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Highly Selective Hydrogenation of α-Pinene Catalyzed by Ru Nanoparticles in Aqueous Micellar Microreactors

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Abstract Ru nanoparticles were prepared using polyoxyethylene–polyoxypropylene–polyoxyethylene triblock copolymer (F127, Mw: 13,000) micelles as stabilizers. The F127-Ru micellar catalyst was used in the hydrogenation of α-pinene to *cis*-pinane. Under very mild conditions, the conversion of α-pinene was 99.9 %, and selectivity for *cis*-pinane reached 99.0 %. The isolated catalyst phase could be reused six times with almost unchanged catalytic activity and selectivity. The improvement in conversion and selectivity was attributed to the formation of micellar microreactors, with the water insoluble substrate solubilized in the hydrophobic core of the micelles. This method offers an effective pathway for the production of a high value-added product from turpentine, and provides a reference for the catalytic hydrogenation of other hydrophobic natural products.

Graphical Abstract
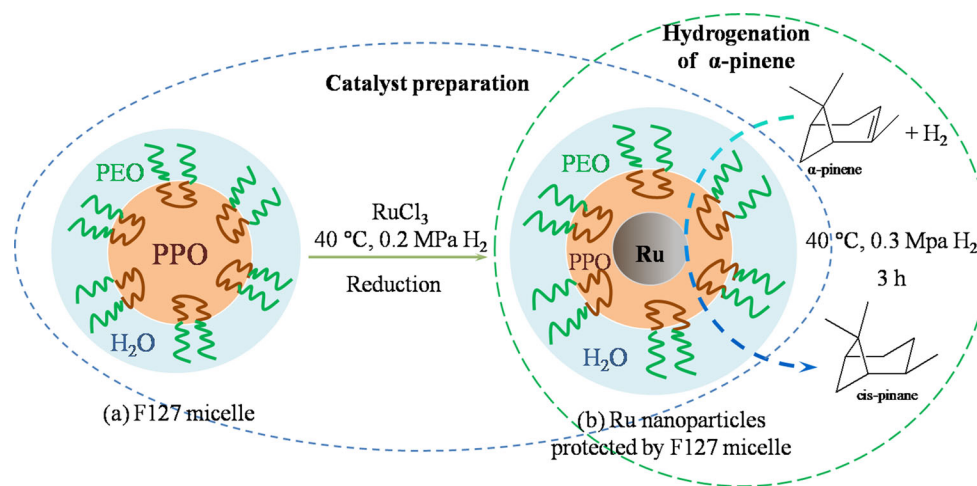
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1 Introduction

α-Pinene is an important product in the wood chemical industry, and occurs widely in nature. It is present in oils obtained from most coniferous tree species, and is the major component of turpentine. Hydrogenation of α-pinene

yields a mixture of *cis*-pinane and *trans*-pinane. *Cis*-pinane is an important chemical intermediate that can be used for the synthesis of high value-added chemicals and specialty pharmaceuticals [1–4]. Supported metallic catalysts are commonly applied in the hydrogenation of α-pinene [5–8]. However, conventional hydrogenation is usually carried out under severe conditions, the catalysts are generally not suitable for reuse, and the selectivity for *cis*-pinane is poor. To obtain superior product selectivity, key factors are the hydrogenation reaction medium and the catalyst. In the 1980s, Rideout and co-workers [9] found that an aqueous reaction medium could greatly improve the reaction rate and selectivity. Water used in organic reactions as a "green solvents" has become an important subject in the field of green chemistry. Some researchers have found that water can accelerate the reactions of both water-soluble and water-insoluble substrates [10, 11]. Our team previously investigated the effect of water on the RuCl$_3$-catalyzed hydrogenation of α-pinene [12] and found that water significantly promoted the hydrogenation. The rate of reaction and the molar ratio of *cis*-pinane to *trans*-pinane were significantly improved. In addition, the product was easy to separate from the catalytic phase. However, the reaction was conducted under high temperature and pressure, and the catalyst was unsuitable for reuse.

Surfactants can improve catalytic activity and chemoselectivity, in addition to improving the reusability of catalysts, through the formation of vesicles or micelles in aqueous solutions. Micellar environments are not just a soapy version of homogeneous catalysis, but rather micelles behave more as nanoreactors characterized by unique features [13–16]. Nowicki and coworkers [17, 18] reported that aqueous Ru nanoparticles stabilized by randomly methylated cyclodextrins was an efficient catalyst for the hydrogenation of various substrates in two liquid phases, such as olefinic and aromatic compounds. They presumed that the cyclodextrins not only enable stabilization of the metallic nanoparticles, but also act as supramolecular shuttles, forming inclusion complexes with the substrate, which could approach the nanoparticle surface. Deng and coworkers [19] reported that the cationic surfactant cetyltrimethylammonium bromide (CTAB) could accelerate the asymmetric transfer hydrogenation of aromatic ketones in aqueous media. Furthermore, the catalyst was effectively recycled. High conversion and enantioselectivity remained even on the 21st run. They assumed that there was a strong interaction between the anionic catalyst and the cationic micelles that enhanced the stability and solubility of the catalyst in water.

Block copolymers of the type polyoxyethylene-polyoxypropylene-polyoxyethylene ((PEO)$_n$–(PPO)$_m$–(PEO)$_n$) are becoming increasingly important, and are fairly biological harmless. These non-ionic amphiphilic copolymers can be used for micellar reactions in aqueous solution. Sakai and co-workers [20] reported that 10 nm gold nanoparticles were obtained in aqueous Pluronic block copolymer solutions at ambient temperature. Yu and co-workers [21] employed [BMMIm]OAc-P123 mixed micelles to stabilize Ni nanoparticles. The mixed-micelle stabilized Ni nanoparticles showed excellent catalytic performance for the selective hydrogenation of C=C and nitro compounds in the aqueous phase under very mild reaction conditions. The nanoparticle system could be recycled at least eight times without obvious loss of catalytic activity. Amphiphilic block copolymers F127 are commonly used as a template in the preparation of mesoporous materials [22–24]. However, nanoparticles prepared using F127 micelles as a stabilizer have seldom been reported. In this paper, we designed a catalyst of Ru nanoparticles protected by F127 micelles in aqueous solution. The catalytic system was used in the hydrogenation of α-pinene to produce *cis*-pinane. The reaction conditions were optimized and the reaction mechanism was explored. The results show that the catalytic system has several advantages. It uses water as the reaction medium, and commercially available polymers as the stabilizer. The synthesis method is environmentally friendly and economical, the reaction conditions are mild, the catalyst is effectively recycled, and the selectivity for *cis*-pinane is high.

2 Experimental

2.1 Preparation of Ru Nanoparticles

In a typical experiment, 2 mL of water and 20 mg of F127 were placed in a stainless steel reactor. The mixture was stirred for 2 h at 25 °C, and then 2.1 mg (0.01 mmol Ru) of RuCl$_3$ (vacuum drying before use) was added to the reactor. Stirring was continued for 0.5 h. The reactor was then sealed, and purged with 1 MPa H$_2$ to remove air. Subsequently, the reactor was pressurized to 0.2 MPa H$_2$, and placed in a 40 °C water bath at a stirring rate of 500 r/min. After stirring for 2 h (Fig S1), the reactor was placed in ice water and the gas was released. Finally, the reactor was vented and a homogeneous dark solution of the catalyst was obtained. Under these conditions, the obtained Ru nanoparticles were dispersed evenly in the system, as shown in Fig. 3a. The nanoparticles were small, at about 2.0–4.0 nm on average. We also measured the valence state of the obtained Ru nanoparticles, with the results indicating that Ru^{3+} was reduced to zero-valence metallic Ru (Fig S2).The obtained catalyst was used directly for the hydrogenation of α-pinene.

2.2 Hydrogenation of α-Pinene

In a typical experiment, 0.2730 g (2 mmol) of α-pinene was added to the catalytic system as described in Sect. 2.1. The reactor was sealed and purged with 1 MPa H_2 to remove air. Then the reactor was pressurized to 0.3 MPa H_2 and placed in a 40 °C water bath. The mixture was stirred for 3 h at a stirring rate of 500 r/min. After the reaction, the remaining products were isolated by liquid–liquid extraction with *n*-heptane and analyzed using gas chromatography (GC). Under these conditions, the conversion for α-pinene was 99.9 %, and the selectivity for *cis*-pinane was 99.0 %. For the recycling procedure, the *n*-heptane remaining in the autoclave was evaporated under vacuum, and the α-pinene charged into the autoclave for subsequent recycling.

3 Results and Discussion

3.1 Influence of Various Reaction Media

A series of Ru nanoparticles protected by F127 was prepared with various reaction media. The results of hydrogenation of α-pinene were shown in Table 1. The reaction was obviously inhibited if the *n*-heptane and other organic solvents were used as reaction medium. However, the conversion was dramatically enhanced when the water was used. The selectivity for *cis*-pinane has the same result. These results were attributed to the formation of micelles in water [25]. Ru nanoparticles were protected by the F127 micelles, and inhibited the Ru nanoparticles aggregated and precipitated [26]. These were also confirmed by transmission electron microscopy (TEM, JP Hitachi-7650) detection. As shown in Fig S4, Ru nanoparticles gathered into clumps when the reaction medium was organic solvents, which decreased the numbers of active sites of the catalyst and reduced the catalytic activity. Furthermore, the

Table 1 Hydrogenation of α-pinene by Ru nanoparticles dispersed in various reaction media

Reaction medium	Conversion (%)	Selectivity (%)	
		Cis-pinane	*Trans*-pinane
n-Heptane	0	0	0
Ethanol	13.2	93.9	6.1
Ethyl acetate	27.3	96.8	3.2
Methanol	35.2	97.3	2.7
Water	99.9	99.0	1.0

Reaction conditions: α-pinene: 0.2730 g; $RuCl_3$: 2.1 mg; F127: 20 mg; reaction medium: 2 mL; stirring rate: 500 r/min; 40 °C; 0.3 MPa H_2; 3.0 h

hydrophobic α-pinene and H_2 were easily solubilized in the hydrophobic interior of the F127 micelles, which was beneficial for promoting the substrate to contact with the Ru nanoparticles. The combination of the aforementioned factors created a highly advantageous condition for acceleration of the reaction [27]. We accordingly selected water as the reaction medium for subsequent experiments. The amount of water influence on the catalytic activity and selectivity for *cis*-pinane was also studied, and the data were plotted in Table S1.

3.2 Influence of Various Metal Precursors

Different metal precursors have different influences on hydrogenation of α-pinene. We examined the catalytic performances of various metal precursors in the F127 system, and the results were shown in Table 2. $RhCl_3$, $PtCl_4$ and $RuCl_3$ exhibited better performance than $PdCl_2$, although these average diameters were similar. The selectivity for *cis*-pinane obtained in the presence of $RuCl_3$ was markedly better than that with other metal precursors, which is similar to the literature result [28]. We investigated the catalytic activity of Pd/C for the hydrogenation of α-pinene [5], which indicated that the reaction rate and selectivity for *cis*-pinane catalyzed by Pd/C were lower than that catalyzed by Ru nanoparticles. We hence selected $RuCl_3$ as the metal precursor for subsequent experiments.

3.3 Influence of F127 Concentration on α-Pinene Hydrogenation

The influence of F127 concentration on α-pinene hydrogenation was further studied, and the data were plotted in Fig. 1. The conversion and selectivity were poor using the catalyst without stabilizer F127. When the F127 concentration increased from 0.19×10^{-3} mol/L to 0.77×10^{-3} mol/L, the conversion of α-pinene rose from 74.7 to 91.3 %. Conversion decreased with further increases in F127 concentration. Interestingly, when the concentration of F127 in the aqueous solution was higher than its critical micelle concentration (CMC), 0.006×10^{-3} mol/L at 40 °C [29], the selectivity for *cis*-pinane was almost unchanged.

Ru nanoparticles aggregated and precipitated in catalyst system without stabilizer F127, and the catalytic hydrogenation activity was decreased [30]. After the concentration of F127 reached its CMC, the hydrophilic PEO blocks extended into the water and the hydrophobic PPO blocks pointed toward the interior. Then the polymer assembled into spherical micelles with a core that protected the Ru nanoparticles. In the hydrogenation reaction, α-pinene tended to dissolve in the hydrophobic interior. The aqueous-organic biphasic interface area increased, which was

Table 2 Hydrogenation of α-pinene catalyzed by nanoparticles derived from various metal precursors

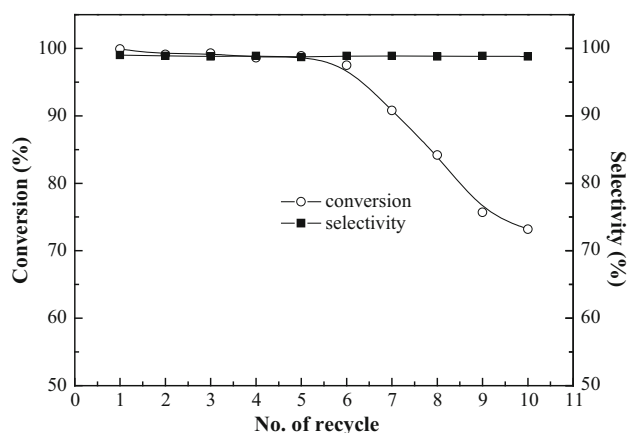| Metal precursor	Average diameter (nm)[a]	Conversion (%)	Selectivity (%)	
			Cis-pinane	*Trans*-pinane
PdCl$_2$	1.8 ± 0.4	82.3	89.3	10.7
RhCl$_3$	1.6 ± 0.4	93.1	95.1	4.9
PtCl$_4$	3.0 ± 0.5	94.7	94.8	5.2
RuCl$_3$	2.8 ± 0.5	91.3	99.1	0.9
Pd/C	–	75.2	87.9	12.1

Reaction conditions: α-pinene: 0.2730 g; metal precursor: 0.01 mmol; F127: 20 mg; water: 2 mL; stirring rate: 500 r/min; 40 °C; 0.3 MPa H$_2$; 2.0 h

[a] Measured using TEM, TEM images were shown in Fig. S5
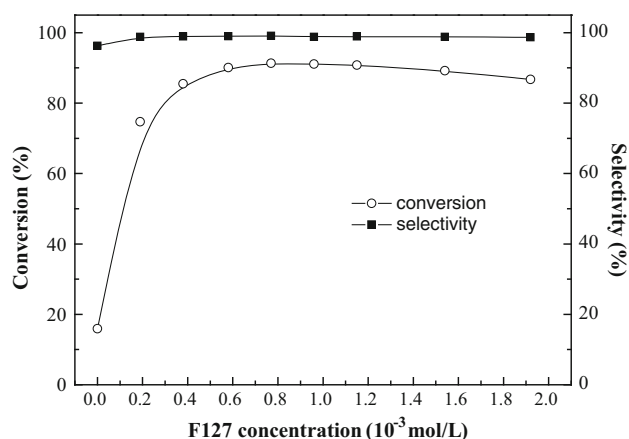
Fig. 1 Influence of F127 concentration on α-pinene hydrogenation. Reaction conditions: α-pinene: 0.2730 g; RuCl$_3$: 2.1 mg; water: 2 mL; stirring rate: 500 r/min; 40 °C; 0.3 MPa H$_2$; 2.0 h

Fig. 2 Reuse of catalyst for the hydrogenation of α-pinene. Reaction conditions: α-pinene: 0.2730 g; RuCl$_3$: 2.1 mg; F127: 20 mg; water: 2 mL; stirring rate: 500 r/min; 40 °C; 0.3 MPa H$_2$; 3.0 h

beneficial for promoting the substrate to contact with the Ru catalyst [27, 31]. Thus, the reaction was accelerated. Because the number of micelles increases with further rising F127 concentration, the interfacial area between two phases would also increase. As a result, the reaction would be further accelerated. The conversion increased until the F127 concentration reached a critical value of 0.77×10^{-3} mol/L. The decreased reactivity was probably due to the dilution effect of the substrate in the micelles and the increased viscosity of the solution, which may interfere with the impingement of reactant molecules [27, 32]. The selectivity for *cis*-pinane increased from 96.3 to 98.8 % as the concentration of F127 increased from 0 to 0.19×10^{-3} mol/L, and the selectivity was almost unchanged when F127 was further increased to 1.92×10^{-3} mol/L. This indicated that the F127 micelles could improve the reaction selectivity, which is the same as those reported by other authors [19]. Therefore, we concluded that the optimal concentration of F127 in the reaction was 0.77×10^{-3} mol/L. We also explored the use of several commercially available surfactants, and our experiment

showed that F127 is the best among those tested (Table S2).

3.4 Recyclability of the Catalyst

In the procedure of α-pinene hydrogenation, several parameters such as stirring rate, temperature, H$_2$ pressure, the amount of catalysts and reaction time were studied, and the results were shown in Fig S6. The optimal conditions found were 500 r/min, 40 °C, 0.3 MPa H$_2$ and 2.1 mg RuCl$_3$ for 3.0 h. We subsequently examined the reproducibility of the reaction, and the results were shown in Fig S7. The maximum deviation of the conversion was ±4 %, and the selectivity for *cis*-pinane was almost unchanged, which was satisfactory.

The recyclability of the catalyst was also studied. After the reaction was complete, the product phase was separated from the catalyst phase. The catalyst was recycled by the addition of fresh α-pinene, and the results were shown in Fig. 2. The catalyst can be reused more than six times with no significant decrease in selectivity or activity. However,
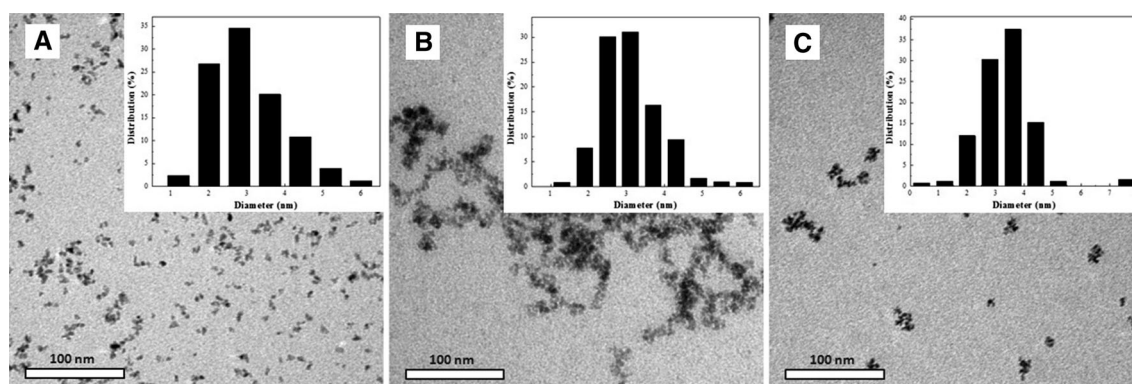
Fig. 3 TEM images of Ru nanoparticles in various recycle stages. **a** Before reaction, **b** after 6 cycles; **c** after 10 cycles

a decrease in catalytic activity was observed after the catalyst was reused seven times. The reduced conversion may be related to the particle size of the Ru nanoparticles. TEM was employed to measure particle size and shape. As shown in Fig. 3, freshly prepared (Fig. 3a) Ru nanoparticles displayed a homogeneous distribution. After six catalytic cycles, the particle size of the Ru nanoparticles increased, and aggregation occurred (Fig. 3b). After ten reaction cycles, some of nanoparticles gathered into clumps (Fig. 3c), presumably leading to the decrease in catalytic activity during the recycling experiments [33, 34].

The amount of Ru leaching during the extraction process was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES, US Leeman, Prodigy XP), and the results were shown in Table S3. The percentage of Ru leaching was 0.13 % after one cycle, and markedly increased to 1.21 % after ten cycles, which might be attributed to micelle damage. Ru nanoparticles without the protection of F127 micelles were exposed to water, and easily entered the product phase. With the loss of Ru catalyst, the catalytic activity gradually decreased. Furthermore, residual extractant may also have an impact on catalytic activity. As described in Table 1, the catalytic activity was very poor when Ru nanoparticles were dispersed in *n*-heptane instead of water. We designed a further set of experiments to explore this assumption. The aforementioned prepared catalyst, with an additional 0.5–2.0 mL *n*-heptane, was used to catalyze the hydrogenation of α-pinene under the same experimental conditions. As shown in Table S4, the conversation of α-pinene decreased 11.2 and 27.6 %, respectively. The addition of *n*-heptane resulted in a gradual decrease in the conversion of α-pinene, which is likely because organic solvents such as *n*-heptane destroy the structure of micelles and affect the catalytic activity [35]. In addition, hydrophobic *n*-heptane can enter the interior of micelles and dilute the α-pinene, which hinders α-pinene contact with the catalyst and leads to a decrease in catalytic activity.

3.5 The Mechanism of Reaction

In the procedure of catalyst preparation, amphiphilic surfactant F127 was dissolved in water. When the concentration reached its CMC, the hydrophilic PEO blocks extended into the water, and the hydrophobic PPO blocks pointed to the interior [36]. Then, the polymer assembled into a spherical micelle with a hydrophobic core, and hydrophobic substrates were easily solubilized in the hydrophobic interior [37], as described in Scheme 1a. With the addition of $RuCl_3$ and H_2 to the mixture, Ru^{3+} was reduced to Ru^0, and Ru nanoparticles were subsequently formed and were embedded in the micelle core (Table S5), as described in Scheme 1b. In the procedure of hydrogenation of α-pinene, Ru nanoparticles protected by F127 micelles can be considered as a microreactor [38]. The bulk α-pinene and H_2 were easily solubilized in the hydrophobic interior of the micelles, and the hydrogenation of α-pinene occurred in these micellar microreactors. In this microcircumstance, the distance between α-pinene and Ru nanoparticles was shorted, which was beneficial for promoting the substrate to contact with the Ru catalyst, and the reaction was accelerated [27, 31]. In addition, The organic phase α-pinene dispersed in the catalyst phase in the form of vesicles with stirring (Fig S8). This structure significantly increased the biphasic interface area, and the energy barrier of phase transfer was effectively minimized [39–41]. The combination of the aforementioned factors created highly advantageous conditions for acceleration of the reaction.

High selectivity for *cis*-pinane is mainly embodied in two aspects. Ru has been found to be a stereoselective catalyst for hydrogenation of α-pinene to obtain *cis*-pinane [28]. Our previous experiments came to the same conclusion (Table 2). This may relate to the structure of Ru nanoparticles (Fig S3). In addition, micelles improve the reaction selectivity to some degree, as demonstrated in Sect. 3.3.

Scheme 1 Mechanism of hydrogenation of α-pinene
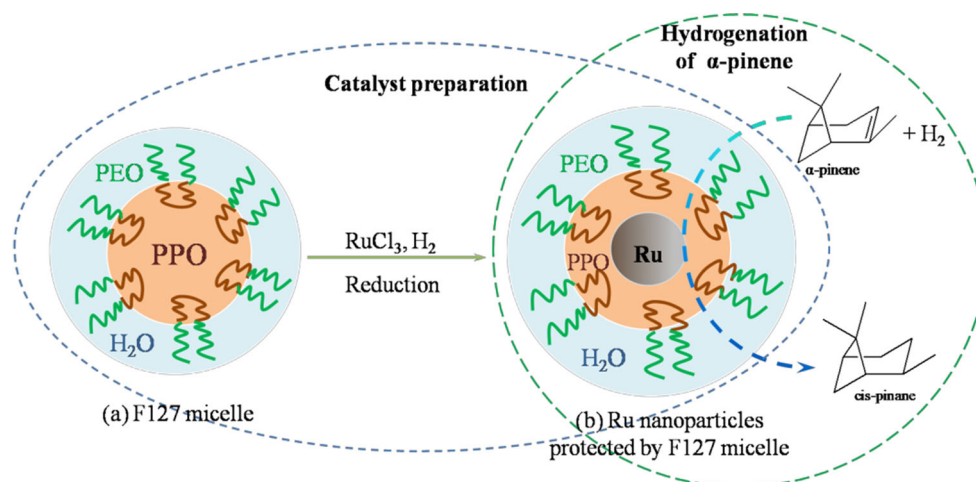
On the basis of these theories, we studied the preliminary kinetics of α-pinene hydrogenation at some typical conditions. As shown in Fig S9, the reaction follows standard pseudo-first-order kinetics for α-pinene at the experimental conditions, which is the same as those reported by many other authors in similar hydrogenation reactions [30, 42].

4 Conclusions

Ru nanoparticles protected by F127 micelles were applied as micellar microreactor for the hydrogenation of α-pinene in an aqueous medium. Under mild conditions, the catalysts showed high activity and high selectivity, and the system exhibited good recycling efficiency for up to six cycles. Analysis of Ru leaching and catalyst recycling experiments showed that Ru nanoparticles can be effectively immobilized in F127 micelles, which significantly improved the stability and reusability of Ru nanoparticles during catalytic cycles. We also demonstrated that hydrogenation of α-pinene in aqueous system can be accelerated by F127 micelles. Benefits of this scheme are that the reaction medium is water, the catalyst preparation and α-pinene hydrogenation are environmentally friendly, and the catalyst system has good prospects for industrial application.

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