Application of a novel phosphonic-functionalized polyether imidazolium ionic liquid in hydroformylation of 1-octene

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Abstract. In this paper, based on the concept of integration of phosphine ligands and ionic liquids, a new phosphine-functionalized polyether imidazolium ionic liquid [Ph(EO)16MIM]3[P(m-C6H4SO3)3] was designed and synthesized. The phosphine-functionalized ionic liquids have the characteristics of both phosphine ligands and ionic liquids. They can be used not only as ligands to complex metal rhodium, but also as catalyst supports. Based on this unique property, we constructed a Rh-[Ph(EO)16MIM]3[P(m-C6H4SO3)3] biphasic catalytic system to catalyze the hydroformylation of 1-octene. The results show that the catalyst is not only easy to separate and recover, but also can obtain 2717 h⁻¹ TOF value within 0.5 h. When the catalyst was reused for 15 times, there was no obvious deactivation of the catalyst, and the total conversion number TTON was as high as 43288.

1. Introduction

Hydroformylation of olefins is a process in which H₂ and CO react with olefins to form aldehydes under the action of rhodium catalyst, and it is also one of the largest homogeneous catalytic reactions in industry [1-3]. Aldehydes and their derivatives produced by hydroformylation are widely used in daily chemicals such as plasticizers, detergents, adhesives and spices [4]. Although the homogeneous hydroformylation catalytic system has the advantages of mild reaction conditions and high catalytic activity, the precious metal rhodium catalyst is difficult to separate and recover, so there is an urgent need to develop a new catalytic system to solve this problem. To this end, a variety of new methods have been explored to solve this problem. Among them, ionic liquid biphasic catalysis has attracted wide attention. Because ionic liquids are chemically stable, their structures can be designed according to requirements, and have good solubility and low vapor pressure, they can be used as "green solvents" for dissolving and carrying catalysts [5-8].

However, the ionic liquid biphasic catalytic system still has great limitations: (1) A large number of ionic liquids are required to support and dissolve transition metal catalysts, no matter from an economic or toxicological point of view, this does not meet the requirements of green chemistry [9]; (2) The use of a large number of ionic liquids increases the mass transfer resistance of substrate molecules and reduces the catalytic activity and selectivity [10-12]; (3) The negative effect of ionic liquids is significant, and excessive impurities may cause oxidation, decomposition, clustering of the catalyst, resulting in lower stability and shorter service life [13]. In order to solve the above problems, in the recent research work, we introduced polyether chain into the cationic structure of ionic liquids and synthesized a kind of phosphine-functionalized polyether guanidinium ionic liquids [14, 15]. This kind of phosphine-functionalized polyether guanidinium ionic liquids integrate phosphine ligands with the...
structure and function of ionic liquids, and can play the dual role of phosphine ligands and solvent ionic liquids, and the introduction of polyether chain can significantly reduce its melting point [16, 17]. In the two-phase hydroformylation of 1-octene, it has high catalytic activity and TOF can reach 2300 h⁻¹.

On the basis of this work, we tried to synthesize a new room temperature phosphine-functionalized polyether imidazolium ionic liquid [Ph(EO)₁₆MIM]₃[PO₃(ch₂so₃)₃] (Fig. 1) by ion exchange reaction of polyether chain ionic liquid [Ph(EO)₁₆MIM][OMs] with monophosphine ligand TPPTS. We constructed a Rh-[Ph(EO)₁₆MIM]₃[P(m-C₆H₄SO₃)₃] biphasic catalytic system for the biphasic hydroformylation of 1-octene, and investigated its reaction activity and cycle life. The catalytic system not only reduces the amount of ionic liquids and the negative effects of ionic liquids, but also is easy to separate and recover.

**Fig. 1.** Synthesis of [Ph(EO)₁₆MIM]₃[P(m-C₆H₄SO₃)₃] and its application in hydroformylation of 1-octene

### 2. Experimental

#### 2.1. General experimental details and materials

All organic solvents were dried, purified, deoxidized and stored in argon atmosphere [18]. All operations were performed in argon atmosphere using standard Schlenck technology [19]. The 1-octene, Rh(acac)(CO)₂ and TPPTS purchased from Aladdin. The product was analyzed by gas chromatography equipped with hydrogen flame ionization detector (FID) and capillary column (OV-101, 50 m × 0.25 mm × 0.33 μm). The ¹³C NMR spectra of ¹H NMR were recorded by Bruker AVANCE 500 and AVANCE III 600 spectrometers. Q-ToFUltimaGlobal mass spectrometer was used for high resolution mass spectrometry analysis.
2.2. Synthesis of Ph(EO)16SO3CH3

Polyethylene glycol phenyl ether 20 g (24 mmol), 3.6 mL (25.2 mmol) triethylamine and 60 mL anhydrous toluene were put into 250 mL three-port flask, stirred well, and placed in ice water bath. When the temperature is below 0 °C, 1.98 mL (25.2 mmol) methanesulfonyl chloride is added drop by drop, and the temperature is kept below 5 °C. After the titration was completed, the reaction device was placed at room temperature for 24 h. After filtration at the end of the reaction, toluene in the filtrate was removed under reduced pressure to obtain a yellowish viscous liquid polyethylene glycol phenyl ether methyl sulfonate with a yield of 98%. 1H NMR (500 MHz, D2O): δ = 7.39 - 7.25 (m, 2H, O-Ph-H), 7.06 - 6.91 (m, 3H, O-Ph-H), 4.39 - 3.39 (m, 66H, OCH2CH2), 3.22 - 3.06 (m, 3H, CH3SO3-).

2.3. Synthesis of [Ph(EO)16MIM][OMs]

Under the protection of argon, 19 g Ph(EO)16SO3CH3 (2.17 mmol), 3.2 g N-methylimidazole (39 mmol) and 60 mL anhydrous toluene were added to the 250 ml Schlenk reaction bottle and reacted at 95 °C for 30 h. At the end of the reaction, toluene was removed under reduced pressure, excess N-methylimidazole was extracted with methyl tert-butyl ether, and the residual methyl tert-butyl ether was removed by vacuum distillation to obtain a yellowish viscous polyether imidazolium ionic liquid [Ph(EO)16MIM][OMs] with a yield of 91%. 1H NMR (500 MHz, D2O): δ = 8.77 (s, 1H, N-CH=N), 7.63-7.44 (m, 2H, N-CH=CH-N), 7.42 (d, J = 7.5 Hz, 2H, O-Ph-H), 7.10 (dd, J = 16.3, 7.7 Hz, 3H, O-Ph-H), 4.42 (s, 2H, O-CH2), 4.26 (d, J = 4.0 Hz, 3H, N-CH3), 4.01-3.59 (m, 67H, OCH2CH2), 2.84 (s, 3H, CH3SO3-); 13C NMR (125.7 MHz, D2O): δ = 70.9, 69.5, 69.4, 63.7, 62.0, 58.0, 48.6, 38.4, 20.4, 19.5; FTMS (ESI): [C42H75O16N2]+ calculated 863.51, found 863.53; [CH3O3S]- calculated 94.08, found 94.98.

2.4. Synthesis of [Ph(EO)16MIM]3[P(m-C6H4SO3)3]

Under the protection of argon, 0.5 g (0.89 mmol) TPPTS, 2.6 g [Ph(EO)16MIM][OMs] (2.67 mmol) and 20 mL CH3CN were added to the 100 ml Schlenk reaction bottle and reacted at room temperature for 72 h. At the end of the reaction, the upper n-heptane was precipitated. The solution product of acetonitrile was added, filtered and decompessed to remove acetonitrile from the filtrate to obtain yellow viscous phosphine-functionalized polyether imidazolium ionic liquid [Ph(EO)16MIM]3[P(m-C6H4SO3)3] with a yield of 94%. 1H NMR (500 MHz, D2O): δ = 8.58 (d, J = 40.8 Hz, 3H, N-CH=N), 7.82-7.65 (d, 6H, P-Ph-H); m, 6H, N-CH=CH-N), 7.51-7.16 (d, 6H, P-Ph-H); d, J = 7.5 Hz, 6H, O-Ph-H), 6.93 (d, J = 7.6 Hz, 9H, O-Ph-H), 4.24 (d, 9H, N-CH3), 3.92-3.18 (m, 192H, OCH2CH2); 13C NMR (126 MHz, D2O): δ = 130.61-129.02, 122.52, 121.76, 114.75, 91.85-83.80, 89.25-83.80, 77.22-73.59, 69.34, 72.79-55.98, 67.78, 66.70, 73.59-19.88, 86.84-19.88, 83.80-19.88, 83.80-19.88, 38.00, 37.51, 24.97, 21.81; 31P NMR (202.4 MHz, D2O): δ = -5.189; FTMS (ESI): [C42H75O16N2]+ calculated 863.51, found 863.53; [C18H12O9PS3]- calculated 166.31, found 166.31.

2.5. Hydroformylation

In Ar atmosphere, Rh(acac)(CO)2 (1.0 mg, 3.88 × 10^-3 mmol) and [Ph(EO)16MIM]3[P(m-C6H4SO3)3] were added to the 60 mL stainless steel autoclave in a certain proportion. The CO/H2 of 1.0 MPa (volume ratio 1:1) was used to replace the air in the autoclave for three times, and then stirred at 80 °C and 5 MPa (CO/H2 = 1:1) for 1 h to prepare Rh-catalyst precursor. At the end of the reaction, cool to room temperature, release the syngas from the kettle, and reduce pressure to remove the solvent. Then, add a certain amount of 1-octene and use n-hexane as the internal standard. The air in the autoclave was replaced three times with 1.0 MPa CO/H2 (volume ratio 1:1), and the reaction was carried out at 110 °C and 5 MPa (CO/H2 = 1:1). After the reaction is over, the reaction is terminated by cooling in ice water. After the syngas was released, the upper organic phase was analyzed by a gas chromatograph equipped with hydrogen flame ionization detector (FID) and capillary column (OV-101, 50 m × 0.25 mm × 0.33 μm).
3. Results and discussion

Based on the above research ideas, a novel phosphine-functionalized polyether imidazolium ionic liquid $[\text{Ph(EO)}_{16}\text{MIM}]_3[\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3)_3]$ was obtained by simple ion exchange reaction between methylimidazolium ionic liquid $[\text{Ph(EO)}_{16}\text{MIM}][\text{OMs}]$ and monophosphine ligand TPPTS at room temperature. The structure was characterized by $^1$H NMR and $^{13}$C NMR, and the yield was as high as 94%. In our study, the hydroformylation of 1-octene was used as the catalytic reaction model, and the activity of Rh-$[\text{Ph(EO)}_{16}\text{MIM}]_3[\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3)_3]$ biphasic catalytic system was evaluated by measuring the turnover frequency (TOF) within 0.5 h before the reaction. The results are shown in Table 1.

| Catalytic system | Solvent | Conv. (%) | Sald (%) | $n/i$ | TOF (h$^{-1}$) |
|------------------|---------|-----------|----------|-------|---------------|
| Biphasic         | None    | 50.7      | 26.8     | 2.9   | 2717          |

reaction conditions: $p(\text{H}_2/\text{CO} = 1:1) = 5.0 \text{ MPa}$, $T = 110 \degree\text{C}$, $t = 0.5 \text{ h}$, Rh(acac)(CO)$_2 = 1.0 \text{ mg}$, P/Rh = 10(molar ratio), alkenes/Rh = 10000(molar ratio). Solvent: none; $^b$ Percent of converted alkenes; $^c$ Selectivity for $n$-nonaldehyde and 2-methyl aldehyde (combined); $^d$ Ratio of normal aldehyde to 2-methyl aldehyde; $^e$ Turnover frequency (TOF): mol (aldehyde) per mol (rhodium) per hour.

We investigated the activity and selectivity of Rh-$[\text{Ph(EO)}_{16}\text{MIM}]_3[\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3)_3]$ catalyst in the biphasic hydroformylation of 1-octene. The data show that the system also has high catalytic activity, with a TOF of 2717 h$^{-1}$, a conversion of 50.7% and a $n/i$ value of 2.9 (Entry 2, Table 1). The reasons for the high activity of the system are as follows: the introduction of polyether chain not only reduces the melting point of ionic liquids, but also reduces its polarity, which can improve the solubility of olefins and the catalytic activity.

Rh-$[\text{Ph(EO)}_{16}\text{MIM}]_3[\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3)_3]$ biphasic catalytic system has high catalytic activity and is easy to be separated and recovered, so we investigate its cycle life. In the cycle experiment, the upper organic phase can be separated by simple precipitation, and then fresh 1-octene is added to start a new cycle. The cycle results are shown in Figure 2. The results show that Rh-$[\text{Ph(EO)}_{16}\text{MIM}]_3[\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3)_3]$ catalyst has a long service life. In 15 consecutive reactions, high conversion (Conv.), good aldehyde selectivity (Sald), and almost constant $n/i$ value were maintained. It is encouraging to note that the total number of conversions (TTON) is as high as 43288.

Figure 2. Cycle of Rh-$[\text{Ph(EO)}_{16}\text{MIM}]_3[\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3)_3]/$1-octene biphasic hydroformylation catalyst system. Reaction conditions: $p(\text{H}_2/\text{CO} = 1:1) = 5.0 \text{ MPa}$, $T = 110 \degree\text{C}$, $t = 5 \text{ h}$, Rh(acac)(CO)$_2$ = 1.0 mg, P/Rh = 20(molar ratio), alkenes/Rh = 5000(molar ratio). Solvent: none.
4. Conclusion

In short, we have synthesized a new type of phosphine-functionalized polyether imidazolium ionic liquid \([\text{Ph}(\text{EO})_{16}\text{MIM}][\text{P}(m-C_6\text{H}_4\text{SO}_3)_3]\) which is liquid at room temperature. By integrating the structure and function of phosphine ligands and ionic liquids, the catalysis can play the dual role of phosphine ligands and solvent ionic liquids at the same time. Based on the unique properties of \([\text{Ph}(\text{EO})_{16}\text{MIM}][\text{P}(m-C_6\text{H}_4\text{SO}_3)_3]\), we constructed a biphasic catalytic system for hydroformylation of 1-octene. The system has high catalytic activity and cycle life, the TOF can reach 2717 h\(^{-1}\), and there is no obvious catalyst deactivation after 15 cycles.

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