

Novel Aqueous/Organic Biphasic System for Thermoregulated Phase-Transfer Catalysis with Rhodium Nanoparticles

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Abstract: An aqueous/1-pentanol biphasic system was developed for thermoregulated phase-transfer catalysis with rhodium nanoparticles in which thermoregulated ligand $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_{22}\text{CH}_3$ -stabilized Rh nanoparticles were used as catalysts for the hydrogenation of olefins. Under the optimized reaction conditions, the conversion of cyclohexene and the yield of cyclohexane were 99%. The catalyst can be easily separated from the product by phase separation and it can be recycled eight times without a loss of activity.

Key words: hydrogenation; rhodium; nanoparticle; olefin; thermoregulated ligand; aqueous/1-pentanol biphasic system

Based on the cloud point (Cp) of thermoregulated ligands, thermoregulated phase-transfer catalysis (TRPTC) in aqueous/organic biphasic systems has been developed and applied to hydrogenation [1], hydroformylation [2], and CO selective reduction of nitroarenes [3]. TRPTC does not have the shortcomings of classical aqueous/organic biphasic catalysis in which the scope of application is limited by the water-solubility of the substrate and it is also a promising approach for the recovery and recycling of noble transition-metal complex catalysts.

Recently, the use of soluble transition-metal nanoparticles in catalysis has received much attention because of their high efficiency and unique properties. However, similar to traditional homogeneous catalysts, an important disadvantage of soluble nanoparticle catalysts is their separation from reaction products [4,5]. TRPTC has provided an approach for recycling transition-metal complex catalysts and, therefore, it can be applied to the corresponding nanoparticle catalysts. Recently, a rhodium nanoparticle catalyst that was stabilized by the thermoregulated ligand $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_{16}\text{CH}_3$ has been certified to have a TRPTC function in an aqueous/1-butanol biphasic system and it was used as an active, stable, and recyclable catalyst for the hydrogenation and hydroformylation of olefins

[6,7]. After this preliminary “proof of concept” study we attempted to extend the aqueous/organic biphasic TRPTC system with a nanoparticle catalyst in which the nanoparticle catalyst is active, stable, and undergoes less leaching in the organic phase.

In this paper, a novel aqueous/1-pentanol biphasic system was used for the thermoregulated phase-transfer catalytic hydrogenation of olefins using thermoregulated ligand $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_{22}\text{CH}_3$ -stabilized Rh nanoparticles as the catalyst.

The thermoregulated ligand $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_{22}\text{CH}_3$ was prepared by the method reported in literature [8]. Rhodium nanoparticles stabilized by $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_{22}\text{CH}_3$ were prepared as follows. Under a N_2 atmosphere, a mixture of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (2 mg, 0.0076 mmol), thermoregulated ligand $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_{22}\text{CH}_3$ (17.75 mg, 0.015 mmol), 1-pentanol (4 ml), and water (4 ml) were added into a 75 ml standard stainless steel autoclave and flushed three times with 2.0 MPa H_2 . This mixture was stirred under hydrogen (4 MPa) at 70 °C for 2 h. The reactor was then cooled to room temperature and depressurized. The color of the aqueous phase changed from light yellow to brownish black indicating the formation of the rhodium nanoparticle catalyst.

All the hydrogenation reactions were carried out in a 75 ml

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standard stainless steel autoclave immersed in a thermostatic oil bath. The stirring rate was the same for all the experiments. The autoclave was charged with the Rh nanoparticle catalyst, 1-pentanol, water, olefins, and flushed three times with 2.0 MPa H_2 . The reactor was pressurized with H_2 up to the required pressure and held at the scheduled temperature with stirring magnetically for a fixed length of time. The reactor was then 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.

Gas chromatography was performed on a Tianmei 7890 GC equipped with a 50 m OV-101 column and a FID detector. GC-MS was performed on a HP 6890/5973 MS instrument. The TEM images were taken with a Philips Tecnai G² 20 TEM at an accelerating voltage of 200 kV.

The choice of the thermoregulated ligand $Ph_2P(CH_2CH_2O)_{22}CH_3$ with the longer polyether chain as a stabilizer of Rh nanoparticles and the use of the aqueous/1-pentanol biphasic system for the TRPTC was for the following reasons. First is that the thermoregulated ligand $Ph_2P(CH_2CH_2O)_{22}CH_3$ with a longer polyether chain will result in the catalyst returning to the aqueous phase more easily after the reaction. The other reason is that the solubility of water in 1-pentanol (7.2%, 30 °C) is lower than our previously reported aqueous/1-butanol biphasic system (20.6%, 30 °C) and this will result in a lower amount of Rh leaching into the organic phase.

Figure 1 shows the aqueous/1-pentanol biphasic system containing the thermoregulated ligand $Ph_2P(CH_2CH_2O)_{22}CH_3$ -stabilized rhodium nanoparticle catalyst. The upper 1-pentanol phase and the lower water phase were immiscible and, therefore, they separated into two layers with a clear interface at room temperature. The rhodium nanoparticle catalyst was in the lower water phase (Fig. 1(a)). When the water/1-pentanol biphasic system was heated gradually to 60 °C (the Cp of the thermoregulated ligand $Ph_2P(CH_2CH_2O)_{22}CH_3$ in the presence of 1-pentanol), we observed that the rhodium nanoparticle catalyst transferred from the lower water phase into the upper 1-pentanol phase (Fig. 1(b)). An indication of this was that the color of both phases changed markedly compared with their respective colors before heating. It should be noted that the

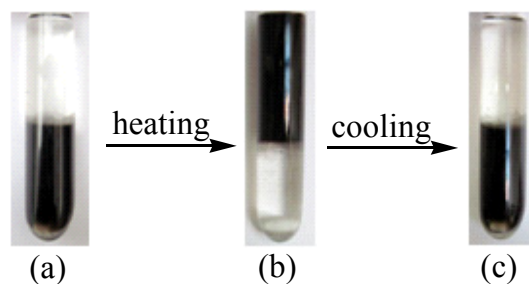


Fig. 1. Scheme of the thermoregulated phase-transfer of the rhodium nanoparticle catalyst stabilized by the thermoregulated ligand $Ph_2P(CH_2CH_2O)_{22}CH_3$ in the aqueous/1-pentanol biphasic system. (a) Freshly prepared Rh nanoparticles in the water phase at room temperature (b) Phase-transfer of Rh nanoparticles from water phase to 1-pentanol phase while heating to 60 °C; (c) Rh nanoparticles after returning to the water phase while cooling to room temperature.

transfer of the rhodium nanoparticle catalyst across the water and 1-pentanol interface was reversible. After cooling to room temperature, the rhodium nanoparticle catalyst returned to the lower water phase from the upper 1-pentanol phase (Fig. 1(c)). The mean diameter of the rhodium nanoparticles was 2.2 nm with a standard deviation of 0.2 nm, and this remained unchanged before and after the transfer (Fig. 2).

To evaluate the catalytic characteristics of the thermoregulated ligand $Ph_2P(CH_2CH_2O)_{22}CH_3$ -stabilized rhodium nanoparticle catalyst, the hydrogenation of olefins was performed. We first studied the hydrogenation of cyclohexene under various conditions and the results are listed in Table 1. Table 1 indicates that upon increasing the temperature, the pressure or by prolonging the reaction time the conversion of cyclohexene increases. At a temperature of 60 °C, a hydrogen pressure of 1 MPa, a substrate/Rh molar ratio of 1000, and a time of 60 min the conversion of cyclohexene and the yield of cyclohexane were 99%. When the temperature was increased from 50 to 60 °C the conversion of cyclohexene increased sharply. This may be a result of the catalyst having transferred into the organic phase and the reaction proceeding homogeneously in the organic phase [9–11]. After the reaction, the upper organic phase separated from the lower catalyst-containing aqueous phase by phase separation and the

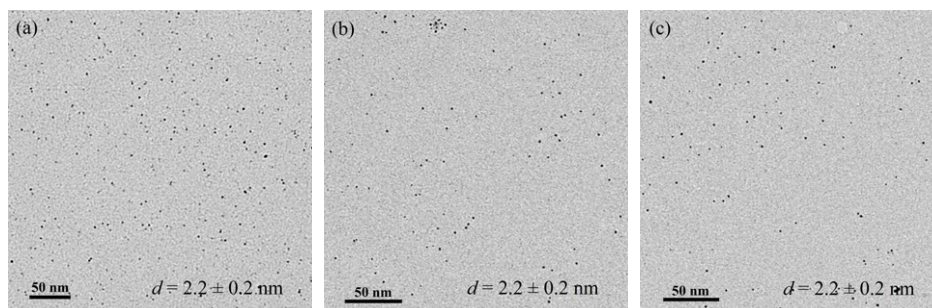


Fig. 2. TEM images of the thermoregulated ligand $Ph_2P(CH_2CH_2O)_{22}CH_3$ -stabilized rhodium nanoparticles. (a) Freshly prepared Rh nanoparticles in the water phase; (b) Rh nanoparticles after transfer to the 1-pentanol phase; (c) Rh nanoparticles after returning to the water phase.

Table 1 Hydrogenation of cyclohexene catalyzed by the thermoregulated ligand $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_{22}\text{CH}_3$ -stabilized rhodium nanoparticles

Entry	Pressure (MPa)	Temperature (°C)	Time (min)	Conversion (%)
1	1	40	60	29
2	1	50	60	56
3	1	60	60	99
4	1	60	10	33
5	1	60	20	49
6	1	60	40	75
7	0.5	60	60	77

Reaction conditions: 4 ml 1-pentanol, 4 ml water containing 7.6×10^{-3} mmol rhodium, substrate/Rh = 1000 (molar ratio).

Table 2 Evaluation of rhodium leaching in the recycling experiments

Recycle number	Rh leaching (%)
0	0.56
1	0.20
2	0.18
3	0.12
4	0.06
5	0.04
6	0.04
7	0.04
8	0.04

aqueous phase was used directly in the next reaction run. The catalyst was recycled eight times without a loss in activity and the size of the Rh nanoparticles increased from 2.2 to 3.0 nm after eight recycles.

In addition, we also studied the leaching of Rh in the 1-pentanol phase (Table 2). The average leaching of Rh was 0.1% (wt. %). To compare with our previously reported results (0.2% in the aqueous/1-butanol biphasic system) the leaching of Rh was markedly lower.

The extension of this hydrogenation reaction to other substrates including styrene, 1-octene, 1-dodecene, and 1,5-cyclooctadiene afforded high conversion, as shown in Table 3.

In conclusion, we demonstrated that the novel aque-

Table 3 Hydrogenation of different olefins catalyzed by the thermoregulated ligand $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_{22}\text{CH}_3$ -stabilized rhodium nanoparticle catalyst

Entry	Substrate	Substrate/Rh (molar ratio)	Time (h)	Pressure (MPa)	Conversion (%)
1	styrene	2000	1	1	100 ^a
2	1-octene	2000	1	1	100
3	1-dodecene	2000	1	1	97
4	1,5-cyclooctadiene	1000	3	2	100 ^b

Reaction conditions: 4 ml 1-pentanol, 4 ml water containing 7.6×10^{-3} mmol rhodium, 60 °C.

^aThe product is ethyl benzene. ^bThe product is cyclooctane.

ous/1-pentanol biphasic system is effective for the TRPTC with nanoparticles in which thermoregulated ligand $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_{22}\text{CH}_3$ -stabilized rhodium nanoparticles are an active and stable catalyst during the hydrogenation of olefins. Of note is that the leaching of Rh in the organic phase is less than that found in our previous work.

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