



Preparation of carbonyl rhodium polyether guanidinium ionic liquids and application in asymmetric hydroformylation based on homogeneous catalysis-biphasic separation system

Ke Wang^a, Xiangxue Liu^a, Baoquan Liu^a, Zhenmei Guo^a, Chao Zhang^{a,b,*}, Zhiguo Lv^{a,*}

^a State Key Laboratory Base for Eco-chemical Engineering, Key Laboratory of Multiphase Flow Reaction and Separation Engineering of Shandong Province, School of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

^b Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin 300071, China

ARTICLE INFO

Article history:

Received 21 February 2021
Revised 16 May 2021
Accepted 7 June 2021
Available online 10 June 2021

Keywords:

Asymmetric hydroformylation
Styrene
Functional ionic liquids
Catalyst recycling

ABSTRACT

Four carbonyl rhodium polyether guanidinium ionic liquids (Rh(CO)₄-PolyGILs) were firstly synthesized by utilizing the ion exchange strategy. This protocol was achieved by introducing polyether guanidinium ionic liquids (PolyGILs) into K[Rh(CO)₄]. Asymmetric hydroformylation (AHF) of styrene was employed as probe reaction to investigate the catalytic performance of the above obtained four functional ionic liquids. The AHF of styrene provided 79.00% conversion, 73.30% yield and 54% enantiomeric excess for 2-phenylpropionaldehyde ([Me(EO)₁₆TMG][Rh(CO)₄] served as catalyst, (R)-BINAP served as chiral ligand at 60°C and 2.0 MPa for 4 h). In addition, based on the unique solubility properties of the above obtained four ionic liquids, a highly effective homogeneous catalysis-biphasic separation (HCBS) system was established for the AHF. HCBS system with [Me(EO)₁₆TMG][Rh((R)-BINAP)(CO)₂] could be reused four times without significantly decrease in the activity. The structure of [Me(EO)₁₆TMG][Rh((R)-BINAP)(CO)₂] was further studied by using the density functional theory (DFT) method, which revealed that the final energy of the molecule was tending to -9460.83 eV and the presence of Ph substituent provided a chiral pocket. The presence of closed rigid chiral pocket could lead to better enantioselectivities.

© 2021 Elsevier B.V. All rights reserved.

1. Introduction

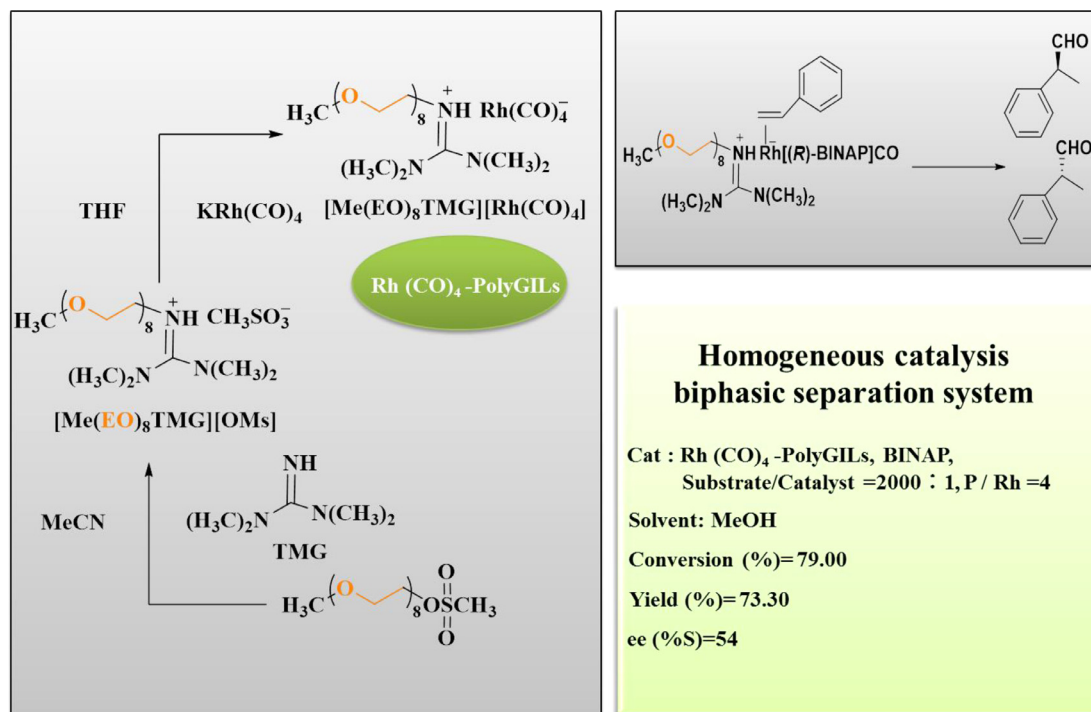
The asymmetric hydroformylation (AHF) is of great significance for the synthesis of drugs, pesticides, fragrances and natural products [1]. At present, there is a growing interest in development of new compounds formed by rhodium with chiral ligands due to their high reactivity and excellent selectivity for AHF [2]. However, there is a considerable difficulty in the separation and recycling of the expensive catalysts [3]. Over the last three decades, several elegant approaches have been explored to overcome this limitation including aqueous-organic biphasic catalysis [4] and fluorinated biphasic catalysis [5], thermoregulated phase transfer catalysis [6] and biphasic IL catalysis [7]. However, there are obviously few reports on the asymmetric hydroformylation reaction of olefins, which due to that oil-soluble phosphine ligands are sulfonated into water-soluble ligands is difficult. Therefore, developing an effective

way for catalyst separation and recycle is highly desirable in asymmetric hydroformylation reaction.

Functionalized ionic liquids (FILs) have received wide attention because of their tunable structures and unique properties [8–11]. Notably, transition metal carbonyls as a widely used catalytic active species has been used in FILs, which makes FILs have both catalytic activity and ionic liquid properties. [bmim][Co(CO)₄], [bmim][HFe(CO)₄], [bmim][Mn(CO)₄] and other new ionic liquids with transition metal carbonyl compounds have been investigated by researchers, which were used as solvents and catalysts for the debromination reaction [12–14]. [bmim][Co(CO)₄] ionic liquid have been prepared and used it for hydrogenation reaction, which proved that [bmim][Co(CO)₄] had high catalytic activity and stability [15]. However, π -sing carbonyl cobalt as catalyst has no longer been used on a commercial scale because of several technical disadvantages (high operating pressure and more by-products). The catalytic activity of rhodium is much higher than that of cobalt, so carbonyl rhodium can be used as catalyst. [bmim][Co(CO)₄] are not suitable for AHF of styrene due to styrene have low water solubility. According to the unique advantages of polyether ionic liquids, Jin Xin used room temper-

* Corresponding author.

E-mail addresses: 1256650347@qq.com (K. Wang), 792122699@qq.com (X. Liu), 285867231@qq.com (B. Liu), huagongguozhenmei@163.com (Z. Guo), chaozhangchem@qust.edu.cn (C. Zhang), lvzhiguo@qust.edu.cn (Z. Lv).



Scheme 1. Synthesis of Rh(CO)₄-PolyGILs and AHF of styrene.

ature phosphine-functionalized polyether guanidinium ionic liquids in a homogeneous catalysis-biphasic separation (HCBS) system to demonstrate the Rh-catalyzed hydroformylation of long chain alkenes [16]. This method can simultaneously maintain the high efficiency and achieve easy separation of the homogeneous catalyst. However, this study is based on the modification of phosphine ligands in homogeneous catalyst system, but the modification of chiral ligands in asymmetric reactions is difficult. The main reasons are as follows: first of all, it is difficult to design and synthesize chiral ligands; secondly, the stereoscopic factors and electronic effects of the substituents of chiral ligands have important effects on the chemical selectivity, regional selectivity and stereoselectivity of the asymmetric synthesis reactions [17,18]; finally, it is difficult for the reactive molecules to enter the transition metal catalytic site due to the large volume of the chiral ligands, thereby affecting the catalytic activity [19]. Therefore, if transition metal ionic liquids catalyst is added to ethoxyl to form HCBS system and the chiral ligands to form asymmetric induction effect, the catalyst with high catalytic activity and effective recovery can be expected to achieve.

Here we report on a series of Rh(CO)₄-PolyGILs of [Me(EO)₈TMG][Rh(CO)₄], [Me(EO)₁₆TMG][Rh(CO)₄], [Ph(EO)₈TMG][Rh(CO)₄] and [Ph(EO)₁₆TMG][Rh(CO)₄] employing ion exchange of PolyGILs with KRh(CO)₄ were designed and synthesized. The four above obtained ionic liquids were characterized by infrared (IR), nuclear magnetic resonance (NMR) and elemental analysis to study their chemical structure and purity. Thermo gravimetric analysis (TGA) also showed that Rh(CO)₄-PolyGILs possessed excellent thermal stability. Afterwards, AHF of styrene as a model reaction was used to demonstrate the HCBS system using the four ionic liquids. Under the optimum condition, the conversion, yield and ee were found to be 79, 73.3 and 54%, respectively. The whole process was shown in Scheme 1. After reaction, introduction of n-heptane led to the formation of biphasic system of the ILs/products, which helped in separating catalyst. Notably, the catalyst had great recyclability.

2. Experimental

2.1. Synthesis of K[Rh(CO)₄]

RhCl₃•nH₂O (0.55 g, 2.2 mmol), freshly ground KOH powder (2 g) and tetrahydrofuran (15 mL) were placed in autoclave. After three times of replacement with argon, CO gas was filled to keep the pressure in the reactor at 1.0-2.0 MPa. After 24 h, KCl and unreacted materials were removed by filtration, affording tetrahydrofuran (THF) solution of KRh(CO)₄.

2.2. Synthesis of Rh(CO)₄-PolyGILs

2.2.1. Preparation of [Me(EO)₈TMG][Rh(CO)₄] and its characterization

A 100 mL schlenk flask was charged with K[Rh(CO)₄] (2.54 g, 10 mmol), [Me(EO)₈TMG][CH₃SO₃] (5.37 g, 10 mmol) and 25 mL of degassed THF under Ar atmosphere. The mixture was stirred at 25°C for 2 h and the reaction solution was filtered after the completion of the reaction. Then, the filtrate was evaporated under reduced pressure to obtain dark red-brown viscous ionic liquids with the yield of 85.3%. ¹HNMR (500 MHz, CDCl₃) δ_H = 3.71-3.54 (m, 35H), 3.38 (s, 3H), 3.03 (s, 12H); ¹³CNMR (126 MHz, CDCl₃) δ_C = 162.8, 71.9, 70.5, 69.7, 59.0, 44.8, 39.9. Elemental Analysis C₂₆H₄₈O₁₂N₃Rh₁: Calcd. C 44.76, H 6.93, N 6.02 %. Found C 44.90, H 7.15, N 6.18 %.

2.2.2. Preparation of [Me(EO)₁₆TMG][Rh(CO)₄] and its characterization

A 100 mL schlenk flask was charged with K[Rh(CO)₄] (2.54 g, 10 mmol), [Me(EO)₁₆TMG][CH₃SO₃] (9.29 g, 10 mmol) and 25 mL of degassed THF under Ar atmosphere. The mixture was stirred at 25°C for 2 h and the reaction solution was filtered after the completion of the reaction. Then, the filtrate was evaporated under reduced pressure to obtain dark red-brown viscous ionic liquids with the yield of 79.8%. ¹HNMR (500 MHz, CDCl₃) δ_H = 3.67-

3.65 (m, 67H), 3.38 (s, 3H), 3.03 (s, 12H); ^{13}C NMR (126 MHz, CDCl_3) $\delta_{\text{C}} = 162.0, 71.9, 71.4, 70.6, 59.0, 44.5, 40.0$. Elemental Analysis $\text{C}_{42}\text{H}_{80}\text{O}_{20}\text{N}_3\text{Rh}_1$: Calcd. C 48.04, H 7.67, N 4.00 %. Found C 48.21, H 7.85, N 4.13 %.

2.2.3. Preparation of $[\text{Ph}(\text{EO})_8\text{TMG}][\text{Rh}(\text{CO})_4]$ and its characterization

A 100 mL schlenk flask was charged with $\text{K}[\text{Rh}(\text{CO})_4]$ (2.54 g, 10 mmol), $[\text{Ph}(\text{EO})_8\text{TMG}][\text{CH}_3\text{SO}_3]$ (6.39 g, 10 mmol) and 25 mL of degassed THF under Ar atmosphere. The mixture was stirred at 25°C for 2 h and the reaction solution was filtered after the completion of the reaction. Then, the filtrate was evaporated under reduced pressure to obtain dark red-brown viscous ionic liquids with the yield of 83.2%. ^1H NMR (500 MHz, CDCl_3) $\delta_{\text{H}} = 7.25$ (d, $J = 8.8$ Hz, 3H), 6.82 (d, $J = 8.8$ Hz, 2H), 4.11 (t, $J = 4.7$ Hz, 2H), 3.84 (t, $J = 5.1$ Hz, 2H), 3.76–3.64 (m, 34H), 2.97 (s, 12H); ^{13}C NMR (126 MHz, CDCl_3) $\delta_{\text{C}} = 162.2, 156.3, 142.4, 127.0, 113.7, 71.3, 70.5, 69.8, 44.4, 39.8$. Elemental Analysis $\text{C}_{31}\text{H}_{53}\text{O}_{12}\text{N}_3\text{Rh}_1$: Calcd. C 48.81, H 7.65, N 5.50 %. Found C 48.97, H 7.87, N 5.63 %.

2.2.4. Preparation of $[\text{Ph}(\text{EO})_{16}\text{TMG}][\text{Rh}(\text{CO})_4]$ and its characterization

A 100 mL schlenk flask was charged with $\text{K}[\text{Rh}(\text{CO})_4]$ (2.54 g, 10 mmol), $[\text{Ph}(\text{EO})_{16}\text{TMG}][\text{CH}_3\text{SO}_3]$ (9.91 g, 10 mmol) and 25 mL of degassed THF under Ar atmosphere. The mixture was stirred at 25°C for 2 h and the reaction solution was filtered after the completion of the reaction. Then, the filtrate was evaporation under reduced pressure to obtain dark red-brown viscous ionic liquids with the yield of 81.5%. ^1H NMR (500 MHz, CDCl_3) $\delta_{\text{H}} = 7.26$ (d, $J = 8.8$ Hz, 3H), 6.82 (d, $J = 8.8$ Hz, 2H), 4.11 (t, $J = 4.8$ Hz, 2H), 3.85 (t, $J = 5.0$ Hz, 2H), 3.68–3.64 (m, 66H), 2.97 (s, 12H); ^{13}C NMR (126 MHz, CDCl_3) $\delta_{\text{C}} = 163.3, 156.4, 142.4, 127.0, 113.8, 71.4, 70.6, 69.8, 44.5, 39.8$. Elemental Analysis $\text{C}_{47}\text{H}_{85}\text{O}_{20}\text{N}_3\text{Rh}_1$: Calcd. C 50.62, H 7.68, N 3.76 %. Found C 50.83, H 7.82, N 3.85 %.

2.3. Asymmetric hydroformylation of styrene catalyzed by $[\text{Me}(\text{EO})_{16}\text{TMG}][\text{Rh}((R)\text{-BINAP})(\text{CO})_2]$

Under Ar atmosphere, $[\text{Me}(\text{EO})_{16}\text{TMG}][\text{Rh}(\text{CO})_4]$, (R)-BINAP, styrene and solvent were charged into the autoclave. The autoclave was sealed and replaced with Ar and CO for 3 times in the same sequence. Then, the autoclave was pressurized with syngas ($\text{CO}:\text{H}_2 = 1:1$) and was maintained at the specified temperature for 4 h. Then, the reactor was cooled to room temperature. After releasing the gas, certain amount of the product was taken out for GC analysis and spectrophotometric determination (conversion of styrene, yield, ee). Next, n-heptane was added to the autoclave to extract the alkene and the aldehyde, and the upper heptane layer was decanted, after which fresh styrene was added to the catalyst present in the lower layer for the next cycle.

2.4. The determination of conversion, yield and ee

Conversion = (converted styrene)/(unconverted styrene + converted styrene) $\times 100\%$, the conversion rate of styrene was determined on GC with a SE-30 MS capillary column.

2-phenylpropionaldehyde selectivity = 2-phenylpropionaldehyde/(benzenepropanal + 2-phenylpropionaldehyde).

Yield = Conversion \times 2-phenylpropionaldehyde selectivity.

l/b is the ratio of benzenepropanal to 2-phenylpropionaldehyde.

The ee of (S)-2-phenylpropionaldehyde was determined by automatic polarizer. The standard conditions of the product were as follows: solvent chloroform, temperature 25°C, and standard value was +192.

The formula of ee:

$$[\alpha]_{\text{D}}^{\text{t}} = \frac{\alpha}{\text{L} \cdot \text{C}}$$

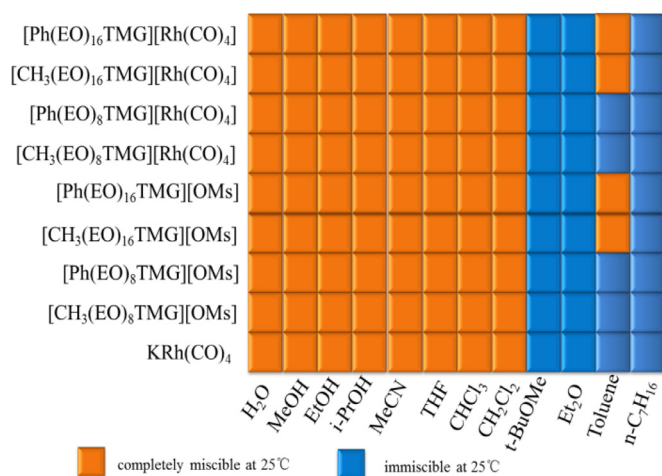


Fig. 1. Solubility of $\text{Rh}(\text{CO})_4$ -PolyGILs in solvents of different polarity.

$$ee = \frac{[\alpha]_{\text{D}}^{\text{t}}}{[\alpha]_{\text{D}}^{\text{t}}_{\text{standard}}} \times 100\%$$

3. Results and discussion

3.1. Solubility of $\text{Rh}(\text{CO})_4$ -PolyGILs

Whether the $\text{Rh}(\text{CO})_4$ -PolyGILs would form homogeneous or biphasic system was dependent on the solubility of $\text{Rh}(\text{CO})_4$ -PolyGILs in various solvents. Fig. 1 showed the solubility of $\text{Rh}(\text{CO})_4$ -PolyGILs in various solvents of different polarity. Complete solubility of the PolyGILs was observed in polar solvents (H_2O , MeOH, EtOH and i-PrOH) and some weakly polar solvents (CHCl_3 and CH_2Cl_2), but in the non-polar solvents ($n\text{-C}_7\text{H}_{16}$) they were immiscible indicating the presence of ionic bond in the PolyGILs. Identical solubility behavior was observed for the $\text{Rh}(\text{CO})_4$ -PolyGIL. This indicated the possibility of using polar solvent as the reaction medium, and non-polar solvent as the extraction medium. These results laid significant foundation for constructing the HCBS system.

3.2. Thermal stability of $\text{Rh}(\text{CO})_4$ -PolyGILs

Taking $[\text{Me}(\text{EO})_{16}\text{TMG}][\text{Rh}(\text{CO})_4]$ as an example, the thermal stability of $\text{Rh}(\text{CO})_4$ -PolyGILs were studied and the result was shown in Fig. 2. The temperature range used for the analysis was from room temperature to 600°C. The first weight loss of about 8% occurred in the temperature range of 35–150°C, due to evaporation of the water confined in the $\text{Rh}(\text{CO})_4$ -PolyGILs and thermal dissociation of carbonyl compounds. Under the low CO partial pressure and high temperature conditions, the carbonyl rhodium may be decomposed to release CO. The major weight loss of about 80% occurred between 150–360°C and could be attributed to the thermal decomposition of the polyether long chains of $\text{Rh}(\text{CO})_4$ -PolyGILs. This result indicated an initial decomposition temperature of 150°C for $[\text{Me}(\text{EO})_{16}\text{TMG}][\text{Rh}(\text{CO})_4]$. Since the reaction temperature of AHF is generally below 100°C, $\text{Rh}(\text{CO})_4$ -PolyGILs met the requirements of AHF.

3.3. Infrared study of $\text{Rh}(\text{CO})_4$ -PolyGILs

FT-IR spectrum of (A) $[\text{Me}(\text{EO})_8\text{TMG}][\text{CH}_3\text{SO}_3]$, (B) $\text{K}[\text{Rh}(\text{CO})_4]$ in THF solution and (C) $[\text{Me}(\text{EO})_8\text{TMG}][\text{Rh}(\text{CO})_4]$ were depicted in Fig. 3. The absorption band at around 2877 cm^{-1} could be

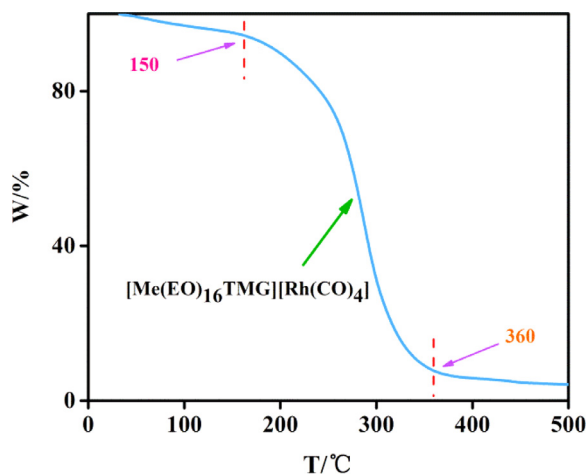


Fig. 2. TG curves of $\text{Rh}(\text{CO})_4$ -PolyGILs.

attributed to the C-H stretching vibration of OCH_2CH_2 in the polyether chains [20]. The carbonyl absorption peak at 1996 cm^{-1} for $\text{K}[\text{Rh}(\text{CO})_4]$ was replaced by new absorption peak at 1976 cm^{-1} for $\text{Rh}(\text{CO})_4$ -PolyGILs [21]. The C=N stretching vibration at 1610 cm^{-1} , represented the presence of tetramethylguanidine [22]. The adsorption band at 1120 cm^{-1} could be attributed to the characteristic peaks of OCH_2CH_2 [20]. These above FT-IR results demonstrated that the $\text{Rh}(\text{CO})_4$ -PolyGILs were successfully synthesized.

3.4. Melting point and viscosity of $\text{Rh}(\text{CO})_4$ -PolyGILs

Ionic liquids are considered as a class of salts that exist as a liquid at room temperature and are composed entirely of anions and cations [23]. At room temperature, the physical state of $\text{Rh}(\text{CO})_4$ -PolyGILs was liquid and hence they could be classified as ionic liquids. The viscosity of $\text{Rh}(\text{CO})_4$ -PolyGILs was also high due to the existence of interionic hydrogen bonds [24]. However, the $\text{Rh}(\text{CO})_4$ -PolyGILs exhibited good fluidity in comparison to the with the traditional ionic liquids containing BF_4^- and PF_6^- as anions. This may be due to the fact that the conventional ionic liquids containing BF_4^- and PF_6^- as anions have two-layer atomic structure, while the ionic liquids synthesized in this article have three-layer atomic structure [25]. In addition, cation also affects the viscosity of ionic liquids in a significant manner. Generally, the introduction of polyether chain reduces the viscosity of the original ionic liquids. However, with the growth of polyether chain, the viscosity of ionic liquids also increases due to the increase of van der Waals forces.

Table 1

Effect of P/Rh molar ratio on AHF of styrene.^a

| P/Rh | Conversion (%) | Yield (%) | b/l | ee(%S) |
|------|----------------|-----------|-------|--------|
| 2 | 47.15 | 35.56 | 7.97 | 34 |
| 4 | 84.21 | 50.34 | 11.60 | 46 |
| 6 | 76.83 | 43.81 | 10.97 | 45 |
| 8 | 77.42 | 43.63 | 10.09 | 44 |
| 10 | 38.87 | 33.56 | 6.48 | 38 |

^a Reaction conditions: styrene, 1.0 g; Substrate/Catalyst = 2000:1; reaction time, 4 h; $T = 60^\circ\text{C}$; syngas ($\text{CO}:\text{H}_2 = 1:1$) pressure, 2.0 MPa; Solvent, toluene; (R)-BINAP as ligand; The catalyst was $[\text{CH}_3(\text{EO})_{16}\text{TMG}][\text{Rh}(\text{CO})_4]$.

3.5. Single factor exploration experiment

3.5.1. Effect of P/Rh molar ratio

Effect of P/Rh molar ratio was studied to investigate the optimized quantity of chiral ligands bond to $\text{Rh}(\text{CO})_4$ -PolyGILs (Table 1). When the molar ratio of P/Rh was 2, the catalyst exhibited poor activity. With increasing molar ratio of P/Rh from 2 to 4, conversion, yield and ee increased significantly. Further increase of the P/Rh molar ratio caused a decrease in conversion, yield and ee. In general, reactions catalyzed by Rh complexes require an excess of chiral ligands in order to prevent the formation of $[\text{HRh}(\text{CO})_4]$. $[\text{HRh}(\text{CO})_4]$ has been used as an active achiral hydroformylation catalyst for the production of racemic aldehydes [26]. A large amount of chiral ligands was conducive to the formation of catalytic active substances containing chiral bisphosphines, which also improved ee of 2-phenylpropanal. However, large steric hindrance led to a decrease in the catalytic activity and selectivity to 2-phenylpropanal. Therefore, P/Rh molar ratio of 4 was found to be the optimized value and was used in the subsequent experiments for AHF.

3.5.2. Effects of temperature, syngas pressure and reaction time

The effects of various reaction parameters including temperature, syngas pressure and reaction time on AHF were studied and the results were depicted in Table 2. We first studied the effect of reaction temperature and found that increase of temperature to 80°C led to lower enantiomeric excess, but when the temperature was decreased to 50°C , the conversion was dramatically reduced to only 69.37%. One of the most important criteria for AHF to take place is the dissociation of CO from the metal center which required high reaction temperature [27]. Unfortunately, at elevated temperature the chiral aldehydes undergo racemization, which due to that amount of the chiral stable conformation varied with temperature. Based on the conversion, yield and ee, an optimal temperature of 60°C was chosen. The syngas pressure also influenced reaction activity. Apparently, the low pressure had a certain resistance to reaction activity, however, too high reaction pressure also led to the production of more by-products such as ethyl benzene.

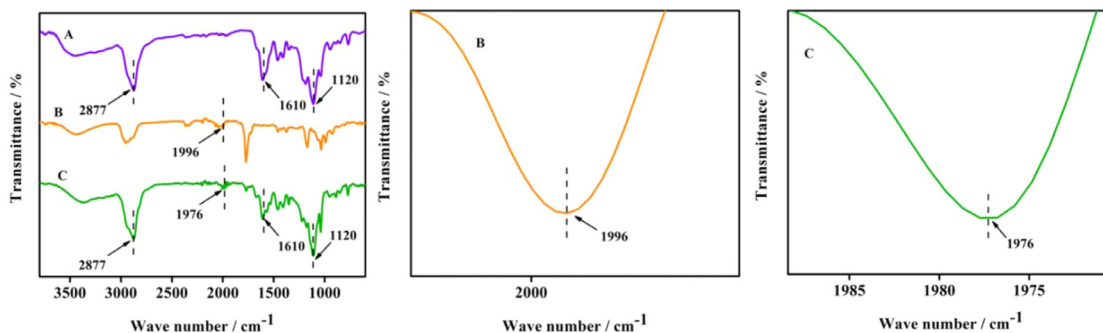


Fig. 3. FT-IR spectra of (A) $[\text{Me}(\text{EO})_8\text{TMG}][\text{CH}_3\text{SO}_3]$, (B) $\text{K}[\text{Rh}(\text{CO})_4]$ in THF solution and (C) $[\text{Me}(\text{EO})_8\text{TMG}][\text{Rh}(\text{CO})_4]$.

Table 2
Effects of temperature, syngas pressure and reaction time on AHF.^a

| T (°C) | P(MPa) | t(h) | Conversion(%) | Yield(%) | b/l | ee(%S) |
|--------|--------|------|---------------|----------|-------|--------|
| 50 | 2 | 4 | 69.37 | 33.11 | 3.14 | 25 |
| 60 | 2 | 4 | 84.21 | 50.34 | 11.60 | 46 |
| 70 | 2 | 4 | 87.03 | 47.21 | 10.41 | 32 |
| 80 | 2 | 4 | 83.11 | 51.07 | 4.88 | 21 |
| 60 | 1 | 4 | 42.04 | 22.34 | 7.75 | 20 |
| 60 | 3 | 4 | 73.06 | 38.67 | 14.31 | 31 |
| 60 | 2 | 2 | 65.55 | 33.07 | 1.28 | 27 |
| 60 | 2 | 3 | 80.57 | 37.24 | 7.97 | 32 |
| 60 | 2 | 5 | 85.1 | 53.2 | 11.15 | 42 |

^a Reaction conditions: styrene, 1.0 g; Substrate/Catalyst = 2000:1; P/Rh = 4; Solvent, toluene; (R)-BINAP as ligand; The catalyst is $[\text{CH}_3(\text{EO})_{16}\text{TMG}][\text{Rh}(\text{CO})_4]$.

Table 3
Effect of catalyst dosage on AHF.^a

| Rh/S | Conversion(%) | Yield (%) | b/l | ee(%S) |
|--------|---------------|-----------|-------|--------|
| 1/2500 | 76.45 | 46.01 | 6.35 | 33 |
| 1/2000 | 84.21 | 50.34 | 11.60 | 46 |
| 1/1500 | 83.25 | 41.05 | 15.02 | 36 |
| 1/1000 | 89.10 | 43.11 | 17.76 | 34 |

^a Reaction conditions: styrene, 1.0 g; P/Rh = 4; reaction time, 4 h; T = 60°C; syngas (CO:H₂ = 1:1) pressure, 2.0 MPa; Solvent, toluene; (R)-BINAP as ligand; The catalyst was $[\text{CH}_3(\text{EO})_{16}\text{TMG}][\text{Rh}(\text{CO})_4]$.

Table 4
Effects of solvent on the asymmetric hydroformylation of styrene.^a

| Solvent | Conversion (%) | Yield (%) | b/l | ee(%S) |
|---------|----------------|-----------|-------|--------|
| MeOH | 79.00 | 73.30 | 14.16 | 54 |
| Toluene | 84.21 | 50.34 | 11.60 | 46 |
| THF | 37.05 | 31.11 | 10.90 | 24 |
| CYH | 10.58 | 8.86 | 5.57 | 10 |

^a Reaction conditions: styrene, 1.0 g; Substrate/Catalyst = 2000:1; P/Rh = 4; reaction time, 4 h; T = 60°C; syngas (CO:H₂ = 1:1) pressure, 2.0 MPa; (R)-BINAP as ligand; The catalyst was $[\text{CH}_3(\text{EO})_{16}\text{TMG}][\text{Rh}(\text{CO})_4]$.

In addition to reaction temperature and syngas pressure, the time of reaction was also varied. The results showed that conversion, yield and ee gradually increased with increasing reaction time in the time range of 2–4 h. However, slight decrease of ee was observed with further extension of the reaction time. Too short reaction time (< 3 h) led to incomplete conversion, and, too long reaction time (> 4 h) led to product racemization. After comprehensive consideration, 4 h was chosen as the optimal reaction time.

3.5.3. Effect of catalyst dosage

The effect of catalyst dosage on the conversion, yield and ee was studied. As evident from Table 3, for Rh/S range of 1/2500–1/2000, there was gradual increase of the conversion, yield and ee. Then, with further increase of Rh/S from 1/2000 to 1/1000, similar conversion was achieved but the yield and the ee for 2-phenylpropionaldehyde decreased linearly. Excessive catalyst dosage led to accelerated hydrogenation step and resulted in the occurrence of phenyl ethane. Excessive catalyst dosage also caused the formation of achiral catalyst $[\text{HRh}(\text{CO})_4]$, which led to the decrease of ee [26].

3.5.4. Catalytic performance of $\text{Rh}(\text{CO})_4$ -PolyGILs in various solvents

The effect of solvent on the conversion, yield and ee under identical conditions were shown in Table 4. Increasing conversion, yield and ee were observed in MeOH as solvent which may be due to the temporary ligand coordination of MeOH with the Rh center promoting the catalytic cycle. Compared to the MeOH, yield and ee

Table 5
Effects of cationic structure of $\text{Rh}(\text{CO})_4$ -PolyGILs on AHF.^a

| ILs | Conversion (%) | Yield (%) | b/l | ee(%S) |
|---|----------------|-----------|-------|--------|
| $[\text{CH}_3(\text{EO})_8\text{TMG}][\text{Rh}(\text{CO})_4]$ | 80.03 | 72.81 | 14.07 | 53 |
| $[\text{CH}_3(\text{EO})_{16}\text{TMG}][\text{Rh}(\text{CO})_4]$ | 79.11 | 73.30 | 14.16 | 54 |
| $[\text{Ph}(\text{EO})_8\text{TMG}][\text{Rh}(\text{CO})_4]$ | 83.56 | 74.63 | 14.21 | 55 |
| $[\text{Ph}(\text{EO})_{16}\text{TMG}][\text{Rh}(\text{CO})_4]$ | 78.33 | 72.20 | 14.03 | 54 |

^a Reaction conditions: styrene, 1.0 g; Substrate/Catalyst = 2000:1; P/Rh = 4; reaction time, 4 h; T = 60°C; syngas (CO:H₂ = 1:1) pressure, 2.0 MPa; Solvent, CH₃OH; (R)-BINAP as ligand; The catalyst is $[\text{CH}_3(\text{EO})_{16}\text{TMG}][\text{Rh}(\text{CO})_4]$.

were rather low in toluene. It might be due to the incomplete dissolution of the hydrophilic polyether chains of $\text{Rh}(\text{CO})_4$ -PolyGILs in toluene which resulted in a micelle-like structure around Rh, and thus inhibiting the activity of Rh. Conversion, yield and ee significantly reduced when the reaction was carried out in non-polar THF and cyclohexane (CYH). This might be due to the fact that the system changed from monophasic to biphasic.

3.5.5. Catalytic performance of $\text{Rh}(\text{CO})_4$ -PolyGILs

Under optimized reaction conditions, the cationic structure of the $\text{Rh}(\text{CO})_4$ -PolyGILs catalysts was varied to investigate the effect of cations on the AHF. It was clearly observed from Table 5, that the cationic structure of $\text{Rh}(\text{CO})_4$ -PolyGILs had no significant effect on the conversion, yield and ee. The reaction rate was related only to the $[\text{Rh}(\text{CO})_4]^+$, but not to the cationic part, which was proved from kinetics of homogeneous catalytic reaction.

3.6. HCBS system and recycling efficiency of catalyst

Schematic demonstration of the catalytic process in HCBS system was shown in Fig. 4. Firstly, $\text{Rh}(\text{CO})_4$ -PolyGILs, (R)-BINAP and styrene were mixed with a certain volume of CH₃OH. The AHF was carried out homogeneously at 60 °C. After completion of the reaction, the system was cooled down to 25 °C. Then, vacuum distillation was used to evaporate CH₃OH followed by the subsequent addition of n-heptane to the system. At room temperature, catalyst containing Rh/(R)-BINAP compounds was insoluble in the upper layer of n-heptane containing the product. Hence, the catalyst could be recovered by simple phase separation. The separated catalyst could then be reused four times without any significant loss of activity (Fig. 5). The results from ICP analysis showed that after four cycles, in the n-heptane phase the content of Rh and P was less than 1% and 2.5%, respectively. And though after five cycles, the Rh content of n-heptane phase was still less than 1%, the P content increased to 5.6%. This result indicated that the binding force between phosphine ligand and ionic liquids was weakened after the catalyst was used repeatedly for 4 times, resulting phosphine ligand cannot be firmly grafted into the ionic liquids structure. The binding force between phosphine and ionic liquid weakened after 4 runs, it might be due to that the oxidation of (R)-BINAP caused the decomposition of $[\text{Me}(\text{EO})_{16}\text{TMG}][\text{Rh}(\text{R})\text{-BINAP}](\text{CO})_2]$. A similar conclusion was also reported in previous literature [28] Fig. 6.

Reaction conditions: styrene, 1.0 g; Substrate/Rh = 2000:1; P/Rh = 4; reaction time, 4 h; T = 60°C; syngas (CO:H₂ = 1:1) pressure, 2.0 MPa; Solvent, CH₃OH; (R)-BINAP as ligand.

3.7. Comparison of the $\text{Rh}(\text{CO})_4$ -PolyGILs with some classic catalyst for AHF

Table 6 compared our catalyst with some classic catalyst. It could be found rhodium catalysts were more active than platinum (entry 1, Table 6). Furthermore, most Pt-catalysts were active at

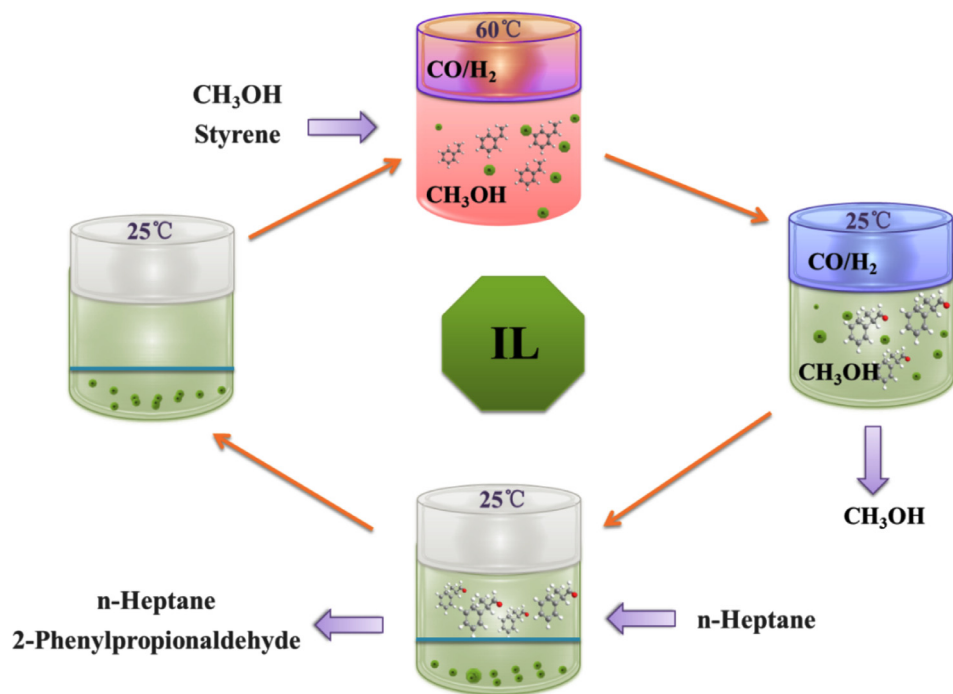


Fig. 4. HCBS system for AHF.

Table 6
Comparison of the $[\text{Me}(\text{EO})_{16}\text{TMG}][\text{Rh}(\text{CO})_4]$ with some classic catalyst for AHF of styrene.

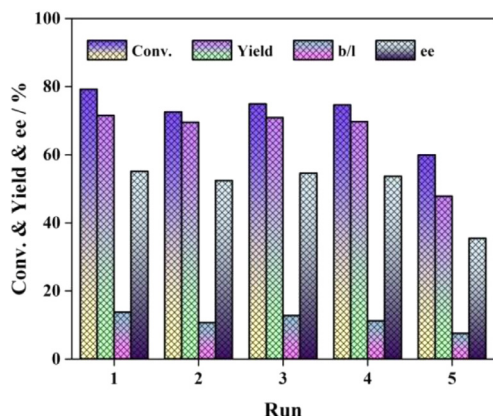
| Entry | Catalyst | Ligand | Conversion(%) | Yield (%) | ee | Recycling number | Ref |
|----------------|---|------------|---------------|-----------|------|------------------|-----|
| 1 ^a | $\text{PtCl}_2[(S)\text{-BINAP}]/\text{SnCl}_2$ | (S)-BINAP | 37 | 12 | 68.8 | 0 | 29 |
| 2 ^b | $\text{Rh}(\text{acac})(\text{CO})_2$ | S(-)-BINAS | 92 | none | 18 | none | 30 |
| 3 ^c | $\text{Rh}(\text{acac})(\text{CO})_2$ | (R)-BINAP | 79 | none | 21.6 | 2 | 31 |
| 4 ^d | $[\text{Me}(\text{EO})_{16}\text{TMG}][\text{Rh}(\text{CO})_4]$ | (R)-BINAP | 79 | 73.3 | 54 | 4 | |

^a Reaction conditions: 35 mL toluene; 0.1 mol styrene; Pt/S = 1/2000; $p(\text{CO}) = p(\text{H}_2) = 40$ bar; $T = 60^\circ\text{C}$.

^b Reaction conditions: substrate/catalyst = 300/1; L/Rh = 4; $p = 100$ bar; $T = 40^\circ\text{C}$.

^c Reaction conditions: ligand/Rh = 1.5 (molar ratio); $\text{Rh}(\text{acac})(\text{CO})_2 = 0.02$ mmol; olefin/Rh = 300 (molar ratio); $\text{CO}/\text{H}_2 = 1$ (molar ratio); pressure = 2.0 MPa; temperature = 333 K.

^d Reaction conditions: styrene, 1.0 g; Substrate/Rh = 2000:1; P/Rh = 4; reaction time, 4 h; $T = 60^\circ\text{C}$; syngas ($\text{CO}:\text{H}_2 = 1:1$) pressure, 2.0 MPa; Solvent, CH_3OH .

Fig. 5. Recycling efficiency of $[\text{CH}_3(\text{EO})_{16}\text{TMG}][\text{Rh}(\text{CO})_4]$ in AHF.

a high pressure, whereas Rh-catalysts exhibited an excellent catalytic activity even at low pressure [29]. The two-phase asymmetric hydroformylation of styrene provided 92% conversion and 18% ee with $\text{Rh}(\text{acac})(\text{CO})_2$ and S(-)-BINAS served as catalyst [30]. The complexes (R)-BINAP-Rh in $\text{BMI}\cdot\text{BF}_4$ -toluene induced 21.6% ee

[31]. The recycling ability of the biphasic asymmetric hydroformylation was better than that of the conventional single-phase (organic solvent) technique, but correspondingly optical yields were lower. From these comparisons, it is found that our catalyst is far superior in catalytic activity and recycling ability. Thus far, the current results remain unparalleled by any existing literature reports.

3.8. Reaction mechanism

For the challenging AHF reaction, the stereochemistry of the reaction products is controlled by the chiral ligands. We employed DFT simulated calculation to further analyze the active species $\text{Rh}[(R)\text{-BINAP}]\text{H}(\text{CO})_2$. After geometric optimization, the system structure energy could reach the minimum (-9460.83 eV). According to the structure of $\text{Rh}[(R)\text{-BINAP}]\text{H}(\text{CO})_2$, the Ph substituent of (R)-BINAP provides a chiral pocket. The closed rigid chiral pocket could lead to better enantioselectivities.

Since Breslow and Heck proposed a conceivable mechanism of hydroformylation in the early 1960s [32], the so-called dissociative mechanism has been theoretically and experimentally investigated intensively in the literature [33-36]. We also adopted the dissociative mechanism in this study. As shown in Scheme 2, blue, orange, and green lines represent the pathways of production of R, S, and linear aldehydes, respectively. The catalytic process includes

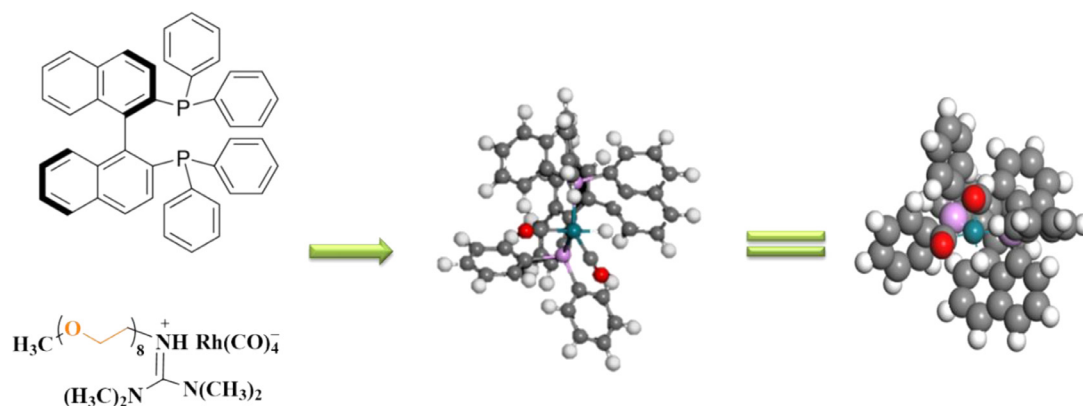
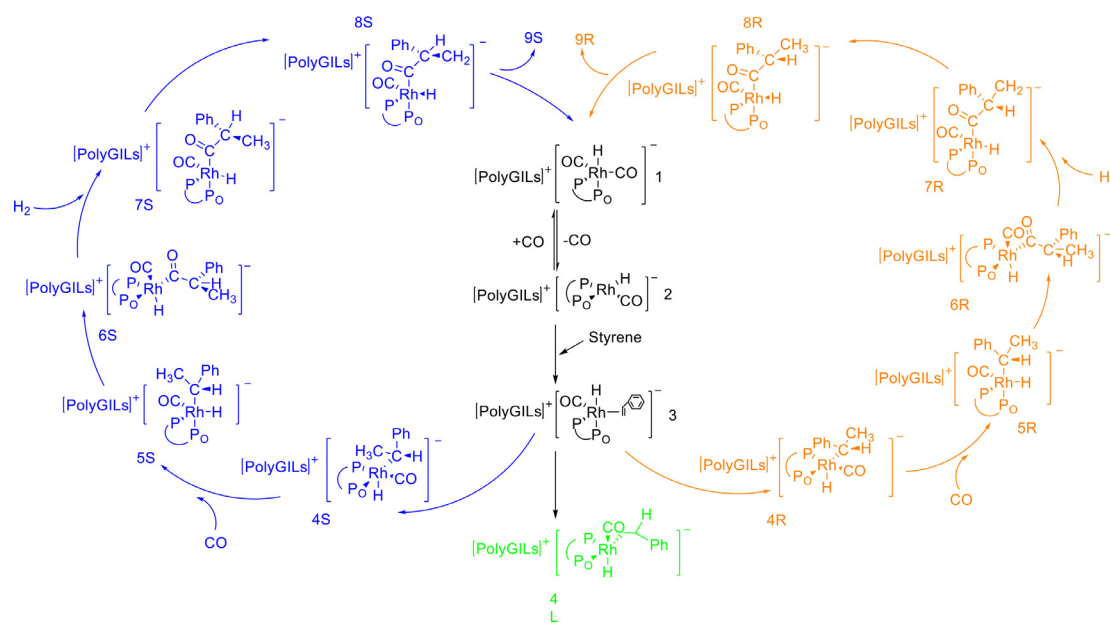


Fig. 6. Space-filling model for $[\text{Me}(\text{EO})_{16}\text{TMG}][\text{Rh}[(R)\text{-BINAP}](\text{CO})_2]$ based on DFT calculation.^a ^a H denotes $[\text{Me}(\text{EO})_{16}\text{TMG}]^+$



Scheme 2. Mechanism of AHF.

four pivotal steps: styrene insertion (3 → 4), CO insertion (5 → 6), H_2 oxidative addition (6 → 8), and aldehyde reductive elimination (8 → 2).

4. Conclusion

In conclusion, novel ionic liquids including $[\text{Me}(\text{EO})_8\text{TMG}][\text{Rh}(\text{CO})_4]$, $[\text{Me}(\text{EO})_{16}\text{TMG}][\text{Rh}(\text{CO})_4]$, $[\text{Ph}(\text{EO})_8\text{TMG}][\text{Rh}(\text{CO})_4]$, $[\text{Ph}(\text{EO})_{16}\text{TMG}][\text{Rh}(\text{CO})_4]$ have been successfully synthesized via ion exchange strategy. These ionic liquids had higher stability compared with the previously reported analogues, which may be due to that interionic bonds and the structure of the polyether chain. Based on solubility property of the $\text{Rh}(\text{CO})_4$ -PolyGILs, HCBS system was established for AHF. The best achieved conversion was 79%, with 73.3% yield and ee 54%. The conversion varied from 79% to 76% and ee varied from 54% to 52%, respectively, at the first and fourth run, indicating that the HCBS catalytic system was stable and easy recoverable. Furthermore, DFT calculation showed the structure energy of $\text{Rh}[(R)\text{-BINAP}]\text{H}(\text{CO})_2$ could reach the minimum of -9460.83 eV. Lastly, we proposed a conceivable mechanism of AHF according to dissociative mechanism and DFT results.

Declaration of Competing Interest

None.

Acknowledgments

This work was supported by grant from the Natural Science Foundation of National (NSFC21978141), the China Postdoctoral Science Foundation funded project (2020M672015), the Open Project of Guangxi Key Laboratory of Petrochemical Resource Processing and Process Intensification Technology (2020K007), the Open Project of Nankai University Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), the Open Project of Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education (KFJJ2021009), and Qingdao Postdoctoral Applied Research Program.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2021.121931](https://doi.org/10.1016/j.jorganchem.2021.121931).

References

- [1] R. Franke, D. Selent, A. Börner, Applied hydroformylation, *Chem. Rev.* 112 (2012) 5675–5732.
- [2] A. Zapf, Homogeneous catalysis. Understanding the art. By Piet W. N. M. van Leeuwen, *Angew. Chem. Int. Ed.* 44 (2005) 1295–1295.
- [3] J.M. Hawkins, T.J.N. Watson, Asymmetric catalysis in the pharmaceutical industry, *Angew. Chem. Int. Ed.* 43 (2004) 3224–3228.
- [4] D. Wu, J. Zhang, Y. Wang, J. Jiang, Z. Jin, Aqueous/organic biphasic hydroformylation of 1-octene catalyzed by $\text{Co}_2(\text{CO})_8/\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{Me}$, *Appl. Organomet. Chem.* 26 (2012) 718–721.
- [5] T. Mathivet, E. Monflier, Y. Castanet, A. Mortreux, J.-L. Couturier, Hydroformylation of higher olefins by rhodium/tris-((1H,1H,2H,2H-perfluorodecyl)phenyl)phosphites complexes in a fluorocarbon/hydrocarbon biphasic medium: effects of fluorinated groups on the activity and stability of the catalytic system, *Tetrahedron* 58 (2002) 3877–3888.
- [6] T. Terashima, M. Ouchi, T. Ando, M. Sawamoto, Thermoregulated phase-transfer catalysis via PEG-armed Ru(II)-bearing microgel core star polymers: Efficient and reusable Ru(II) catalysts for aqueous transfer hydrogenation of ketones, *J. Polym. Sci., Part A: Polym. Chem.* 48 (2010) 373–379.
- [7] H.F. Ramalho, K.M.C. di Ferreira, P.M.A. Machado, R.S. Oliveira, L.P. Silva, M.J. Prauchner, P.A.Z. Suarez, Biphasic hydroformylation of soybean biodiesel using a rhodium complex dissolved in ionic liquid, *Ind. Crops Prod.* 52 (2014) 211–218.
- [8] J. Huddleston, R.Swatloski Willauer, R.Rogers Visser, Room temperature ionic liquids as novel media for 'clean' liquid-liquid extraction, *Chem. Commun.* 16 (1998) 1765–1766.
- [9] K.S. Egorova, E.G. Gordeev, V.P. Ananikov, Biological activity of ionic liquids and their application in pharmaceuticals and medicine, *Chem. Rev.* 117 (2017) 7132–7189.
- [10] Z. Lei, B. Chen, Y.M. Koo, D.R. Macfarlane, Introduction: Ionic liquids, *Chem. Rev.* 117 (2017) 6633–6635.
- [11] C. Dai, J. Zhang, C. Huang, Z. Lei, Ionic liquids in selective oxidation: catalysts and solvents, *Chem. Rev.* 117 (2017) 6929–6983.
- [12] R. Brown, P. Dyson, D. Ellis, T. Welton, 1-butyl-3-methylimidazolium cobalt tetracarbonyl [bmim][Co(CO)₄]: A catalytically active organometallic ionic liquid, *Chem. Commun.* 18 (2001) 1862–1863.
- [13] T.J. Geldbach, P.J. Dyson, A versatile ruthenium precursor for biphasic catalysis and its application in ionic liquid biphasic transfer hydrogenation: Conventional vs task-specific catalysts, *J. Am. Chem. Soc.* 126 (2004) 8114–8115.
- [14] T.J. Geldbach, G. Laurenczy, R. Scopelliti, P.J. Dyson, Synthesis of imidazolium-tethered ruthenium(II)-arene complexes and their application in biphasic catalysis, *Organometallics* 25 (2006) 733–742.
- [15] Z. Guo, H. Wang, Z. Lv, Z. Wang, T. Nie, W. Zhang, Catalytic performance of [Bmim][Co(CO)₄] functional ionic liquids for preparation of 1,3-propanediol by coupling of hydroesterification-hydrogenation from ethylene oxide, *J. Organomet. Chem.* 696 (2011) 3668–3672.
- [16] X. Jin, J. Feng, H. Song, J. Yao, Q. Ma, M. Zhang, C. Yu, S. Li, S. Yu, Integration of phosphine ligands and ionic liquids both in structure and properties—a new strategy for separation, recovery, and recycling of homogeneous catalyst, *Green Chem* 21 (2019) 3583–3596.
- [17] R. Gómez Arrayás, J. Adrio, J.C. Carretero, Recent applications of chiral ferrocene ligands in asymmetric catalysis, *Angew. Chem. Int. Ed.* 45 (2006) 7674–7715.
- [18] S.P. Flanagan, P.J. Guiry, Substituent electronic effects in chiral ligands for asymmetric catalysis, *J. Organomet. Chem.* 691 (2006) 2125–2154.
- [19] S. Liu, C. Xie, S. Yu, F. Liu, Z. Song, Hydrogenation of 2-Ethylhexenal using thermoregulated phase-transfer catalyst for production of 2-Ethylhexanol, *Ind. Eng. Chem. Res.* 50 (2015) 2478–2481.
- [20] Z. Lv, Y. Jiang, C. Zhou, Z. Guo, X. Ma, Q. Chen, T. Nie, H. Song, Synthesis and evaluation of stable, efficient, and recyclable carbonylation catalysts: Polyether-substituted imidazolium carbonyl cobalt ionic liquids, *J. Mol. Catal. A: Chem.* 415 (2016) 89–95.
- [21] X. Zheng, C. Liu, In-situ infrared spectroscopy of Rh/TPPTS and Rh/PPH₃ catalysts in syngas, *J. Catal.* 18 (1997) 447–448.
- [22] N. Fattahi, A. Ramazani, H. Ahankar, P.A. Asiabi, V. Kinzhybalov, Tetramethylguanidine-functionalized Fe₃O₄/chloro-silane core-shell nanoparticles: An efficient heterogeneous and reusable organocatalyst for aldol reaction, *Silicon* 11 (2019) 1441–1450.
- [23] K.R. Seddon, Ionic liquids for clean technology, *J. Chem. Technol. Biotechnol.* 68 (1997) 351–356.
- [24] O.O. Okoturo, T.J. VanderNoot, Temperature dependence of viscosity for room temperature ionic liquids, *J. Electroanal. Chem.* 568 (2004) 167–181.
- [25] F.G. Deng, B. Hu, W. Sun, J. Chen, C.G. Xia, Novel pyridinium based cobalt carbonyl ionic liquids: Synthesis, full characterization, crystal structure and application in catalysis, *Dalton Trans* 38 (2007) 4262–4267.
- [26] A. Muhammad, M.I. Abdul Mutalib, T. Murugesan, Z. Man, A. Bustam, Density and viscosity estimation of 1-hexyl-3-methyl imidazolium based ionic liquids with [BF₄] and [PF₆] anions at high pressures, *J. Appl. Sci.* 11 (2011) 2452–2455.
- [27] C. Chen, X.Q. Dong, X. Zhang, Chiral ligands for rhodium-catalyzed asymmetric hydroformylation: A personal account, *Chem. Rec.* 16 (2016) 2674–2686.
- [28] Q. Lin, W. Jiang, H. Fu, H. Chen, X. Li, Hydroformylation of higher olefin in halogen-free ionic liquids catalyzed by water-soluble rhodium-phosphine complexes, *Appl. Catal. A-Gen.* 328 (2007) 83–87.
- [29] L. Kollár, P. Sándor, G. Szalontai, Temperature dependence of the enantioselective hydroformylation with PtCl₂[(S)-BINAP] + SnCl₂ catalyst and the dynamic NMR study of the catalytic precursor, *J. Mol. Catal.* 67 (1991) 191–198.
- [30] R.W. Eckl, T. Priermeier, W.A. Herrmann, IX. 1Mono- and biphasic asymmetric hydroformylation with rhodium catalysts of the diphosphine ligand NAPHOS and its sulfonated derivatives, *J. Organomet. Chem.* 532 (1997) 243–249.
- [31] C. Deng, G. Ou, J. She, Y. Yuan, Biphasic asymmetric hydroformylation and hydrogenation by water-soluble rhodium and ruthenium complexes of sulfonated (R)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl in ionic liquids, *J. Mol. Catal. A-Chem.* 270 (2007) 76–82.
- [32] R.F. Heck, D.S. Breslow, The reaction of cobalt hydrotetracarbonyl with olefins, *J. Am. Chem. Soc.* 83 (1961) 4023–4027.
- [33] X. Zhang, B. Cao, Y. Yan, S. Yu, B. Ji, X. Zhang, Synthesis and application of modular phosphine-phosphoramidite ligands in asymmetric hydroformylation: Structure-selectivity relationship, *Chem.-Eur. J.* 16 (2010) 871–877.
- [34] D. Evans, G. Yagupsky, G. Wilkinson, The reaction of hydridocarbonyltris(triphenylphosphine) rhodium with carbon monoxide, and of the reaction products, hydridodicarbonylbis(triphenylphosphine) rhodium and dimeric species, with hydrogen, *J. Chem. Soc. A* 90 (1968) 2660–2665.
- [35] C.K. Brown, G. Wilkinson, Homogeneous hydroformylation of alkenes with hydridocarbonyltris(triphenylphosphine)rhodium(I) as catalyst, *J. Chem. Soc. A* 17 (1970) 2753–2764.
- [36] D. Evans, J.A. Osborn, G. Wilkinson, Hydroformylation of alkenes by use of rhodium complex catalysts, *J. Chem. Soc. A.* (1968) 3133–3142 0.