温控离子液体/有机两相体系中纳米 Rh 催化烯烃氢甲酰化反应

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摘要: 将具有“高温混溶、室温分相”功能的离子液体 $[\text{CH}_3(\text{OCH}_2\text{CH}_2)_{16}\text{N}^+\text{Et}_3][\text{CH}_3\text{SO}_3^-]$ ($\text{IL}_{\text{PEG750}}$) 与甲苯-正庚烷组成的两相体系用于纳米 Rh 催化的烯烃氢甲酰化反应中, 在优化的反应条件下, 1-辛烯转化率和醛收率分别为 99% 和 91%。催化剂经简单分相即可与产物分离, 且可连续使用 8 次, 其活性基本保持不变。

关键词: 氢甲酰化; 铑; 纳米粒子; 烯烃; 温控离子液体/有机两相体系

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Rh Nanoparticles Catalyzed Hydroformylation of Olefins in a Thermoregulated Ionic Liquid/Organic Biphasic System

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Abstract: Rh nanoparticles were investigated as a catalyst for hydroformylation of olefins in thermoregulated ionic liquid/organic biphasic systems composed of an ionic liquid, namely $[\text{CH}_3(\text{OCH}_2\text{CH}_2)_{16}\text{N}^+\text{Et}_3][\text{CH}_3\text{SO}_3^-]$ ($\text{IL}_{\text{PEG750}}$), and an organic solvent. This enables not only a homogeneous reaction but also easy biphasic separation. Under the optimized reaction conditions, the conversion of 1-octene and yield of aldehyde were 99% and 91%, respectively. The catalyst was easily separated from the product by phase separation and used eight times without evident loss of activity.

Key words: hydroformylation; rhodium; nanoparticle; olefin; thermoregulated ionic liquid/organic biphasic system

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近年来, 可溶性过渡金属纳米催化剂因其独特高效的催化性能而广受关注, 但与传统的均相催化剂一样, 存在催化剂与产物的分离回收和循环使用问题^[1,2]。为解决该难题, 已有多种方法见诸文献, 其中主要集中在液/液两相体系的研究上, 如: 氟/有机两相体系^[3,4], 温控 PEG 两相体系^[5], 水/有机两相体系^[6,7]和离子液体两相体系^[8,9]。

最近, 本课题组研究发现, 含离子液体

$[\text{CH}_3(\text{OCH}_2\text{CH}_2)_{16}\text{N}^+\text{Et}_3][\text{CH}_3\text{SO}_3^-]$ ($\text{IL}_{\text{PEG750}}$) 稳定的 Rh 纳米催化剂的 $\text{IL}_{\text{PEG750}}$ /有机两相催化体系具有“高温混溶、室温分相”的功能, 在烯烃加氢反应中 Rh 纳米催化剂表现出良好的催化活性和稳定性, 反应结束后, 通过简单分相即可实现催化剂的分离回收及循环使用 (见图 1)^[10]。

目前, Rh 纳米催化剂大多用于加氢反应中, 而用于氢甲酰化反应的较少^[11~14]。为进一步拓展温控

图 1 含有 IL_{PEG750} 稳定的 Rh 纳米催化剂的温控离子液体/有机两相体系

Fig. 1. Thermoregulated ionic liquid/organic biphasic system with IL_{PEG750}-stabilized Rh nanoparticles.

IL_{PEG750}/有机两相体系中 Rh 纳米催化剂的应用范围, 本文将其用于烯烃氢甲酰化反应中。

根据文献[15]合成离子液体 IL_{PEG750}。将含有 RhCl₃·3H₂O (20 mg, 0.076 mmol) 的 IL_{PEG750} (7.0 g, 7.6 mmol) 加入 75 ml 不锈钢高压釜中, 用 1.0 MPa 的 H₂ 置换体系 3 次后, 充至 4 MPa, 在 70 °C 搅拌反应 2 h。然后取出高压釜, 冷却至室温, 泄压开釜, 得到含有纳米 Rh 的 IL_{PEG750} 溶液备用。离子液体 IL_{PEG750} 和甲苯-正庚烷组成的两相体系的混溶温度测定方法参见文献[15]。

将含有纳米 Rh (2.6×10⁻³ mmol) 的 IL_{PEG750} 溶液 (0.25 g)、1-辛烯 (0.6 g, 5.2 mmol)、甲苯 (3.8 g)、正庚烷 (0.3 g) 和内标正癸烷 (0.1 g) 加到 75 ml 的不锈钢高压釜中, 用 1.0 MPa 的 CO 置换体系 3 次后, 充入合成气 (CO:H₂ = 1:1) 至设定压力。将高压釜置于已预先升至反应温度的恒温油浴中, 在恒速搅拌下反应至设定时间后, 取出高压釜, 冷却至室温后泄压开釜, 通过简单分相取出上层含产物的有机相。产物分析在天美公司 GC-7890 II 型气相色谱仪上进行: OV-101 毛细管柱 (50 m × 0.25 mm), FID 检测器, N₂ 作为载气。在 HP 6890 GC/5973 MSD 型气相色谱/质谱联用仪上进行样品的定性分析: HP-5MS 柱 (30 m × 0.25 mm), He 作为载气。样品的透射电镜 (TEM) 照片在 Philips Tecnai G² 20 型 (200 kV) 仪器上获得。采用美国 Perkin Elmer 公司 Optima 2000 DV 型仪器 (ICP-AES) 检测 Rh 的流失。

表 1 为 Rh 纳米催化剂上 1-辛烯氢甲酰化反应结果。1-辛烯转化率和醛收率均随着合成气压力的增加而增加 (实验 1~4); 当温度从 70 升到 90 °C 时, 1-辛烯转化率和醛收率提高 (实验 3, 5 和 6), 100 °C

表 1 IL_{PEG750} 稳定的纳米 Rh 催化 1-辛烯氢甲酰化反应

Table 1 Hydroformylation of 1-octene catalyzed by IL_{PEG750}-stabilized Rh nanoparticles

Entry	Pressure (MPa)	Temperature (°C)	Time (h)	Conversion (%)	Aldehyde yield (%)	n/b ^a
1	3.0	90	15	40	22	4.7
2	4.0	90	15	68	54	2.8
3	5.0	90	15	93	86	1.5
4	6.0	90	15	99	87	1.4
5	5.0	70	15	83	58	1.8
6	5.0	80	15	88	80	2.5
7	5.0	100	15	96	83	1.2
8	5.0	90	17	99	90	1.4
9	5.0	90	20	99	91	1.4
10 ^b	5.0	90	15	48	43	2.3
11 ^c	5.0	90	15	94	86	1.4

Other conditions: IL_{PEG750} 0.25 g (containing 2.6×10^{-3} mmol of Rh), toluene 3.8 g, *n*-heptane 0.3 g, CO:H₂ = 1:1, substrate:Rh = 2000:1 (molar ratio), internal standard *n*-decane 0.1 g, the miscibility temperature of the system is 80 °C.

^aThe molar ratio of normal to branched aldehydes.

^bUsing *n*-heptane as the sole upper-phase organic solvent.

^cUsing toluene as the sole upper-phase organic solvent.

时 1-辛烯转化率略有升高, 但醛收率下降 (实验 7)。延长反应时间可提高 1-辛烯转化率和醛收率 (实验 3, 8 和 9)。产物醛的正/异比 (1.2~4.7) 与相关文献值一致^[11,13]。值得注意的是, 当仅以正庚烷为有机相时, 1-辛烯转化率明显降低 (实验 10), 这是由于在反应温度下, IL_{PEG750} 和正庚烷不能混溶为一相所致。由此可见, 选择合适的上层有机相是实现加热条件下两相体系变为均相进行反应的关键。

在优化的反应条件下 (表 1 实验 3), 考察了 IL_{PEG750} 稳定的 Rh 纳米催化剂的循环使用性能, 结果见图 2。反应结束后, 经简单的相分离, 将下层含

图 2 IL_{PEG750} 稳定的 Rh 纳米催化剂在 1-辛烯氢甲酰化反应中的循环使用效果

Fig. 2. Recycling efficiency of IL_{PEG750}-stabilized Rh nanoparticle catalyst for hydroformylation of 1-octene.

催化剂的 IL_{PEG750} 相直接用于下一次反应. 由图可以看出, 催化剂连续使用 8 次后, 其活性未见明显降低.

为了进一步了解 Rh 纳米催化剂粒径的变化情况, 对循环使用前后 Rh 的纳米催化剂进行了 TEM 表征, 结果见图 3. 可以看出, 新制备的 Rh 纳米粒子平均粒径为 2.1 nm, 标准偏差 0.3 nm. 经连续使用 8 次后, Rh 纳米粒子平均粒径为 2.6 nm, 标准偏差 0.7 nm, 可见 Rh 粒径未见明显增加.

此外, 我们还采用 ICP-AES 法分析了催化剂循环使用过程上层有机相中 Rh 的流失, 结果见表 2.

表 2 上层有机相中的 Rh 流失

Table 2 Leaching of Rh in the upper organic phase

Recycle number	Leaching of Rh (%)
1	4.3
2	2.1
3	1.0
4	0.5
5	0.3
6	0.3
7	0.3
8	0.3

可以看出, Rh 流失随着循环使用次数增加而减少, 平均 Rh 流失为 1.1%.

将底物拓展到环己烯、1-十四碳烯和苯乙烯进行氢甲酰化反应, 结果见表 3. 可以看出, 各反应均具有较高的烯烃转化率和醛收率.

表 3 IL_{PEG750} 稳定的纳米 Rh 催化不同烯烃氢甲酰化反应
Table 3 Hydroformylation of different olefins catalyzed by IL_{PEG750}-stabilized Rh nanoparticles

Olefin	Pressure (MPa)	Temperature (°C)	Time (h)	Conversion (%)	Aldehyde yield (%)	n/b
Cyclohexene	5.0	120	12	99	85	2.0
1-Tetradecene	5.0	90	20	92	84	2.2
Styrene	5.0	90	15	99	98	0.2

Reaction conditions: IL_{PEG750} 0.25 g (containing 2.6×10^{-3} mmol of Rh), CO:H₂ = 1:1, internal standard *n*-decane 0.1 g, substrate:Rh = 2000:1 (molar ratio), the miscibility temperature of the system is 80 °C.

综上所述, IL_{PEG750} 稳定的 Rh 纳米催化剂在温控离子液体/有机两相体系的烯烃氢甲酰化反应中表现出高的催化活性和稳定性. Rh 纳米催化剂经简单分相即可与产物分离, 连续使用 8 次后, 其活性基本保持不变.

图 3 IL_{PEG750} 稳定的 Rh 纳米粒子的 TEM 照片

Fig. 3. TEM images of IL_{PEG750}-stabilized Rh nanoparticles. (a) Fresh sample; (b) After eight cycles of use.

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英 译 文

English Text

The catalytic behavior of soluble transition-metal nanoparticles has been a very active research field in recent decades because of the high efficiency and unique properties of such catalysts. However, as is the case with traditional homogeneous catalysts, one of the main disadvantages of soluble nanoparticle catalysts is the problem of separating the catalyst from the products [1,2]. A range of methods for overcoming this problem have been reported, with most studies focusing on liquid/liquid biphasic systems, for example, the use of fluorous/organic biphasic systems [3,4], thermoregulated poly(ethylene glycol) biphasic systems [5], aqueous/organic biphasic systems [6,7], and ionic liquid biphasic systems [8,9].

Recently, a novel thermoregulated ionic liquid/organic biphasic system containing Rh nanoparticles stabilized by the ionic liquid $[\text{CH}_3(\text{OCH}_2\text{CH}_2)_{16}\text{N}^+\text{Et}_3][\text{CH}_3\text{SO}_3^-]$ ($\text{IL}_{\text{PEG750}}$) was used in the hydrogenation of olefins. This achieved a highly efficient catalytic hydrogenation reaction and also easy separation and reuse of the catalyst as a result of the

thermoregulated phase-transition properties of the $\text{IL}_{\text{PEG750}}$ /organic biphasic system (see Fig. 1) [10].

Although Rh nanoparticle catalyzed hydrogenation has been extensively studied, less attention has been paid to hydroformylation [11–14]. In this study, we extended the application of $\text{IL}_{\text{PEG750}}$ -stabilized Rh nanoparticle catalysts to the hydroformylation of olefins in thermoregulated ionic liquid/organic biphasic systems.

$\text{IL}_{\text{PEG750}}$ was prepared by a method reported in the literature [15]. Rh nanoparticles stabilized by $\text{IL}_{\text{PEG750}}$ were prepared as follows. A mixture of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (20 mg, 0.076 mmol) and $\text{IL}_{\text{PEG750}}$ (7.0 g, 7.6 mmol) was added to a 75-ml standard stainless-steel autoclave and stirred under H_2 (4 MPa) at 70 °C for 2 h. The reactor was then cooled to room temperature and depressurized. The Rh nanoparticle catalyst was obtained as an $\text{IL}_{\text{PEG750}}$ solution and was used for olefin hydroformylation. The miscibility temperature of a system composed of $\text{IL}_{\text{PEG750}}$, toluene, and *n*-heptane was determined by a method reported in the literature [15].

In a typical hydroformylation reaction, $\text{IL}_{\text{PEG750}}$ (0.25 g, containing 2.6×10^{-3} mmol of Rh), 1-octene (0.6 g, 5.2 mmol), toluene (3.8 g), *n*-heptane (0.3 g), and *n*-decane as an internal standard (0.1 g) were charged into a 75-ml stainless-steel autoclave. The autoclave was sealed and flushed three times with CO at 1.0 MPa, pressurized with syngas ($\text{CO}:\text{H}_2 = 1:1$) to the required pressure, and held at the designated temperature, with magnetic stirring, for a fixed length of time. The autoclave was then cooled to room temperature and depressurized. The upper organic phase was separated by phase separation and immediately subjected to GC and GC-MS analyses.

GC analysis was performed on a Tianmei 7890 GC instrument equipped with an OV-101 column (50 m $\times$ 0.25 mm) and a flame-ionization detector; N_2 was used as the carrier gas. GC-MS measurements were performed on an HP 6890 GC/5973 MSD instrument with an HP-5MS column (30 m $\times$ 0.25 mm); He was used as the carrier gas. Transmission electron microscopy (TEM) images were taken with a Philips Tecnai G² 20 TEM (Philips, Eindhoven, The Netherlands) at an accelerating voltage of 200 kV. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses of Rh were carried out using an Optima 2000 DV (Perkin Elmer, USA).

Optimization of the reaction conditions was carried out using the hydroformylation of 1-octene as a model reaction. As shown in Table 1, the conversion of 1-octene and the yield of aldehyde increased with increasing reaction pressure (entries 1–4). The effects of temperature on the reaction were studied. In the range of 70–90 °C, the conversion of 1-octene and the yield of aldehyde increased with increasing reaction temperature (entries 3, 5, and 6). Further increasing the temperature to 100 °C achieved a slightly improved conver-

sion, but the yield of aldehyde decreased a little (entry 7). It is also evident from the data in Table 1 that prolonged reaction times led to increases in the conversion of 1-octene and aldehyde yields (entries 3, 8, and 9). The molar ratios of normal to branched aldehydes ($n/b = 1.2\text{--}4.7$) obtained with IL_{PEG750}-stabilized Rh nanoparticles were similar to the ratios previously reported for reactions catalyzed by Rh nanoparticles [11,13]. It should be noted that when *n*-heptane was used as the organic phase instead of a toluene/*n*-heptane mixture, much lower conversion was obtained (entry 10). This result implies that for reactions carried out in a homogeneous system under heating, the choice of an appropriate organic phase is crucial, because we observed that IL_{PEG750} and *n*-heptane cannot mix to form a homogeneous phase at the reaction temperature.

The recycling efficiency of the Rh nanoparticle catalyst was investigated under the optimized reaction conditions (Table 1, entry 3). After reaction, the lower IL_{PEG750} phase containing the catalyst was separated from the upper organic phase by phase separation and directly used in the next run. The catalyst was used eight times without evident loss of activity, as shown in Fig. 2.

TEM images were used to examine the morphologies of

the Rh nanoparticle catalyst before and after reaction, as shown in Fig. 3. The mean diameter of the freshly prepared Rh nanoparticles was 2.1 nm, with a standard deviation of 0.3 nm (see Fig. 3(a)). Analysis of the Rh nanoparticles after eight cycles of use showed an average diameter of 2.6 nm, with a standard deviation of 0.7 nm (see Fig. 3(b)). TEM analysis indicated that there was no apparent size increase.

We also studied the leaching of Rh in the upper organic phase (see Table 2). ICP-AES analysis showed that the loss of Rh decreases with increasing recycling number. The average leaching of Rh was 1.1%.

Extension of the hydroformylation reaction to other substrates, including cyclohexene, 1-tetradecene, and styrene, also afforded good conversions, as shown in Table 3.

In conclusion, we have demonstrated that IL_{PEG750}-stabilized Rh nanoparticles are an active, stable, and recyclable catalyst for olefin hydroformylation in thermoregulated ionic liquid/organic biphasic systems. The catalyst can be recovered readily by simple phase separation and reused, without evident loss of activity after eight catalytic cycles.

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