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Mild water-promoted ruthenium nanoparticles as an efficient catalyst for the preparation of cis-rich pinane

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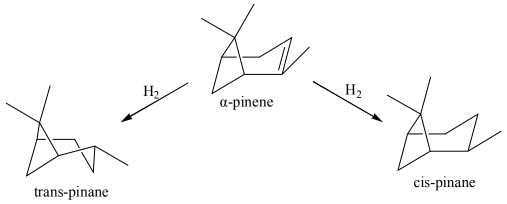
Abstract:

Ruthenium (Ru) nanoparticles were prepared using polyoxyethylene-polyoxypropylene-polyoxyethylene triblock copolymer (P123) micelles in water as the stabilizing agent. The P123-Ru micellar catalyst was first used in the hydrogenation of α-pinene to pinane, and the selectivity for cis-pinane reached 98.9%. This result is attributed to the formation of vesicles. The isolated catalyst phase could be used seven times with no treatment, and its catalytic activity and selectivity were almost unchanged. The preparation process of catalyst and hydrogenation reaction of α-pinene was under mild and environmentally friendly conditions. This research offers an effective method for the hydrogenation of α-pinene and provides a reference for other hydrophobic natural products in hydrogenation reactions.

Keywords: α-pinene, hydrogenation, micelle, water, Ru nanoparticles.

1. Introduction

Biomass is the only renewable carbon resource that can be converted into liquid chemicals and liquid fuels, biomass and biomass derived compounds holds great potential in synthesis of high value-added chemicals.[1] For instance, α-pinene, mainly obtained from pine trees, is valuable raw materials for fine organic synthesis.[2] Cis-pinane is produced by the hydrogenation of α-pinene, it can be used for the synthesis of specialty chemicals and pharmaceuticals such as linalool, dihydromyrcenol and other terpene series spices.[3] As the hydrogenation of other biomass, Pd/C[4,5] and other supported metallic catalysts[6,7] are commonly applied in the hydrogenation of α-pinene. However, conventional hydrogenation technology yields a mixture of cis- and trans- pinanes (Scheme 1), furthermore, the processes for such reactions are usually conducted under high reaction temperatures and pressures, and the catalysts are generally not suitable for reuse. Recently, Pd/C[8,9] was used to catalyze hydrogenation of α-pinene under carbon dioxide of high pressure. The results showed that although the yield of pinane was very high, the selectivity of cis-pinane was poor. In order to obtain superior product selectivity, the hydrogenation reaction medium and catalyst are key factors.



Scheme 1. Hydrogenation of α-pinene

It has been known since the 1980s that water as the reaction medium can greatly accelerate reactions.[10] Thus, scientists have been extensively exploring this usage. Some researchers[11,12] have determined that the hydrophobic effect and the donor-acceptor hydrogen bonding ability of water enhance productivity and enantioselectivity and catalyst recycling in several catalytic reactions. Our team investigated[13] the effect of water on the hydrogenation of α-pinene catalyzed by $RuCl_3$. The results showed that water significantly promoted the hydrogenation; the rate of reaction and the molar ratio of cis- and trans-pinane were significantly improved. However, the catalyst was not suitable for reuse.

Amphiphilic surfactants tend to mediate between the two phases in the presence of water and immiscible organic species. When the amount of surfactant is more than a certain minimum concentration (CMC) in water, nanoscale micelles can be formed by the aggregation of monomers. Similar to enzymes, nanoscale micelles can cause an acceleration of chemical reaction, which has been recognized since 1975.[14] Subsequent studies have determined that surfactants can improve catalytic activity and chemoselectivity in addition to the reusability of catalysts through the formation of vesicles or micelles in aqueous solutions.[15,16] The activity and selectivity depended strongly on the property of the surfactants in a given chemical reaction.[17] Because weak inhibition effects occur by unfavorable interactions of functional groups of the surfactant, which compete with the substrate for the binding site of the catalyst, the distribution of substrate and product within the microheterogeneous medium strongly affects both the reaction rate and the separation procedure of the products.[18] Block copolymers with the type $(PEO)_n$-$(PPO)_m$-$(PEO)_n$ have many excellent properties, such as lack of toxicity, low price, and wide range of solubilities.[19] These non-ionic amphiphiles can be used for micellar reactions similar to surfactants. Toshio Sakai and co-workers[20] reported that 10 nm gold nanoparticles were obtained at ambient temperature by simply mixing an aqueous hydrogen tetrachloroaureate-(III) hydrate ($HAuCl_4 \cdot 3H_2O$) solution with an aqueous Pluronic block copolymer (P123) solution. We designed the catalyst of Ru nanoparticles protected by P123 micelles in aqueous solutions. The catalytic system was used in the hydrogenation of α-pinene to produce cis-pinane, and the mechanism of the reaction was explored. The reaction conditions, such as temperature, hydrogen pressure, reaction time and so on, were also optimized herein.

2. Experimental

2.1 Materials

A-pinene (purity: 98%) was supplied by Jiangxi Hessence (China) Chemicals Co. Ltd., $RuCl_3$ (Ru content≥37.5%) was supplied by Aladdin (China) Industrial Corporation, $PdCl_2$, $RhCl_3$ and $PtCl_4$ were supplied by CIVI-Chem (China) Industrial Corporation, $Ru(NO)(NO_3)_3$ was supplied by Alfa Aesar (China) Chemicals Co. Ltd.. $Ru_3(CO)_{12}$ was supplied by Tokyo Chemical Industry Co. Ltd.. P123 and other surfactants were purchased from Sigma-Aldrich (China) Co.. H_2 (purity≥99.9%) was supplied by Heli (China) Co.. Water was double distilled and deionized before use. Other reagents were of analytical grade purity.

2.2 Preparation of Ru nanoparticles

In a typical experiment, P123 (PEO_{20}-PPO_{70}-PEO_{20}, Mw: 5800, 30mg), $RuCl_3$ (2.1 mg, 0.01 mmol) and water (2 mL) were placed in a stainless steel autoclave (75mL) equipped with a Teflon-liner. The mixture was stirred for 2 h at 25 °C. Then the autoclave was sealed, and the air in the autoclave was replaced four times with 1 MPa H_2. The autoclave was pressurized to 0.5 MPa H_2 and placed in a 40 °C water bath. After stirring for 1 h, the reactor was cooled to ambient temperature and vented. The obtained dark homogeneous solution was used directly for the hydrogenation of α-pinene.

2.3 Hydrogenation of α-pinene

In a typical experiment, α-pinene (0.272 g, 2 mmol) was added into the catalytic system as described above (section 2.2). The autoclave was sealed, and the air in the autoclave was replaced four times with 1 MPa H_2. Then H_2 was admitted to the system at a constant pressure up to 0.7 MPa. The mixture was stirred for 2 h at 40 °C. After the reaction, the products were extracted by n-heptane and analyzed by using gas chromatography (GC). The GC analysis was performed in a GC9790 (Fuli) gas chromatography equipped with a flame ionization detector (FID) detector and an OV 1701 (50 m, 0.25 mm i.d.) column. Under these conditions, the conversion of α-pinene was 99.9%, and the selectivity of cis-pinane was 98.9%. For the recycling procedure, the n-heptane remaining in the autoclave was evaporated under a vacuum, and the α-pinene was charged into the autoclave for subsequent recycling.

2.4 Characterization

The reaction time was determined according to ultraviolet-visible absorption spectra (UV-Vis, Varian Cary 500); 1 mL of the micellar solution was diluted to 20 mL with distilled water before measurement. The UV-Vis absorption spectra are shown in Fig. S1.

The particle sizes and shapes of the Ru nanoparticles were measured by transmission electron microscopy (TEM, Hitachi-7650). The specimens were prepared by placing a drop of the micellar dispersion on a copper grid and then evaporating the solvent. The particle diameters were measured from the enlarged TEM photographs. A particle size distribution histogram was obtained on the basis of the measurements of about 400 particles.

The valence of Ru nanoparticles was tested by X-ray photoelectron spectroscopy

(XPS, Kratos Axis Ultra DLD). A mono Al Kα (hv=1486.6 eV) X-ray source was used at a power of 150 W (15 kV). Binding energies were calibrated by using the C_{1s} hydrocarbon peak at 284.60 eV. The samples were prepared by drying the Ru nanoparticles by rotator evaporation. The results are shown in Fig. S2.

The amount of Ru leaching during the reaction was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Prodigy XP, Leeman,). A certain amount of sample was dissolved in 5mL aqua regia. The mixture was then transferred to a 10 mL volumetric flask, diluted to 10mL, and tested by ICP analysis.

The mean diameter of the P123 micelles containing Ru nanoparticles was determined by dynamic light scattering (DLS, Nano ZS90, Malvern). The analysis of the recorded correlation functions was conducted by using the cumulant method.

The vesicle-microreactor photographs were captured by using a confocal laser scanning microscope (CLSM, TCS-SP5-II, Leica).

3 Results and discussions

3.1 Influence of various molecular weights of P123

A series of Ru nanoparticles was prepared with different molecular weights of P123 under the same conditions. Their properties and selectivity upon hydrogenation of α-pinene were investigated, the results are listed in Table 1.

Table 1 Influence of various molecular weight of P123 on the reaction results

molecular weight	Average diameter (nm) [a]	Average diameter (nm) [b]	Conversion (%)	Selectivity (%) [c]
1100	-	-	27.1	95.9
2900	3.15±0.7	26.3	60.1	97.1
5800	2.8±0.4	23.5	90.3	98.4
8400	2.8±0.4	20.4	89.5	98.4
13000	3.0±0.5	22.4	88.2	98.1

Reaction conditions: P = 1.0 MPa, T = 40 °C, t = 1 h. α-pinene: 2 mmol, metal precursor: $RuCl_3$ (0.01 mmol), surfactants: 30 mg, reaction medium: water (2 mL)

[a]:measured by TEM (Fig 2). [b]: measured by DLS (Fig 3). [c]: Selectivity: The percentage of cis-pinane in the product.

The conversion of α-pinene was low when the molecular weight of P123 was 1100. Because the chain length of P123 was too short to stabilize the particles, the Ru nanoparticles aggregated and precipitated.[20,21] With an increase in the molecular weight, P123 provided effective protection against agglomeration, thus enabling increases in the conversion of α-pinene and the selectivity for cis-pinane. When the molecular weight of P123 was 5800, the conversion of α-pinene reached the maximum, 90.3%. Further increases in the molecular weight of P123, only slightly reduced the conversion of α-pinene and selectivity for cis-pinane. The results may be related to the particle size of nanoparticles and the diameter of micelles in the reaction.

The diameter of P123-Ru micelles was tested by DLS. As shown in Table 1, the average diameter of all the micelles was about 20-30nm. Because micelles were in thermodynamic equilibrium where monomers rapidly exchanged among aggregates, these differences were too small to affect the reaction. The particle size of Ru nanoparticles was tested by TEM; the results are shown in Table 1 and Fig.1.All of the particles had small sizes of about 2.0-4.0 nm in average. Ru nanoparticles were dispersed evenly in the system, as shown in Fig.1 (B). However, as described in Fig.1 (A), (C), and (D), some of nanoparticles gathered into clumps, which decreased the numbers of active sites of the catalyst and reduced the catalytic activity.[22,23]Therefore, the conversion of α-pinene decreased. All of the nanoparticles were extremely stable without precipitation for at least six months at room temperature, because the amphiphilic block copolymers were able to self-assemble into micelles in the aqueous solution and on the surface of nanoparticles. These micelles could be exploited as nanocontainers to protect the Ru nanoparticles.[24,25] The vesicle-microreactor formed during the reaction of hydrogenation of α-pinene was observed by CLSM, as shown in Fig. 2. Dispersion for vesicles in samples in (B), (C), and (D) was better than that for (A); those in (B), with a molecular weight of 5800, had the best distribution. These results are consistent with those of TEM and catalytic reactivity. Thus, we selected the molecular weight of 5800 (P123) as the stabilizer for subsequent experiments. We also explored the use of several commercially available surfactants; our experiment showed that P123 is the best among those tested (Table S1).

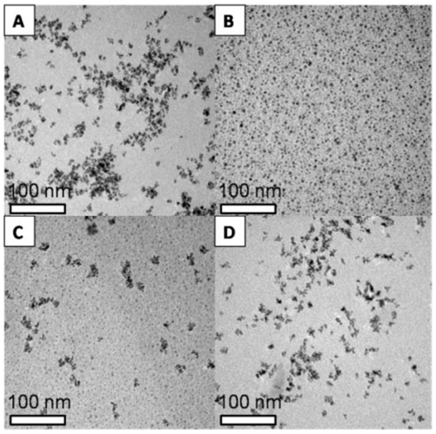


Fig.1 TEM images of Ru nanoparticles protected by P123 with various molecular weights
A: 2900, B: 5800, C: 8400, D: 13000

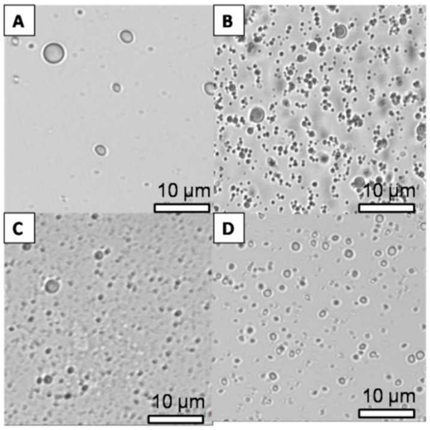


Fig.2 CLSM images of vesicles during the hydrogenation of α-pinene with various molecular weights of P123.
A: 2900, B: 5800, C: 8400, D: 13000

3.2 Influence of various reaction media

A series of Ru nanoparticles protected by P123 was prepared with various reaction media. Their size and conversion of α-pinene were shown in Table 2.

Table 2. Hydrogenation of α-Pinene by Ru nanoparticles dispersed in various reaction media

Entry	Reaction medium	Average diameter (nm)[b]	Conversion (%)	Selectivity (%)	TOF (h^{-1})
1	n-heptane	-	-	-	-
2	carbon tetrachloride	-	-	-	-
3	ethanol	3.8±0.5	6.0	95.2	6
4	ethyl acetate	2.7±0.4	17.5	97.3	17.5
5	methanol	3.2±0.4	33.2	98.6	33.2
6	ethanol: water(1:1) [a]	2.4±0.4	36.0	97.8	36.0
7	water	2.8±0.4	99.9	98.9	99.9

TOF: Turnover frequency measured in [mol product] [mol metal]$^{-1}$ h^{-1}.

Reaction conditions: P = 1.0 MPa, T = 40 °C, t = 2 h, α-pinene: 2 mmol, metal precursor: $RuCl_3$ (0.01 mmol), surfactants: P123 (Mw: 5800, 30 mg), reaction medium: 2 mL.

[a]: 1mL ethanol and 1 mL water. [b]: measured by TEM, TEM images are shown in Fig. S3.

As shown in Table 2, $RuCl_3$ in nonpolar reaction media such as n-heptane and CCl_4 (entries 1 and 2) cannot be reduced to Ru nanoparticles. In polar organic reaction media such as ethanol, ethyl acetate, and methanol and in an aqueous solution, varied diameters of nanoparticles were obtained. Despite their similar particle sizes, the stability of Ru nanoparticles and the conversion of α-pinene in the aqueous reaction medium were markedly better than those in the organic reaction media. When the concentration of P123 in the aqueous solution was higher than its CMC,[26] the hydrophilic PEO blocks extended into the water, and the hydrophobic

PPO blocks pointed to the interior. Then, the polymer assembled into a spherical micelle with a core[27,28] that protected the Ru nanoparticles. In the hydrogenation reaction, microreactors were formed. α-pinene was dissolved in the hydrophobic interior of the microreactors, and Ru nanoparticles were enriched in the interface of the microreactors.[29] It was beneficial to promote the substrate to transfer to the interface and to contact the Ru nanoparticles catalyst, thereby accelerating the reaction rate. We accordingly selected water as the reaction medium for subsequent experiments. The amount of water influence on the catalytic activity and selectivity of Ru nanoparticles was also studied; the data are plotted in Table S2.

3.3 The influence of various metal precursors

We sequentially examined the catalytic performances of various metal precursors in the P123 system; the results are shown in Table 3. $Ru_3(CO)_{12}$ displayed bad solubility in water and negligible reaction. Nearly identical catalytic reactivity was observed for three different metal precursors: $RhCl_3$, $PtCl_4$ and $RuCl_3$. Although all exhibited better performance than $PdCl_2$ and $Ru(NO)(NO_3)_3$,the selectivity obtained in the presence of $RuCl_3$, 98.6%, was markedly better than that with other catalysts. This result could be related to the higher surface hydrophilicity caused by adsorbed Cl,[30] which increased the mobility of interface between two phases, thereby increasing the mass transfer rate and the reaction rate.[27,29]We hence selected $RuCl_3$ as the metal precursor for subsequent experiments.

Table 3. Hydrogenation of α-pinene catalyzed by nanoparticles derived from various metal precursors.

Entry	Metal precursors	Conversion (%)	Selectivity (%)	TOF (h^{-1})
1	$PdCl_2$	86.6	91.2	173.2
2	$RhCl_3$	91.2	96.1	182.4
3	$PtCl_4$	92.0	96.2	184.0
4	$RuCl_3$	90.5	98.6	181.0
5	$Ru(NO)(NO_3)_3$	81.6	96.9	163.2
6	$Ru_3(CO)_{12}$	3.6	0	7.2

TOF: Turnover frequency measured in [mol product] [mol metal]$^{-1}$ h^{-1}.

Reaction conditions: P = 1.0 MPa, T = 40 °C, t = 1 h, α-pinene: 2 mmol, metal precursor: 0.01 mmol, surfactants: P123 (Mw: 5800, 30 mg), reaction medium: water (2 mL).

3.4 Influence of P123 concentration on α-pinene hydrogenation

The influence of P123 concentration on the catalytic activity and selectivity of Ru nanoparticles was studied; the data are plotted in Fig. 3. When the P123 concentration increased from 0 to 2.6×10^{-3} mol L^{-1}, the conversion of α-pinene rose from 21.7% to 92.8%. Conversions decreased with further increases in P123 concentration. Interestingly, the selectivity for cis-pinane increased from 93.5% to 98.9% as the concentration of P123 increased from 0 to 2.6×10^{-3} mol L^{-1}, and no obvious decrease for selectivity was noted when the concentration of P123 further increased to 5.3×10^{-3} mol L^{-1}.

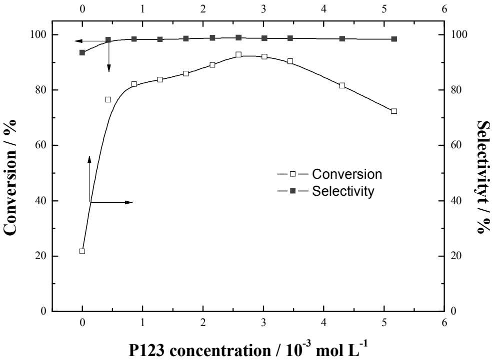


Fig.3. Influence of P123 concentration on α-pinene hydrogenation

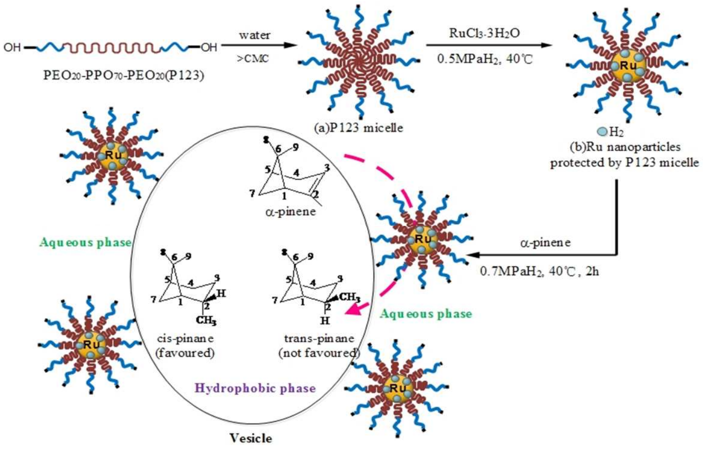
Reaction conditions: $P = 1.0$ MPa, $T = 40$ °C, $t = 1$ h, α-pinene: 2 mmol, metal precursor: $RuCl_3$ (0.01 mmol), surfactants: P123 (Mw: 5800), reaction medium: water (2 mL).

To explain this phenomenon, we performed a series of experiments; the results are shown in Table S3. These phenomena are attributed mainly to the formation of P123 micelles. After the concentration of P123 reached its CMC, the number of micelles increased along with the concentration of P123. In the progression of the reaction, the number of vesicle-microreactors increased. As a result, the interfacial area between two phases enlarged during the reaction. The local concentration of α-pinene in the vesicles increased significantly, and the concentration of Ru nanoparticles increase obviously in the interfacial layer. These conditions are more favorable for the coordination of α-pinene with Ru nanoparticles; thus, the reaction was accelerated. However, the decreased reactivity observed as the P123 concentration exceeded a certain value is due likely to the dilution effect of the substrate in the micelles and an increase in the viscosity of the solution, which may have interfered with the impingement of reactant molecules.[31-33] Therefore, the best concentration of P123 in the reaction was 2.6×10^{-3}mol L^{-1}.

3.5 The mechanism of reaction

In the procedure of catalyst preparation, P123 was added to the water. When the concentration reached its CMC, the hydrophilic PEO blocks extended into the water, and the hydrophobic PPO blocks pointed to the interior. Then, the polymer assembled into a spherical micelle with a core, as described in Scheme 2 (a). With the addition of $RuCl_3$ and H_2 to the mixture, $Ru^{3+}$was reduced in certain conditions to Ru^0, and Ru nanoparticles were subsequently formed and were protected in the core by the P123 micelles (Scheme 2 (b)).

In the procedure of reducing the substrate, the vesicles were formed in the reaction system when the hydrogenation of α-pinene occurred. The structures of internal and external phases were separated by the vesicles. As described in Scheme 2, every vesicle can be considered as a microreactor in the reaction. The Ru nanoparticles protected by P123 micelles in the vesicle-microreactor system were similar to the enzymes in the cells.[34]A special role was played by the vesicle-microreactor for the separated reaction spaces. The bulk α-pinene and H_2 were easily solubilized in the hydrophobic interior of the vesicle-microreactor; thus, the local concentration of α-pinene in vesicles was extremely high. The Ru nanoparticles were enriched in the interface of the vesicle-microreactor.[35]In this micro-circumstance, the distance of α-pinene from the interior of the vesicle to the interface was shortened, which was beneficial for promoting the substrate to contact with the Ru catalyst. Furthermore, this structure significantly increased the biphasic interface area, and the energy barrier of phase transfer was effectively minimized. The combination of the aforementioned factors created a highly advantageous condition for acceleration of the reaction.[36] In addition, the special spatial structure of the P123 micelles protected the Ru nanoparticles. This allowed only the endo surface of α-pinene with a small space steric to contact with the catalyst, which increased the selectivity of cis-pinane. In addition, compared with other precious metals (Table 3), Ru is more suitable for the highly selective hydrogenation of α-pinene.[13]



Scheme 2. Mechanism of hydrogenation of α-pinene

3.6 Optimal conditions of α-pinene hydrogenation

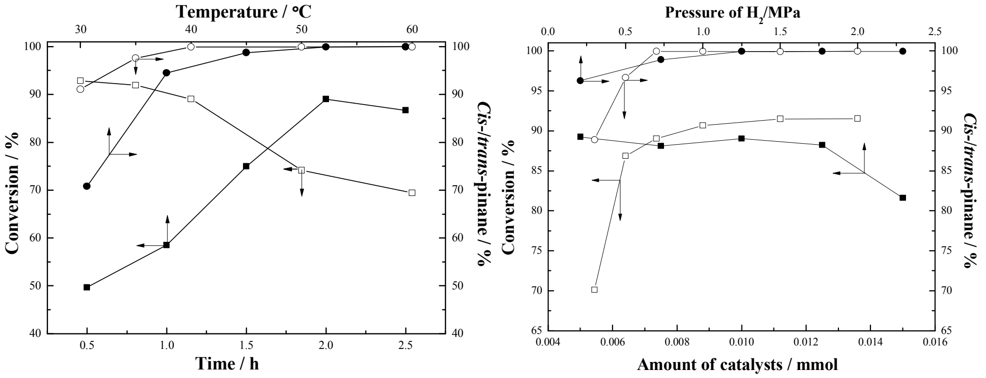


Fig. 4 The influence of reaction time, temperature, pressure of H_2 and catalyst amount on the reaction

Reaction conditions: P = 0.5-2.0 MPa, T = 30-60 °C, t = 0.5-2.5 h, α-pinene: 2 mmol, metal precursor: $RuCl_3$ (0.005-0.015 mmol), surfactants: P123 (Mw: 5800, 30mg), reaction medium: water (2 mL).

To further study the influence of the catalyst on the hydrogenation of α-pinene, several parameters such as temperature, H_2 pressure, reaction time, and catalyst amount were studied; the results are shown in Fig.4. The conversion of α-pinene increased with increasing temperature. When the temperature was higher than 40°C, the influence of temperature on the conversion was not obvious. Chou and co-workers[37] demonstrated that low temperature favors the production of cis-pinane from α-pinene. Thus, we selected the temperature of 40°C for subsequent experiments. The conversion and selectivity increased with increasing H_2 pressure. However, the use of high pressure would increase the capital costs for the hydrogenation plant facility. Examination of the catalyst amount revealed 0.01mmol as the best value. Considering the analysis results of the four factors, the optimum conditions were determined to be: P = 0.7 MPa, T = 40 °C, t = 2 h, 0.01 mmol $RuCl_3$, 2 mmol α-pinene. Furthermore, the influence of stirring rate on α-pinene hydrogenation was also studied, the data are plotted in Table S4. Our experiment showed that 500 r/min is the best stirring rate. Under these conditions, the conversion of α-pinene was 99.9%, and the selectivity of cis-pinane was 98.9%.

3.7 Recyclability of the catalyst

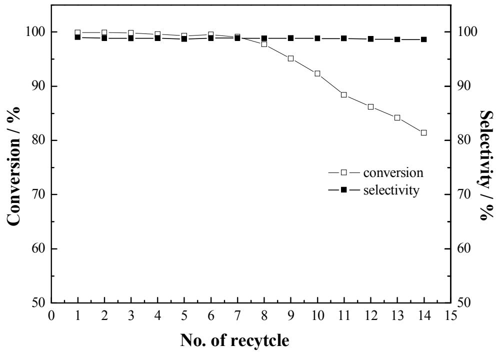


Fig. 5 Catalyst recycle data for the hydrogenation of α-pinene promoted by Ru nanoparticles Reaction conditions: P = 0.7 MPa, T = 40 °C, t = 2 h. [substrate] : [catalyst]=200 : 1, α-pinene: 2 mmol, metal precursor: $RuCl_3$ (0.01 mmol), surfactants: P123 (Mw: 5800, 30 mg), reaction medium: water (2 mL).

After the reaction, the product phase was separated from the catalyst phase. The catalyst was directly recycled by the addition of fresh α-pinene. As shown in Fig. 5, the catalyst can be reused more than seven times with no significant decline in selectivity or activity. Nearly no appreciable Ru leaching into the organic phase was observed, as indicated by ICP analysis results of 0.79ppm. The selectivity remained almost unchanged during the experiments. These results occurred because P123 micelles protected the Ru nanoparticles from poisoning and accumulation.[18] Therefore, the new catalytic system of P123-Ru shows excellent stability.

After eight catalytic cycles, the aggregation of Ru nanoparticles was confirmed by TEM (Fig.S4). The freshly prepared Ru nanoparticles had an average particle size of 2.8 ± 0.4 nm, and the nanoparticles displayed a homogeneous distribution. After eight catalytic cycles, the particle size of the Ru nanoparticles increased, and aggregation occurred. After 14 reaction cycles, an average size particle size of 4.0 ± 0.5 nm was observed, presumably leading to the decrease in catalytic activity during the recycling experiments.

The content of Ru leaching determined by ICP was 5.0 ppm (Table S5) after 14 catalytic cycles, which might be attributed to damaged micelles. Ru nanoparticles without the protection of P123 micelles were exposed to water, and they easily entered the product phase. With the loss of Ru catalyst, the catalytic activity gradually decreased. Furthermore, the residual extractant may also have an impact on catalytic activity.

This theory might partly account for the loss of activity as well as the possible deactivation of the catalyst during the recycling procedure. As described in Table 2, the catalytic activity was very poor when Ru nanoparticles were dispersed in n-heptane instead of water. When 0.5-2.0 mL excess n-heptane was added to the prepared catalytic system of P123-Ru in water, the conversation of α-pinene decreased 6.3% and 24.4%, respectively (Table S6). These results indicate that the residual n-heptane in the emulsions likely affects the assembling behavior of polymer-based catalysts, resulting in negative effects for the reduction of substrates. Furthermore, this substance destroys the structure of micro-reactors to some extent.

4 Conclusions

In summary, a new mild and environmentally beneficial methodology has been developed for efficient hydrogenation of α-pinene in a aqueous medium based on the generation of Ru nanoparticles protected by P123 micelles. This new catalytic system has been demonstrated to be suitable for environmentally clean reduction of α-pinene. The hydrogenation of α-pinene by the P123-Ru micellar catalyst in the aqueous phase resulted in effective conversion of α-pinene and selectivity for cis-pinane under very mild conditions. The catalyst can be reused more than seven times with no significant decline in selectivity or activity. The P123 micelles can protect the Ru nanoparticles from poisoning and accumulation. This study provides a reference for the study of other hydrophobic natural products in hydrogenation reactions.

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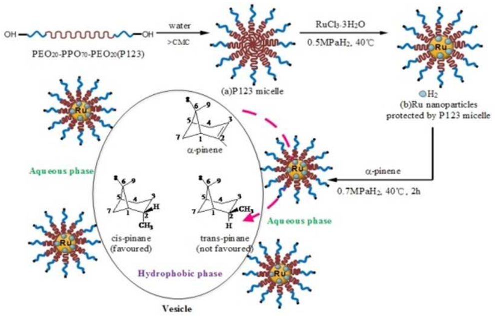
ABSTRACT

Ruthenium (Ru) nanoparticles were prepared using polyoxyethylene-polyoxypropylene-polyoxyethylene triblock copolymer (P123) micelles in water as the stabilizing agent. The P123-Ru micellar catalyst was first used in the hydrogenation of α-pinene to pinane, and the selectivity for cis-pinane reached 98.9%. This result is attributed to the formation of vesicles. The isolated catalyst phase could be used seven times with no treatment, and its catalytic activity and selectivity were almost unchanged. The preparation process of catalyst and hydrogenation reaction of α-pinene was under mild and environmentally friendly conditions. This research offers an effective method for the hydrogenation of α-pinene and provides a reference for other hydrophobic natural products in hydrogenation reactions.



In the procedure of catalyst preparation, P123 was added to the water. When the concentration reached its CMC, the hydrophilic PEO blocks extended into the water, and the hydrophobic PPO blocks pointed to the interior. Then, the polymer assembled into a spherical micelle with a core, as described in Scheme (a). With the addition of $RuCl_3$ and H_2 to the mixture, Ru^{3+} was reduced in certain conditions to Ru0, and Ru nanoparticles were subsequently formed and were protected in the core by the P123 micelles (Scheme (b)).

In the procedure of reducing the substrate, the vesicles were formed in the reaction system when the hydrogenation of α-pinene occurred. The structures of internal and external phases were separated by the vesicles. As described in Scheme, every vesicle can be considered as a microreactor in the reaction. The Ru nanoparticles protected by P123 micelles in the vesicle-microreactor system were similar to the enzymes in the cells. A special role was played by the vesicle-microreactor for the separated reaction spaces. The bulk α-pinene and H_2 were easily solubilized in the hydrophobic interior of the vesicle-microreactor; thus, the local concentration of α-pinene in vesicles was extremely high. The Ru nanoparticles were enriched in the interface of the vesicle-microreactor. In this micro-circumstance, the distance of α-pinene from the interior of the vesicle to the interface was shortened, which was beneficial for promoting the substrate to contact with the Ru catalyst. Furthermore, this structure significantly increased the biphasic interface area, and the energy barrier of phase transfer was effectively minimized. The combination of the aforementioned factors created a highly advantageous condition for acceleration of the reaction. In addition, the special spatial structure of the P123 micelles protected the Ru nanoparticles. This allowed only the endo surface of α-pinene with a small space steric to contact with the catalyst, which increased the selectivity of cis-pinane. In addition, compared with other precious metals, Ru is more suitable for the highly selective hydrogenation of α-pinene.