温控相分离纳米 Rh 催化 1,5-环辛二烯选择性加氢反应

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摘要: 发现离子液体 $[\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{N}^+\text{Et}_3][\text{CH}_3\text{SO}_3^-]$ (IL_{PEG} , $n = 12, 16, 22$) 具有临界溶解温度特性, 据此确证了以 IL_{PEG} 为稳定剂制得的 Rh 纳米催化剂具有温控相分离催化功能, 并将其用于 1,5-环辛二烯 (1,5-COD) 选择性加氢制环辛烯 (COE) 的反应中. 在优化的反应条件下, 1,5-COD 转化率和 COE 选择性分别为 99% 和 90%; Rh 纳米催化剂经简单分相即可与产物分离, 催化剂循环使用 10 次, 其活性和选择性无明显降低.

关键词: 温控相分离催化; 离子液体; 铑纳米粒子; 选择性加氢; 1,5-环辛二烯

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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

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为解决均相催化反应中催化剂与产物的分离难题, 基于膦配体在有机溶剂中的临界溶解温度 (CST) 特性, 本课题组提出了温控相分离催化 (TPSC) 概念. 其基本原理如下: 室温时 (低于 CST) 催化剂不溶于上层有机溶剂而自成一相; 当加热至反应温度时 (高于 CST), 催化剂可溶于有机溶剂中, 体系变为均相; 反应结束后, 冷却至室温时催化剂

又从上层有机相中析出, 故通过简单分相, 即可将产物与催化剂分离. 该催化体系兼具均相反应的高活性和多相体系易分离的特点, 已成功用于 Rh 和 Ru 络合物催化的烯烃氢甲酰化和加氢反应中^[1~3].

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倍受关注, 但传统的均相催化剂一样, 存在催化剂与产物分离回收难的问题. 因

此, 人们主要采用氟/有机两相体系^[4,5]、温控 PEG 两相体系^[6]、温控相转移两相体系^[7]和离子液体两相体系^[8,9]等液/液两相体系。

最近, 本课题组以含聚醚链的离子液体 $[\text{CH}_3(\text{OCH}_2\text{CH}_2)_{16}\text{N}^+\text{Et}_3][\text{CH}_3\text{SO}_3^-]$ ($\text{IL}_{\text{PEG}750}$) 为稳定剂制备了 Rh 纳米催化剂。研究发现, 含该 Rh 纳米催化剂的离子液体相与甲苯、正庚烷组成的两相体系存在“高温混溶, 室温分相”的功能, 即高温均相反应, 室温分相而实现催化剂的分离回收及循环使用。这种含 Rh 纳米催化剂的温控离子液体/有机两相催化体系兼具均相和两相催化反应的优点, 已成功用于烯烃的加氢和氢甲酰化反应中^[10,11]。

在上述工作基础上, 本文进一步探究了含聚醚链离子液体 $[\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{N}^+\text{Et}_3][\text{CH}_3\text{SO}_3^-]$ (IL_{PEG} , $n = 12, 16$ 和 22 时分别记作 $\text{IL}_{\text{PEG}550}$, $\text{IL}_{\text{PEG}750}$ 和 $\text{IL}_{\text{PEG}1000}$) 在甲苯、正庚烷混合溶剂中的溶解性能, 首次发现其具有 CST 特性, 并将其用于 1,5-环辛二烯 (1,5-COD) 的选择性加氢反应中。

根据文献[12]合成离子液体 $\text{IL}_{\text{PEG}550}$, $\text{IL}_{\text{PEG}750}$ 和 $\text{IL}_{\text{PEG}1000}$ 。稳定的 Rh 纳米催化剂的制备方法如下: 将 $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (11.30 mg, 0.043 mmol) 和 $\text{IL}_{\text{PEG}1000}$ (5.0 g, 4.3 mmol) 加入 75 ml 的不锈钢高压釜中, 用 2.0 MPa 氢气置换体系 5 次后, 充压至 4.0 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 Rh 纳米催化剂的 $\text{IL}_{\text{PEG}1000}$ 备用。

将含有 Rh 纳米催化剂的 $\text{IL}_{\text{PEG}1000}$ (0.3 g, 含有 2.6×10^{-3} mmol Rh)、1,5-COD (0.6 g, 5.2 mmol)、甲苯 (3.5 g) 和正庚烷 (0.9 g) 加入 75 ml 的不锈钢高压釜中。用 2.0 MPa 氢气置换体系 5 次后, 充至反应压力, 将高压釜置于已预先升至反应温度的恒温油浴中, 在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。产物分析在上海天美科学有限公司的 GC-7890 II 型气相色谱仪上进行: OV-101 毛细管柱 (长 50 m, 内径 0.25 mm), FID 检测器 (N_2 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 (长 30 m, 内径 0.25 mm), He 作为载气。透射电镜 (TEM) 照片在 Tecnai G² 20 Spirit 型 (120 kV) 仪器上获得。采用美国 Perkin Elmer 公司 Optima 2000 DV 型电

感耦合等离子体发射光谱仪 (ICP-AES) 检测上层有机相中 Rh 含量。

$\text{IL}_{\text{PEG}550}$, $\text{IL}_{\text{PEG}750}$ 和 $\text{IL}_{\text{PEG}1000}$ 在甲苯和正庚烷混合溶剂中的溶解性质如图 1 所示。可以看出, 这三种离子液体具有 CST 特性, 即 $\text{IL}_{\text{PEG}550}$, $\text{IL}_{\text{PEG}750}$ 和 $\text{IL}_{\text{PEG}1000}$ 在甲苯和正庚烷混合溶剂中的溶解度存在陡增现象, 至 60 °C 时 $\text{IL}_{\text{PEG}1000}$ 完全溶解在有机溶剂中。另外, 在相同的温度下, 随着 IL_{PEG} 中聚醚链增长, 它在有机溶剂中的溶解度减小, 因此, $\text{IL}_{\text{PEG}1000}$ 更宜用作过渡金属纳米催化剂分离回收及循环使用过程中的稳定剂。

图 1 离子液体 $\text{IL}_{\text{PEG}550}$, $\text{IL}_{\text{PEG}750}$ 和 $\text{IL}_{\text{PEG}1000}$ 在甲苯和正庚烷混合溶剂中的溶解性能

Fig. 1. Solubility of $\text{IL}_{\text{PEG}550}$, $\text{IL}_{\text{PEG}750}$, and $\text{IL}_{\text{PEG}1000}$ in the mixture of toluene and *n*-heptane as a function of temperature.

基于 IL_{PEG} 的 CST 特性, 提出了含 Rh 纳米催化剂的温控相分离催化概念, 其基本原理如图 2 所示。室温时 ($T < \text{CST}$), 下层含 Rh 纳米催化剂的

图 2 含 Rh 纳米催化剂的温控相分离催化基本原理

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

IL_{PEG} 相与上层含底物的有机相不互溶. 当加热至 $T > \text{CST}$ 时, 含 Rh 纳米催化剂的 IL_{PEG} 相与上层有机相混溶, 在反应温度下 ($T > \text{CST}$), 整个体系为均相, 反应可顺利进行. 反应结束冷至室温 ($T < \text{CST}$) 后, 含 Rh 纳米催化剂的 IL_{PEG} 相又可从上层有机相中析出, 体系重新变为两相, 即上层含产物的有机相和下层含 Rh 纳米催化剂的离子液体相. 通过简单分相即可实现产物与催化剂的分离, 下层含催化剂的离子液体相可直接循环使用.

将上述含 Rh 纳米催化剂的温控相分离催化体系用于 1,5-COD 选择性加氢制环辛烯 (COE) 的反应中, 结果见表 1. 可以看出, 1,5-COD 转化率随着反应温度的升高而增加; 但产物选择性在 60 °C 达最高 (实验 1~4), 1,5-COD 转化率为 99%, COE 选择性为 90%, 高于文献[13,14]报道的 Ir 催化剂. 值得注意的是, 当温度从 50 °C 升至 60 °C 时, 反应活性明显提高, 这主要是由于反应体系从两相变为均相所致. 如实验 3, 5~7 所示, 增大反应压力有利于提高 1,5-COD 转化率, 但产物 COE 选择性在 1.0 MPa 时最高. 还可以看出, 随着反应时间的延长, 1,5-COD 转化率增加, 而产物选择性于 20 min 时达最高 (实验 3、8~10). 可见适宜反应条件为 60 °C, 1.0 MPa, 20 min. 结果还表明, IL_{PEG1000} 稳定的 Rh 纳米催化剂催化 1,5-环辛二烯选择性加氢反应的 TOF 值高于文献报道的 Pd 纳米催化剂^[6].

表 1 IL_{PEG1000} 稳定的纳米 Rh 催化 1,5-环辛二烯选择性加氢反应

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.

反应结束后, 经简单分相, 将含催化剂的离子液体相直接用于下一次反应, 结果见图 3. 可以看出, 在优化的反应条件下 Rh 纳米催化剂可循环使用 10 次, 其活性和选择性无明显降低. 图 4 为新鲜的和循环使用 10 次后的 Rh 纳米催化剂的 TEM 照片. 由图可见, 循环使用 10 次后, Rh 纳米催化剂的粒径从 1.7 ± 0.2 nm 略增至 2.5 ± 0.4 nm.

过渡金属纳米催化剂在反应中通常都会有流失, 尤其是广泛应用于催化反应中的第八族金属^[15]. 本文测定了反应结束后甲苯和正庚烷混合溶剂相中 Rh 含量. 结果表明, 反应中 Rh 的流失低于仪器检测下限 (0.005 µg/ml).

图 3 IL_{PEG1000} 稳定的 Rh 纳米催化剂在 1,5-环辛二烯选择性加氢反应中的循环使用效果

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

图 4 IL_{PEG1000} 稳定的 Rh 纳米粒子 TEM 图

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).

综上所述, 基于 IL_{PEG} 在甲苯和正庚烷混合溶剂中的 CST 特性, 确证了 Rh 纳米催化剂的温控相分离催化功能, 且 IL_{PEG1000} 稳定的 Rh 纳米催化剂在 1,5-环辛二烯选择性加氢反应中表现出高的催化活性、选择性和良好的循环使用性能。尤为重要的是, 含纳米催化剂的温控相分离催化体系将为可溶性过渡金属纳米催化剂, 尤其是贵金属纳米催化剂的分离回收及循环使用开辟一条新途径。

参 考 文 献

- 1 Wang Y H, Jin Z L. In: Cornils B, Herrmann W A, Muhler M, Wong C H eds. *Catalysis from A to Z*. Weinheim: Wiley-VCH, 2007. 1409
- 2 Jin Z L, Wang Y H, Zheng X L. In: Cornils B, Herrmann W A eds. *Aqueous-Phase Organometallic Catalysis*. Weinheim: Wiley-VCH, 2004. 301
- 3 Wang Y H, Jiang J Y, Wu X W, Cheng F, Jin Z L. *Catal Lett*, 2002, **79**: 55
- 4 Chechik V, Crooks R M. *J Am Chem Soc*, 2000, **122**: 1243
- 5 Moreno-Mañas M, Pleixats R, Villarroya S. *Organometallics*, 2001, **20**: 4524
- 6 Huang T S, Wang Y H, Jiang J Y, Jin Z L. *Chin Chem Lett*, 2008, **19**: 102
- 7 Li K X, Wang Y H, Jiang J Y, Jin Z L. *Catal Commun*, 2010, **11**: 542
- 8 Dupont J, de Souza R F, Suarez P A Z. *Chem Rev*, 2002, **102**: 3667
- 9 Mu X D, Meng J Q, Li Z C, Kou Y. *J Am Chem Soc*, 2005, **127**: 9694
- 10 Zeng Y, Wang Y H, Jiang J Y, Jin Z L. *Catal Commun*, 2012, **19**: 70
- 11 曾艳, 王艳华, 徐贻成, 宋颖, 赵家骐, 蒋景阳, 金子林. 催化学报(Zeng Y, Wang Y H, Xu Y Ch, Song Y, Zhao J Q, Jiang J Y, Jin Z L. *Chin J Catal*), 2012, **33**: 402
- 12 Tan B, Jiang J Y, Wang Y H, Wei L, Chen D J, Jin Z L. *Appl Organometal Chem*, 2008, **22**: 620
- 13 Moura F C C, dos Santos E N, Lago R M, Vargas M D, Araujo M H. *J Mol Catal A*, 2005, **226**: 243
- 14 Moura F C C, Lago R M, dos Santos E N, Araujo M H. *Catal Commun*, 2002, **3**: 541
- 15 Durán Pachón L, Rothenberg G. *Appl Organometal Chem*, 2008, **22**: 288

英 译 文

English Text

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 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 [$\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{N}^+\text{Et}_3$][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 system 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 G² 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_{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. Additionally, 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 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 H₂. 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 H₂ 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 H₂ pressure benefits the conversion of 1,5-COD, but higher pressure decreases the selectivity towards COE. The best H₂ 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].

As the lifetime is an important feature in evaluating a catalyst, 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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