



Thermoregulated phase-transfer rhodium nanoparticle catalyst for hydrogenation in an aqueous/organic biphasic system

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ABSTRACT

A simple, effective and reversible aqueous/organic phase-transfer method for rhodium nanoparticles was developed on the basis of the cloud point (Cp) of thermoregulated ligand. The rhodium nanoparticles stabilized by thermoregulated ligand $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ ($n = 16$) could transfer from aqueous phase to 1-butanol phase and vice versa by means of changing temperature. This thermoregulated phase-transfer rhodium nanoparticle catalyst evaluated in the hydrogenation of olefins in an aqueous/1-butanol biphasic system exhibited high activity and stability.

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1. Introduction

Soluble transition-metal nanoparticles in catalysis have drawn much attention due to their high efficiency and unique properties. However, very similar to traditional homogeneous catalysts, one of the main disadvantages of soluble nanoparticle catalysts is the problem of separation the catalyst from the products [1,2]. To deal with this problem, a range of methods has 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] and ionic liquid biphasic system [6,7].

Thermoregulated phase-transfer catalysis (TRPTC) in aqueous/organic biphasic system was suggested by Jin and co-workers based on the cloud point (Cp) of thermoregulated ligands. Thermoregulated ligands exhibit an inverse-temperature-dependent solubility in water, that is, their aqueous solution will undergo a phase separation on heating to Cp and become water soluble again on cooling to a temperature lower than the Cp [8–10]. The general principle of TRPTC is illustrated in Scheme 1. The character of this catalytic process can be described as follows: the system consists of aqueous and organic phases. At a temperature lower than the Cp, the catalyst would remain in the aqueous phase. On heating to a temperature higher than the Cp, however, the catalyst would

transfer into the organic phase. Thus, the catalyst and the substrate will be in the same phase and the reaction proceeds in the organic phase. As soon as the reaction is completed and the system is cooled to a temperature lower than the Cp, the catalyst would return to the aqueous phase. Therefore, by simple phase separation the catalyst can be separated from products. TRPTC is not only free from the shortcomings of classical biphasic catalysis, in which the scope of application is restrained by the water-solubility of the substrate, but also a promising approach for recovery and recycling of noble transition-metal complex catalyst. Till now, several catalytic reactions have been achieved in TRPTC system such as hydroformylation [11], hydrogenation [12], CO selective reduction of nitroarenes [13] and Heck reaction [14]. Although employing thermoregulated ligand as stabilizing agent for rhodium has been explored in the hydroformylation of 1-octene [15], transition-metal nanoparticle catalyst with the function of TRPTC has not previously been reported.

In this paper, rhodium nanoparticle catalyst stabilized by thermoregulated ligand $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ ($n = 16$) was first certified to be with the function of TRPTC and used as an active, stable and recyclable catalyst for hydrogenation of olefins.

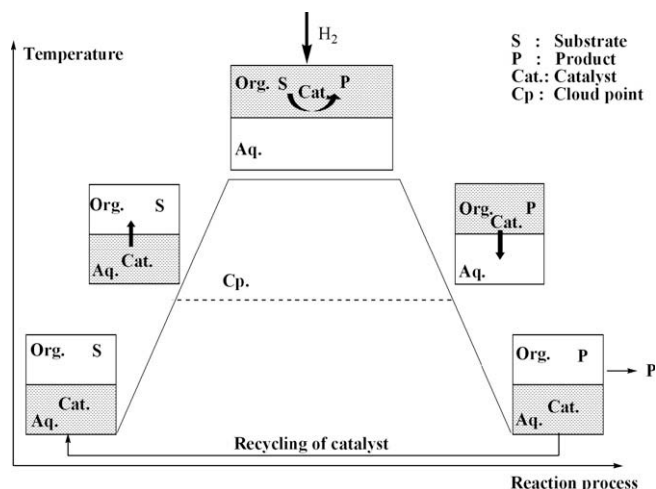
2. Experimental

2.1. Materials and analyses

1-Butanol, cyclohexene and styrene were of analytical grade and were purchased from Kermel. 1-Dodecene and 1,5-cyclooctadiene

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Scheme 1. General principle of TRPTC.

were supplied from Fluka. 1-Octene was obtained from Acros. All these chemical agents were purified by distillation from an appropriate drying agent under inert atmosphere. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was received from Beijing Research Institute of Chemical Industry and used without further purification. Thermoregulated ligand $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ ($n = 16$) was prepared according to the method reported in the literature [16] (^1H NMR (400 MHz, CDCl_3): $\delta = 2.38$ (t, 2H), 3.35 (s, 3H), 3.52–3.63 (m, 71H), 7.30–7.41 (m, 10H) ppm; ^{13}C NMR (100 MHz, CDCl_3): $\delta = 28.24$ (d), 58.42 (s), 67.82 (d), 69.58–71.38 (m), 127.88–137.88 (m) ppm; ^{31}P NMR (400 MHz, CDCl_3): $\delta = -22.01$ ppm). Gas chromatography was performed on a Tianmei 7890 GC with an FID detector equipped with a 50 m OV-101 column. GC–MS measurement was performed on a HP 6890/5973 MS instrument. ICP–AES analyses of rhodium were carried out on Optima 2000DV (Thermo Elemental, USA).

2.2. Preparation of the rhodium nanoparticle catalyst

In a typical experiment, a mixture of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (2 mg, 0.0076 mmol), thermoregulated ligand $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ ($n = 16$) (13.9 mg, 0.015 mmol), 1-butanol (4 mL) and water (4 mL) 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 color of the aqueous

phase turned from light yellow to brownish black, indicating the formation of rhodium nanoparticle catalyst.

2.3. TEM of the rhodium nanoparticle catalyst

The size of rhodium nanoparticle catalyst was characterized by transmission electron microscopy (TEM). The solution containing the rhodium nanoparticle catalyst was diluted with ethanol. Then, a drop of the aqueous solution (or 1-butanol) was placed onto a carbon-coated copper grid, which was 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

All hydrogenation reactions were carried out in a 75 mL standard stainless-steel autoclave immersed in a thermostatic oil bath. The stirring rate was the same for all experiments performed. The autoclave was charged with rhodium nanoparticle catalyst, 1-butanol, water and olefin and flushed three times with 2 MPa H_2 . The reactor was pressurized with H_2 up to the required pressure and held at the scheduled temperature with magnetic stirring for a fixed length of time. Then, 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 by GC and GC–MS.

3. Results and discussion

3.1. Thermoregulated phase-transfer of thermoregulated ligand $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ ($n = 16$)-stabilized rhodium nanoparticles

A range of methods for the phase-transfer of transition-metal nanoparticles has been reported [17–19]. However, at present no reports on using the thermoregulated ligand to realize the phase-transfer of transition-metal nanoparticle catalyst. Thermoregulated ligand is generally defined as one kind of nonionic surface-active phosphine ligands containing polyoxyethylene chains as the hydrophilic group in the molecular structure, which demonstrates a special property of inverse-temperature-dependent solubility in water (Cp). Seeing that the thermoregulated ligand possesses the property of Cp, meanwhile it can act as a stabilizing agent for transition-metal nanoparticles, here we developed a simple and effective phase-transfer approach of noble transition-metal nanoparticles

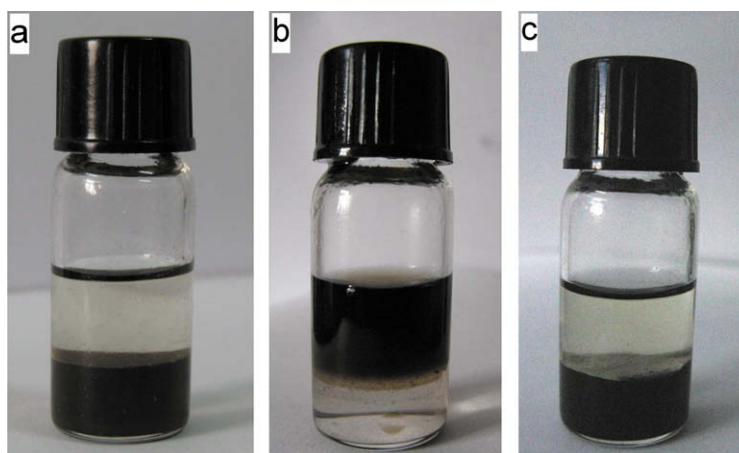


Fig. 1. Photographs showing the thermoregulated phase-transfer of rhodium nanoparticle catalyst stabilized by thermoregulated ligand $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ ($n = 16$). (a) Freshly prepared Rh nanoparticle catalyst in water at room temperature. (b) Phase-transfer of Rh nanoparticle catalyst from water phase to 1-butanol phase while heating to 60 °C. (c) Phase-transfer of Rh nanoparticle catalyst from 1-butanol phase to water phase on cooling to room temperature.

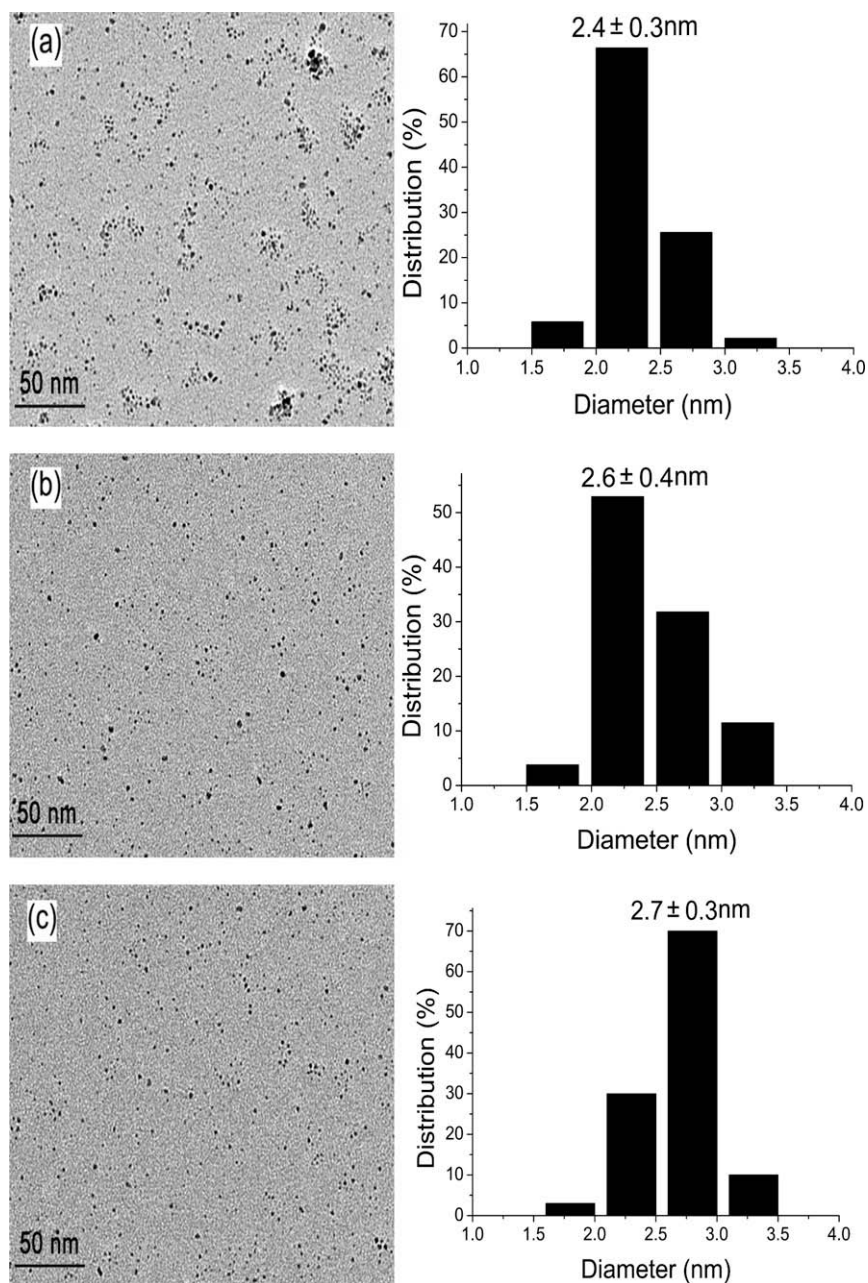


Fig. 2. TEM images and particle size histogram of rhodium nanoparticles during the thermoregulated phase-transfer process. (a) Freshly prepared Rh nanoparticles in water phase (120 particles); (b) Rh nanoparticles after transferring into 1-butanol phase (105 particles); and (c) Rh nanoparticles after going back to water phase (112 particles).

stabilized by the thermoregulated ligand. Among the various methods available for the generation of nanoparticles we employed reduction of corresponding transition-metal salt and adopted thermoregulated ligand $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ ($n = 16$) as stabilizing agent to prepare rhodium nanoparticle catalyst.

Fig. 1 shows a biphasic water/1-butanol mixture containing thermoregulated ligand $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ ($n = 16$)-stabilized rhodium nanoparticle catalyst. The upper 1-butanol phase and the lower water phase were immiscible with each other and therefore they separated into two layers with a clear interface when the stirring ceased at room temperature. The rhodium nanoparticle catalyst was in the lower water phase (see Fig. 1a). Afterwards, the water/1-butanol mixture was heated gradually to 60°C (the Cp of thermoregulated ligand $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ ($n = 16$) in the presence of 1-butanol) under stirring. Stopping the stirring and

controlling the temperature at 60°C , we observed that the mixture separated into two phases and the rhodium nanoparticle catalyst transferred from the lower water phase into the upper 1-butanol phase (see Fig. 1b). An evident indication was that the color of both two phases changed greatly as compared to the respective color before heating. It should be noted that the transferring of rhodium nanoparticle catalyst across the water and 1-butanol interface was reversible. After cooling to room temperature, the rhodium nanoparticle catalyst could go back to the lower water phase from the upper 1-butanol phase (see Fig. 1c). These thermoregulated phase-transfer phenomena relating to thermoregulated ligand $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ ($n = 16$)-stabilized rhodium nanoparticle catalyst shown in Fig. 1 are very similar to our previously reported TRPTC by using transition-metal complex as catalyst [8–10]. Here, thermoregulated ligand $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ ($n = 16$) not only

Table 1
Hydrogenation of cyclohexene under various conditions.^a

Entry	S/Rh ^b	P_{H_2} (MPa)	T (°C)	Time (min)	Conversion (%)	TOF ^c (h ⁻¹)
1	1000	1	40	15	15	600
2	1000	1	50	15	31	1240
3	1000	1	60	15	59	2360
4	1000	1	70	15	73	2920
5	1000	1	80	15	86	3440
6	1000	1	90	15	100	4000
7	1000	1	60	30	85	1700
8	1000	1	60	45	96	1280
9	1000	1	60	60	100	1000
10	1000	2	60	20	100	3000
11	5000	4	60	60	100	5000

^a Reaction conditions: 1-butanol 4 mL, water 4 mL containing 7.6×10^{-3} mmol rhodium.

^b Molar ratio of substrate to rhodium.

^c Turnover frequency, calculated as the number of moles of product formed per mol of rhodium per hour.

serves as stabilizing agent, but also endows the rhodium nanoparticle catalyst with the thermoregulated phase-transfer property.

To further know the size change of the rhodium nanoparticle catalyst before and after the thermoregulated phase-transfer, TEM images were recorded as shown in Fig. 2. The mean diameter of the freshly prepared rhodium nanoparticles in water phase was 2.4 nm with a standard deviation of 0.3 (see Fig. 2a). When transferring into 1-butanol phase, the mean diameter of rhodium nanoparticles was 2.6 nm with a standard deviation of 0.4 (see Fig. 2b). After going back to water phase, analysis of the rhodium nanoparticles gave average diameter of 2.7 nm with a standard deviation of 0.3 (see Fig. 2c). TEM analysis indicated that no obvious size increasing of the transferred nanoparticles occurred.

3.2. Catalytic properties of thermoregulated ligand

$Ph_2P(CH_2CH_2O)_nCH_3$ ($n = 16$)-stabilized rhodium nanoparticles for hydrogenation

To evaluate the catalytic characteristics of thermoregulated ligand $Ph_2P(CH_2CH_2O)_nCH_3$ ($n = 16$)-stabilized rhodium nanoparticle catalyst, hydrogenation of alkenes was performed. We first studied the hydrogenation of cyclohexene at various conditions and the results were listed in Table 1. The conversion of cyclohexene with cyclohexane as the only product and the TOF of the reaction increased with increasing of temperature (entries 1–6). However, prolonging the reaction time could increase the conversion but decrease the TOF of the reaction (entries 3, 7–9). Meanwhile, we can

Table 2
Evaluation of rhodium leaching in the recycling experiments.

Recycle number	0	1	2	3	4	5	6
Rh leaching (wt.%)	1.10	0.23	0.09	0.07	0.06	0.06	0.06

also see from Table 1 that by means of increasing temperature, pressure or prolonging reaction time the conversion of cyclohexene could all reach 100% (entries 6, 9–11). Under the conditions of hydrogen pressure (4 MPa) at 60 °C with a S/Rh of 5000, the TOF of the reaction reached up to 5000, suggesting that the thermoregulated ligand $Ph_2P(CH_2CH_2O)_nCH_3$ ($n = 16$)-stabilized rhodium nanoparticle catalyst was very active for hydrogenation.

The recycling efficiency of the rhodium nanoparticle catalyst was investigated. After reaction, the upper organic phase was separated from the lower catalyst-containing aqueous phase by phase separation. And the aqueous phase was directly used in the next reaction run. Under the reaction conditions of 1-butanol 4 mL, water 4 mL containing 7.6×10^{-3} mmol rhodium, $T = 60$ °C, hydrogen pressure = 1 MPa, cyclohexene/Rh = 1000 (molar ratio), reaction time = 60 min, the catalyst could be recycled for six times remaining a 100% yield. And no apparent aggregation and size change of the rhodium nanoparticles have been observed, as shown by the TEM images in Fig. 3.

The leaching of transition-metal nanoparticle catalyst is frequent, especially for the catalytically active group VIII metals [20]. Therefore, we studied the leaching of the aqueous/1-butanol biphasic system in the recycle experiments by determination of the rhodium content in the 1-butanol phase at the end of the

Table 3
Hydrogenation of different olefins catalyzed by thermoregulated ligand $Ph_2P(CH_2CH_2O)_nCH_3$ ($n = 16$)-stabilized rhodium nanoparticle catalyst.^a

Entry	Substrate	S/Rh ^b	Time (h)	Conversion (%)	TOF ^c (h ⁻¹)
1	Styrene	2000	1	100 ^d	2000
2	1-Octene	2000	1	95	1900
3	1-Dodecene	2000	1	87	1740
4	1,5-Cyclooctadiene	1000	2	100 ^e	500

^a Reaction conditions: 1-butanol 4 mL, water 4 mL containing 7.6×10^{-3} mmol rhodium, $T = 60$ °C, $P_{H_2} = 1$ MPa.

^b Molar ratio of substrate to rhodium.

^c Turnover frequency, calculated as the number of moles of product formed per mol of rhodium per hour.

^d Product is ethyl benzene.

^e Product is cyclooctane.

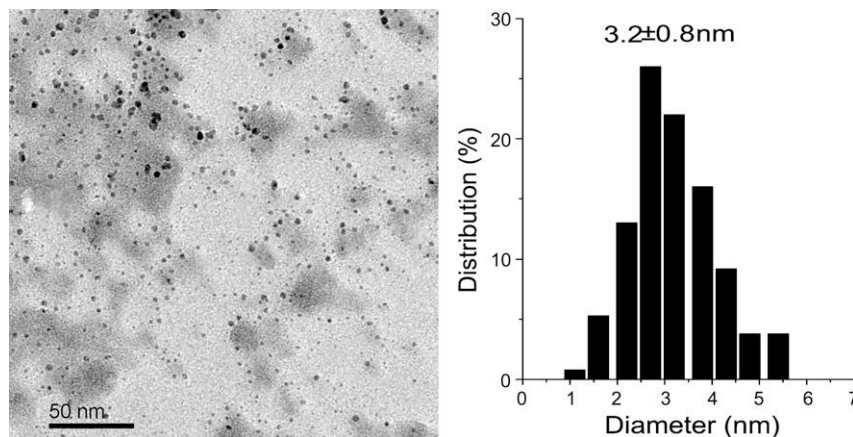


Fig. 3. TEM image and particle size histogram of rhodium nanoparticles after six recycling at 60 °C (160 particles).

reaction. The leaching of rhodium was detected by ICP-AES and the results were presented in Table 2. It can be seen that the leaching of rhodium decreases with the increase of recycle number. The reason for this needs further investigation. Nevertheless, compared with our previous complex catalyst in TRPTC system, the average leaching of rhodium (0.2 wt.%) is lower.

Extension of the hydrogenation reaction to other substrates including styrene, 1-octene, 1-dodecene and 1,5-cyclooctadiene afforded the high conversion as shown in Table 3. Both styrene and 1,5-cyclooctadiene could completely convert into ethyl benzene and cyclooctane, respectively, at 60 °C and initial H₂ pressure of 1 MPa (entries 1 and 4).

4. Conclusions

To summarize, we have demonstrated for the first time that the thermoregulated ligand Ph₂P(CH₂CH₂O)_nCH₃ (*n* = 16)-stabilized rhodium nanoparticles are not only with the property of TRPTC but also active, stable and recyclable catalyst for hydrogenation of olefins in the aqueous/1-butanol biphasic system. Perhaps most importantly, however, the methodology of TRPTC of nanoparticles is simple to realize and the catalyst is easy to separate from the product and recycle. Therefore, it opens up a new avenue for recovery and recycling of soluble transition-metal nanoparticle catalyst, especially for noble transition-metal nanoparticle catalyst.

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