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Communication

Thermoregulated Phase-Separable Catalysis for Rh Nanoparticle Catalyzed Selective Hydrogenation of 1,5-Cyclooctadiene

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Abstract: Through the study of the critical solution temperature of ionic liquids $[CH_3(OCH_2CH_2)_nN^+Et_3][CH_3SO_3^-]$ (IL_{PEG}, n = 12, 16, 22), IL_{PEG}-stabilized Rh nanoparticle catalysts have been found to function as thermoregulated phase-separable catalysts and have been shown to be efficient and recyclable for the selective hydrogenation of 1,5-cyclooctadiene (1,5-COD) to cyclooctene (COE). Under optimized conditions, the conversion of 1,5-COD and selectivity for COE were 99% and 90%, respectively. The Rh catalyst could be recovered by simple phase separation and reused for ten times without loss of activity or selectivity.

Key words: thermoregulated phase-separable catalysis; ionic liquid; rhodium nanoparticle; selective hydrogenation; 1,5-cyclooctadiene

To overcome the greatest drawback of homogeneous catalysis, namely the separation of the catalyst from the product, we previously developed a thermoregulated phase-separable catalysis (TPSC) based on the critical solution temperature (CST) of phosphine ligands in organic solvents. The catalytic process of TPSC can be described as follows: before the reaction, at room temperature (T < CST), the system is biphasic and the catalyst is insoluble in the upper organic solvent. When heated to T > CST, the catalyst becomes soluble in the solvent and at the reaction temperature (T > CST) the whole system remains homogeneous. After the reaction, the reaction mixture is cooled to room temperature (T < CST) and the catalyst precipitates out of the organic phase. Thus, by simple phase separation, the products can be easily separated from the catalyst. TPSC allows not only for a highly efficient homogeneous catalytic reaction, but also for the easy separation and reuse of catalyst. It has found application in Rh or Ru complex catalyzed hydroformylation or hydrogenation [1–3].

In recent years, soluble transition-metal nanoparticles in catalysis have drawn much attention because of their high efficiency and unique properties. However, as with traditional homogeneous catalysts, one of the main disadvantages of soluble nanoparticle catalysts come from difficulties in separating the catalyst from the products. To overcome these drawbacks, several methods have been reported, with most studies focusing on liquid/liquid biphasic systems such as the use of fluorous/organic biphasic systems [4,5], thermoregulated polyethylene glycol (PEG) biphasic systems [6], thermoregulated phase-transfer biphasic systems [7], and ionic liquid biphasic systems [8,9].

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. A series of ionic liquids $[CH_3(OCH_2CH_2)_nN^+Et_3][CH_3SO_3^-]$ (IL_{PEG}, n = 12, 16, 22 abbreviated as IL_{PEG550}, IL_{PEG750}, and $IL_{PEG1000}$, respectively) has been developed and IL_{PEG750} specifically was employed as the ionic liquid. This ionic liquid exhibits a unique solubility in organic solvents depending on the temperature. Namely, IL_{PEG750} is immiscible in a mixture of toluene and n-heptane at room temperature, but becomes homogeneous when the temperature is increased beyond a certain point. Consequently, the reaction proceeds in a homogeneous system with heating, and on cooling to room temperature, separates into a biphasic sys-

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tem composed of an ionic liquid phase containing the Rh catalyst and an organic phase containing the products. Such a process provides both the advantages of a classic monophasic and a biphasic system, i.e., highly catalytic efficiency and good recyclability [10,11].

Aiming to understand the above-mentioned unique solubility of IL$_{\mathrm{PEG}}$ more clearly and enlightened by TPSC, we initiated a study on the CST of ionic liquids IL$_{\mathrm{PEG550}}$, IL$_{\mathrm{PEG750}}$, and IL$_{\mathrm{PEG1000}}$ in the mixture of toluene and *n*-heptane. Herein, IL$_{\mathrm{PEG}}$-stabilized Rh nanoparticle catalyst has been demonstrated to function as a TPSC and was shown to be highly active, selective, and recyclable for the selective hydrogenation of 1,5-COD.

Ionic liquids IL$_{\mathrm{PEG550}}$, IL$_{\mathrm{PEG750}}$, and IL$_{\mathrm{PEG1000}}$ were prepared according to the reported method [12]. Rh nanoparticles stabilized by IL$_{\mathrm{PEG1000}}$ were prepared as follows. In a typical experiment, a mixture of $\mathrm{RhCl_3 \cdot 3H_2O}$ (11.30 mg, 0.043 mmol) and IL$_{\mathrm{PEG1000}}$ (5.0 g, 4.3 mmol) was added to a 75 ml standard stainless-steel autoclave. The autoclave was flushed five times with 2.0 MPa H_2 and stirred under hydrogen (4.0 MPa) at 70 °C for 2 h. The reactor was then cooled to room temperature and depressurized. The IL$_{\mathrm{PEG1000}}$-stabilized Rh nanoparticles thus obtained were used for the following selective hydrogenation of 1,5-COD.

Selective hydrogenation reactions were performed in a 75 ml stainless-steel autoclave. In a typical experiment, the IL$_{\mathrm{PEG1000}}$ with Rh nanoparticles (0.3 g, containing 2.6×10^{-3} mmol Rh), 1,5-COD (0.6 g, 5.2 mmol), toluene (3.5 g), and *n*-heptane (0.9 g) were added to the autoclave and purged five times with 2.0 MPa H_2. Subsequently, the autoclave was pressurized with H_2 to the desired pressure and held at the desired temperature with stirring in a thermostatic oil bath for the desired length of time. After the reaction, the autoclave was cooled to room temperature and depressurized. The upper organic phase was separated from the lower ionic liquid phase by simple phase separation and analyzed by GC and GC-MS. Gas chromatography analyses was performed on a Tianmei 7890 GC instrument (Shanghai Techcomp Instrument Ltd, Shanghai, China) equipped with a 50 m OV-101 column (inner diameter 0.25 mm) and an FID detector (N_2 as a carrier gas). GC-MS measurements were performed on a HP 6890 GC/5973 MSD instrument (with a 30 m HP-5MS column, inner diameter 0.25 mm, and He as a carrier gas). The transmission electron microscopy (TEM) images were taken with a Tecnai G^2 20 Spirit microscope at an acceleration voltage of 120 kV. ICP-AES analyses of Rh were carried out on Optima 2000 DV (Perkin Elmer, USA).

The solubility of IL$_{\mathrm{PEG550}}$, IL$_{\mathrm{PEG750}}$, and IL$_{\mathrm{PEG1000}}$ in the mixture of toluene and *n*-heptane were investigated and are shown in Fig. 1. These ILs possess a distinctive CST, at which the solubility of IL$_{\mathrm{PEG550}}$, IL$_{\mathrm{PEG750}}$, and IL$_{\mathrm{PEG1000}}$ in the mixture of toluene and *n*-heptane increased dramatically. At 60 °C, IL$_{\mathrm{PEG1000}}$ was completely dissolved in the organic solvent. Additionally, at the same temperature the decrease of solubility with increasing of *n* value in IL$_{\mathrm{PEG}}$ suggested that IL$_{\mathrm{PEG1000}}$ would be a better stabilizer for recycling transition-metal nanoparticle catalysts.

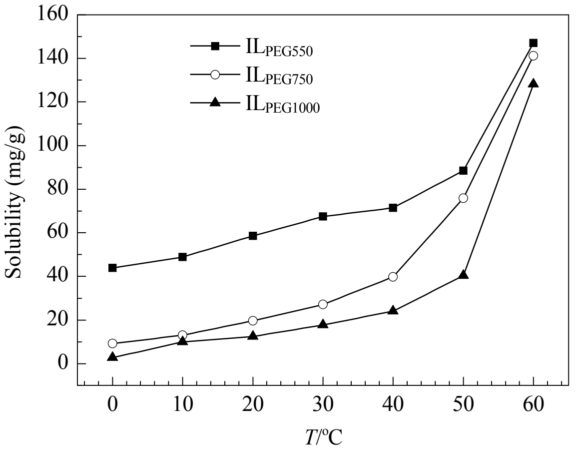

Fig. 1. Solubility of IL$_{\mathrm{PEG550}}$, IL$_{\mathrm{PEG750}}$, and IL$_{\mathrm{PEG1000}}$ in the mixture of toluene and *n*-heptane as a function of temperature.

Based on the CST of IL$_{\mathrm{PEG}}$, TPSC using a Rh nanoparticle catalyst is illustrated in Fig. 2. Before the reaction, at room temperature (T< CST), the lower IL$_{\mathrm{PEG}}$ phase containing IL$_{\mathrm{PEG}}$-stabilized Rh nanoparticle catalyst is immiscible with the upper organic phase containing the substrate. When heated to T > CST, the IL$_{\mathrm{PEG}}$-stabilized Rh nanoparticle catalyst becomes miscible with the organic phase. At the reaction temperature (T > CST), the whole system is homogeneous and the reaction proceeds smoothly. After the reaction, on cooling to room temperature (T < CST), the IL$_{\mathrm{PEG}}$-stabilized Rh nanoparticle catalyst precipitates from the organic phase, thus forming a biphasic system again, in which the upper organic phase contains products while the lower IL$_{\mathrm{PEG}}$ phase contains the Rh nanoparticle catalyst. By simple phase separation, the lower IL$_{\mathrm{PEG}}$ phase with IL$_{\mathrm{PEG}}$-stabilized Rh nanoparticle catalyst can be recovered and reused in the next reaction run.

The practicality of this TPSC with a IL$_{\mathrm{PEG1000}}$-stabilized Rh

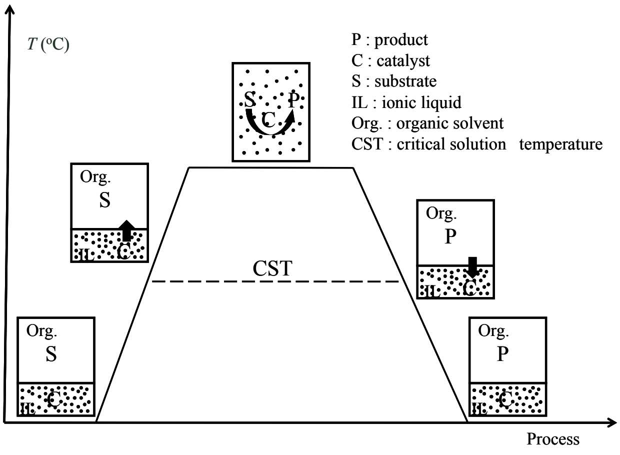

Fig. 2. General principle of TPSC of Rh nanoparticle catalyst.

Table 1 Selective hydrogenation of 1,5-COD catalyzed by IL$_{PEG1000}$-stabilized Rh nanoparticles

Entry	Temperature (°C)	Pressure of H_2 (MPa)	Time (min)	Conversion (%)	COE selectivity (%)	TOF (h^{-1})
1	40	1.0	20	52	83	2590
2	50	1.0	20	58	82	2854
3	60	1.0	20	99	90	5346
4	70	1.0	20	100	83	4980
5	60	0.1	20	13	47	367
6	60	0.5	20	67	81	3256
7	60	1.5	20	100	74	4440
8	60	1.0	10	57	81	5540
9	60	1.0	15	80	89	5696
10	60	1.0	25	100	73	3504

Reaction conditions: IL$_{PEG1000}$ 0.3 g (containing 2.6×10^{-3} mmol Rh), toluene 3.5 g, *n*-heptane 0.9 g, 1,5-COD/Rh = 2000 (molar ratio).

TOF: turnover frequency, calculated as the number of moles of product formed per mol of rhodium per hour.

nanoparticle catalyst was demonstrated by the selective hydrogenation of 1,5-COD to COE. The effects of different reaction parameters have been investigated in detail and the results are summarized in Table 1. The effect of temperature was studied over the range of 40–70 °C at 1.0 MPa pressure of H_2. The conversion of 1,5-COD increased with increasing temperature, but past 60 °C it led to a decrease in selectivity (Table 1, entries 1–4). At 60 °C, 99% conversion, and 90% COE selectivity were obtained, respectively, which are higher than the reported Ir catalyst [13,14]. It was worth noting that the conversion of 1,5-COD increased remarkably when the temperature increased from 50 to 60 °C. This result was ascribed to the increase in the solubility of IL$_{PEG1000}$ over the CST, causing the biphasic system to transform into a monophasic system. The effect of H_2 pressure on the reaction was also investigated over the range of 0.1 to 1.5 MPa (Table 1, entries 3 and 5–7). Increasing H_2 pressure benefits the conversion of 1,5-COD, but higher pressure decreases the selectivity towards COE. The best H_2 pressure was 1.0 MPa. In addition, the conversion of 1,5-COD and the selectivity towards COE are dependent on the reaction time (Table 1, entries 3 and 8–10). The optimized reaction time was 20 min. The TOF value in the present study is higher than the reported Pd-catalyzed selective hydrogenation of 1,5-COD [6].

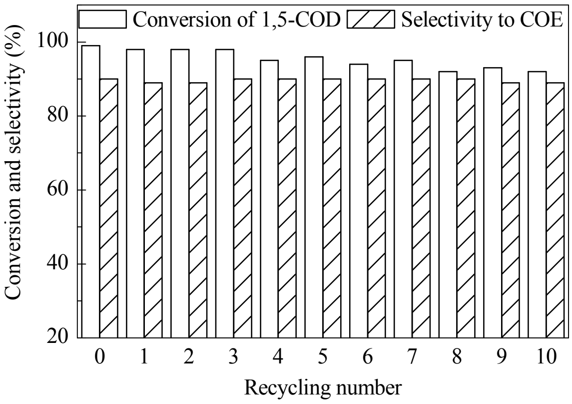

Fig. 3. Recycling efficiency of the IL$_{PEG1000}$-stabilized Rh nanoparticle catalyst for the selective hydrogenation of 1,5-COD.

As the lifetime is an important feature in evaluating a cata-

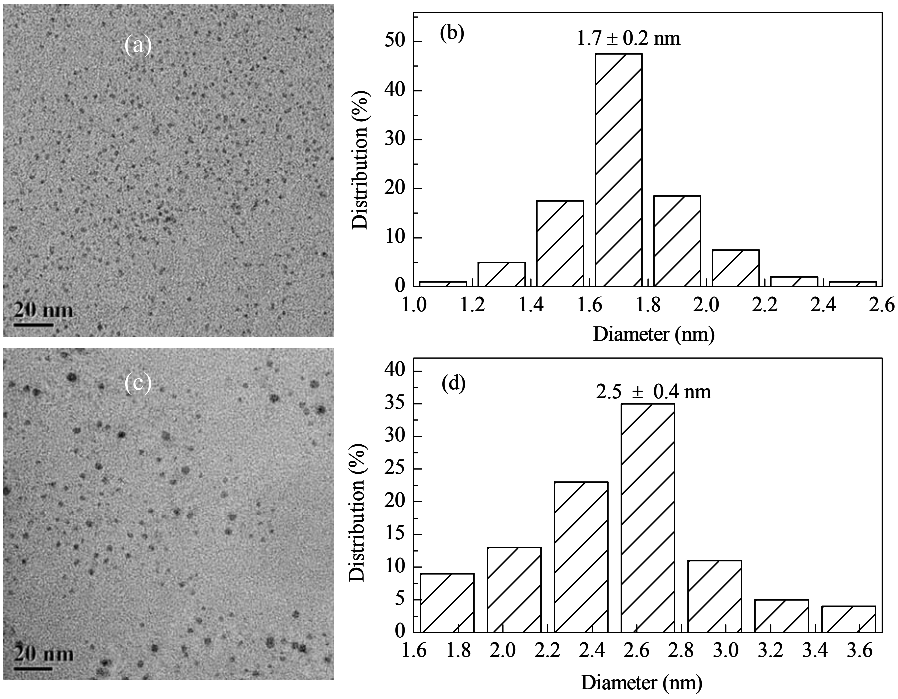

Fig. 4. TEM images and particle size histograms of the IL$_{PEG1000}$-stabilized Rh nanoparticles newly prepared (a, b) and after ten recycles (c, d) (200 and 100 particles, respectively).

lyst, the reusability of the Rh nanoparticles was examined. After the reaction, the upper organic phase was separated from the lower catalyst-containing phase by simple phase separation. This lower, catalyst-containing phase was directly used in the next reaction run. Under identical reaction conditions to entry 3 in Table 1, the recovered Rh nanoparticles exhibited high catalytic efficiency without loss of activity or selectivity after the catalyst was reused ten times (Fig. 3). Comparison of the TEM images between the newly prepared Rh nanoparticles and those after ten recycles showed only a slight increase of particle size from the original 1.7 ± 0.2 nm to 2.5 ± 0.4 nm (Fig. 4).

The leaching of transition-metal nanoparticle catalyst is frequently a problem, especially for the catalytically active group VIII metals [15]. Therefore, we studied the Rh leaching of the $IL_{PEG1000}$/toluene/*n*-heptane biphasic system in the recycle experiments by measuring the Rh content in the toluene/*n*-heptane phase at the end of the reaction. The Rh concentration was measured by ICP-AES and the results indicated that the Rh content was under the minimum detectable amount (0.005 μg/ml).

In summary, for the first time, a IL_{PEG}-stabilized Rh nanoparticle catalyst was demonstrated to act as a TPSC by investigation of the CST of IL_{PEG} in the mixture of toluene and *n*-heptane. Furthermore, the $IL_{PEG1000}$-stabilized Rh nanoparticle catalyst was also shown to be highly active, selective, and recyclable for the selective hydrogenation of 1,5-COD. More to the point, the methodology of TPSC of nanoparticles provides a new approach to the recovery and recycling of soluble transition-metal nanoparticle catalysts, especially for noble transition-metal nanoparticle catalysts.

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