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Thermoregulated ionic liquids and their application for the hydroformylation of 1-dodecene catalyzed by Rh/TPPTS complex

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Based on the synthesis of a new kind of room temperature ionic liquids, quaternary ammonium alkanesulfonate salts tailed with polyether chain to their alkyl group, a thermoregulated ionic liquid biphase system composed of IL_{PEG750}, *n*-heptane and toluene was developed. The system was applied in the hydroformylation of 1-dodecene catalyzed by Rh/TPPTS complex. Under the optimum conditions, the conversion of 1-dodecene and yield of aldehyde are 99% and 97%, respectively. In addition, the catalyst could be easily separated from products by phase separation and efficiently recovered. Copyright © 2008 John Wiley & Sons, Ltd.

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Keywords: thermoregulated biphase catalysis; ionic liquid; hydroformylation; 1-dodecene; rhodium complex

Introduction

Separation of noble metal catalysts from hydroformylation mixtures has been a challenge and continues to be the focus of intense research on homogeneous catalysis.[1] Several elegant approaches including aqueous[2,3] and fluorous biphasic catalysis,[4,5] reactions in supercritical media[6–9] and catalyst immobilization onto solid support materials[10–13] have been explored over the past decades.

Room temperature ionic liquids as environmentally benign solvent alternatives in biphase catalysis are investigated with great interest and there are some excellent reviews.[14–23] Several ionic liquids biphasic systems that are 'homogeneous at high temperature and biphasic at low temperature' have been established, such as the ionic liquid-water system for hydrogenation of but-2-yne-1, 4-diol,[24] fluorous-containing ionic liquid for hydrosilylation of alkenes[25] and the ionic liquid–acetonitrile–fatty acid ester ternary system for Diels–Alder reaction.[26] These systems are based on imidazolium salt ionic liquids whose toxicities are still questioned. Liberation of harmful hydrogen halide has posed a serious problem and some imidazolium-based ionic liquids are considered to be more toxic than traditional solvents.[27–29] Compared with imidazolium salt ionic liquids, quaternary ammonium salts are relatively safer and biphasic systems based on this kind of ionic liquids would be of importance.

In this paper, a series of quaternary ammonium alkanesulfonates with polyether chain in their alkyl group (IL_{PEGx}, $x = 350$, 550 and 750) have been synthesized. Based on these ionic liquids, a thermoregulated ionic liquid biphase system, where the ionic liquid phase contains Rh/TPPTS (trisodium triphenylphosphine-3-3′-3″-trisulfonate) complex catalyst and the organic phase contains substrate, is established and applied for the hydroformylation of 1-dodecene.

Experimental

Organic solvents for the synthesis of ionic liquids were purified by distillation from appropriate drying agents under inert atmosphere. 1-Dodecene, $MeO(CH_2CH_2O)_nH$ ($M_w = 350$, 550, 750) and TPPTS were purchased from Aldrich. $RhCl_3 \cdot 3H_2O$ was purchased from Beijing Institute of Chemical Engineering and used without any further purification. The catalyst Rh–TPPTS complex was prepared *in situ*.

^1H- and ^{13}C-NMR spectra were recorded on a Varian INOVA 400 MHz NMR instrument. Differential scanning calorimetry measurements of the ionic liquids were performed on Netzsch DSC 204 instrument. The decomposition temperatures of the ionic liquids were measured with a Mettler Toledo TGA/SDTA 851e Thermal Gravimetric Analyzer. The hydroformylation products were analyzed using a gas chromatography (Temp 5890 II Analyzer, capillary column, OV-101, 50 m × 0.3 mm equipped with a Shimadu C-R3A integrator). Measurement of the leaching of rhodium in organic phase was carried out on an Optima 2000DV ICP-AES instrument.

Synthesis of IL_{PEGx}

Preparation of IL_{PEG750}

$MeO(CH_2CH_2O)_nH$ ($M_w = 750$) was converted to the corresponding methanesulfonates by reaction with methanesulfonyl chloride according to the published method.[30] Then, the methanesulfonates reacted with an excess of triethylamine in THF (tetrahydrofuran) under reflux for 2 weeks under N_2. The reaction mixture

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$$\mathrm{MeO(CH_2CH_2O)_nH + CH_3SO_2Cl \xrightarrow[\text{toluene}\ <\ 10\,^{\circ}\mathrm{C}]{NEt_3} Me(OCH_2CH_2)_nOSO_2CH_3}$$

$$\mathrm{CH_3(OCH_2CH_2)_nOSO_2CH_3 + NEt_3 \xrightarrow[80\,^{\circ}\mathrm{C}]{THF} CH_3(OCH_2CH_2)n\overset{+}{N}Et_3\ CH_3SO_3^{-}}$$

$\mathrm{IL_{PEG750}}$ n = 16
$\mathrm{IL_{PEG550}}$ n = 12
$\mathrm{IL_{PEG350}}$ n = 7

Scheme 1. The synthesis of $\mathrm{IL_{PEGx}}$; $x = 350$, 550 and 750.

was evaporated under vacuum to give a waxy product $\mathrm{IL_{PEG750}}$ (Scheme 1). The product was characterized by NMR (solvent: $CDCl_3$) and the chemical shifts are as follows: ^{1}H-NMR δ: 1.38(t, 9H, $CH_2\mathit{CH_3}$), 2.62(s, 3H, -$SO_3\mathit{CH_3}$), 3.38(s, 3H, -$O\mathit{CH_3}$), 3.50(6H, dd, $\mathit{CH_2}CH_3$), 3.56, 3.64, 3.76, 3.88 [m, 59H($O\mathit{CH_2CH_2}$)$_n$]; ^{13}C-NMR (solvent : $CDCl_3$) δ: 7.85, 39.5, 59.0, 46.2, 53.9, 56.9, 64.6, 70.2 and 71.9. The glass-transition temperature and the thermal decomposition temperature of $\mathrm{IL_{PEG750}}$ are 24 and 315 °C, respectively.

$\mathrm{IL_{PEG550}}$ and $\mathrm{IL_{PEG350}}$ were prepared in a similar method to that mentioned above, except that $MeO(CH_2CH_2O)_nH$ ($M_w = 550$) and $MeO(CH_2CH_2O)_nH$ ($M_w = 350$) were employed, respectively. These two ionic liquids were characterized by NMR (solvent: $CDCl_3$) and the chemical shifts are as follows. $\mathrm{IL_{PEG550}}$: ^{1}H-NMR (solvent : $CDCl_3$) δ: 1.38(t, 9H, $CH_2\mathit{CH_3}$), 2.62(s, 3H, -$SO_3\mathit{CH_3}$), 3.38(s, 3H, -$O\mathit{CH_3}$), 3.50(dd, 6H, $\mathit{CH_2}CH_3$), 3.56, 3.64, 3.76, 3.88 [m, 48H ($O\mathit{CH_2CH_2}$)$_n$]; ^{13}C-NMR (solvent: $CDCl_3$) δ: δ 46.2, 53.9, 56.9, 64.6, 70.2, 71.894, 7.85, 39.5, 59.0. $\mathrm{IL_{PEG350}}$: ^{1}H-NMR (solvent : $CDCl_3$) δ: 1.38(t, 9H, $CH_2\mathit{CH_3}$), 2.62 (s, 3H, -$SO_3\mathit{CH_3}$), 3.38 (s, 3H, -$O\mathit{CH_3}$), 3.50(dd, 6H, $\mathit{CH_2}CH_3$), 3.56, 3.64, 3.76, 3.88 [m, 24H ($O\mathit{CH_2CH_2}$)$_n$]; ^{13}C-NMR (solvent: $CDCl_3$) δ: , 53.9, 56.9, 64.6, 70.2, 71.9, 7.85, 39.5, 59.0.

The glass-transition temperature and the thermal decomposition temperature of $\mathrm{IL_{PEG550}}$ are 5 and 305 °C, respectively. For $\mathrm{IL_{PEG350}}$, the glass-transition temperature and the thermal decomposition temperature are −12 and 277 °C, respectively.

Hydroformylation of 1-dodecene

Hydroformylation reactions were carried out in a 75 ml stainless-steel autoclave with a magnetic stirring bar. $RhCl_3 \cdot 3H_2O$, TPPTS, 1-dodecene, $\mathrm{IL_{PEG750}}$, toluene, *n*-heptane and *n*-decane (internal standard) were charged into the autoclave. The autoclave was sealed and flushed five times with 1.0 MPa CO. Then the reactor was pressurized with syngas ($CO:H_2 = 1:1$) and held at the designated temperature with magnetic stirring for a fixed length of time. Then, the reactor was cooled to room temperature and depressurized. The upper organic phase was separated by phase separation from the lower $\mathrm{IL_{PEG750}}$ phase and immediately analyzed by gas chromatography.

Results and Discussion

Thermoregulated ionic liquid biphase system

Based on the solubility property of $\mathrm{IL_{PEGx}}$, $x = 350$, 550 and 750, in *n*-heptane and toluene, the thermoregulated ionic liquid biphase system was chosen to be composed of $\mathrm{IL_{PEGx}}$, $x = 350$, 550 and 750, *n*-heptane and toluene. The phase diagram for the system of $\mathrm{IL_{PEGx}}$–*n*-heptane–toluene is shown in Fig. 1. To get this phase diagram, miscibility tests were carried out in a glass autoclave at 298 and 363 K. Given amounts of $\mathrm{IL_{PEGx}}$, *n*-heptane and toluene were added to the autoclave and heated in an oil bath until the mixture became homogeneous and remained stable as one phase. Through this investigation, the bigger miscibility gap of the $\mathrm{IL_{PEG750}}$–*n*-heptane–toluene system facilitated a good operation range. Therefore, it was selected as the thermoregulated biphase system for the hydroformylation of 1-dodecene. The system composed of different compositions of $\mathrm{IL_{PEG750}}$–*n*-heptane–toluene may be changed from biphasic to monophasic by increasing the temperature.

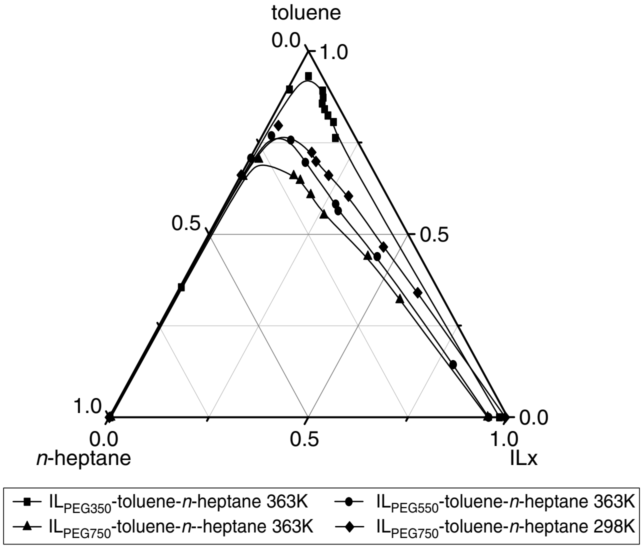

Figure 1. The phase diagram of $\mathrm{IL_{PEGx}}$–toluene -*n*-heptane.

Besides the phase switch property of the above-mentioned ternary system, anionic phosphine ligand TPPTS can be easily immobilized in the ionic liquid phase through metathesis between the sodium cation of TPPTS and the ammonium cation of the ionic liquids. The process of catalysis in the thermoregulated $\mathrm{IL_{PEG750}}$–*n*-heptane–toluene biphase system is schematically depicted in Fig. 2. At room temperature ($T < T_m$, where T_m = miscibility temperature), $\mathrm{IL_{PEG750}}$ phase containing Rh/TPPTS complex is immiscible with the upper organic phase that contains substrate. On heating to the reaction temperature ($T > T_m$), the system becomes monophasic and the reaction proceeds homogeneously. After reaction, on cooling to room temperature ($T < T_m$), the system switches back to two phases again. By simple phase separation, the ionic liquid phase containing catalyst can be separated from the organic phase containing the product and reused in subsequent reaction runs.

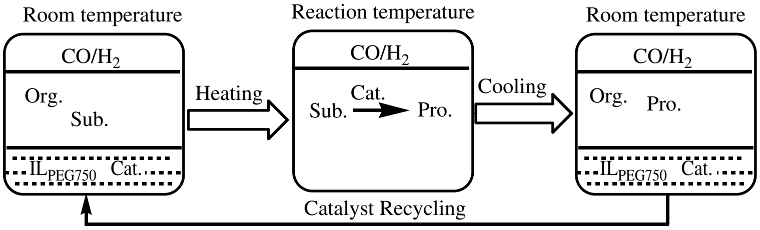

Figure 2. Thermoregulated ionic liquid biphase catalytic process. Org., organic phase; Sub., substrate; Ald., aldehydes.

Table 1. Effect of P/Rh molar ratio on the hydroformylation of 1-dodecene catalyzed by Rh/TPPTS complex[a]

Entry	P : Rh (molar ratio)	Conversion of 1-dodecene (%)	Aldehyde yield (%)	TOF[b] (h^{-1})
1	3	90	85	264
2	8	97	95	295
3	12	97	95	295
4	16	98	96	298
5	20	98	96	298
6	30	90	74	230

[a] Reaction conditions: $RhCl_3{\bullet}3H_2O$; 1.0 mg (0.0038 mmol); $T = 110\,^\circ C$; syngas ($CO{:}H_2 = 1{:}1$) pressure, 5.0 MPa; reaction time, 5 h; IL_{PEG750}, 0.5 g; toluene, 4.3 g; *n*-heptane, 0.5 g; *n*-decane (inner standard), 0.2 g; and 1-dodecene, 1.0g (5.9 mmol). The miscibility temperature (T_m) of the system was 108 °C.

[b] Turnover frequency (TOF) in moles of aldehyde per mole of catalyst per hour.

Table 2. Effects of different reaction parameters on the hydroformylation of 1-dodecene[a]

Entry	Temperature (°C)	Syngas pressure (MPa)	Reaction time (h)	Conversion of 1-dodecene (%)	Aldehyde yield (%)	TOF (h^{-1})
7	110	5.0	5.0	97	95	295
8	110	5.0	2.0	56	53	165
9	110	5.0	4.0	85	84	261
10	110	5.0	6.0	98	96	298
11	90	5.0	5.0	23	21	65
12	100	5.0	5.0	40	36	112
13	120	5.0	5.0	98	96	298
14[b]	100	5.0	5.0	98	97	301
15[c]	110	5.0	5.0	24	22	68
16	110	3.0	5.0	60	44	137
17	110	4.0	5.0	90	88	273
18	110	6.0	5.0	99	96	298

[a] Reaction conditions: P : Rh molar ratio 8; other conditions are the same as in Table 1.

[b] Only toluene was used as organic solvent.

[c] Only heptane was used as organic solvent.

Table 3. Recycling efficiency of Rh/TPPTS complex catalyst[a]

Entry	Conversion (%)	Aldehyde yield (%)	Rh leaching in organic phase (wt%)
19[b]	98	96	0.53
20	97	96	0.67
21	99	97	0.60
22	97	95	0.65
23	99	97	0.82
24	98	96	0.73
25	98	97	0.45
26	98	97	0.64

[a] Reaction conditions: P : Rh molar ratio 8; *n*-heptane, 0.8 g; other conditions the same as those in Table 1.

[b] P : Rh molar ratio 8; *n*-heptane, 0.5 g; other conditions the same as in Table 1.

Hydroformylation of 1-dodecene in IL_{PEG750}/*n*-heptane/toluene system catalyzed by Rh/TPPTS complex

Effect of P/Rh molar ratio

The hydroformylation of 1-dodecene catalyzed by Rh/TPPTS complex was conducted in a system composed of IL_{PEG750}, *n*-heptane and toluene. The miscibility temperature of the system is 108 °C. The effects of different P : Rh molar ratios on the reaction were examined under a reaction temperature of 110 °C and a syngas pressure of 5.0 MPa for 5 h. Generally, reactions using metal complex as catalyst require excessive ligands in order to increase the stability of the catalyst. However, large amounts of ligands will decrease the catalyst. activity. The effect of P : Rh molar ratio on the hydroformylation of 1-dodecene is shown in Table 1. It can be seen that the conversion of 1-dodecene and the yield of aldehyde remain nearly the same (97–98%) when the P : Rh molar ratio is changed from 8 to 20. However, too low or high a P : Rh molar ratio will decrease the conversion of 1-dodecene and yield of aldehyde. Thus, the optimum P : Rh molar ratio is chosen to be 8.

Effects of other reaction parameters

The effects of other reaction parameters, including reaction time, temperature and syngas pressure, on the hydroformylation of 1-dodecene were studied and the results are listed in Table 2. With increasing syngas pressure and reaction temperature, both the conversion of 1-dodecene and yield of aldehyde increased as well. When the temperature increased from 100 to 110 °C, the conversion of 1-dodecene increased sharply. This may be due to the fact that the system changes from biphase to monophase. In order to prove the inference, hydroformylation of 1-dodecene was tested by using only toluene as the upper layer organic solvent at 100 °C (the system was homogeneous; entry 14, Table 2) and *n*-heptane as the upper layer organic solvent at 110 °C (the system was biphasic; entry 15, Table 2). The results indicate that IL_{PEG750}–*n*-heptane–toluene biphase system changes from biphase to monophase between 100 and 110 °C.

Recycling efficiency of the Rh/TPPTS complex catalyst

When the reaction was complete, the upper organic phase was separated from the lower catalyst-containing IL_{PEG750} phase by phase separation. Then, by adding fresh solvent and substrate, the catalyst was directly recycled. Considering that a small amount of toluene is desolved in IL_{PEG750} phase, which will the change the T_m of the system, from the second reaction run an additional 0.3 g *n*-heptane was added to keep the T_m of the system the same. Table 3 illustrates the results of catalyst recovery efficiency on the hydroformylation of 1-dodecene. Under the conditions of $T = 110\,^\circ C$, $P = 5.0$ MPa, P:Rh = 8; the Rh–TPPTS complex catalyst could be reused eight times without loss of activity. The leaching of rhodium in organic phase was less than 1% (wt%) in every recycling run.

Conclusion

Based on the synthesis of a new kind of room temperature ionic liquid quaternary ammonium alkanesulfonate salts tailed with polyether chain to their alkyl group, a thermoregulated ionic liquid biphase system composed of IL_{PEG750}, *n*-heptane and toluene was developed. By using this system, hydroformylation of 1-dodecene catalyzed by Rh–TPPTS complex was systematically investigated. Under the optimum conditions, the conversion of 1-dodecene and yield of aldehyde were 99 and 97%, respectively. In addition, the catalyst could be easily separated from products by phase separation and efficiently reused.

Supporting information

Supporting information may be found in the online version of this article.

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