

Thermoregulated *n*-heptane/poly(ethylene glycol) monoalkyl ether biphasic system and its application in PETPP/Ru complex catalyzed hydrogenation

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Abstract

A thermoregulated biphasic system composed of *n*-heptane and poly(ethylene glycol) (PEG) monoalkyl ether, which underwent a reversible change from biphasic to monophasic regulated by temperature, was reported and used for PETPP/Ru (PETPP = P-[*p*-C₆H₄O(CH₂CH₂O)_{*n*}H]₃, 3*n* = 14) complex catalyzed hydrogenation. Under the optimal reaction conditions: *T* = 80 °C, time = 3 h, *P* = 5 MPa, the yield of *n*-octane reached up to 100% and the TOF was 332 h⁻¹. After reaction, on cooling to room temperature, the catalyst-containing poly(ethylene glycol) monoalkyl ether phase could be easily separated from the product-containing *n*-heptane phase by simple decantation and reused directly for the next run. Catalytic activity remained almost the same within ten successive runs. Analysis of ICP-AES demonstrated that Ru leaching to the *n*-heptane phase was under the detection limit of the instrument in this thermoregulated biphasic system.

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1. Introduction

Liquid/liquid biphasic catalysis has received increasing attention due to its facile catalyst recycling and reuse after reaction [1]. However, a major disadvantage attached to this approach is the reduced activity resulted from the mass-transport limitation.

To achieve efficient catalyst recovery while maintaining reactivity and selectivity of homogeneous catalysis, numerous approaches have been studied. Among them, based on the cloud point (Cp) of nonionic tensioactive phosphine ligands a aqueous/organic biphasic process termed as thermoregulated phase transfer catalysis (TRPTC) was proposed by Jin et al. [2]. This process has been successfully applied to the hydroformylation of long chain α -olefins [3–6]. Very recently, studies focusing on thermoregulated biphasic solvent systems, including fluorous biphasic system (FBS) [7–11], thermoregulated phase-separable catalytic system [12–14], polymer/polar biphasic systems [15], PEG biphasic systems [16,17], ionic

liquid–water biphasic system [18] and other polar/nonpolar biphasic systems [19,20], have attracted considerable attention. These systems, which exhibit a reversible two phase-single phase transformation regulated by temperature, combine the desirable activity and selectivity of homogeneous catalysis with the simplicity of catalyst recovery associated with heterogeneous catalysis. After reaction, the catalyst-containing phase could be easily separated from the product-containing phase by simple decantation (Fig. 1).

Herein, a novel thermoregulated catalytic system composed of *n*-heptane and poly(ethylene glycol) monoalkyl ether was reported and applied in PETPP/Ru complex catalyzed hydrogenation. PETPP was chosen as the ligand because PETPP had an analogous structure with PEG monoalkyl ether and PETPP/Ru complex could selectively dissolve in PEG monoalkyl ether.

2. Experimental

2.1. General methods

PETPP was prepared according to our previously reported procedure [21]. *n*-Heptane was distilled from sodium before use. MeOPEG₃₅₀, MeOPEG₅₅₀ and all the long chain α -olefins

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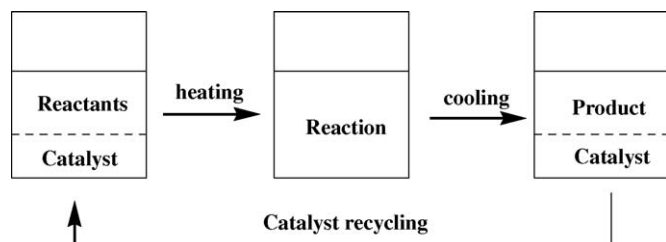


Fig. 1. Illustration of thermoregulated biphasic catalysis.

were from Fluka and were used as received. Triethylene glycol monoalkyl ether and other reagents were commercially available and had an analytical grade. Other poly(ethylene glycol) monoalkyl ethers were prepared according to the literature [22] and the polymeric degrees were determined by ^1H NMR. ^1H NMR measurement was performed on Varian INOVA spectrometer at 400 MHz using TMS as internal standard and CDCl_3 as solvent. GC analysis was run on GC-7890 instrument (OV101) (50 m capillary column, carrier gas: 3 atm N_2 , FID detector). ICP-AES measurements were carried out on Optima 2000DV instrument. GC-MS measurement was performed on HP 6890/5973 MS instrument.

BuOPEG₃₅₀ (1): ^1H NMR (CDCl_3): $\delta = 0.66\text{--}0.70$ (t, 3H, CH_3), 1.12–1.14 (m, 2H, CH_3CH_2), 1.31–1.34 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2$), 3.21–3.24 (t, 2H, $\text{CH}_3(\text{CH}_2)_2\text{CH}_2$), 3.35–3.47 (m, 32H, PEGH).

BuOPEG₅₅₀ (2): ^1H NMR (CDCl_3): $\delta = 0.73\text{--}0.76$ (t, 3H, CH_3), 1.17–1.22 (m, 2H, CH_3CH_2), 1.37–1.41 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2$), 3.27–3.30 (t, 2H, $\text{CH}_3(\text{CH}_2)_2\text{CH}_2$), 3.39–3.54 (m, 48H, PEGH).

OctOPEG₃₅₀ (3): ^1H NMR (CDCl_3): $\delta = 0.70\text{--}0.73$ (t, 3H, CH_3), 1.11–1.18 (m, 10H, $\text{CH}_3(\text{CH}_2)_5$), 1.39–1.41 (m, 2H, $\text{CH}_3(\text{CH}_2)_5\text{CH}_2$), 3.26–3.30 (t, 2H, $\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{CH}_2$), 3.41–3.54 (m, 32H, PEGH).

OctOPEG₅₅₀ (4): ^1H NMR (CDCl_3): $\delta = 0.72\text{--}0.75$ (t, 3H, CH_3), 1.13–1.21 (m, 10H, $\text{CH}_3(\text{CH}_2)_5$), 1.41–1.45 (m, 2H, $\text{CH}_3(\text{CH}_2)_5\text{CH}_2$), 3.29–3.32 (t, 2H, $\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{CH}_2$), 3.42–3.57 (m, 48H, PEGH).

2.2. General procedure for hydrogenation of olefins

Hydrogenation experiments were performed in a 75 ml stainless steel autoclave equipped with a magnetic stirrer. Hydrogenation catalyst PETPP/Ru complex was prepared in situ. The autoclave was charged with $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, PETPP, triethylene glycol monomethyl ether, *n*-heptane and olefin. The system was flushed three times with 2 MPa H_2 . Then, the autoclave was pressurized with 5 MPa H_2 and brought to the required temperature in a thermostatic oil bath. After appropriate time, the homogeneous reaction mixture was cooled to room temperature and the upper organic layer was analyzed by GC and ICP-AES. The lower catalyst-containing triethylene glycol monomethyl ether layer was directly used for the next cycle.

3. Results and discussion

3.1. Studies on the miscibility temperature in *n*-heptane/poly(ethylene glycol) monoalkyl ether biphasic system

The solubility of PEG in organic solvents has been reported in previous literature [23]. As we have known, PEG is insoluble with *n*-heptane. Considering that the solubility of PEG in *n*-heptane may be improved by introducing an alkyl group to PEG, PEG alkyl ether was chosen as the other phase to form a biphasic system with *n*-heptane. Preliminary study revealed that *n*-heptane-triethylene glycol monomethyl ether biphasic system underwent a reversible two phase-single phase transformation depending upon temperature. However, *n*-heptane-MeOPEG₃₅₀ and *n*-heptane-MeOPEG₅₅₀ didn't show this property. By changing the alkyl group and the length of PEG monoalkyl ether, we determined their miscibilities with *n*-heptane (Fig. 2). The results showed that PEG monoalkyl ethers (BuOPEG₃₅₀, OctOPEG₃₅₀, BuOPEG₅₅₀, OctOPEG₅₅₀) were soluble with *n*-heptane at certain temperature. PEG monoalkyl ethers with longer PEG chain length showed poorer miscibility with *n*-heptane. On the other hand, PEG monoalkyl ethers with a larger alkyl group showed better miscibility with *n*-heptane. Therefore, by changing the length of PEG, the alkyl group and the composition of biphasic system, the miscibility temperature of the biphasic system could be regulated. This thermoregulated system may provide a potential method for homogeneous reactions combined with advantages of biphasic separation.

3.2. Hydrogenation of 1-octene catalyzed by PETPP/Ru complex

To test the efficiency of this new thermoregulated system, PETPP/Ru complex catalyzed hydrogenation of 1-octene was

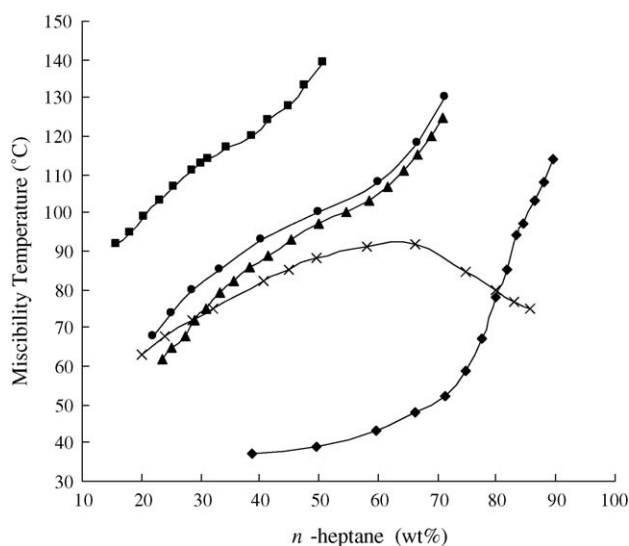


Fig. 2. Phase diagram of *n*-heptane and poly(ethylene glycol) monoalkyl ether. *n*-Heptane/triethylene glycol monomethyl ether (x), *n*-heptane/BuOPEG₅₅₀ (■), *n*-heptane/BuOPEG₃₅₀ (●), *n*-heptane/OctOPEG₅₅₀ (▲), *n*-heptane/OctOPEG₃₅₀ (◆).

Table 1
PETPP/Ru complex catalyzed hydrogenation of 1-octene in *n*-heptane/triethylene glycol monomethyl ether biphasic solvent system^{a,b}

Entry	<i>T</i> (°C)	<i>P</i> (MPa)	Time (h)	Yield (%) ^c	TOF (h ⁻¹) ^d
1	80	5	3	100	332
2	70	5	3	96	319
3	60	5	3	93	308
4	50	5	3	82	273
5	80	4	3	94	314
6	80	3	3	85	284
7	80	2	3	84	279
8	80	5	2	90	448
9	80	5	1	86	859

^a Reaction conditions—1-octene: 6.25×10^{-3} mol; 1-octene/Ru: 1000 (molar ratio); PETPP/Ru: (molar ratio), 2 g *n*-heptane, 4 g triethylene glycol monomethyl ether.

^b The miscibility temperature of the reaction system is 78 °C.

^c GC yield.

^d TOF calculated as the number of moles of *n*-octane formed per mol of ruthenium per hour.

investigated. PETPP/Ru complex catalyzed hydrogenation of 1-octene in *n*-heptane/triethylene glycol monomethyl ether biphasic solvent system was first studied because triethylene glycol monomethyl ether was commercially available and had an analytical grade. The effect of the reaction conditions on hydrogenation in the binary solvent system was examined and the results were summarized in Table 1. As can be seen from Table 1, the yield of *n*-octane reach up to 100% when the pressure was 5 MPa, and the reaction time was 3 h at 80 °C (entry 1).

To further study the efficiency of the thermoregulated biphasic system we performed the recycling experiments under the optimal reaction conditions and the results were shown in Table 2. Much to our surprise, the Ru content leaching into the upper product-containing phase was too low to be detected within the ten successive runs. Meanwhile, no obvious decrease

Table 2
Recycling efficiency of PETPP/Ru complex catalyst on hydrogenation of 1-octene^a

Cycle	Yield (%) ^b	TOF (h ⁻¹) ^c	Leaching of Ru (%) ^d
0	100	332	n.d. ^e
1	98	327	n.d.
2	98	324	n.d.
3	97	324	n.d.
4	98	325	n.d.
5	98	326	n.d.
6	98	326	n.d.
7	97	324	n.d.
8	98	326	n.d.
9	98	326	n.d.
10	98	326	n.d.

^a Reaction conditions—*T*: 80 °C; time: 3 h; *P*: 5 MPa; 1-octene: 6.25×10^{-3} mol; 1-octene/Ru: 1000 (molar ratio); PETPP/Ru: 5 (molar ratio), 2 g *n*-heptane, 4 g triethylene glycol monomethyl ether.

^b GC yield.

^c TOF calculated as the number of moles of *n*-octane formed per mol of ruthenium per hour.

^d Loss of Ru in the upper product layer, detection limit of ICP-AES was 5 ppb.

^e Not detected.

Table 3
PETPP/Ru complex catalyzed hydrogenation in *n*-heptane/triethylene glycol monomethyl ether biphasic system^a

Entry	Substrate	Product ^b	Yield (%) ^c	TOF (h ⁻¹) ^d
1	1-Decene	<i>n</i> -Decane	97	323
2	1-Dodecene	<i>n</i> -Dodecane	86	286
3	Styrene	Phenylethane	94	314
4	Cyclohexene	Cyclohexane	73	245
5	Crotonaldehyde	Butanal	100	333

^a Reaction conditions—*T*: 80 °C; time: 3 h; *P*: 5 MPa; RuCl₃·3H₂O: 6.23×10^{-6} mol; substrate/Ru: 1000 (molar ratio); PETPP/Ru: 5 (molar ratio), 2 g *n*-heptane, 4 g triethylene glycol monomethyl ether.

^b The product is determined by GC–MS.

^c GC yield.

^d TOF calculated as the number of moles of product formed per mol of Ru per hour.

in the reactivity and selectivity was observed. This is may be ascribed to the fact that the ligand PETPP bearing three PEG chains could selectively dissolve in the lower triethylene glycol monomethyl ether phase.

To demonstrate the applicability of this thermoregulated system, we chose a variety of compounds containing the C=C bond as the substrates and the results were shown in Table 3. From Table 3 it can be seen that cyclohexene gave the lowest yield. However, crotonaldehyde could be selectively hydrogenated and the corresponding product was butanal according to GC–MS.

In order to investigate the influence of the alkyl group as well as the length of the PEG chain on the recyclability of the catalyst, the leaching content of Ru in the upper phase in different thermoregulated biphasic system was measured. The results in Table 4 indicated that only very small amount of Ru leaching in the upper product phase was detected. With increasing of PEG chain, the loss of Ru decreased. The leaching of Ru was not detected in *n*-heptane/OctoOPEG₅₅₀ biphasic system while in *n*-

Table 4
PETPP/Ru complex catalyzed hydrogenation of 1-octene in *n*-heptane/poly(ethylene glycol) monoalkyl ether biphasic solvent systems

Entry	Solvent System	Yield (%) ^a	TOF (h ⁻¹) ^b	Leaching of Ru (wt.%) ^c
1 ^{d,e}	<i>n</i> -Heptane/OctoOPEG ₃₅₀	99	331	0.18
2 ^{d,f}	<i>n</i> -Heptane/OctoOPEG ₅₅₀	99	329	n.d. ^g
3 ^{h,i}	<i>n</i> -Heptane/BuOPEG ₃₅₀	100	332	0.034
4 ^{h,j}	<i>n</i> -Heptane/OctoOPEG ₃₅₀	100	333	–

^a GC yield.

^b TOF calculated as the number of moles of *n*-octane formed per mol of ruthenium per hour.

^c Loss of Ru in the upper product layer, detection limit of ICP-AES was 5 ppb.

^d Reaction conditions—*T*: 90 °C; time: 3 h; *P*: 5 MPa; 1-octene: 6.25×10^{-3} mol; 1-octene/Ru: 1000 (molar ratio); PETPP/Ru: 5 (molar ratio).

^e 3 g OctoOPEG₃₅₀, 1.7 g *n*-heptane.

^f 3 g OctoOPEG₅₅₀, 1.7 g *n*-heptane.

^g Not detected.

^h Reaction conditions—*T*: 80 °C; time: 3 h; *P*: 5 MPa; 1-octene: 6.25×10^{-3} mol; 1-octene/Ru: 1000 (molar ratio); PETPP/Ru: 5 (molar ratio).

ⁱ 3 g BuOPEG₃₅₀, 0.5 g *n*-heptane.

^j 3 g OctoOPEG₃₅₀, 0.5 g *n*-heptane.

heptane/OctOPEG₃₅₀ biphasic system it accounted for 0.18% (wt.%). As for the alkyl group, the larger the alkyl group is, the higher leaching of Ru would be. In *n*-heptane-BuOPEG₃₅₀ biphasic system, the Ru leaching content was only 0.034% (wt.%). Under the same conditions, the *n*-heptane-OctOPEG₃₅₀ binary system became homogeneous at room temperature.

4. Conclusions

In summary, a thermoregulated biphasic system composed of *n*-heptane/poly(ethylene glycol) monoalkyl ether was developed and applied in PETPP/Ru (PETPP=P-[*p*-C₆H₄O(CH₂CH₂O)_{*n*}H]₃, 3*n*=14) complex catalyzed hydrogenation. The catalyst could be successfully recycled and reused for several runs without loss of catalytic activity.

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