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Communication

Thermoregulated phase-transfer Rh nanoparticle catalyst for selective hydrogenation of *ortho*-chloronitrobenzene

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ABSTRACT

The use of a thermoregulated phase-transfer Rh nanoparticle catalyst for the selective hydrogenation of *ortho*-chloronitrobenzene (*o*-CNB) to *ortho*-chloroaniline (*o*-CAN) in an aqueous/1-pentanol biphasic system was studied. Under the optimized reaction conditions, the conversion of *o*-CNB and the selectivity for *o*-CAN were 100% and 98%, respectively. The catalyst was easily separated from the product by phase separation and reused eight times without evident loss of activity and selectivity.

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The catalytic hydrogenation of *ortho*-chloronitrobenzene (*o*-CNB) is an important method for the preparation of *ortho*-chloroaniline (*o*-CAN), which is an intermediate in the syntheses of pharmaceuticals, dyes, and pesticides. Among the investigated catalysts, transition-metal nanoparticles are of interest because of their high catalytic efficiencies. Nanoparticles such as Ru [1], Rh [2], Pd [3], Ag [4], Au [5], and Pt [6,7] have been reported to be efficient in the catalytic hydrogenation of *o*-CNB. However, considering the cost and limited sources of these noble transition-metals, the development of recyclable catalysts with high activities and selectivities is desirable. In our previous work, soluble transition-metal nanoparticle catalysts for thermoregulated poly(ethylene glycol) biphasic catalysis [8–10], thermoregulated phase-separable catalysis [11–13], and thermoregulated phase-transfer catalysis (TRPTC) were developed [14–17]. These catalysts provide promising approaches to the recovery and recycling of soluble transition-metal nanoparticle catalysts, especially noble transi-

tion-metal nanoparticle catalysts.

TRPTC has been used in Rh-nanoparticle-catalyzed hydrogenation, hydroformylation, and hydroaminomethylation of olefins [14–17]. In this study, based on our earlier work, we used $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_{22}\text{CH}_3$ -stabilized Rh nanoparticles as an efficient and recyclable catalyst in a thermoregulated phase-transfer biphasic system for the selective hydrogenation of *o*-CNB to *o*-CAN (Fig. 1).

The thermoregulated ligand $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_{22}\text{CH}_3$ was prepared using a previously reported method [18]. $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_{22}\text{CH}_3$ -stabilized Rh nanoparticles were prepared as follows. A mixture of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (1 mg, 0.0038 mmol), $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_{22}\text{CH}_3$ (8.88 mg, 0.008 mmol), 1-pentanol (4 mL), and water (4 mL) was added to a 75-mL standard stainless-steel autoclave under a N_2 atmosphere and flushed three times with 3.0 MPa H_2 . The mixture was stirred under H_2 (4 MPa) at 70 °C for 2 h. The reactor was cooled to room temperature and depressurized. The color of the aqueous phase

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Fig. 1. Hydrogenation of *o*-CNB to *o*-CAN using thermoregulated phase-transfer Rh nanoparticles as catalyst.

changed from light yellow to brownish black, indicating formation of the Rh nanoparticle catalyst.

All hydrogenation reactions were carried out in a 75-mL standard stainless-steel autoclave immersed in a thermostated oil bath. The stirring rate was the same for all experiments performed. The autoclave was charged with the Rh nanoparticle catalyst, 1-pentanol, water, and *o*-CNB and flushed three times with 3.0 MPa H₂. The reactor was pressurized with H₂ up to the required pressure and held at the scheduled temperature, with magnetic stirring, for a fixed length of time. The reactor was cooled to room temperature and depressurized. The upper organic phase was separated by phase separation from the lower aqueous phase and immediately analyzed using gas chromatography (GC) and GC-mass-spectrometry (GC-MS).

GC analysis was performed using a Tianmei 7890 GC instrument equipped with an OV-101 column (50 m × 0.25 mm) and a flame-ionization detector; N₂ was used as the carrier gas. GC-MS measurements were performed using an HP 6890 GC/5973 MSD instrument with an HP-5MS column (30 m × 0.25 mm); He was used as the carrier gas. Transmission electron microscopy (TEM) images were obtained using a Philips Tecnai G² 20 instrument at an accelerating voltage of 200 kV. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) determination of Rh was performed using an Optima 2000 DV instrument.

First, we studied the effects of the reaction conditions on the selective hydrogenation of *o*-CNB; the results are listed in Table 1. It shows that increasing the temperature, pressure, or reaction time increases the conversion of *o*-CNB, but the selectivity for *o*-CAN remains nearly the same. Under the conditions *T* = 70 °C, H₂ pressure = 3 MPa, *o*-CNB/Rh = 1000 (molar ratio), and time = 2 h, the conversion of *o*-CNB and the selectivity for *o*-CAN were 100% and 98%, respectively. The catalytic efficiency was comparable to that reported for a Ni/TiO₂ catalyst [19,20]. It is worth noting that when the temperature is increased from 50 to 60 °C, the conversion of *o*-CNB increases sharply. This is mainly because the catalyst has been transferred into the organic phase, in which the reaction proceeds homogeneously [17].

Table 1

Selective hydrogenation of *o*-CNB catalyzed by Ph₂P(CH₂CH₂O)₂₂CH₃-stabilized Rh nanoparticles.

Entry	Temperature (°C)	Pressure (MPa)	Time (h)	Conversion (%)	Selectivity (%)
1	40	3	2	41	99
2	50	3	2	55	99
3	60	3	2	88	98
4	70	3	2	100	98
5	70	1	2	45	98
6	70	2	2	54	98
7	70	3	1	69	97
8	70	3	1.5	87	98

Reaction conditions: 1-pentanol 4 mL, water 4 mL containing 0.0038 mmol Rh, *o*-CNB/Rh = 1000 (molar ratio), Ph₂P(CH₂CH₂O)₂₂CH₃/Rh = 2.

We then investigated the recycling efficiency of the Rh nanoparticle catalyst. After the initial reaction, the lower aqueous phase containing the catalyst was separated from the upper organic phase by simple phase separation and reused without any further treatment in the next reaction run under the optimized reaction conditions (Table 1, entry 4). The Rh nanoparticles maintained their efficiency for up to at least eight cycles, as shown in Fig. 2.

TEM was used to examine the morphologies of the Rh nanoparticle catalyst before and after reaction; the images are shown in Fig. 3. The mean diameter of the freshly prepared Rh nanoparticles was 2.2 nm, with a standard deviation of 0.2 nm. Analysis of the Rh nanoparticles after eight recycles showed an average diameter of 5.6 nm and a standard deviation of 0.7 nm (Fig. 3(b)). It is known that catalytic activity is sometimes sensitive to particle size. We deduced from the results of the recycling experiments that this reaction is insensitive to nanoparticle catalyst size in the range 2.2–5.6 nm.

We also studied the leaching of Rh in the upper organic phase (Fig. 4). ICP-AES analysis of the 1-pentanol layer showed that Rh loss decreases with increasing recycling number. The average leaching of Rh was 1.8 wt%.

To determine whether the catalyst is heterogeneous or homogeneous, a Hg-poisoning experiment was carried out. Hg(0) (0.38 g, 500 equiv with respect to Rh) was added to the freshly prepared Rh nanoparticle catalyst, and the mixture was stirred

Fig. 2. Recycling efficiency of Ph₂P(CH₂CH₂O)₂₂CH₃-stabilized Rh nanoparticle catalyst for selective hydrogenation of *o*-CNB.

Fig. 3. TEM images of thermoregulated ligand $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_{22}\text{CH}_3$ -stabilized Rh nanoparticles. (a) Fresh Rh nanoparticles; (b) Rh nanoparticles after eight recycles.

at room temperature for 2 h. Hydrogenation was then performed under the reaction conditions in Table 1, entry 4. The *o*-CNB conversion of 14% indicated that the Rh nanoparticle catalyst was heterogeneous.

In summary, we have demonstrated for the first time that thermoregulated ligand $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_{22}\text{CH}_3$ -stabilized Rh nanoparticles are an active, selective, and recyclable catalyst for the hydrogenation of *o*-CNB to *o*-CAN in an aqueous/1-pentanol biphasic system. TRPTC achieves homogeneous reactions under reaction conditions, and subsequent efficient

separation of the catalysts from the products is achieved by cooling the reaction mixtures. It is therefore anticipated that TRPTC will find various applications in reactions catalyzed by Rh and other transition-metal nanoparticles.

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Fig. 4. Leaching of Rh in upper organic phase.

Graphical Abstract

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An active selective and recyclable thermoregulated phase-transfer rhodium nanoparticle catalyst was applied to the hydrogenation of *ortho*-chloronitrobenzene to *ortho*-chloroaniline.

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温控相转移纳米铈催化邻氯硝基苯选择性加氢反应

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摘要: 研究了水/1-戊醇两相体系中铈纳米催化剂在邻氯硝基苯选择性还原制邻氯苯胺反应中的催化性能. 在优化的反应条件下, 邻氯硝基苯的转化率和邻氯苯胺的选择性分别为100%和98%. 铈纳米催化剂经简单分相后可循环使用8次, 其催化活性和选择性基本保持不变.

关键词: 温控配体; 铈纳米粒子; 邻氯硝基苯; 选择性加氢; 水/1-戊醇两相体系

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