A new thermoregulated PEG biphasic system and its application for hydroformylation of 1-dodecene

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Abstract

The development of a new thermoregulated polyethylene glycol (PEG) biphasic system composed of PEG-400/1,4-dioxane/n-heptane is reported in this paper. By applying this system in the hydroformylation of 1-dodecene catalyzed by Rh complexes modified with phosphite ligand containing PEG chains, TMPGP (P[O(CH$_2$CH$_2$O)$_n$CH$_3$]$_3$, n = 8), the conversion of 1-dodecene and the yield of aldehydes reached up to 96% and 94%, respectively. The catalyst, after being recycled twenty-three times, showed no appreciable loss of catalyst activity. The average Rh loss was 0.65% each run.

1. Introduction

Recovery of catalysts poses a serious problem for industrial application of homogeneous catalysis. This is the main reason why homogeneous catalysis only amounts to less than 20% in industrial catalytic processes [1]. So far, intensive work has been focused on developing efficient catalytic systems to deal with this problem [2,3]. Among them, liquid–liquid biphasic catalysis is probably the most elegant method, such as aqueous/organic [4], fluorous/organic [5,6], ionic liquids [7,8], soluble polymer-supported catalysts [9,10], supercritical fluids [11] and organic/organic biphasic systems [12].

As one of the non-toxic and inexpensive solvents with low volatility, PEG (polyethylene glycol) has been used as an efficient, recyclable and environmentally benign reaction medium for the recycling of homogeneous catalysts in Heck reaction [13], hydrogenation [14], hydroformylation [15,16], asymmetric dihydroxylation [17], epoxidation [18], Baylis–Hillman reaction [19] and Suzuki cross-coupling reaction [20]. However, additional procedures such as extraction by ethers or alkanes were necessary to separate catalysts from products in most of the above-mentioned catalytic reactions [13,17–20], or

the reactions were carried out under biphasic conditions that resulted in mass transfer problem between two phases [15,16]. Loh and coworkers first developed a novel solvent system composed of PEG-3350, n-heptane and either dichloromethane or methanol for the Rh-catalyzed hydrogenation of 1-hexene. The reaction was carried out in a single phase at higher temperature, and the separation of product phase from catalyst phase was achieved by simple decantation at a lower temperature [14]. Later, Behr and coworkers reported a temperature-dependent solvent system based on PEG-1000. This catalytic system, which consisted of PEG-1000, toluene, conjugated methyl linoleate (CML) together with Rh catalysts modified with phophorous ligands with PEG chains, was applied in the rhodium-catalyzed cooligomerization of CML with ethylene [21].

In our previous work, a thermoregulated PEG biphasic system, which was composed of PEG-4000, toluene, n-heptane together with a Rh catalyst modified with a phosphite ligand OPGPP (n = 19), was applied in the hydroformylation of p-isobutylstyrene. The catalyst was recycled seven times and the average leaching of rhodium in the upper organic phase was found to be 6.5% [22,23].

In this paper, in order to further decrease the loss of catalyst in the product phase, a new thermoregulated PEG biphasic system consisting of PEG-400, 1,4-dioxane, n-heptane and TMPGP (tri-(methoxy poly ethylene glycol) phosphite,

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P[O(CH$_2$CH$_2$O)$_n$CH$_3$]$_3$, $n = 8$) was developed and applied in the Rh-catalyzed hydroformylation of 1-dodecene.

2. Experimental

2.1. Materials

Organic solvents were purified by distillation from appropriate drying agents under an inert atmosphere. 1-Dodecene was purchased from Aldrich. PEG-400 was purchased from Acros and used without further treatment. Rh(acac)(CO)$_2$ was purchased from Beijing Institute of Chemical Engineering. Phosphite ligand TMPGP (P[O(CH$_2$CH$_2$O)$_n$CH$_3$]$_3$, $n = 8$) was prepared according to our previous work [22]. The catalyst was prepared in situ with Rh(acac)(CO)$_2$ as the catalyst precursor and TMPGP as the ligand.

2.2. Hydroformylation of 1-dodecene

All hydroformylation reactions were performed in a 200ml stainless-steel autoclave equipped with a magnetic stirrer. Given amounts of Rh(acac)(CO)$_2$, TMPGP, 1-dodecene, PEG-400, 1,4-dioxane, n-heptane and the internal standard n-decane were charged into the autoclave, which was flushed four times with 2.0 MPa of CO. Then the autoclave was pressurized with syn-gas (CO/H$_2$ = 1:1) to the required pressure and held at the designated temperature in a thermostatic oil bath. After the designated time, the reactor was cooled to room temperature and depressurized. The upper organic phase was separated from the PEG phase by decantation and analyzed by gas chromatograph. After addition of fresh solvents and substrate, the PEG phase containing the catalyst was recycled directly. Recycling experiments were conducted under the optimum reaction conditions.

2.3. Analysis

The reaction products were analyzed on a gas chromatograph (GC-8810) equipped with a FID, a capillary column (OV-101, 50 m × 0.3 mm, carrier gas: 0.1 MPa N$_2$) and a Shimadu C-R3A integrator. n-Decane was used as the internal standard. ICP-AES analysis was carried out on an Optima 2000DV instrument. The concentration of phosphite ligand in the upper organic phase was determined according to the known procedure [24].

3. Results and discussion

3.1. Partition coefficients of PEG and TMPGP (n = 8) in PEG biphasic system and phase diagram of PEG-400/n-heptane/1,4-dioxane

It is known that PEG with low molecular weight (e.g. PEG-400) is immiscible with alkanes or higher olefins at both room and high temperature but is miscible with many other kinds of organic solvents at room temperature [25]. Therefore, PEG biphasic system with the feature of being "single-phase at high temperature and two-phase at low temperature" could be obtained through adding a proper organic solvent to the mixture of PEG-400/n-heptane. Moreover, because thermoregulated PEG biphasic system is characterized by the combination of PEG and phosphite ligand modified with PEG chain, the partition coefficients of PEG and those of phosphite ligand in the thermoregulated PEG biphasic system must be considered. Here, TMPGP (P[O(CH$_2$CH$_2$O)$_n$CH$_3$]$_3$, $n = 8$), a phosphite ligand with PEG chains, was chosen as the model ligand. The loss of PEG and ligand in the upper organic phase and their partition coefficients between two phases in several systems are given in Table 1.

In Table 1, among the systems, which have the same miscibility temperature of 125 °C, the system of PEG-400/1,4-dioxane/n-heptane has the lowest loss of PEG and phosphite ligand in the upper organic phase. This indicates that PEG and TMPGP exhibit the highest partition coefficients in the system of PEG-400/1,4-dioxane/n-heptane. Therefore, the system of PEG-400/1,4-dioxane/n-heptane is chosen as that in PEG biphasic catalysis.

The phase diagram of the ternary system PEG-400/1,4-dioxane/n-heptane at temperatures of 293 K, 323 K and 353 K is depicted in Fig. 1. The diagram shows that the biphasic region reduces with the increase of temperature. According to the phase diagram, a certain ternary solvent system with a

Table 1

Loss of PEG and phosphite ligand (TMPGP ($n = 8$)) in the upper organic phase and their partition coefficients between two phases in the systems of different organic solvents/PEG-400/n-heptane with miscibility temperature of 125 °C[a]

Solvents	Amount of solvents (g)	Loss of PEG in organic phase (wt.%)[b]	Partition coefficients of PEG[c]	Loss of TMPGP in organic phase (mol.%)[d]	Partition coefficients of TMPGP[e]
n-Butanol	1.56	2.51	38.8	0.81	122
2-Butanone	2.73	4.13	23.2	0.58	171
Ethyl acetate	3.33	3.34	28.9	0.51	195
Butyl acetate	3.51	4.74	20.1	0.56	178
THF	3.12	4.26	22.5	0.53	188
Toluene	5.00	3.39	28.5	0.68	145
1,4-Dioxane	3.15	0.75	132	0.050	2000

[a] In all systems, the amounts of PEG-400 and n-heptane are 3.00 g and 3.00 g, respectively.

[b] Loss of PEG (wt.%) = (total PEG in organic phase)/(total PEG in the system).

[c] Partition coefficient of PEG (wt.) = (total PEG in PEG phase)/(total PEG in organic phase).

[d] Loss of TMPGP (mol.%) = (total TMPGP in organic phase)/(total TMPGP in the system).

[e] Partition coefficient of TMPGP (mol.) = (total TMPGP in PEG phase)/(total TMPGP in organic phase).
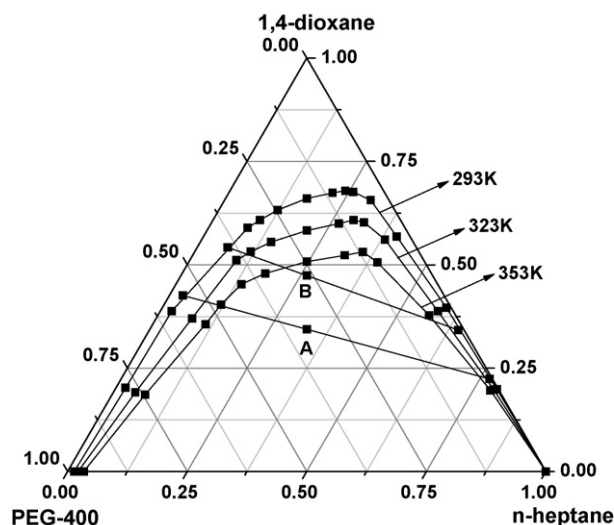
Fig. 1. Phase diagram of the ternary system PEG-400/1,4-dioxane/*n*-heptane at temperatures of 293 K, 323 K and 353 K.

given composition, which is biphasic at room temperature but miscible at high temperature, can be determined. For example, the solvent systems with a composition of A (3.00 g PEG-400, 3.15 g 1,4-dioxane, 3.00 g *n*-heptane) and B (3.00 g PEG-400, 5.40 g 1,4-dioxane, 3.00 g *n*-heptane) have the miscibility temperatures of 125 °C and 95 °C, respectively. Both are biphasic at 20 °C. It can also be seen from the phase diagram that the solvent system with a composition of A has lower PEG loss in the upper organic phase and lower solubility of *n*-heptane in PEG phase. Therefore, the solvent system with a composition of A (3.00 g PEG-400, 3.15 g 1,4-dioxane, 3.00 g *n*-heptane) is chosen for the catalytic reaction.

3.2. Catalytic hydroformylation of 1-dodecene

In this paper, using phosphite as the ligand for the hydroformylation of higher olefins in PEG biphasic system is based on two points: one is the high catalytic activity of Rh catalyst modified by phosphite ligand for hydroformylation, the other is the instability of phosphite ligand in aqueous systems due to hydrolysis [26,27].

As higher olefins have almost the same solubility as *n*-heptane in PEG, the amount of *n*-heptane is reduced accordingly to maintain the same miscible temperature when given amounts of higher olefins or other long chain alkanes are added to the system. So, a typical reaction mixture (3.00 g PEG-400, 3.15 g 1,4-dioxane, 1.78 g *n*-heptane, 1.00 g 1-dodecene, 0.22 g *n*-decane) is selected for the catalytic reaction. This system has a miscible temperature of 126 °C.

3.2.1. Effect of the reaction temperature

Table 2 shows that both the conversion of 1-dodecene and the yield of aldehydes increase with the increase of the reaction temperature. At 130 °C, the conversion of 1-dodecene and the yield of aldehydes reach up to 96% and 94%, respectively. Interestingly, the conversion of 1-dodecene and the yield of aldehydes increase sharply between 120 °C and 130 °C. This

Table 2
Effects of the reaction temperature on the hydroformylation of 1-dodecene[a]

Entry	Reaction temperature (°C)	Conversion (%)	RCHO (%)	n/i	TOF (h^{-1})
1	110	76	75	1.5	127
2	120	81	80	1.2	135
3	130	96	94	1.0	160
4	140	99	96	1.0	167
5	130[b]	64	62	0.6	107
6	120[c]	93	92	1.3	155

[a] *Reaction conditions*: $P = 5.0$ MPa (CO/H$_2$ = 1); 1-dodecene 1.00 g; S/Rh = 1000 (molar ratio); P/Rh = 10; PEG-400 3.00 g; *n*-heptane 1.78 g; 1,4-dioxane 3.15 g; *n*-decane (internal standard) 0.30 ml (0.22 g); 6.0 h.
[b] Only using *n*-heptane and PEG-400 as solvents.
[c] Only using 1,4-dioxane and PEG-400 as solvents.

may be due to the fact that the whole catalysis system is one phase at the reaction temperature of 130 °C but biphasic at the reaction temperature lower than 126 °C. In order to prove the above inference, hydroformylation of 1-dodecene was studied by using only 1,4-dioxane as the organic solvent (the system was homogeneous) at 120 °C (entry 6 in Table 2) and using only *n*-heptane as organic solvent (the system was biphasic) at 130 °C (entry 5 in Table 2). When only *n*-heptane is used as the solvent, the conversion of 1-dodecene and the yield of aldehydes are 64% and 62%, respectively at 130 °C, much lower than those with only 1,4-dioxane used as solvent at 120 °C (93% and 92%, respectively). These results indicate that PEG biphasic system changes from two phases to one phase between 120 °C and 130 °C.

3.2.2. Effect of the total pressure of syn-gas

Table 3 lists the effect of the total pressure of syn-gas (CO/H$_2$ = 1:1) on the hydroformylation of 1-dodecene. With increase of the total pressure, both the conversion of 1-dodecene and the yield of aldehydes increase. When the total pressure exceeds 5.0 MPa, there are only slight increases in the conversion of 1-dodecene and the yield of aldehydes. Therefore, the optimum total pressure should be 5.0 MPa.

3.2.3. Effect of the reaction time

Data in Table 4 illustrate the effect of reaction time on the hydroformylation of 1-dodecene. When the reaction time is less than 6 h, the conversion of 1-dodecene and the yield of aldehydes increase with increase of reaction time. However, when the reaction time is more than 6 h, there are only slight increases

Table 3
Effects of the total pressure of syn-gas on the hydroformylation of 1-dodecene

Entry	Pressure (MPa)	Conversion (%)	RCHO (%)	n/i	TOF (h^{-1})
1	2.0	13	13	1.3	22
2	3.0	41	40	1.2	68
3	4.0	69	67	1.1	115
4	5.0	96	94	1.0	160
5	6.0	98	95	1.0	163

Reaction conditions are the same as those of entry 3 in Table 2 except the total pressure of syn-gas.

Table 4
Effects of the reaction time on the hydroformylation of 1-dodecene

Entry	Reaction time (h)	Conversion (%)	RCHO (%)	n/i	TOF (h^{-1})
1	1	20	20	1.3	200
2	2	57	56	1.1	285
3	3	71	70	1.1	237
4	4	77	76	1.1	193
5	5	87	85	1.1	174
6	6	96	94	1.0	160
7	7	99	95	1.0	141

Reaction conditions are the same as those of entry 3 in Table 2 except the reaction time.

of conversion and yield. Therefore, 6 h is the optimum reaction time.

3.2.4. Effect of the P/Rh molar ratio

Generally, reactions using a metal complex as catalyst need excessive ligands in order to increase the stability of the catalyst. However, large excess of ligands will decrease the catalyst activity. Table 5 summarizes the effect of *P*/Rh molar ratio on the hydroformylation of 1-dodecene. It can be seen that the conversion of 1-dodecene and the yield of aldehydes increase significantly with increase of *P*/Rh molar ratio from 0 to 10, then decrease when the *P*/Rh molar ratio is over 10. Thus, the optimum *P*/Rh molar ratio is chosen to be 10.

In summary, the optimum reaction conditions are as follows: $P = 5.0$ MPa (CO/H$_2$ = 1), 1-dodecene 1.00 g, S/Rh = 1000 (molar ratio), *P*/Rh = 10, PEG-400 3.00 g, *n*-heptane 1.78 g, 1,4-dioxane 3.15 g, *n*-decane (internal standard) 0.30 ml (0.22 g), $t = 130\,^\circ$C, 6.0 h.

3.2.5. Recycling efficiency of the Rh/TMPGP complex catalyst

The use of the PEG-400/*n*-heptane/1,4-dioxane system affords an easy separation of the catalyst phase and the product phase. The PEG phase containing the catalyst was separated from the product phase by decantation and was used directly in the next run by adding fresh organic solvents (not including PEG-400) and substrate. Because the GC analysis results show that more than 98% of *n*-heptane, *n*-decane and aldehydes but only 32% of 1,4-dioxane reside in the upper organic phase, the amounts of *n*-heptane, *n*-decane and substrate added to the catalytic system are the same as those in

Table 5
Effects of the *P*/Rh molar ratio on the hydroformylation of 1-dodecene

Entry	P/Rh molar ratio	Conversion (%)	RCHO (%)	n/i	TOF (h^{-1})
1	0	70	68	0.6	117
2	5	76	75	0.8	127
3	10	96	94	1.1	160
4	15	95	93	1.1	158
5	20	94	92	1.2	157

Reaction conditions are the same as those of entry 3 in Table 2 except the *P*/Rh molar ratio.
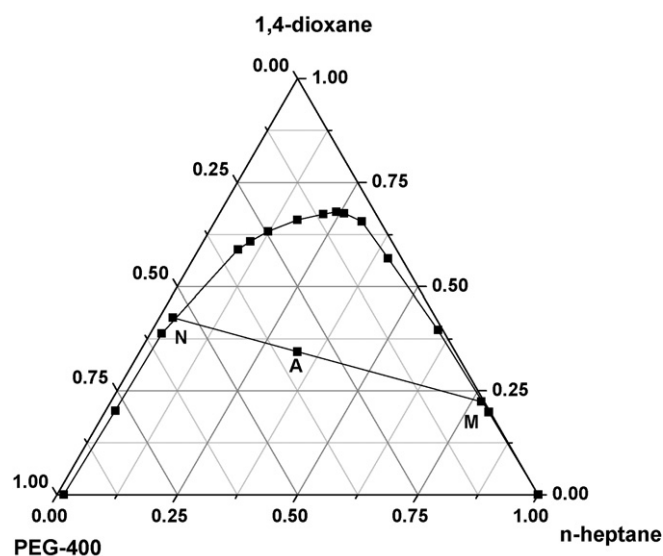

Fig. 2. Phase diagram of the ternary system PEG-400/1,4-dioxane/*n*-heptane at temperature of 293 K.

the first run except that the suitable amount of 1,4-dioxane added to the catalytic system should be 1.00 g after the first run in the process of recycling the catalyst. This can also be determined according to the phase diagram of the ternary system of PEG-400/1,4-dioxane/*n*-heptane at 293 K (shown in Fig. 2). The solvent system of PEG-400/1,4-dioxane/*n*-heptane with a composition of A (3.00 g PEG-400, 3.15 g 1,4-dioxane, 3.00 g *n*-heptane) turns into two phases at room temperature. One phase is the PEG phase with a composition of N and the other phase is the organic phase with a composition of M. Based on the calculation from the phase diagram, there are about 2.15 g of 1,4-dioxane in the PEG phase and 1.00 g of 1,4-dioxane in the upper organic phase, respectively. These calculation results are in agreement with the GC analysis results. Therefore, the suitable amount of 1,4-dioxane added to the catalytic system should be 1.00 g in the process of the catalyst's recycling.

Fig. 3 illustrates the recycling efficiency of the Rh/TMPGP complex catalyst on the hydroformylation of 1-dodecene. It can be seen that there is almost no decrease of catalytic activity after 23 times recycling. ICP-AES analysis shows that the Rh
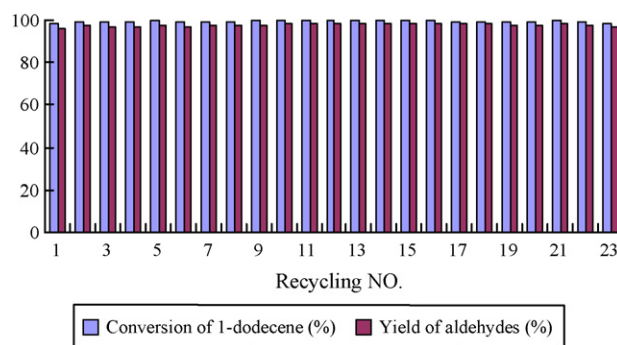

Fig. 3. Recycling efficiency of the Rh/TMPGP complex catalyst on the hydroformylation of 1-dodecene.

leaching in the upper product phase of the first reaction run is 1.12% and the average Rh leaching in the upper product phase is 0.65% each run, which are much less than the results reported previously [14,21,23].

4. Conclusions

A new thermoregulated PEG biphasic catalysis system composed of PEG-400/1,4-dioxane/*n*-heptane was developed and applied in the Rh-catalyzed hydroformylation of 1-dodecene. Under the optimum reaction conditions, the conversion of 1-dodecene and the yield of aldehydes are 96% and 94%, respectively. The catalyst, after being recycled 23 times, shows no evident loss of catalytic activity. The average Rh leaching into the upper product phase is 0.65% each run. This new system exhibits better recycling efficiency of catalyst.

Acknowledgments

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