Ammonium salts with polyether-tail: new ionic liquids for rhodium catalyzed two-phase hydroformylation of 1-tetradecene

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By attaching the polyether chains to ammonium salts, a novel class of ionic liquid termed polyether melt is prepared. Such polyether melt contains no fluoride and hence is environmentally more benign. Applying this polyether melt as a polar phase, the hydroformylation of 1-tetradecene catalyzed by Rh complex catalyst in two-phase medium was investigated. The rhodium catalyst immobilized in this polyether melt is readily separated from the aldehyde product phase by decantation and has been reused for seven times without obvious loss of activity.

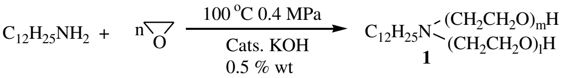
KEY WORDS: ionic liquid; polyether; hydroformylation; two-phase.

1. Introduction

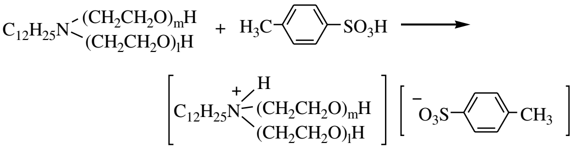
To avoid the problem of separation of products from catalyst in homogeneous catalysis, liquid–liquid two-phase systems have been developed. In those systems the catalyst complex remains in one-phase while the product remains in a second, immiscible phase [1]. Aqueous biphasic systems have been applied commercially in the Rhurchemie-Rhone Poulene process for the hydroformylation of propylene to butanal using a water-soluble rhodium triphenylphosphine trisulphonate (TPPTS) catalyst [2]. Unfortunately, this process is limited to C_2–C_5 olefins due to the low solubility of higher olefins in water [3]. Later, perfluorohydrocarbons have been proposed as a non-aqueous polar phase for the two-phase catalysis; however, to solubilize rhodium complexes in the "fluorous" phase, special fluorinated ligands have to be designed [4–7]. With respect to the use of more environmentally benign solvents, a series of novel solvents known as ionic liquids are suggested [8,9]. Ionic liquids are salts that are liquid at low temperature (< 100). The most commonly used ionic liquids are salts in which imidazolium, pyridinium, ammonium and phosphonium as cations and tetrafluoroborate and hexafluorophosphate as anions. In our research work concerning with polyether modified phosphine ligands used for "thermoregulated phase transfer catalysis," [10] we have noticed a common phenomenon that many solid phosphine compounds such as tri(*p*-hydroxyphenyl)phosphine, after being attached with polyethylene glycol chains, will become a viscous liquid. So an idea to introduce polyether chains to ammonium salt and thus to prepare a novel ionic liquid seems reasonable.

2. Results and discussion

We have prepared some quite viscous polyether-tailored ammonium salts by protonation of the polyether-tailored amine **1** [the products by ethoxylation reaction, equation (1)] with stoichiometric amount of *p*-toluenesulfonic acid [equation (2)] (Scheme 1). Such kind of ionic liquid can also be called polyether melt according to Murray [11] description. As there is no fluoride used, such polyether melt are environmentally more benign.



(1)



(2)

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As a low molecular polymer, the polyether melt **2** did not have exact melting points. Thus the glass transition temperature T_g, taken as the inflection temperatures on the DSC (Differential Scanning Calorimetry) heating curves, was determined to show its phase behavior. The T_g of **2** is −41.3 °C which means that **2** is a viscous liquid at room temperature. On the other hand, the SDTA T_g spectrum implies that **2** does not decompose until 230 °C and the density of **2** is 1.1213 g/cm^3. All of these properties implied the possibility of **2** using as a polar phase in the two-phase catalysis.

Hydroformylation of higher olefins (C > 6) is an important industrial process. The resulting long chain

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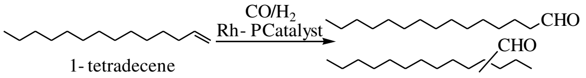
aldehydes can be converted into alcohols for plasticizers (C_6–C_{11}) and detergents (C_{12}–C_{20}) [12]. A number of publications concerned with this reaction have appeared, in the search for more active and selective rhodium catalysts coupled with easy catalyst separation and recycling [13]. Chauvin [14] has first described the two-phase hydroformylation of penta-1-ene catalyzed by $[Rh(CO)_2acac]$/triphenylphosphine in 1-butyl-3-methyl-imidazolium hexafluorophosphate ($[BMIM]PF_6$) ionic liquid medium. Wasserscheid *et al.* [15] described the successful application of cobaltocenium ligands or guanidinium-modified diphosphine ligands with a xanthene backbone [16] in the Rh-catalyzed hydroformylation of oct-1-ene in hexafluorophosphate ionic liquids. Here, we report the application of polyether melt **2** as a polar phase to immobilize Rh complex to catalyze the hydroformylation of 1-tetradecene [see Scheme 2 Equation (3)].



(3)

The reactions were performed in polyether melt **2**/heptane two-phase medium under a temperature of 105 °C and a syn gas pressure of 5.0 MPa for 10 h. At the end of each hydroformylation run, the autoclave was cooled and the pressure was released. The liquid organic phase was separated and the products were analyzed by GC, GC-MS. The results for the rhodium leaching in organic phase were measured by atomic absorption for several samples. The results were shown in table 1. The remaining polyether melt ionic liquid layer containing catalyst remained in the autoclave for the next run.

In the reaction with classical lipophilic ligand PPh_3 (table 1, entry 1), good catalytic activity was observed, but the Rh contained in organic phase was 25% of the total Rh added after the reaction mixture was cooling to room temperature.

Previously we [17] had reported the use of octylpolyethyleneglycol-phenylene-phosphite (OPGPP, **3**) in the rhodium catalyzed hydroformylation of higher olefins. Since both polyether melt **2** and OPGPP contain polyether moiety, we also tested OPGPP (table 1, entries 2–4) as ligand. Rh–OPGPP catalyst gives a reasonable TOF somewhat lower than that of Rh–PPh_3. But the leakage of Rh into the organic phase decreased markedly (only 1.75% table 1, entry 2). The recycle experiments results were also quite reasonable (table 1, entries 3 and 4).

In order to immobilize Rh complex catalyst in the polyether melt ionic liquid, a polar ligand should be applied. For this purpose, the sodium salts of TPPTS had been selected as ligand. The Rh–TPPTS complex in the polyether melt showed satisfactory activity toward the hydroformylation of 1-tetradecene (table 1, entries 5–12). The results in table 1 entry 5–7 show that the catalyst activity increased during the first three runs and meanwhile, as prospective, the ratio of linear to branched aldehyde products (*n*/*i*) decreased with the increase of the reaction conversion. Catalyst activity reached a stable higher activity state after the third recycling run. Such a behavior was attributed to catalyst pre-formation period which was proved by the following experiment. Without addition of 1-tetradecene, the same reaction procedure was performed for 20 h for the formation of the complex catalyst. Then 1-tetradecene was added and the first catalytic run was carried out (table 1, entry 10). Catalyst activity reaches to the highest level this time. After the first catalytic run, only 0.5% of the used Rh was found in the organic layer (table 1, entry 10). These results revealed good

Table 1
Polyether melt **2**/ *n*-heptane two-phase hydroformylation of 1-tetradecene based on rhodium catalysts

Entry	Ligand (cycle)	Conversion (%)[a]	Aldehyde yield (%)	*n*:Iso[b]	TOF[c] (h^{-1})	Rh leaching (%)
1	PPh_3(1)	95.1	94.4	1.0	95	25
2	OPGPP(1)	83.1	82.8	0.2	83	1.75
3	OPGPP(2)	82.1	81.6	0.2	82	
4	OPGPP(3)	80.6	79.2	0.2	81	
5	TPPTS(1)	16.7	16.4	3.9	16	
6	TPPTS(2)	56.6	56.1	1.0	57	
7	TPPTS(3)	94.5	93.7	0.4	95	
8	TPPTS(4)	94.3	92.8	0.4	95	
9	TPPTS(7)	88.2	87.8	0.4	88	
10	TPPTS(1)[d]	93.8	92.4	0.4	94	0.5
11	TPPTS(2)[d]	94.3	92.8	0.4	94	
12	TPPTS(7)[d]	87.1	86.9	0.4	87	

[a] Conversion = [(initial 1-tetradecene)−(1-tetradecene after reaction)]/(initial 1-tetradecence).

[b] Ratio of linear to branched aldehyde products.

[c] Turnover frequency (TOF) in mol of aldehyde per mol of Rh per h.

[d] After 20 h pre-formation of the active catalyst.

Reaction conditions: polyether melt **2**: 2.0 g; $CO/H_2 = 1/1$; $P(CO/H_2) = 5.0$ MPa; organic solvent (*n*-heptane): 2 mL; 1-tetradecene: 1 mL; ligands/Rh (mol/mol) = 15/1; Rh-precursor: $RhCl_3$; $T = 105\ ^{\circ}C$; $t = 10$ h; internal standard: *n*-decane (0.2 mL); Rh/S(mol/mol) = 1/1000.

immobilization of the Rh–TPPTS complex in the polyether melt phase. After seven consecutive runs, an overall turnover number of 6300 mol aldehyde per mol Rh-catalyst has been obtained (table 1, entries 10–12). Efforts were also made to determine in which phase the hydroformylation really takes place when Rh–TPPTS complex was used in the polyether melt. After the first catalytic run (table 1, entry 10), the reaction mixture was transferred into a glass autoclave and then the glass autoclave we heated from room temperature (under normal nitrogen atmosphere) to 105 °C and kept for 6 h while stirring. When stirring was stopped, it was found that the reaction mixture settled again into two clear immiscible phases. Besides, the amount of 1-tetradecene dissolved in the polyether melt phase has been measured to be 1.0% by weight. Such a concentration is sufficient to ensure good reaction rates in the polyether melt. Thus, in case of the Rh–TPPTS complex was applied, the reaction is mainly taking place in the lower polyether melt phase.

3. Conclusion

Several other polyether melts were prepared by changing the cation and the anion, and they also appear as liquid at room temperature. Studies are now under way to investigate the possibility of finding a smart polyether melt, which can be fully soluble in an organic solvent at a higher temperature and separate from the organic solvent at a lower temperature. This feasibility could be matched by careful tailoring the ionic composition of the polyether melt, such as introducing lipophilic polypropylene glycol chains to the organic amine or using a more lipophilic anionic group. This type of polyether melt could be applied to form a catalytic system which is capable of one-phase catalysis (at higher temperature) coupled with two-phase separation (at lower temperature).

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