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Highly efficient and recyclable rhodium nanoparticle catalysts for hydrogenation of quinoline and its derivatives[†]

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PEG-stabilized rhodium nanoparticles exhibited high activity, selectivity and recyclability for the hydrogenation of quinoline and its derivatives. The selectivity of 1,2,3,4-tetrahydroquinoline was higher than 99%. The catalysts were recycled ten times with a total turnover number of 10 592, which is the highest value ever reported for quinoline.

1,2,3,4-Tetrahydroquinoline (1,2,3,4-THQ) and its derivatives are very important for the production of fine chemicals, pharmaceuticals, agrochemicals and petrochemicals. Although there are various preparation methods, the catalytic hydrogenation of quinoline and its derivatives is considered to be the best one due to its simplicity and high atomic efficiency. The catalysts most often used for this reaction are transition metals either in homogeneous or heterogeneous form, such as Ru,¹ Rh,^{2,3g,h} Pd,³ Ir,^{2f,4} Au,⁵ and Ni.⁶ Catalytic systems that are directed towards mild reaction conditions or green solvents have been reported.^{1i,2d,3b} As we have known, homogeneous catalysts are active and selective, but they face the problem of separation. On the contrary, heterogeneous catalysts can be separated easily from the products, but their activity is low. Therefore, developing a new catalytic system that combines the merits of homogeneous and heterogeneous catalyses remains challenging but rewarding. Recently, we have advanced a thermoregulated poly(ethylene glycol) (PEG) biphasic system towards transition metal nanoparticle catalysts, which can realize a totally homogeneous reaction medium under a certain reaction temperature and achieve subsequent efficient separation into two phases by cooling the reaction mixture to room temperature. Namely, the PEG phase containing PEG-stabilized transition metal nanoparticles is immiscible with a mixture of toluene and *n*-heptane at room temperature, but the phases become homogeneous when the temperature is increased to a certain point. Consequently, the reaction proceeds virtually in a homogeneous system under heating, and on cooling to room temperature, it separates into a biphasic system composed of a PEG phase with the transition metal nanoparticle catalysts and an organic phase containing the products. Such a process provides both the advantages of homogeneous and heterogeneous catalyses. Until now, this thermoregulated PEG biphasic system has been applied for the hydroformylation of alkenes,^{7a} hydrogenation of cinnamaldehyde^{7b} and semihydrogenation of alkynes.^{7c} Driven by our long-standing interest in searching for effective biphasic catalytic systems and inspired by the aforementioned results, herein, we originally explore the thermoregulated PEG biphasic system involving the PEG-stabilized Rh nanoparticle catalysts for the hydrogenation of quinoline and its derivatives.

Our investigations started with the preparation of PEGstabilized Rh nanoparticle catalysts. In a typical experiment, RhCl₃·3H₂O (1.35 mg, 0.005 mmol) dissolved in PEG₄₀₀₀ (PEG with an average molecular weight of 4000 g mol⁻¹, 3.0 g, 0.75 mmol) was added into a 75 mL standard stainless steel autoclave and stirred under hydrogen (4.0 MPa) at 70 °C for 3 h. Then, the reactor was cooled to room temperature and depressurized. The PEG₄₀₀₀-stabilized Rh nanoparticles thus obtained were characterized by transmission electron microscopy (TEM). As depicted in Fig. 1, the TEM image shows that the average diameter of the Rh nanoparticles is 1.5 ± 0.4 nm.



Fig. 1 TEM image and particle size histogram of the PEG_{4000} -stabilized Rh nanoparticles (newly prepared, 200 particles).

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Fig. 2 Schematic illustration of the hydrogenation of quinoline in the thermoregulated PEG biphasic system with the PEG_{4000} -stabilized Rh nanoparticles.

Next, the PEG4000-stabilized Rh nanoparticle-catalyzed hydrogenation of quinoline in a thermoregulated PEG biphasic system was first examined and the schematic illustration of the process is shown in Fig. 2. All the quinoline 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 the experiments performed. The autoclave was loaded with the Rh nanoparticle catalyst, toluene, n-heptane, n-decane (internal standard), and quinoline and was flushed three times with 1.0 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 reaction time. Then, the reactor was cooled to room temperature and depressurized. The upper organic phase was carefully removed from the lower PEG phase by a syringe and immediately analyzed by GC and GC-MS.

The main results are summarized in Table 1. The major product is 1,2,3,4-THQ, and the selectivity is more than 99%. The effect of the reaction temperature was studied in the range of 80–120 °C at 3.0 MPa H_2 pressure. As shown in Table 1, when the temperature is increased from 80 °C to 100 °C, the conversion of quinoline increased evidently (Table 1, entry 1 *vs.* entry 2). This can be explained by the fact that the catalytic system changed from a biphase to a monophase (the miscibility temperature of the system is 98 °C) and therefore benefited the mass transfer process. With a further





increase in the temperature to 120 °C, the conversion of quinoline remained nearly the same (Table 1, entry 3). The effect of H₂ pressure on the reaction was then studied (Table 1, entries 2 and 4-6). In the range from 1.0 to 3.0 MPa, the conversion of quinoline increased with increasing pressure and 97% conversion was achieved at 3.0 MPa. When the H₂ pressure was increased to 4.0 MPa, the 97% conversion remained unchanged. It was also clear from the data in Table 1 (entries 2 and 7-9) that prolonging the reaction time led to an increase in the conversion of quinoline. Under the optimized reaction conditions, the conversion of quinoline and the selectivity of 1,2,3,4-THQ were 97% and more than 99%, respectively (Table 1, entry 2). The TOF was 320 h^{-1} and the TON was 960. In order to gain further insight into the nature of the catalysis, namely heterogeneous or homogeneous, a mercury poisoning experiment was carried out. 0.5 g of Hg(0) (500 equiv. of Rh) was added to the catalytic system at the beginning of the reaction (Table 1, entry 10) or after 1 h (Table 1, entry 11). Whenever Hg was introduced, the catalysts were completely deactivated (Table 1, entries 7, 10, and 11). As we know, Hg(0) is a well-known poison for heterogeneous catalysts due to its adsorption on the catalyst surface or amalgamation with the metal catalyst. Therefore, this

Table 1 Hydrogenation of quinoline catalyzed by the PEG ₄₀₀₀ -stabilized Rh nanoparticle catalysts ^a												
Entry	Temperature (°C)	Pressure (MPa)	Time (h)	Conversion (%)	Selectivity ^b (%)	$\mathrm{TOF}^{c}\left(\mathbf{h}^{-1}\right)$	TON ^d					
1	80	3.0	3	55	>99	182	546					
2	100	3.0	3	97	>99	320	960					
3	120	3.0	3	98	>99	323	969					
4	100	1.0	3	79	>99	261	783					
5	100	2.0	3	91	>99	300	900					
6	100	4.0	3	97	>99	320	960					
7	100	3.0	1	77	>99	762	762					
8	100	3.0	2	92	>99	455	911					
9	100	3.0	6	98	>99	162	972					
10^e	100	3.0	3	4	>99	13	39					
11^f	100	3.0	3	78	>99	257	771					

^{*a*} Reaction conditions: PEG_{4000} 3.0 g (containing 5.0 × 10⁻³ mmol of Rh), quinoline/Rh = 1000 (molar ratio), toluene 3.0 g, *n*-heptane 1.0 g, *n*-decane 0.2 g (internal standard). ^{*b*} Selectivity of 1,2,3,4-THQ. ^{*c*} Turnover frequency (TOF): calculated as the number of moles of 1,2,3,4-THQ per mole of Rh per hour. ^{*d*} Turnover number (TON): moles of product formed per mole of rhodium. ^{*e*} For the mercury poisoning experiment, 0.5 g of Hg(0) (500 equiv. of Rh) was added at the beginning of the reaction. ^{*f*} For the mercury poisoning experiment, 0.5 g of Hg(0) (500 equiv. of Rh) was added at the beginning of the reaction. ^{*f*} For the mercury poisoning experiment, 0.5 g of Hg(0) (500 equiv.



Fig. 4 TEM image and particle size histogram of the PEG_{4000} -stabilized Rh nanoparticles (after ten recycles, 200 particles).

result implied the heterogeneous nature of the Rh nanoparticle catalysts.

The lifetime is an important aspect concerning the use of catalysts; therefore, 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 in the autoclave under open air conditions. By adding a new batch of substrate and solvent, the lower catalyst-containing phase can be directly used in the next reaction run. Under the same reaction conditions as entry 2 in Table 1, the recovered Rh nanoparticle catalyst could be reused ten times without evident loss in activity and selectivity (Fig. 3). The average particle size of the Rh nanoparticles after ten recycles was 1.7 nm, which only increased slightly compared with the freshly prepared Rh nanoparticles (Fig. 4). The total TON is 10592, which is higher than the reported value of 940 for a heterogeneous Rh catalyst 2a and 1528 for the homogeneous one.^{2h} The better stability of the PEG4000-stabilized Rh nanoparticles is perhaps due to the following two aspects. One is the complexation of oxygen in PEG with Rh through the formation of pseudo-crown ether structures.⁸ The other reason probably results from the steric effects of the PEG chain.

The leaching of transition metal nanoparticle catalysts is frequent, especially for the catalytically active group VIII metals.⁹ Therefore, we studied Rh leaching in the recycle experiments by determination of the Rh content in the upper organic phase at the end of the reaction. The leaching of Rh was detected by ICP-AES, and the results indicated that the average leaching of Rh in the upper organic phase was 1.0 wt%. Although further optimization is necessary to minimize the Rh leaching, the PEG₄₀₀₀-stabilized Rh nanoparticle catalysts are not only really easy to handle but also active, selective and recyclable for the hydrogenation of quinoline.

To expand the application scope of the catalytic system, various quinoline derivatives including 2-methylquinoline, 3-methylquinoline, 6-methylquinoline, 8-methylquinoline and 6-methoxyquinoline were screened as substrates. Under the optimized reaction conditions, they also afforded their corresponding tetrahydroquinolines with high conversion and >99% selectivity as shown in Table 2.

Conclusions

In summary, a thermoregulated PEG biphasic system combining the merits of homogeneous and heterogeneous catalyses was explored for the hydrogenation of quinoline and its derivatives with PEG_{4000} -stabilized Rh nanoparticles as catalysts. These catalysts were not only active and selective but were also easy to separate from the products by simple phase separation and were recycled ten times without evident loss in activity and selectivity. To the best of our knowledge, these

Table 2 Hydrogenation of quinoline derivatives catalyzed by the PEG ₄₀₀₀ -stabilized Rh nanoparticle catalysts ^a											
Entry	Substrate	Product	Time (h)	Conversion (%)	Selectivity ^{<i>b</i>} (%)	$\operatorname{TOF}^{c}(\mathrm{h}^{-1})$	TON ^a				
1			12	93	>99	77	921				
2			7	99	>99	140	980				
3	N		4	99	>99	245	980				
4	N	N H	4	99	>99	245	980				
5	H ₃ CO	H ₃ CO	6	95	>99	157	941				

^{*a*} Reaction conditions: PEG_{4000} 3.0 g (containing 5.0×10^{-3} mmol of Rh), $P_{H_2} = 3.0$ MPa, T = 100 °C, substrate/Rh = 1000 (molar ratio), toluene 3.0 g, *n*-heptane 1.0 g, *n*-decane 0.2 g (internal standard). ^{*b*} Selectivity of the corresponding products. ^{*c*} Turnover frequency (TOF): calculated as the number of moles of product per mole of Rh per hour. ^{*d*} Turnover number (TON): moles of product formed per mole of rhodium.

 PEG_{4000} -stabilized Rh nanoparticle catalysts exhibited the highest TON of 10 592 for the hydrogenation of quinoline.

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