene oxide to organic compounds with active hydrogen is a main route to prepare nonionic surfactants [18]. We extend this method to prepare nonionic water-soluble phosphines with polyoxyethylene substituents. As outlined in Scheme 1, mono-, di-, and tri-*p*-hydroxytriphenylphosphines **2a**–**2c** were readily ethoxlated to afford a series of poly (ethylene oxide)-substituted triphenylphosphines **1a**–**1c** in the presence of anhydrous sodium acetate as the catalyst. Solubility determination shows that PEO-TPPs are completely soluble in water if the average ethylene oxide units per molecule *N* is larger than 8. An outstanding advantage of this method lies in that it is facile to control the length of polyether chains by varying the amount of ethylene oxide added during the course of ethoxylation. As a result, some properties of the adductive products, such as water solubility, cloud point and phase-transfer function, which may be essential to their catalytic applications, could be adjusted deliberately.

3.1.1. Inverse temperature-dependent water solubility

It is well known that the water solubility of nonionic surfactants with polyoxyethylene moieties as the hydrophilic groups is based on the hydrogen bonds formed between the polyether chain and water [18]. The solubility of this class of compounds in water decreases with the raise of the temperature, and undergoes a miscibility gap on heating to a lower critical solution temperature – cloud point. In addition, such a process is reversible since the water solubility could be restored on cooling to a temperature lower than the C_p. A common explanation attributes this phenomenon to the cleavage of hydrogen bonds on heating [18].

As we have expected, the modification of organophosphines with polyoxyethylene chains also grants them with the property of inverse temperature-dependent water solubility. With appropriate hydrophobe to hydrophile ratio, PEO-TPPs have distinct cloud points range from 26°C to 95°C as shown in Table 1. Moreover, it is available to control the C_p by varying the microstructure of the molecule such as the length of polyether chains. Therefore, special catalyst designs

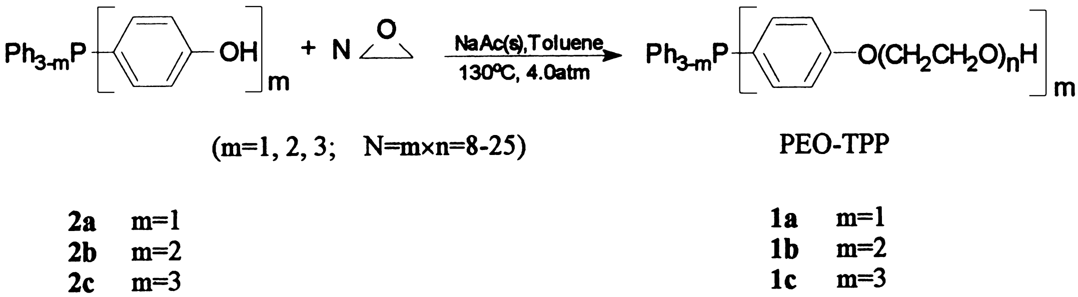
Table 1
Cloud points of PEO-TPPs

PEO-TPP	*m*	*N*[a]	C_p[b] (°C)	HLB[c]
1a	1	8	26	11.7
1a	1	16	52	14.7
1a	1	25	75	16.2
1b	2	15	55	14.3
1b	2	20	71	15.8
1c	3	18	95	15.2

[a] Average ethylene oxide units per molecule.

[b] Cloud point, determined in 3% (w/w, aq) solutions of PEO-TPPs.

[c] $HLB=20\times M_H/(M_H+M_L)$, M_H and M_L stand for the molecular weights of hydrophilic and hydrophobic parts of PEO-TPPs, respectively.



Scheme 1.

based on these ligands may be accessible. It is worthy to point out that there have been several papers involving the synthesis of polyether-bound phosphines previously [19–21], but these ligands could hardly present a cloud point since the hydrophobic and hydrophilic parts of the molecule are not matched.

3.1.2. Anti-Arrhenius kinetic behavior

The inverse temperature-dependent water solubility of PEO-TPPs could play an important role in the catalytic behaviors of their complexes. The hydrogenation of a water-soluble unsaturated substrate, allyl alcohol, was designed to investigate the effect of temperature on the reaction rates in the presence of $RhCl_3$/**1b** (N=15) as the catalyst. The hydrogen-uptake as a function of the reaction time at different temperatures are presented in Fig. 1. Ligand **1b** (N=15) had a C_p of 55°C at 3.0% concentration by the weight in H_2O. After adding $RhCl_3$ and allyl alcohol to the reaction system, the C_p was lowered to 52°C. As shown in Fig. 1, an interesting anti-Arrhenius kinetic behavior has been observed. At 30°C, a temperature lower than the C_p, the reaction system was homogeneous and gradual uptake of H_2 indicated the hydrogenation was taking place in the aqueous phase. The average turnover frequency (TOF) of this stage was 4.3 h^{-1}. On heating to 70°C, a temperature higher than the C_p, the TOF was lowered to 0.6 h^{-1}, which meant the reaction rate decreased by a factor of 7. According to the normal Arrhenius kinetics, however, such a temperature change should lead to a reaction proceeding about 20-fold faster. The loss in the reactivity of the catalyst was due to its inverse temperature-dependent water solubility. The catalyst reached its C_p on heating which changed the former homogeneous system to a "heterogeneous" (clouding) one. It was found this process was reversible. When the temperature was lowered to 30°C again, the uptake of H_2 resumed since the lost hydrated shell of the catalyst recovered.

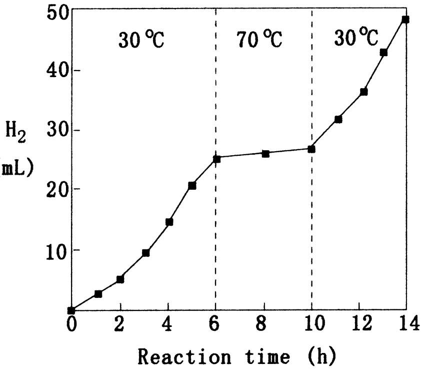


Fig. 1. Atmosphere-pressure hydrogenation of allyl alcohol catalyzed by Rh/PEO-TPP (**1b**, N=15) in water at different temperatures (P/Rh=12.5, allyl alcohol/Rh=250, H_2O 15 ml).

The analogous phenomenon was first reported by Bergbreiter et al. [22,23]. In the presence of phosphorus-bonded block copolymers of ethylene oxide and propylene oxide as ligands ("smart ligands"), rhodium-catalyzed hydrogenation of a variety of water-soluble unsaturated compounds in the aqueous phase demonstrates the similar anti-Arrhenius reactivity. Obviously, the existence of such a unusual temperature-dependent phenomenon provides a fundamental support for the concept of the TRPTC. By introducing an extra organic phase containing a water-immiscible substrate into the reaction system, the catalyst being precipitated from the aqueous phase on heating to its cloud point would transfer into the organic phase so as to ensure the reaction to take place in the organic phase.

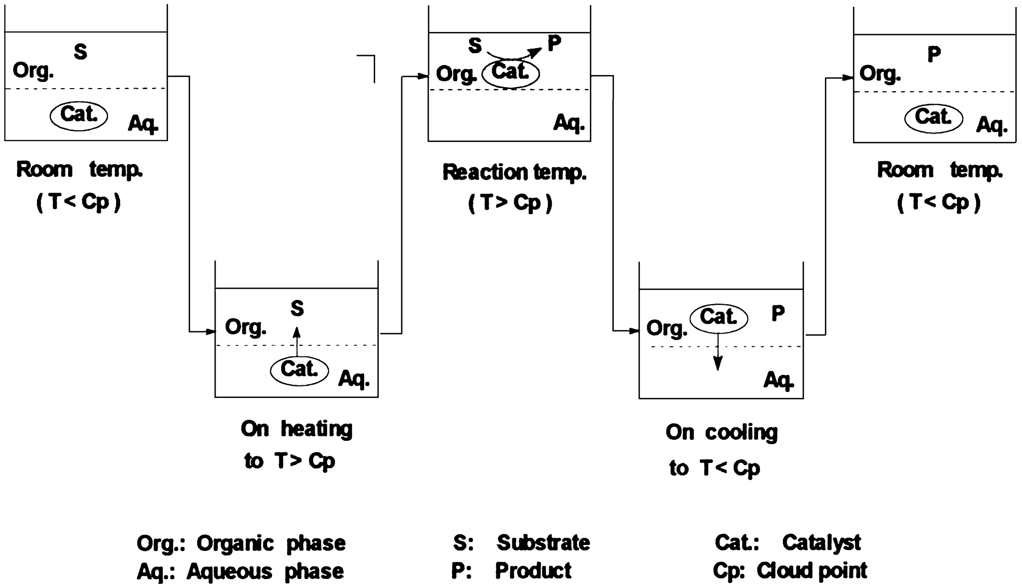


Fig. 2. General principle of the thermoregulated phase-transfer catalysis (TRPTC).

3.2. Hydroformylation of high olefins by the TRPTC

It is very attractive to extend the method of aqueous/organic two-phase catalysis to the reaction of substrates with very low water-solubility [9]. Based on the inverse temperature-dependent water-solubility of polyoxyethylene-substituted nonionic water-soluble ligands, we developed a new concept of two-phase catalysis – thermoregulated phase-transfer catalysis. The general principle of the TRPTC are outlined in Fig. 2. A basic feature of the TRPTC is that the catalyst could transfer into the organic phase to catalyze a reaction at a temperature higher than the cloud point. Thus, the water solubility of the substrate is no longer a factor in control of the reaction rates.

The two-phase hydroformylation of higher olefins was chosen as a model reaction to investigate the tentative idea of the TRPTC. A major drawback associated with such a reaction lies in the limited water-solubility of higher olefins, which prevents the reaction from viable catalytic rates [10]. For example, Rh/TPPTS (sodium salt of triphenylphosphine trisulfonate) complex, a perfect catalyst used in the two-phase hydroformylation of propene in the RCH/RP process, if was applied to higher olefins, only gave conversions about 20% [24].

The results of the hydroformylation of higher olefins catalyzed by Rh/PEO-TPP are listed in Table 2. It was observed that PEO-TPPs showed increasing TOFs with the following sequence: **1c**<**1b**<**1a** (entries 1–3). In the presence of **1a** ($N=25$) as the ligand, a TOF of 180 h^{-1} for 1-dodecene (entry 12) has been achieved. Even the hydroformylation of cyclohexene, an inner olefin, gave a TOF of 137 h^{-1} (entry 13). Rh(acac)$(CO)_2$ is a better catalyst precursor in comparison with $RhCl_3$. An induction period of more than 2 h was observed if $RhCl_3$ was employed as the precursor (entry 9). This period may be attributed to the time-necessity to transform Rh(III) species to Rh(I) active intermediates under the reaction conditions. The recycling effect of the catalyst was also examined. Rh/**1a** ($N=25$) catalyst containing aqueous solution after phase separation was used for five times. Nearly no loss in the reactivity has been detected (entries 4–8).

The concept of the TRPTC provides a reasonable explanation for the satisfactory catalytic reactivity of Rh/PEO-TPP complexes. At a temperature lower than the C_p, PEO-TPP modified rhodium catalyst would remain in the aqueous phase because the partitioning of the catalyst between water and nonpolar aprotic solvents strongly favors the former. On heating to a temperature higher than the C_p, however, the catalyst

Table 2
Two-phase hydroformylation of olefins catalyzed by Rh/PEO-TPP catalysts[a]

Entry	Cycle[b]	Ligand (N^c)	Olefin	Temperature (°C)	Time (h)	Conversion (%)	RCHO (%)	TOF[d] (h^{-1})
1	0	**1c** (18)	1-Hexene	100	5	82	80	160
2	0	**1b** (20)	1-Hexene	100	5	85	83	166
3	0	**1a** (16)	1-Hexene	100	5	95	91	182
4	1	**1a** (25)	1-Hexene	100	5	96	91	182
5	2	**1a** (25)	1-Hexene	100	5	94	87	174
6	3	**1a** (25)	1-Hexene	100	5	95	89	178
7	4	**1a** (25)	1-Hexene	100	5	94	91	182
8	5	**1c** (25)	1-Hexene	100	5	92	87	174
9[e]	0	**1b** (25)	1-Hexene	100	8	93	87	109
10	0	**1a** (25)	1-Octene	100	5	97	91	182
11	0	**1a** (25)	1-Decene	100	5	93	90	180
12	0	**1a** (25)	1-Dodecene	100	5	96	90	180
13	0	**1a** (25)	Cyclohexene	120	6	83	82	137
14	0	**1a** (25)	Styrene	80	2	96	94	470

[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).
[b] Number of catalyst recycles.
[c] Average ethylene oxide units per molecule.
[d] Average turnover frequency, TOF=mol(aldehyde)/mol(Rh)/h.
[e] With $RhCl_3{\cdot}3H_2O$ (0.01 mmol) added as the catalyst precursor.

loses its hydrated shell and then transfers into the organic phase where alkenes are transformed to aldehydes. As soon as the reaction is complete and the system is cooled to a temperature lower than the C_p, the catalyst regains its hydrated shell and returns to the aqueous phase to be separated from the products.

It deserves to emphasize that the reaction site of the TRPTC is the organic phase rather than the aqueous phase or the aqueous/organic interface. To verify such a conclusion, the competitive hydroformylation of equimolar 1-hexene and 1-decene has been checked. This method was previously established by Horvath [25] to monitor the role of the solubility of olefins in

Table 3
Hydroformylation of equimolar mixture of 1-hexene and 1-decene as a evidence of the TRPTC[a]

Entry	Catalyst	Temperature (°C)	Time (h)	Hexene		Decene	
				Conversion (%)	RCHO (%)	Conversion (%)	RCHO (%)
1′	Rh/**1a** (N=25)	100	1.5	50	49	49	48
			3.0	82	79	80	77
2′	Rh/PPh_3	80	0.5	65	63	61	60
			1.0	97	94	95	92
3′	Rh/TPPTS	100	10.0	46	45	9	9
			24.0	81	78	16	15
4′	Rh/TPPTS/PEG 600[b]	100	10.0	51	49	13	13
			24.0	93	90	25	24

[a] Reaction conditions: $Rh_{(acac)}(CO)_2$ 0.01 mmol, olefin 10 mmol (1-hexene/1-decene=1/1), P/Rh=12, toluene 2.0 ml, H_2O 3.0 ml, P=5.0 MPa (CO/H_2=1/1).
[b] With added poly(ethylene glycol), M_w=600, 0.12 g.

the reaction rates. As shown in Table 3, the hydroformylation rates of both 1-hexene and 1-decene are almost identical in the presence of Rh/PPh_3 complex as the catalyst (entry 2′), which means the size of terminal olefins may not have an effect on the catalytic reactivity for a homogeneous system. Comparatively, the reaction rate of 1-hexene is significantly faster than the rate of 1-decene for a standard aqueous/organic two-phase system catalyzed by Rh/TPPTS complex (entry 3′) due to the water-solubility of the former is higher than the latter [25]. Even when a phase-transfer reagent, poly(ethylene glycol) 600, was added to the reaction system, the rates of two olefins are still quite different (entry 4′). Interestingly, while Rh/PEO-TPP (**1a**, N=25) was used as the catalyst, roughly the same reaction rates of 1-hexene and 1-decene at different conversion levels have been observed although the reaction media were aqueous/organic two-phase system (entry 1′). These results suggest that a reaction of TRPTC-type takes place in the organic phase and hence the water solubility of substrates may hardly play a role in the reaction.

4. Conclusion

A new line of aqueous/organic two-phase catalysis termed the thermoregulated phase-transfer catalysis has been developed and shown to be very effective for the hydroformylation of higher olefins. The TRPTC utilizes a series of polyoxyethylene-substituted nonionic water-soluble phosphines as ligands. The existence of a process of the TRPTC is supported by several experimental phenomena. Firstly, PEO-TPPs have distinct cloud points. Secondly, anti-Arrhenius kinetic behavior has been observed during the aqueous-phase hydrogenation of allyl alcohol. Thirdly, Rh/PEO-TPP catalyst transforms 1-hexene and 1-decene nearly at the same rates, whereas for Rh/TPPTS catalyst, the rates are deeply affected by the size of the olefins.

In comparison with the classical aqueous/organic two-phase catalysis, the process of the TRPTC is more "homogeneous" to some extent because the catalyst and substrates remain in the same organic phase at the reaction temperature. In addition, the TRPTC is also quite different from the fluorous biphase system [16]. While the initial fluorous/organic two-phase of the FBS becomes one-phase at an appropriate higher temperature, the TRPTC would maintain the aqueous/organic two-phase system throughout the reaction. It is the "mobile" catalyst that transfers between two-phase in response to temperature changes. Thus, the TRPTC could be regarded as a promising avenue for the further exploration of the two-phase catalysis.

Acknowledgements

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