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A Novel Thermoregulated Ionic Liquid and Organic Biphasic System With Rh Nanoparticles for Olefin Hydroformylation

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Abstract A thermoregulated ionic liquid and organic biphasic system composed of quaternary ammonium-based ionic liquid *N*,*N*-dimethyl-*N*-(2-(2-methoxyethoxy)ethyl)-*N*-(2-(2-octyloxyethoxy)ethyl) ammonium methanesulfonate (**1**) and cyclohexane was first applied for the Rh nanoparticle catalyzed hydroformylation of olefins, which allows for not only a highly efficient homogeneous catalytic reaction, but also an easy separation and reuse of catalyst. Under the optimized conditions, various olefins could be converted completely with ≥98 % selectivity for aldehydes. After reaction, the Rh nanoparticle catalyst could be recovered by simple phase separation and reused for five times without evident loss of activity.

Keywords Thermoregulated ionic liquid and organic biphasic system · Rhodium · Nanoparticle · Olefin · Hydroformylation

1 Introduction

In recent years, considerable attention has been directed toward the soluble transition-metal nanoparticle catalysts due to their high efficiency and unique properties. However, very similar to traditional homogeneous catalysts, one of the main disadvantages of soluble nanoparticle catalyst is the problem of separation the catalyst from the product [1, 2]. To deal with this problem, a range of methods has been reported, with most studies focusing on the liquid/liquid biphasic system, for example, the use of fluorous/organic biphasic system [3, 4], thermoregulated polyethylene glycol (PEG) biphasic system [5], thermoregulated phase-transfer biphasic system [6] and ionic liquid biphasic system [7, 8]. Ionic liquids with negligible vapor pressure have been explored as stabilizers for transition-metal nanoparticles. However, in most cases, the reaction systems involving ionic liquids are either monophase allowing for rapid transformation or biphase facilitating separation of product from catalyst [8–13]. Therefore, to search for new catalyst systems that might combine the advantages of both homogeneous and heterogeneous catalysis will have a significant impact.

Very recently, our group has developed an effective approach for Rh nanoparticle catalyzed hydrogenation and hydroformylation of olefins in a thermoregulated ionic liquid and organic biphasic system [14, 15], wherein $[CH_3(OCH_2CH_2)_{16}N^+Et_3][CH_3SO_3^-]$ (IL_{PEG750}) was employed as ionic liquid. This ionic liquid exhibits very unique solubility in organic solvent depending on the temperature. Namely, IL_{PEG750} is immiscible with the mixed toluene and *n*-heptane at room temperature, but becomes homogeneous when the temperature is increased to a certain point. Consequently, the reaction proceeds virtually in a homogeneous system under heating, and upon cooling to room temperature, separates into a biphasic system composed of ionic liquid phase containing Rh catalyst and organic phase containing the products. Such a process provides both the advantages of classic monophasic and biphasic system, i.e., highly catalytic efficiency and good recyclability.

With the aim to broaden the scope of this interesting technology, herein, we report on a novel and more efficient catalytic system for the biphasic hydroformylation of olefins by using Rh nanoparticles in a quaternary ammonium-based ionic liquid *N*,*N*-dimethyl-*N*-(2-(2-methoxyethoxy)ethyl)-*N*-(2-(2-octyloxyethoxy)ethyl)ammonium methanesulfonate

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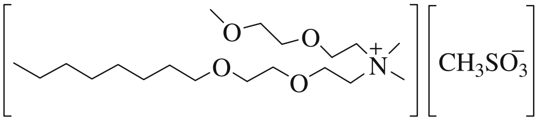

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Scheme 1 The structure of ionic liquid **1**

(abbreviated as **1**, Scheme 1) as the lower catalyst-containing phase and cyclohexane as the upper substrate- and product-containing phase. Higher activity and selectivity for aldehydes were obtained and recycling of Rh nanoparticle catalyst was realized.

2 Experimental

2.1 General Remarks

Cyclohexane and *n*-heptane were purchased from Kermel and distilled from sodium under inert atmosphere before use. $RhCl_3 \cdot 3H_2O$ and $Rh(acac)(CO)_2$ were received from Beijing Research Institute of Chemical Industry and used without any further purification. 1-Octene was obtained from Acros. 1-Decene, 1-dodecene and cyclohexene were supplied by Fluka. Ionic liquid **1** was prepared according to our previous reported method [16]. Gas chromatography analyses were performed on a Tianmei 7890 GC instrument equipped with a 50 m OV-101 column and an FID detector (N_2 as a carrier gas). GC–MS measurement was performed on a HP 6890 GC/5973 MSD instrument (with a 30 m HP-5MS column, He as a carrier gas). ICP-AES analyses of rhodium were carried out on Optima 2000 DV (Perkin Elmer, USA). The IR spectrum was recorded on a Fourier transform infrared (FTIR) spectrometer (Nicolet Avatar 360) using the KBr disc technique.

2.2 Preparation of Ionic Liquid **1**-Stabilized Rh Nanoparticles

In a typical experiment, a mixture of $RhCl_3 \cdot 3H_2O$ (7.42 mg, 0.028 mmol) and ionic liquid **1** (5.0 g, 11.3 mmol) was added in a 75 mL standard stainless-steel autoclave. The autoclave was flushed five times with 2 MPa H_2 and stirred under hydrogen (4 MPa) at 70 °C for 2 h. Then, the reactor was cooled to room temperature and depressurized. The nanoparticles thus obtained as ionic liquid **1** solution were used for the following hydroformylation of olefins.

2.3 TEM Images of Rhodium Nanoparticle Catalyst

The ionic liquid **1** solution containing the rhodium nanoparticle catalyst was diluted with ethanol. Then, a drop of the solution was placed onto a carbon-coated copper grid, and dried at ambient temperature. The transmission electron microscopy (TEM) images were taken with a Philips Tecnai G^2 20 TEM at an accelerating voltage of 200 kV.

2.4 General Procedure for Hydroformylation of Olefins

All hydroformylation reactions were carried out in a 75 mL stainless-steel autoclave equipped with a magnetic bar. The autoclave was charged with ionic liquid **1** solution of rhodium nanoparticles (0.30 g, containing 1.7×10^{-3} mmol Rh), olefin (1.7 mmol), cyclohexane (2.50 g) and *n*-heptane (0.05 g, as internal standard). Then, flushed five times with 2 MPa H_2, and pressurized with syngas ($CO/H_2 = 1$) up to an appointed pressure. The reactor was held at a scheduled temperature under stirring in a thermostatic oil bath for a fixed length of time. After the reaction, the reactor was cooled to room temperature and depressurized. The upper organic phase was separated from the lower ionic liquid phase and submitted immediately to GC and GC–MS analysis. The lower ionic liquid phase was reused to catalyze the hydroformylation of the next run.

3 Results and Discussion

Rh nanoparticles were synthesized by simple H_2 reduction of $RhCl_3 \cdot 3H_2O$ in ionic liquid **1**. The TEM image of the Rh nanoparticles was shown in Fig. 1. A relatively narrow size distribution with a diameter of 1.3 ± 0.2 nm was observed.

As shown in Fig. 2, this novel thermoregulated ionic liquid **1**/cyclohexane biphasic system with ionic liquid **1**-stabilized Rh nanoparticles also possessed the thermoregulated phase-transition property. Namely, at room temperature, the lower ionic liquid phase containing Rh nanoparticles was immiscible with the upper cyclohexane phase (**a** in Fig. 2). Interestingly, when the temperature was elevated gradually to 118 °C, the biphasic system merged into a homogeneous single phase (**b** in Fig. 2). Then, by cooling to room temperature, the biphasic system recovered completely to its original form as **a** (**c** in Fig. 2). This phenomenon implies that the thermoregulated ionic liquid **1**/cyclohexane biphasic system with ionic liquid **1**-stabilized Rh nanoparticles can realize a reaction under homogeneous conditions and achieve subsequent efficient separation of catalyst from products by cooling the reaction mixture to room temperature. One of the most notable advantages has been discussed above, the availability and cost of the ionic liquid **1** are analogous with the most reported ionic liquids. Till now, Rh nanoparticle catalyzed hydrogenation has been extensively studied, but less attention has been paid to hydroformylation [17–21]. Therefore, this novel thermoregulated ionic liquid

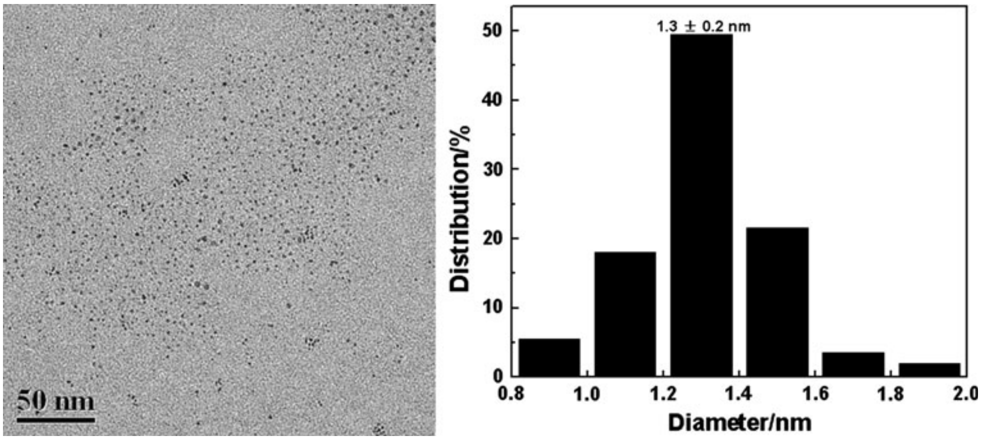

Fig. 1 TEM image of ionic liquid **1**-stabilized Rh nanoparticles (newly prepared, 200 particles)

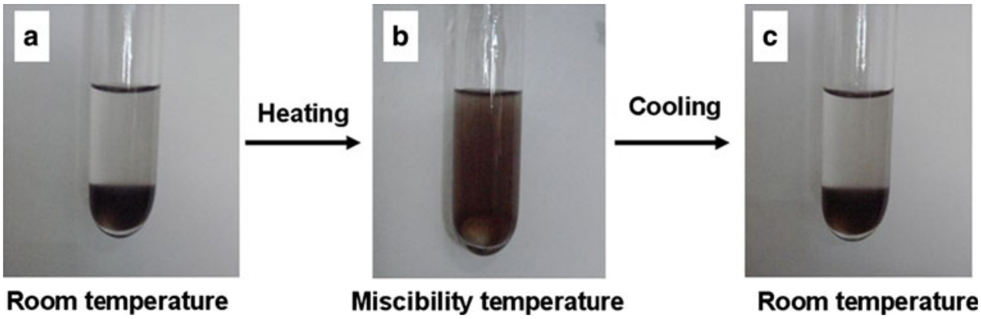

Fig. 2 Thermoregulated phase-transition property of ionic liquid **1**/cyclohexane biphasic system with ionic liquid **1**-stabilized Rh nanoparticles

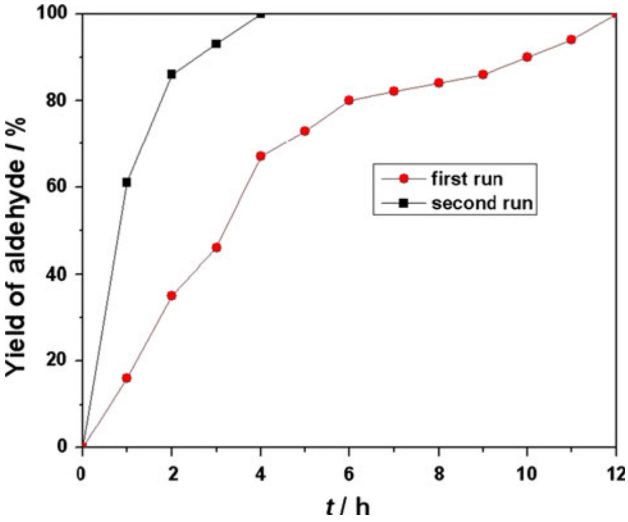

Fig. 3 Aldehyde yield as a function of time for hydroformylation of 1-octene

1/cyclohexane biphasic system with ionic liquid **1**-stabilized Rh nanoparticles was first employed for the hydroformylation of olefins.

The hydroformylation of 1-octene was investigated as a model reaction. The aldehyde yield as a function of time was shown in Fig. 3, which revealed a significant induction period in the first run. However, the reaction started again without any noticeable induction period in the second run, thereby leading to >99 % aldehyde yield within 4 h at 120 °C. The reaction rate is faster than the Rh nanoparticle catalyst prepared in 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (BMI·BF_4) ionic liquid [17]. The phenomenon of induction period was very similar to the previously reported results, which was associated with the dispersion process or attributed to the transformation of the nanoparticles into catalytically active species [17, 22]. According to the TEM images of ionic liquid **1**-stabilized Rh nanoparticles (Fig. 1 and see below Fig. 5), we speculate that the latter of the above-mentioned hypotheses is more possible.

The effects of temperature, pressure of syngas and reaction time on the hydroformylation of 1-octene catalyzed by ionic liquid **1**-stabilized Rh nanoparticles were summarized in Table 1. The effect of temperature was studied in the range of 80–120 °C, at a 5 MPa total syngas pressure ($CO/H_2 = 1$). At 80 °C, 32 % conversion was observed after 4 h of reaction time. At temperature of 90 °C and higher, conversion was virtually complete. The selectivity for aldehydes increased with increasing of temperature (entries 1–4). It is worth noting that the conversion of 1-octene increased sharply when the temperature increased from 80 to 90 °C. This may be due to the fact that the reaction system changed from biphase to

Table 1 Hydroformylation of 1-octene catalyzed by ionic liquid **1**-stabilized Rh nanoparticles

Entry	Temperature (°C)	Pressure (MPa)	Time (h)	Conversion (%)	Y_{ald}^{a} (%)	Y_{iso}^{b} (%)	*n*/b
1	80	5	4	32	24	8	1.6
2	90	5	4	98	84	14	1.4
3	100	5	4	100	87	13	1.4
4	120	5	4	100	>99	<1	1.2
5	120	2	4	100	40	60	0.8
6	120	3	4	100	58	42	0.7
7	120	4	4	100	87	13	0.8
8	120	5	1	99	61	38	1.4
9	120	5	2	100	86	14	1.0
10	120	5	3	100	93	7	0.8
11[c]	120	5	4	99	70	29	1.2

Reaction conditions: ionic liquid **1** 0.30 g (containning 1.7×10^{-3} mmol Rh), **1**/Rh = 400 (molar ratio), substrate/Rh = 1,000 (molar ratio), 1-octene 0.19 g (1.7 mmol), cyclohexane 2.50 g, internal standard *n*-heptane 0.05 g, $CO/H_2 = 1$, *n*/b molar ratio of normal to branched aldehyde. The recovered catalyst from the first run was used

[a] Y_{ald} yield of aldehydes

[b] Y_{iso} yield of isomeric octenes

[c] $Rh(acac)(CO)_2$ (1.7×10^{-3} mmol) was used as catalyst

Table 2 Hydroformylation of different olefins catalyzed by ionic liquid **1**-stabilized Rh nanoparticles

Entry	Olefin	Pressure (MPa)	Time (h)	Conversion (%)	Aldehyde yield (%)
1	1-Decene	5	4	100	99
2	1-Dodecene	5	4	100	98
3	Cyclohexene	6	5	100	99

Reaction conditions: ionic liquid **1** 0.30 g (containning 1.7×10^{-3} mmol Rh nanoparticles), **1**/Rh = 400 (molar ratio), substrate/Rh = 1,000 (molar ratio), cyclohexane 2.50 g, internal standard *n*-heptane 0.05 g, T = 120 °C, $CO/H_2 = 1$

monophase (the miscibility temperature of the system was 85 °C in the presence of aldehydes). The effect of syngas pressure on the reaction was studied in the range from 2 to 5 MPa. The conversion of 1-octene remained 100 %, and the selectivity for aldehydes increased with increasing pressure. At 2 MPa two-thirds of the substrate was converted to by-products from isomerization, whereas at 5 MPa by-products account for only less than 1 % (entries 4–7). In addition, selectivity for aldehydes also increased with prolonging reaction time in the range studied (entries 4, 8–10). The molar ratios of normal to branched aldehydes (*n*/b = 0.7–1.6) obtained with ionic liquid **1**-stabilized Rh nanoparticles were similar to the ratios previously reported for reactions catalyzed by Rh nanoparticles [17, 18]. Furthermore, a catalytic experiment using $Rh(acac)(CO)_2$ as molecular Rh precursor has been performed in the same conditions as the ionic liquid **1**-stabilized Rh nanoparticles. In both cases, virtually complete conversion was observed, but the yield of aldehydes was lower with $Rh(acac)(CO)_2$ as catalyst (entry 4 vs. entry 11).

In addition, this novel thermoregulated ionic liquid **1**/cyclohexane biphasic system with ionic liquid **1**-stabilized Rh nanoparticles was also tested with 1-decene, 1-dodecene and less reactive cyclohexene as substrates (see Table 2). 100 % conversion and ≥ 98 % selectivity for aldehydes were obtained. The catalytic activity and selectivity for aldehydes of this novel sytem is superior to our previously reported results [15].

The recycling efficiency of Rh nanoparticle catalyst was also investigated. After reaction, the upper cyclohexane phase containing product was separated from the lower ionic liquid phase containing catalyst by simple phase separation. And the lower catalyst-containing ionic liquid phase was directly used in the next reaction run. Under the identical reaction conditions to entry 4 in Table 1, the recovered ionic liquid **1**-stabilized Rh nanoparticle catalyst exhibited highly catalytic efficiency without evident loss of activity after the catalyst was recycled for five times (Fig. 4). Comparison of the TEM images of Rh nanoparticles between newly prepared and after six runs (Fig. 1 vs. Fig. 5) showed a slight increase of particle size from

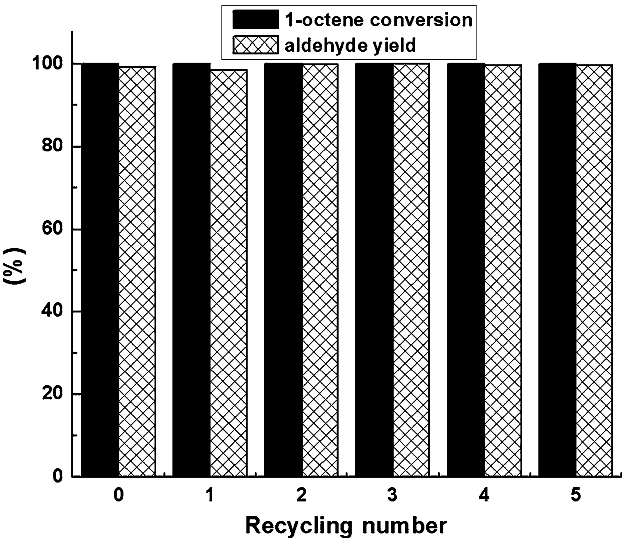

Fig. 4 Recycling efficiency of ionic liquid **1**-stabilized Rh nanoparticle catalyst on the hydroformylation of 1-octene

original 1.3 nm to 2.4 nm. ICP-AES analysis of the upper colorless cyclohexane phase separated from the first run indicated that the leaching of Rh was 0.3 wt%. The IR spectrum of ionic liquid **1**-stabilized Rh nanoparticles with vibrations at 1,988 and 2,060 cm^{-1} is an indication of the presence of Rh-CO band (Fig. 6). However, the nature of catalysis for Rh nanoparticle catalyzed hydroformylation, namely homogeneous or heterogeneous, is still open. Some results point out that the nature of the catalyst is heterogeneous [23], whereas other studies show that the active species are probably Rh complexes [17–19]. Although the presence of Rh-CO band has been detected, at this stage of our studies we still cannot certify the existence of molecular Rh species, as it requires different analytical techniques that are difficult to combine for the study of metal nanoparticles. Nevertheless, in order to make the catalytic nature of the Rh nanoparticle catalyzed hydroformylation reaction more clearly, the in situ high-pressure FTIR and ^{1}H-NMR measurements will be helpful.

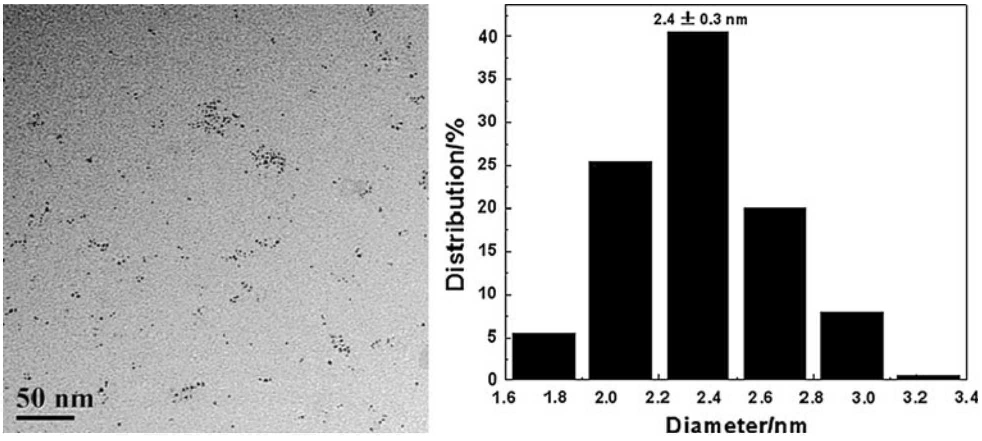

Fig. 5 TEM image of ionic liquid **1**-stabilized Rh nanoparticles (after six runs, 200 particles)

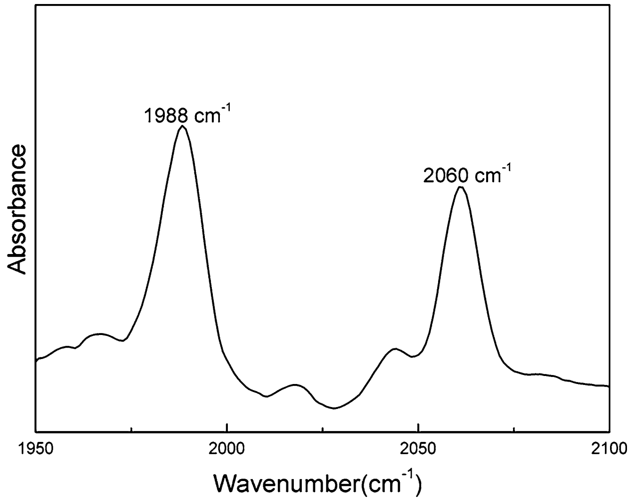

Fig. 6 Part of the IR spectrum of the ionic liquid **1**-stabilized Rh nanoparticles

4 Conclusions

In summary, we have developed a novel thermoregulated ionic liquid **1**/cyclohexane biphasic system with ionic liquid **1**-stabilized Rh nanoparticles, which possessed the thermoregulated phase-transition property. The ionic liquid **1**-stabilized Rh nanoparticle catalyst exhibited high activity and selectivity for aldehydes in the hydroformylation of olefins. And the Rh nanoparticle catalyst could be separated from product by simple phase separation and reused for five times without evident loss of activity. More applications of this novel thermoregulated ionic liquid and organic biphasic system are now under further investigation and will be reported in due course.

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