

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 $[\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{N}^+\text{Et}_3][\text{CH}_3\text{SO}_3^-]$ (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 ($T < \text{CST}$), the system is biphasic and the catalyst is insoluble in the upper organic solvent. When heated to $T > \text{CST}$, the catalyst becomes soluble in the solvent and at the reaction temperature ($T > \text{CST}$) the whole system remains homogeneous. After the reaction, the reaction mixture is cooled to room temperature ($T < \text{CST}$) 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 fluorinated/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 $[\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{N}^+\text{Et}_3][\text{CH}_3\text{SO}_3^-]$ (IL_{PEG} , $n = 12, 16, 22$ abbreviated as $\text{IL}_{\text{PEG}550}$, $\text{IL}_{\text{PEG}750}$, and $\text{IL}_{\text{PEG}1000}$, respectively) has been developed and $\text{IL}_{\text{PEG}750}$ specifically was employed as the ionic liquid. This ionic liquid exhibits a unique solubility in organic solvents depending on the temperature. Namely, $\text{IL}_{\text{PEG}750}$ 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_{PEG} more clearly and enlightened by TPSC, we initiated a study on the CST of ionic liquids IL_{PEG550}, IL_{PEG750}, and IL_{PEG1000} in the mixture of toluene and *n*-heptane. Herein, IL_{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_{PEG550}, IL_{PEG750}, and IL_{PEG1000} were prepared according to the reported method [12]. Rh nanoparticles stabilized by IL_{PEG1000} were prepared as follows. In a typical experiment, a mixture of RhCl₃·3H₂O (11.30 mg, 0.043 mmol) and IL_{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 H₂ 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_{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_{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 H₂. Subsequently, the autoclave was pressurized with H₂ 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 (N₂ 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 G²20 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_{PEG550}, IL_{PEG750}, and IL_{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_{PEG550}, IL_{PEG750}, and IL_{PEG1000} in the mixture of toluene and *n*-heptane increased dramatically. At 60 °C, IL_{PEG1000} was completely dissolved in the organic solvent. Addi-

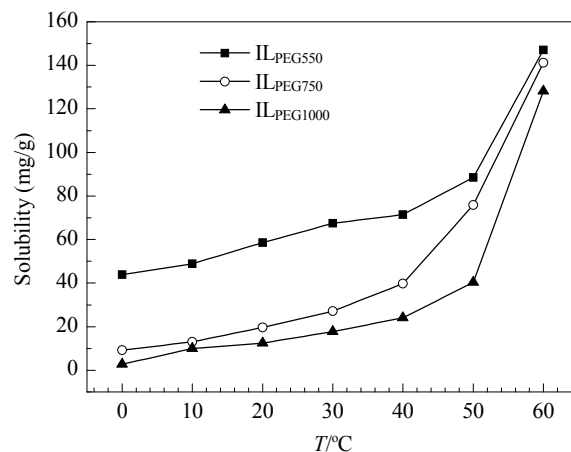


Fig. 1. Solubility of IL_{PEG550}, IL_{PEG750}, and IL_{PEG1000} in the mixture of toluene and *n*-heptane as a function of temperature.

tionally, at the same temperature the decrease of solubility with increasing of *n* value in IL_{PEG} suggested that IL_{PEG1000} would be a better stabilizer for recycling transition-metal nanoparticle catalysts.

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

The practicality of this TPSC with a IL_{PEG1000}-stabilized Rh

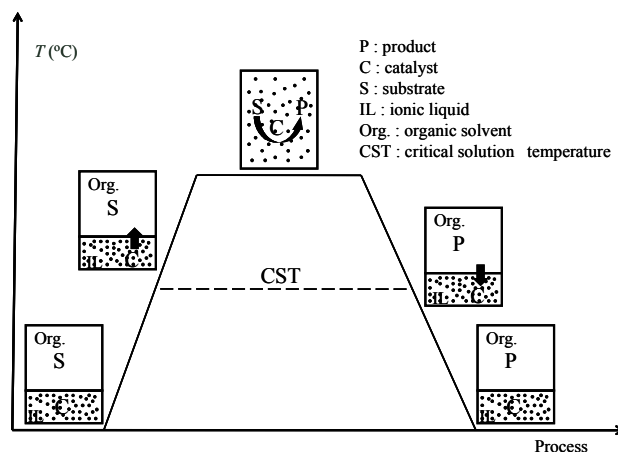


Fig. 2. General principle of TPSC of Rh nanoparticle catalyst.

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