



Short Communication

Rh nanoparticle catalyzed hydrogenation of olefins in thermoregulated ionic liquid and organic biphasic system

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ABSTRACT

Rh nanoparticle catalyzed hydrogenation of olefins in a biphasic system composed of $[\text{CH}_3(\text{OCH}_2\text{CH}_2)_{16}\text{N}^+\text{Et}_3][\text{CH}_3\text{SO}_3^-]$ ($\text{IL}_{\text{PEG}750}$) ionic liquid and organic solvent allows for not only a highly efficient homogeneous catalytic reaction, but also an easy separation and reuse of catalyst attributed to the thermoregulated phase-transition property of the $\text{IL}_{\text{PEG}750}$ and organic biphasic system. Under the optimized conditions, various alkenes could be hydrogenated to the corresponding alkanes as the sole product with 100% conversion. The Rh nanoparticles can be recovered by simple phase separation and reused for nine times without evident loss of activity.

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1. Introduction

Transition-metal nanoparticles in homogeneous catalysis have attracted growing interest owing to the highly catalytic efficiency and unique properties. However, the recycling and stabilization of the nanoparticles remain a considerable challenge [1,2]. To overcome these drawbacks, several methods have been reported, with most studies focusing on the liquid/liquid biphasic system, for example, the use of fluorinated/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 monophasic allowing for rapid transformation or biphasic facilitating separation of product from catalyst [9–14]. Therefore, to search for new catalyst systems that might combine the advantages of both homogeneous and heterogeneous catalysis will have a significant impact.

Recently, we have developed an effective approach for Rh-catalyzed hydroformylation of olefins in a thermoregulated ionic liquid/organic biphasic system [15], wherein $[\text{CH}_3(\text{OCH}_2\text{CH}_2)_{16}\text{N}^+\text{Et}_3][\text{CH}_3\text{SO}_3^-]$ ($\text{IL}_{\text{PEG}750}$) was employed as ionic liquid. This ionic liquid exhibits very unique solubility in organic solvent depending on the temperature. Namely, $\text{IL}_{\text{PEG}750}$ 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 novel process provides both the advantages of classic monophasic and biphasic system, i.e., highly catalytic efficiency and good recyclability.

To best use this interesting technology as well as to make the catalytic process more effective, we initiated a study of Rh nanoparticle catalyzed reaction in this thermoregulated biphasic system because, in addition to the thermoregulated phase-transition property, the PEG-based ionic liquid is also anticipated to be acting to stabilize the Rh nanoparticles via the interaction of PEG linear chain and Rh, and ultimately, improving the recyclability of the nanoparticles. Herein, we disclose that the $\text{IL}_{\text{PEG}750}$ -stabilized Rh nanoparticle is a highly efficient, stable, and reusable catalyst for the hydrogenation of olefins.

2. Experimental

2.1. Materials and analyses

Toluene and *n*-heptane were purchased from Kermel and purified by distillation according to the standard method. Cyclohexene and styrene were analytical grade and were purchased from Kermel. 1-Dodecene was supplied by Fluka. 1-Octene was obtained from Acros. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was received from Beijing Research Institute of Chemical Industry and used without further purification. $\text{IL}_{\text{PEG}750}$ was prepared according to the reported method [15]. Gas chromatographic analyses were performed on a Tianmei 7890 GC instrument equipped with a

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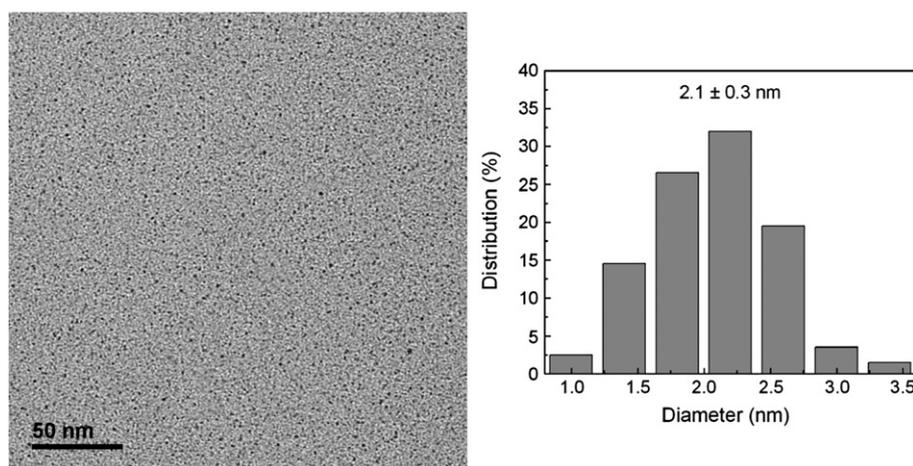


Fig. 1. TEM images and particle size histogram of Rh nanoparticles stabilized by IL_{PEG750} (200 particles).

50 m OV-101 column (inner diameter 0.25 mm) and an FID detector (N₂ as a carrier gas; injector and detector temperature 260 °C; oven temperature 70 °C). GC–MS measurement was performed on a HP 6890 GC/5973 MSD instrument (with a 30 m HP-5MS column, inner diameter 0.25 mm; He as a carrier gas; injector temperature 300 °C; oven temperature 60 °C). ICP–AES analyses of rhodium were carried out on Optima 2000 DV (Perkin Elmer, USA).

2.2. Preparation of the IL_{PEG750}-stabilized rhodium nanoparticles

A mixture of RhCl₃·3H₂O (20 mg, 0.076 mmol) and IL_{PEG750} (7.0 g, 7.6 mmol) was added in a 75 mL standard stainless-steel autoclave 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 IL_{PEG750} solution were used for the following hydrogenation of olefins.

2.3. TEM image of the rhodium nanoparticle catalyst

The IL_{PEG750} 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 TEM images were taken with a Philips Tecnai G² 20 TEM at an accelerating voltage of 200 kV.

2.4. Hydrogenation of olefins

A 75 mL stainless-steel autoclave charged with IL_{PEG750} solution of rhodium nanoparticles (0.5 g, containing 5.5×10^{-3} mmol Rh), olefin (5.5 mmol), toluene (3.5 g), *n*-heptane (0.7 g), and a magnetic bar

was flushed three times with 1.0 MPa H₂. The reactor was then pressurized with H₂ up to an appointed pressure and heated at a scheduled temperature under stirring. 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 analyses. The lower ionic liquid phase was reused to catalyze the hydrogenation of the next run.

3. Results and discussion

3.1. TEM image and thermoregulated phase-transition property of IL_{PEG750} and organic biphasic system with IL_{PEG750}-stabilized Rh nanoparticles

Rh nanoparticles were prepared by the reduction of RhCl₃·3H₂O with H₂ in the IL_{PEG750} media. As depicted in Fig. 1, TEM image showed that the Rh nanoparticles thus obtained display a homogeneous distribution in IL_{PEG750} with an average particle size of 2.1 ± 0.3 nm in diameter. This observation suggested that reductive hydrogenation is a reliable and simple method for the synthesis of Rh nanoparticles.

The thermoregulated phase-transition property of the IL_{PEG750} and organic biphasic system with IL_{PEG750}-stabilized Rh nanoparticles is shown in Fig. 2. At room temperature, the lower ionic liquid phase containing Rh nanoparticles was immiscible with the upper organic phase consisting of toluene and *n*-heptane (a in Fig. 2). Interestingly, when the temperature was elevated gradually to 60 °C, the biphasic system merged into a clear single phase (b in Fig. 2). Finally, by decreasing the temperature to room temperature, the biphasic system recovered completely to its original form as a (c in Fig. 2). The

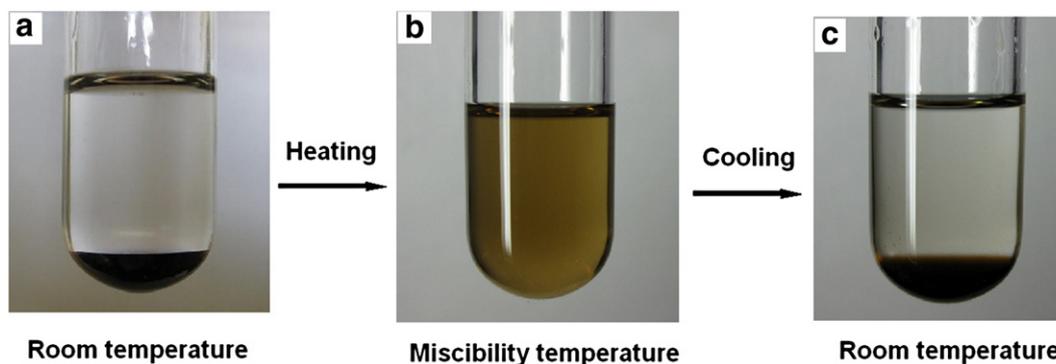


Fig. 2. Thermoregulated phase-transition property of the IL_{PEG750} and organic biphasic system with IL_{PEG750}-stabilized Rh nanoparticles.

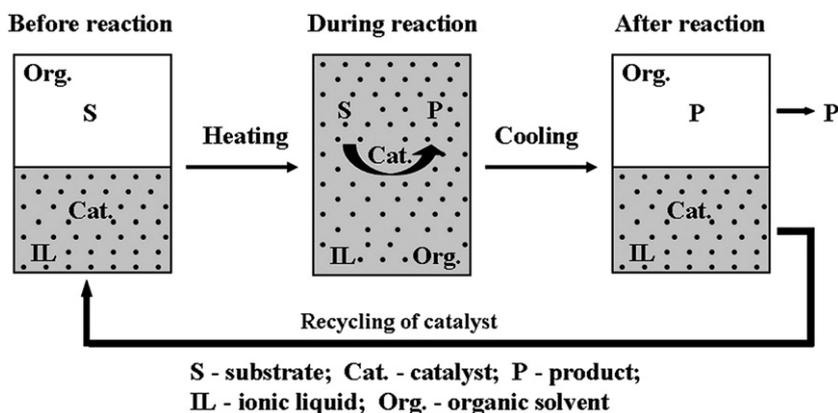


Fig. 3. Schematic illustration of thermoregulated phase-transition process for Rh nanoparticle catalyzed reaction.

observation of a colorless organic phase in c implies that after a heating and cooling cycle, no or only negligible Rh nanoparticles remain in organic phase.

The observed thermoregulated phase-transition process would provide a simple, atom-efficient, and environmentally benign way for various Rh-catalyzed reactions when the reaction procedure is appropriately designed. As illustrated in Fig. 3, for a reaction whose product is soluble in organic phase, one can make the reaction proceed in a homogeneous phase under heating (middle panel in Fig. 3). When the reaction is completed, the product and the catalyst are collected easily from the organic and ionic liquid phase, respectively, just by cooling the reaction system to room temperature (right panel in Fig. 3). The recovered catalyst can be reused without further purification or activation (right to left panel in Fig. 3).

3.2. Catalytic properties of IL_{PEG750}-stabilized Rh nanoparticles for hydrogenation

The practicality of the newly developed approach was demonstrated by the hydrogenation of olefins. Here, the hydrogenation of cyclohexene was first employed as a model reaction. The results are listed in Table 1. A general observation is that under various conditions, cyclohexane was provided as a single product. However, both the conversion and turnover frequency are influenced by the reaction parameters such as temperature (entry 1 vs. entry 2), reaction time (entries 2–5), and pressure (entry 2 vs. entry 6). The optimized reaction conditions are heating the reaction mixture at 60 °C for 1 h under 1.0 MPa of H₂ pressure (entry 2). Under these conditions, 100% conversion as well as 1000 TOF was observed. The TOF was comparable to that of the Rh nanoparticle catalysts in the ionic liquid *n*-butylmethyl-imidazolium tetrafluoroborate ([BMIm⁺][BF₄⁻]) [16–18]. It

should be noted that when using *n*-heptane instead of the mixed toluene and *n*-heptane as organic phase, a much lowered conversion and TOF were obtained (entry 7). These results further confirmed that a proper choice of organic phase that enables the reaction to be carried out in a homogeneous system under heating is crucial because we observed that ionic liquid IL_{PEG750} and *n*-heptane cannot be merged into a homogeneous phase under the reaction temperature.

With the optimized reaction conditions established, we examined the scope of this thermoregulated phase-transition process by varying structures of olefins. 100% conversion was also occurred for styrene, 1-octene, and 1-dodecene to afford the corresponding hydrogenated products.

Finally, the reusability of the Rh nanoparticles was examined. Under the identical reaction conditions to entry 2 in Table 1, the recovered Rh nanoparticles exhibited highly catalytic efficiency without evident loss in activity after the catalyst was reused for nine times (Fig. 4). Detection of the Rh content in the upper organic phase after each run by using ICP-AES revealed that the Rh leaching was under the minimum detectable amount (0.005 µg/mL). TEM image showed that the morphology of the nanoparticles remained unchanged after nine recycles (Fig. 5).

The good reusability and high stability of the Rh nanoparticles presented herein are in good agreement with our original assumption (vide supra). Namely, the presence of PEG linear chain in the IL_{PEG750} may be acting to stabilize the Rh nanoparticles via the complexation of oxygen with Rh. To compare with the classic ionic liquids which stabilize the Rh nanoparticles via the electrostatic interaction and/or steric effects [19], it is assumed that the introduction of complexation effect as an extra factor should play an important role in stabilizing the nanoparticles, although the detailed reasons deserve a further clarification.

Table 1
Hydrogenation of cyclohexene catalyzed by IL_{PEG750}-stabilized Rh nanoparticle catalyst.^a

| Entry | T (°C) | Time (min) | Pressure (MPa) | Conversion (%) | TOF (h ⁻¹) ^b |
|----------------|--------|------------|----------------|----------------|-------------------------------------|
| 1 | 50 | 60 | 1.0 | 83 | 830 |
| 2 | 60 | 60 | 1.0 | 100 | 1000 |
| 3 | 60 | 30 | 1.0 | 58 | 1160 |
| 4 | 60 | 40 | 1.0 | 74 | 1110 |
| 5 | 60 | 50 | 1.0 | 89 | 1068 |
| 6 | 60 | 60 | 0.5 | 75 | 750 |
| 7 ^c | 60 | 50 | 1.0 | 15 | 180 |

^a Reaction conditions: IL_{PEG750} 0.5 g (containing 5.5×10^{-3} mmol rhodium), substrate/Rh = 1000 (molar ratio), toluene 3.5 g, *n*-heptane 0.7 g, miscibility temperature of the system is 60 °C.

^b Turnover frequency (TOF), calculated as the number of moles of product formed per mol of rhodium per hour.

^c *n*-Heptane as the only organic solvent.

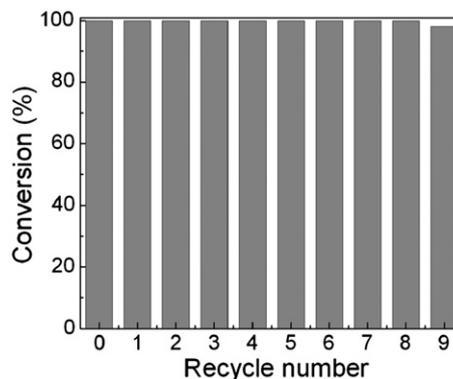


Fig. 4. The recycling efficiency of IL_{PEG750}-stabilized Rh nanoparticle catalyst.

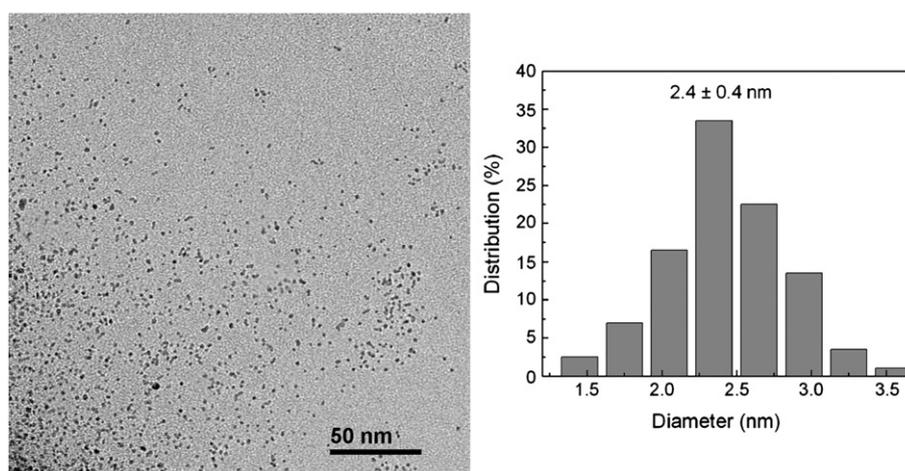


Fig. 5. TEM images and particle size histogram of Rh nanoparticles stabilized by IL_{PEG750} after nine recycles at 60 °C (200 particles).

4. Conclusions

In conclusion, we have demonstrated that IL_{PEG750}-stabilized Rh nanoparticles are active, stable and recyclable catalyst for hydrogenation of olefins. More importantly, the method represents the very few examples for easy recovery and efficient reuse of soluble transition-metal nanoparticle catalyst. Finally, the results presented in this work would have further implications beyond this work and would provide a new ideal for the development of more efficient systems aimed at practical application.

Acknowledgments

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