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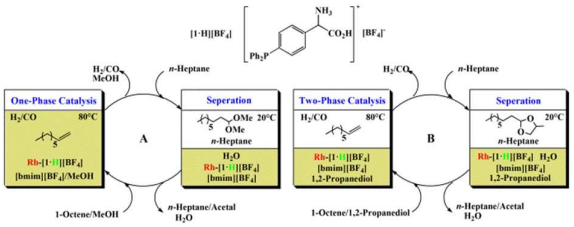

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PAPER

Highly effective tandem hydroformylation-acetalization of olefins using a long-life Brønsted acid-Rh bifunctional catalyst in ionic liquid/alcohol systems

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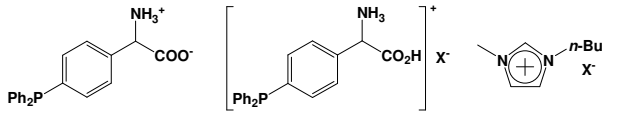
A robust and highly effective tandem hydroformylation-acetalization of olefins using a Brønsted acid-Rh bifunctional catalyst (ARBC) in ionic liquid/alcohol systems is reported. The key feature of the ARBC is its use of a zwitterionic phosphine ligand bearing an amino acid tag. This novel ARBC shows excellent catalytic efficiency and long service life without significant drop in both the hydroformylation efficiency and the acetalization efficiency or Rh loss for more than seventeen cycles. We believe that the long-term high activity and acetal selectivity mainly benefit from the synergy between the acidic active site and the Rh active site on the ARBC and the highly effective immobilization and recycling of ARBC in ionic liquid/alcohol systems due to the strong affinity of ARBC with the ionic liquid.

Introduction

The isolation and recycling of noble metal catalysts in homogeneous catalytic reactions have remained a challenge in green chemistry for the past 20 years.[1] The highly effective one-pot catalytic synthesis of chemicals and fine chemicals has also been an research focus in green chemistry, since it improves atom economy and reduces emission, E factor ($kg_{waste}/kg_{product}$), and consumption of energy and raw materials.[2] Rh-catalyzed hydroformylation is an important method for the functionalization of alkenes to produce aldehydes in industrial applications. Due to their versatile chemical properties,[3] aldehydes can be further transformed into other important chemicals. Based on the principles of atom economy and low energy consumption in green chemistry, the hydroformylation of alkenes can be combined with numerous other organic reactions to form tandem reaction sequences that can be achieved directly under the hydroformylation condition.[4] Examples include tandem hydroformylation-reduction, hydroformylation-nucleophilic addition, hydroformylation-aldol condensation, *etc*. Among them, an important application is the tandem hydroformylation-acetalization, in which the formation of acetal may be used to protect the sensitive aldehyde group or to further synthesize fine chemicals such as perfume, pharmaceuticals and agricultural chemicals. Such one-pot synthesis procedure enables multiple catalytic reactions in series, which avoids the formation of side products and circumvents the complex steps for the separation and purification of aldehyde intermediates.[2]

Although many efforts have been devoted to the research of Rh-catalyzed one-pot hydroformylation and acetalization process,[5] most of the related works are focused on catalysts, kinetics and scope of the reaction, and the separation and recycling of the expensive Rh-catalyst in this homogeneous catalysis reaction are rarely investigated. To date, no reported catalytic system can realize the combination of high activity, high acetal selectivity and longer service life of catalyst in tandem hydroformylation-acetalization of olefins, mainly due to difficulties in the efficient immobilization and recycling of the Rh-catalyst.

In recent years, biphasic hydroformylation using ionic liquid (IL) as reusable supports of Rh-catalyst has received extensive attention.[6] The key issue in IL biphasic hydroformylation is the effective immobilization of Rh-catalyst in IL to avoid Rh loss. Since the tandem hydroformylation-acetalization normally uses alcohol as the reaction medium,[5a-l] if the Rh-catalyst can be effectively immobilized in IL/alcohol systems, it would then be possible to enable the efficient separation and recycling of Rh-catalyst in the tandem hydroformylation-acetalization of olefins. To the best of our knowledge, catalyst recycling in IL/alcohol systems for the hydroformylation-acetalization of olefins has not been described yet.



Scheme 1 The zwitterionic phosphine ligand with a glycine tag (**1**), its ammonium salts ([**1**·H]X) and the imidazole-based ILs.

To achieve long-term recycling of Rh-catalyst while maintaining high catalytic efficiency in the tandem hydroformylation-acetalization of alkenes, we report the catalytic systems consisting of Brønsted acid-Rh bifunctional catalysts, imidazole-based ionic liquids (Scheme 1) and alcohols using a

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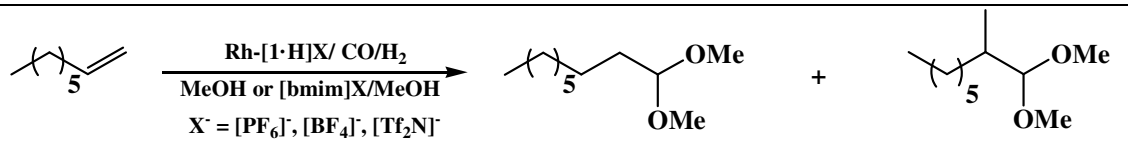
Table 1 One-pot hydroformylation-acetalization of 1-octene using the ARBCs (Rh-[**1**·H]X) in MeOH or [bmim]X/MeOH systems (X^- = $[PF_6]^-$, $[BF_4]^-$ and $[Tf_2N]^-$).[a]



Entry	Ligand	Reaction medium	Conversion [b] (%)	S_{oxo} [c] (%)	E_{ace} [d] (%)	S_{iso} [e] (%)	*l* : *b* [f]	Rh loss [g] (%)
1	[**1**·H][BF_4]	MeOH	98	95	94	3	78:22	—
2	[**1**·H][PF_6]	MeOH	99	94	96	2	70:30	—
3	[**1**·H][Tf_2N]	MeOH	99	97	94	1	76:24	—
4	**1**	MeOH	99	98	0.5	1	78:22	—
5	PPh_3	MeOH	99	99	1	1	84:16	—
6	[**1**·H][BF_4]	[bmim][BF_4]/MeOH	99	97	95	1	75:25	0.03
7	[**1**·H][PF_6]	[bmim][PF_6]/MeOH	94	99	95	1	77:23	0.6
8	[**1**·H][Tf_2N]	[bmim][Tf_2N]/MeOH	99	98	92	1	77:23	0.7
9	**1**	[bmim][BF_4]/MeOH	99	97	51	1	82:18	37
10	**1**	[bmim][PF_6]/MeOH	99	97	5	1	86:14	52
11	**1**	[bmim][Tf_2N]/MeOH	99	95	4	3	84:16	39

[a] *p* (H_2/CO = 1/1) = 5 MPa, *T* = 80 °C, *t* = 2 h, $Rh(acac)(CO)_2$ 1.0 mg, ligand/Rh = 10, 1-octene/Rh = 1000, cyclohexane as internal standard, 1 g IL, 3 mL MeOH. The ammonium salts [**1**·H]X (X^- = $[BF_4]^-$, $[PF_6]^-$, $[Tf_2N]^-$) can be easily prepared in methanol through an acid-base neutralization reaction of **1** with equimolar HX (HX/**1**/Rh = 10/10/1), and the ammonium salts can be either first isolated or used directly, which does not alter the result. [b] Percent of converted 1-alkene, determined by GC. [c] Selectivity of total oxo products based on 1-alkene consumed, determined by GC. Total oxo products mainly consist of linear aldehyde, branched aldehyde, linear acetal and branched acetal. [d] Acetalization efficiency: E_{ace} = (linear acetal + branched acetal)/(linear aldehyde + branched aldehyde + linear acetal + branched acetal). [e] Selectivity of isomerized alkenes that are mainly 2-alkene and 3-alkene, determined by GC. [f] Ratio of linear acetal to branched acetal. [g] Percentage of leached Rh in the total Rh charged, determined by ICP-AES.

glycine tagged zwitterionic phosphine ligand[7] and its ammonium salts (Scheme 1, **1** and [**1**·H]X). The first successful application of catalyst recycling via IL/alcohol systems in tandem hydroformylation-acetalization of olefins here is demonstrated.

Results and discussion

The acetalization of aldehydes is normally catalyzed by Lewis acids or Brønsted acids in alcohols or orthoesters.[8] Therefore, all currently reported Rh-catalyzed tandem hydroformylation-acetalization of olefins are carried out in alcohols [5a-l] or orthoesters [5m-q] in the presence of Lewis acids or Brønsted acids as co-catalysts. The acidic co-catalysts usually need to be added separately [5j-q] and are sometimes generated *in situ*.[5g-i, p, 9] However, because the Rh-catalyst and the acidic co-catalysts exist independently, their simultaneous immobilization and recycling become difficult. The Brønsted acid-Rh bifunctional catalysts (ARBCs) that we report here elegantly resolve this problem by empolying a glycine-tagged zwitterionic phosphine ligand **1** in the form of an internal salt, which can form ammonium salts with equimolar amount of Brønsted acids HX (X^- = $[PF_6]^-$, $[BF_4]^-$ and $[Tf_2N]^-$). The ammonium salt [**1**·H]X can then be complexed with Rh precursor under hydroformylation condition to form the ARBCs Rh-[**1**·H]X. The advantages of the ARBCs are as follows. (1) The ammonium salts [**1**·H]X can be easily prepared and can be either isolated and added separately or used directly. There is no need to add other acid co-catalysts, which makes the reaction greener. (2) The ARBCs embed both the Rh active site that catalyzes the hydroformylation and the acidic active site that catalyzes the acetalization, which promotes the synergy between both catalytic active sites and enables the simulatneous immobilization and recycling of both the Rh catalyst and the acid co-catalyst. (3) The formation of the ammonium salts [**1**·H]X increases the electric charge of the ARBCs molecule, which improves the affinity of the ARBCs with ILs [bmim]X as catalyst carriers and effectively reduces catalyst loss.

In Table 1 (entries 1–3), the tandem hydroformylation-acetalization of 1-octene in methanol is used as a model reaction to evaluate the catalytic efficiency of ARBCs for the hydroformylation and acetalization reactions. The conversion of alkene and S_{oxo} (selectivity for total oxo products including aldehyde and acetal) characterize the hydroformylation efficiency of the Rh active site, while E_{ace} characterizes the acetalization efficiency of the acidic active site formed on the glycine side chain of Rh-[**1**·H]X. Gratifyingly, in MeOH the ARBCs (Rh-[**1**·H]X) exhibit excellent hydroformylation efficiency with high conversion of alkene (98%–99%), high selectivity for oxo products (94%–97%) and low selectivity for isomerized alkenes (1%–3%), as well as good acetalization efficiency (94%–96%) and moderate regioselectivity for the linear acetal (70%–78%), and the type of Brønsted acid does not affect the acetalization efficiency. In comparison, the zwitterionic ligand **1** and triphenylphosphine (PPh_3) are exmined under identical conditions. It can be seen that Rh-**1** and Rh-PPh_3 have similar catalytic behavior (Table 1, entries 4 and 5), both giving high hydroformylation efficiency but essentially no catalytic activity for the acetalization reaction. This demonstrates that the glycine side chain of the internal salt **1** does not possess an effective acidic active site that can provide adequate concentration of H^+ to

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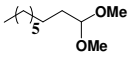
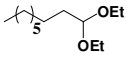
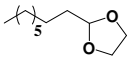
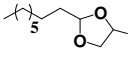
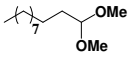
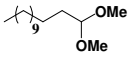
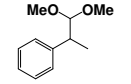
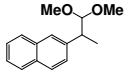
Table 2 One-pot hydroformylation-acetalization of different alkenes using Rh-[**1**·H][BF_4] in [bmim][BF_4]/alcohols systems.[a]

Entry	Alkene	Main product	Conver. (%)	S_{oxo} (%)	E_{ace} (%)	*l* : *b*
1			99	97	95	75:25
2			98	84	91	74:26
3			99	94	96	76:24
4			99	97	99	77:23
5 [b]			99	90	93	70:30
6 [c]			99	88	91	70:30
7			100	99	99	8:92
8 [d]			63	99	95	8:92

[a] The reaction conditions are the same as in Table 1; **1**/HBF_4 = 1/1, **1**/Rh = 10, alkenes/Rh = 1000, 1 g [bmim][BF_4], 3 mL methanol, 5 mL ethanol, 0.5 mL glycol, 0.5 mL 1,2-propanediol. [b] 6 mL methanol, *n*-octane as internal standard. [c] 11 mL methanol, *n*-decane as internal standard. [d] 10 mL methanol, *n*-decane as internal standard.

catalyze the acetalization reaction.

In our opinion, the addition of one equivalent of Brønsted acid allows the formation of a carboxylic acid from the protonation of the carboxylate group of the internal salt **1**. This carboxylic acid is the true acidic active site for catalyzing acetalization, since the carboxylic acid moeity is more acidic than the ammonium functional group. Pneumatikakis *et al.*[5p] reported a hydroformylation-acetalization promoted by a Rh/thioamino acid system, in which the thioamino acid is generated *in situ* under hydroformylation condition. Nevertheless, the tandem hydroformylation-acetalization of olefins using bifunctional catalysts containing both glycine and Rh remains unprecedented.

Subsequently, we selected the most commonly used IL [bmim]X (X^- = $[BF_4]^-$, $[PF_6]^-$ and $[Tf_2N]^-$) as the catalyst carrier to evaluate the catalytic and immobilization efficiency of ARBCs (Rh-[**1**·H]X) in the [bmim]X/MeOH systems (Table 1, entries 6–8). It can be seen that both the hydroformylation efficiency and the acetalization efficiency of Rh-[**1**·H]X in [bmim]X/MeOH are comparably high to those in MeOH alone. To evaluate the immobilization efficiency of ARBCs in ILs, methanol was removed by vacuum evaporation and the products were extracted with *n*-heptane, and the Rh loss to the *n*-heptane phase was analyzed by ICP-AES. The results show that Rh-[**1**·H]X can be effectively immobilized in [bmim]X and the Rh losses are all less than 1%. In particular, [bmim][BF_4] shows the best immobilization effect for Rh-[**1**·H][BF_4] with only 0.03% Rh loss. In contrast, when using Rh-**1** as the catalyst in the [bmim]X/MeOH systems (Table 1, entries 9–11), only a moderate amount of acetal can be obtained with the highest acetalization efficiency being only 51%, which is due to the presence of minor amount of acidic impurities in the ILs. Besides, ICP analysis shows that significant amount of Rh is leached from the ILs into the extraction phase.

The above results demonstrate that the ligand **1** with weak charge does not have strong electrostatic interaction with the ILs and thus cannot effectively immobilize Rh in the ILs. In contrast, the ammonium salts ([**1**·H]X) of **1** are strongly charged, which results in the strong electrostatic attraction between the ARBCs and the ILs. In particlar, the same X^- anion in Rh-[**1**·H]X and [bmim]X further increases the affinity between the ARBCs and the ILs and significantly reduces Rh loss.

To explore the scope of the reaction, different alcohols were used for the hydroformylation-acetalization of 1-octene with Rh-[1·H][BF_4] in [bmim][BF_4]/alcohols (Table 2, entries 1–4), in which the alcohols mainly serve as the reactant. In certain cases (e.g., Table 2, entries 5, 6 and 8) where a large excess of alcohol is used, the alcohol also serves as the solvent. Besides methanol, we have especially focused on ethanol, ethylene glycol, and 1,2-propanediol. Using ethanol results in lower acetalization efficiency than using methanol, while using ethylene glycol and 1,2-propanediol results in higher acetalization efficiency of 96% and 99%, which is in agreement with literature report.[5i] These acetalization reactions have important applications in chemical synthesis. For example, the diethyl and cyclic acetals of nonanal are important perfumes.

The scope of the reaction was also evaluated by using different 1-alkenes in the [bmim][BF_4]/MeOH system (Table 2, entries 5–8). For linear 1-alkenes, the conversion is always very high, and the selectivity for oxo products and the acetalization efficiency decrease slightly from 1-octene to 1-dodecene, but the acetalization efficiency is still always higher than 90%. In contrast, 100% conversion, 99% oxo products selectivity and 99% acetalization efficiency are obtained for styrene with excellent regioselectivity (92%) toward the branched acetal. The conversion of 2-vinylnaphthalene is low (63%) mainly due to its low solubility in MeOH, but the oxo products selectivity, acetalization efficiency and regioselectivity are still at high levels.

GC and GC/MS analyses show that, in all reactions, except for the water generated from the acetalization reaction, other minor byproducts include aldehydes (linear aldehydes and branched aldehydes), alkene hydrogenation product (<1%), as well as isomerized alkenes (2-alkenes and 3-alkenes) and their corresponding aldehydes and acetals from hydroformylation-acetalization.

To investigate the recycling and service life of the ARBCs in the IL/alcohol systems, the phase behavior and miscibility of the IL/alcohol/1-alkene systems were first characterized (see supporting information). The investigation focused particularly on the [bmim][BF_4]/MeOH (or EtOH)/1-alkenes (1-octene, 1-decene or 1-dodecene) and [bmim][BF_4]/diols (ethylene glycol or 1,2-propanediol)/1-octene systems. The results show that [bmim][BF_4] and 1-alkenes are both readily soluble in MeOH or EtOH, but [bmim][BF_4] and 1-alkenes are not miscible. Therefore, the mixture of [bmim][BF_4], 1-alkenes and MeOH (or EtOH) at an appropriate ratio and above a certain temperature can

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become a homogeneous system. The miscibility determinations were carried out by cloud titration method according to literature report.[10] The system with fixed amount of IL, 1-alkene and internal standard was maintained at a fixed temperature (*T*), and the minimum amount of alcohol (MeOH or EtOH) to make the system miscible is measured by dropwise addition. It was also noted that when the system became miscible, the system would become biphasic again when the temperature dropped below *T* and return to homogeneous when the temperature came back to *T* or exceeded *T*. Further studies showed that the introduction of minor amount of ligand and Rh had no influence on the phase behavior and miscibility of the system.

The biphasic hydroformylation of alkene in IL[6] and the biphasic hydroformylation-acetalization of 1-hexene in ethylene glycol[5b] have been confirmed by literature reports. For our [bmim][BF_4]/diols (ethylene glycol or 1,2-propanediol)/1-octene systems, because [bmim][BF_4] and the diols (ethylene glycol or 1,2-propanediol) are completely miscible whereas 1-octene is not miscible with [bmim][BF_4] and diols (ethylene glycol or 1,2-propanediol) from room temperature up to the hydroformylation reaction temperature (80–120 °C), the mixture of [bmim][BF_4], diols (ethylene glycol or 1,2-propanediol) and 1-octene can form a biphasic reaction system. The cloud titration indicated that the system is biphasic throughout from room temperature to reaction temperature.

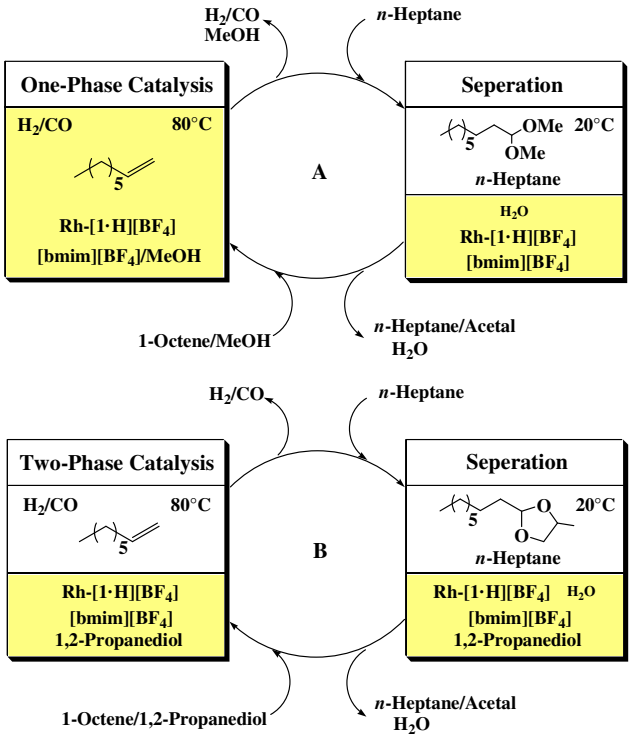

Fig. 1 The separation and recycling diagram of ARBC in [bmim][BF_4]/alcohol systems for the hydroformylation-acetalization of 1-octene (A: one-phase catalysis in [bmim][BF_4]/MeOH; B: two-phase catalysis in [bmim][BF_4]/1,2-propanediol).

Based on the phase behavior and miscibility of the hydroformylation-acetalization systems, the separation and recycling of ARBC are shown in Fig. 1 using Rh-[**1**·H][BF_4] as model catalyst and the hydroformylation-acetalization of 1-octene in [bmim][BF_4]/MeOH and [bmim][BF_4]/1,2-propanediol as model reaction systems. In [bmim][BF_4]/MeOH system (Fig. 1, A), by adjusting the temperature and the ratio between [bmim][BF_4], 1-octene and MeOH, the hydroformylation-acetalization can proceed in the homogeneous system. After completing the reaction and cooling to room temperature, the reaction system remains homogeneous. The volatile methanol and the water generated from acetalization can be readily removed under reduced pressure, and the acetal product is extracted with *n*-heptane and separated from the IL phase by decanting. The [bmim][BF_4] phase in the bottom layer containing the ARBC is separated and carried through the next cycle. In the [bmim][BF_4]/1,2-propanediol system (Fig. 1, B), the hydroformylation-acetalization proceeds in the biphasic system consisting of a [bmim][BF_4]/1,2-propanediol phase dissolving the ARBC and an 1-octene phase. After completing the reaction and cooling to room temperature, the product acetal is extracted with *n*-heptane and water is removed *in vacuo*. The [bmim][BF_4]/1,2-propanediol phase in the bottom layer is carried through the next cycle after 1,2-propanediol is replenished.

Table 3 Recycling and reuse of the Rh-[**1**·H][BF_4] catalyst for the tandem hydroformylation-acetalization of 1-octene in [bmim][BF_4]/alcohols [a]

Alcohol	Run	Conver. (%)	S_{oxo} (%)	E_{ace} (%)	*l* : *b*	Rh loss (%)
methanol	1	99	97	95	75:25	0.03
	2	99	97	98	74:26	—
	4	99	96	96	75:25	0.05
	6	98	94	97	75:25	—
	8	97	94	97	74:26	0.06
	10	97	95	97	74:26	—
	12	98	82	94	73:27	—
1,2-propanediol	1	99	97	99	77:23	0.08
	3	98	95	98	75:25	—
	5	98	94	99	75:25	—
	7	98	94	99	74:26	0.07
	9	98	92	99	75:25	—
	12	97	90	99	74:26	0.1
	15	82	83	98	74:26	—
	17	72	81	98	75:25	—

[a] The reaction conditions are the same as in Table 1, **1**/HBF_4=1/1, **1**/Rh = 10, 1-octene/Rh=1000, 1 g [bmim][BF_4], 3 mL methanol, 0.5 mL 1,2-propanediol.

Table 3 shows the recycling experimental results of Rh-[**1**·H][BF_4] in both systems (Fig. 1, A and B). Both catalytic systems exhibit high catalytic efficiency and long service life of catalyst, with no significant deterioration in conversion, oxo products selectivity, acetalization efficiency or Rh loss for more than twelve and seventeen cycles, respectively. This result for the tandem hydroformylation-acetalization is thus far unparalleled in published literature. The high hydroformylation-acetalization efficiency and long service life of ARBC can be attributed to the structural motif of ARBC and efficient recycling strategy. The synergy between the acidic active site and the Rh active site on the ARBC ensures that the aldehyde formed at the Rh active site

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can be rapidly transformed into acetal by the acidic active site on the glycine side chain in each catalytic cycle. Because the ARBC embed both the Rh active site and the acidic active site, catalyst recycling is significantly improved. Most importantly, the ammonium salt structure strongly enhances the affinity between ARBC and IL, which ensures very low Rh loss (0.03%–0.1%) and increases the stability and reusability of ARBC in ILs, thus extending the service life of ARBC.

Conclusion

In conclusion, a highly effective and long-life one-pot hydroformylation-acetalization catalytic system has been established based on Brønsted acid-Rh bifunctional catalysts and ILs. In the IL/alcohol systems, the ARBCs showed excellent hydroformylation and acetalization efficiency for a wide scope of olefins and alcohols. We believe that the high catalytic efficiency mainly relies on the synergy between the acidic active site and the Rh active site on the ARBCs. The analysis of Rh loss and catalyst recycling experiments showed that ARBCs have strong affinity with IL and can be effectively immobilized in IL, which significantly improved the stability and reusability of ARBCs during long-term catalytic cycles. No significant loss of catalytic efficiency or Rh was observed for more than twelve and seventeen cycles when reacting with MeOH and 1,2-propanediol, respectively.

Experimental

General

The linear 1-alkenes, styrene and 2-vinylnaphthalene were purchased from Acros company. The rhodium catalysts precursor $Rh(acac)(CO)_2$ was purchased from ABCR company. 1-Butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium bis [(trifluoromethyl)sulfonyl]imide were obtained commercially from Shanghai Chengjie Chemical Co., and all ILs contained <0.2 wt % water and <150 ppm halide. The alcohols, HBF_4 (40% aq.), HPF_6 (60% aq.) and Tf_2NH were obtained from commercial sources. The 4-(diphenyl-phosphino)-DL-phenylglycine (**1**) was synthesized by a published method.[7] The hydroformylation-acetalization was carried out in a 60 ml homemade stainless steel autoclave with Teflon lining and magnetic stirring under an argon atmosphere using standard Schlenk techniques. The solvents and reagents were rigorously deoxygenated prior to use. The products of hydroformylation-acetalization were analyzed by GC technique (OV-101 capillary column, FID detector). The conversion and selectivity were determined by GC using cyclohexane (for 1-octene and styrene), *n*-octane (for 1-decene) or *n*-decane (for 1-dodecene and 2-vinylnaphthalene) as internal standards. The column temperature is maintained at 80°C for 2 min, then is raised to 200°C by a programming rate of 6°C/min and maintained at 200°C for 20 min.The products have been identified by GC-MS (Agilent 6890/5973 GC-MS apparatus with a DB-35MS capillary column) and by comparison of their GC retention times with those of reference samples. ICP-AES was made with an IRIS Istrepid II XSP apparatus for determining the loss of Rh.

One-phase hydroformylation-acetalization of 1-octene using acid-Rh bifunctional catalyst Rh-[1·H]X (X^- = $[BF_4]^-$, $[PF_6]^-$ or $[Tf_2N]^-$) in MeOH

In a typical experiment, under an argon atmosphere, ligands **1** (3.87×10^{-2} mmol) was dissolved in 3 mL of degassed MeOH. The equimolar HPF_6 (60% aq.), HBF_4 (40% aq.) or Tf_2NH was added. The solution was allowed to stir for 60 min at 50°C to give the ammonium salts [**1**•H]X (X^- = $[PF_6]^-$, $[BF_4]^-$ or $[Tf_2N]^-$). The ammonium salts can be isolated or used immediately for the hydroformylation-acetalization. 1-octene (0.6 mL, 3.82 mmol), internal standard (cyclohexane, 0.1 mL), $Rh(acac)(CO)_2$ (1.0 mg, 3.87×10^{-3} mmol) and the preceding ammonium salts ([**1**·H]X) of **1** in 3 mL MeOH were placed in a 60 mL stainless steel autoclave. Then the reactor was pressurized with syngas to 5.0 MPa, and the reaction system was heated to 80°C. After 2 h the autoclave was rapidly cooled with ice, and the conversion and selectivity were analysed by GC.

One-phase hydroformylation-acetalization of 1-octene using acid-Rh bifunctional catalyst Rh-[1·H]X in [bmim]X/MeOH (X^- =[$BF_4]^-$, $[PF_6]^-$ or $[Tf_2N]^-$)

In a typical experiment, 1-octene (0.6 mL, 3.82 mmol), internal standard (cyclohexane, 0.1 mL), $Rh(acac)(CO)_2$ (1.0 mg, 3.87×10^{-3} mmol), [bmim]X (1.0 g) and the preceding ammonium salts ([**1**·H]X) of **1** in 3 mL MeOH were placed in a 60 mL stainless steel autoclave. Then the reactor was pressurized with syngas to 5.0 MPa, and the reaction system was heated to 80°C. After 2 h the autoclave was rapidly cooled with ice, and the conversion and selectivity were analysed by GC. Subsequently, the MeOH and generated water were removed *in vacuo* and the top product layer was separated by extracting with *n*-heptane (3 mL). New 1-octene and methanol were added into the IL for next catalytic recycling.

Two-phase hydroformylation-acetalization of 1-octene using acid-Rh bifunctional catalyst Rh-[1·H][BF_4] in [bmim][BF_4]/1,2-propanediol

In a typical experiment, under an argon atmosphere, 1-octene (0.6 mL, 3.82 mmol), internal standard (cyclohexane, 0.1 mL), $Rh(acac)(CO)_2$ (1.0 mg, 3.87×10^{-3} mmol), [bmim][BF_4] (1.0 g), 1,2-propanediol (0.5 mL), ligands **1** (3.87×10^{-2} mmol) and equimolar HBF_4 (40% aq.) were placed in a 60 mL stainless steel autoclave. The reactor was pressurized with CO/H_2 (1:1) to 5.0 MPa, and the reaction system was stirred at 80°C ([**1**·H][BF_4] here was generated *in situ* for use). After 2h the system was rapidly cooled on ice. The top product was extracted with 3 mL *n*-heptane under atmospheric condition. The water was removed under reduced pressure. The new 1-octene and replenished 1,2-propanediol (0.3 mL) were added into the [bmim][BF_4] for next recycling.

One-phase hydroformylation-acetalization of 1-decene using acid-Rh bifunctional catalyst Rh-[1·H][BF_4] in [bmim][BF_4]/ MeOH

The 1-decene (0.72 mL, 3.80 mmol), internal standard (*n*-octane, 0.1 mL), $Rh(acac)(CO)_2$ (1.0 mg, 3.87×10^{-3} mmol), [bmim][BF_4]

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(1.0 g) and ammonium salts ([**1**·H][BF_4]) of **1** (3.87×10^{-2} mmol) in 6 mL MeOH were combined in a 60 mL stainless steel autoclave in a procedure identical to that given for 1-octene in [bmim]X/MeOH system with Rh-[**1**·H]X. The conversion and selectivity were analysed by GC.

One-phase hydroformylation-acetalization of 1-dodecene using acid-Rh bifunctional catalyst Rh-[1·H][BF_4] in [bmim][BF_4]/MeOH

The 1-dodecene (0.85 mL, 3.83 mmol), internal standard (*n*-decane, 0.1 mL), Rh(acac)$(CO)_2$ (1.0 mg, 3.87×10^{-3} mmol), [bmim][BF_4] (1.0 g) and ammonium salts ([**1**·H][BF_4]) of **1** (3.87×10^{-2} mmol) in 11 mL MeOH were combined in a 60 mL stainless steel autoclave in a procedure identical to that given for 1-octene in [bmim]X/MeOH system with Rh-[**1**·H]X. The conversion and selectivity were analysed by GC.

One-phase hydroformylation-acetalization of styrene using acid-Rh bifunctional catalyst Rh-[1·H][BF_4] in [bmim][BF_4]/MeOH

The styrene (0.45 mL, 3.93 mmol), internal standard (cyclohexane, 0.1 mL), Rh(acac)$(CO)_2$ (1.0 mg, 3.87×10^{-3} mmol), [bmim][BF_4] (1.0 g) and ammonium salts ([**1**·H][BF_4]) of **1** (3.87×10^{-2} mmol) in 3 mL MeOH were combined in a 60 mL stainless steel autoclave in a procedure identical to that given for 1-octene in [bmim]X/MeOH system with Rh-[**1**·H]X. The conversion and selectivity were analysed by GC.

One-phase hydroformylation-acetalization of 2-vinylnaphthalene using acid-Rh bifunctional catalyst Rh-[1·H][BF_4] in [bmim][BF_4]/MeOH

The 2-vinylnaphthalene (0.6 g, 3.89 mmol), internal standard (*n*-decane, 0.1 mL), Rh(acac)$(CO)_2$ (1.0 mg, 3.87×10^{-3} mmol), [bmim][BF_4] (1.0 g) and ammonium salts ([**1**·H][BF_4]) of **1** (3.87×10^{-2} mmol) in 10 mL MeOH were combined in a 60 mL stainless steel autoclave in a procedure identical to that given for 1-octene in [bmim]X/MeOH system with Rh-[**1**·H]X. The conversion and selectivity were analysed by GC.

One-phase hydroformylation-acetalization of 1-octene using acid-Rh bifunctional catalyst Rh-[1·H][BF_4] in [bmim][BF_4]/EtOH

The 1-octene (0.6 mL, 3.82 mmol), internal standard (cyclohexane, 0.1 mL), Rh(acac)$(CO)_2$ (1.0 mg, 3.87×10^{-3} mmol), [bmim][BF_4] (1.0 g) and ammonium salts ([**1**·H][BF_4]) of **1** (3.87×10^{-2} mmol) in 5 mL EtOH were combined in a 60 mL stainless steel autoclave in a procedure identical to that given for 1-octene in [bmim]X/MeOH system with Rh-[**1**·H]X. The conversion and selectivity were analysed by GC.

Two-phase hydroformylation-acetalization of 1-octene using acid-Rh bifunctional catalyst Rh-[1·H][BF_4] in [bmim][BF_4]/ethylene glycol

The 1-octene (0.6 mL, 3.82 mmol), internal standard (cyclohexane, 0.1 mL), Rh(acac)$(CO)_2$ (1.0 mg, 3.87×10^{-3} mmol), [bmim][BF_4] (1.0 g), ethylene glycol (0.5 mL), ligands **1** (3.87×10^{-2} mmol) and equimolar HBF_4 (40% aq.) were combined in a 60 mL stainless steel autoclave in a procedure identical to that given for 1,2-propanediol. The conversion and selectivity were analysed by GC.

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Notes and references

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