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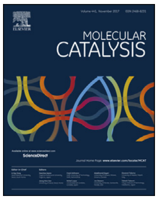

Research Paper

Highly selective hydrogenation of α-pinene in aqueous medium using PVA-stabilized Ru nanoparticles

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ABSTRACT

Polyvinyl alcohol (PVA)-stabilized ruthenium nanoparticles in water were synthesized and characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and confocal laser scanning microscope (CLSM). The Ru-PVA catalyst was highly effective for the hydrogenation of α-pinene, exhibiting higher selectivity for *cis*-pinane as well as high conversion. The selectivity could reach approximately 99%. The catalyst phase could be recycled at least eight times without obvious loss in the catalytic activity and selectivity. Furthermore, both the preparation of catalyst and hydrogenation of α-pinene were under mild experimental conditions. Using water as the reaction medium and PVA as the stabilizing agent made the hydrogenation process environmentally friendly. This catalytic system may also be used to convert a range of cyclenes and long chain alkenes, in particular aromatic compounds to corresponding hydrogenated products.

1. Introduction

As a part of a sustainable supply chain to fine chemicals, biomass-derived substrates have attracted more and more attention [1,2]. Among them, turpentine is a kind of natural aromatic oil originated from pine trees with the largest output in the world. As the major component of turpentine, α-pinene plays an important role in chemistry and industry of forest products [3,4]. Hydrogenation of α-pinene yields a mixture of *cis*-pinane and *trans*-pinane. Pinane is a vital chemical intermediate that can be applied in the synthesis of valuable fragrance compounds and drug components such as rose musk, linalyl acetate and vitamin E [5,6]. Compared with *trans*-pinane, *cis*-pinane possesses higher reaction activity. Therefore, the content of *cis*-pinane is required to be as high as possible so as to ensure the quality of subsequent products in industrial applications. To obtain *cis*-rich pinane, the challenge is to design and develop a novel catalytic system with optimal efficiency and selectivity [7].

During the last decades, researchers have been continually seeking *cis*-rich selective catalytic systems, including unsupported and supported metallic catalysts [8–11]. Nickel nanoparticles applied in the hydrogenation of α-pinene showed good catalytic activity, and the selectivity to *cis*-pinane (94.3%) was higher than that with Pd/C [12]. Palladium colloidal catalyst was also effective for hydrogenation of α-pinene [13]. The conversion of α-pinene exceeded 99%, while the selectivity for *cis*-pinane was 81.3%. Mark et al. found that ruthenium was a stereoselective catalyst for the hydrogenation of α-pinene to *cis*-pinane [14]. Ru nanoparticles protected by amine-functionalized magnetite nanoparticles ($Fe_3O_4/NH_2/Ru$) were utilized to catalytic hydrogenation of α-pinene [15]. Under the optimal conditions, the α-pinene conversion and the selectivity for *cis*-pinane could reach 98.6% and 98.1%, respectively. Nonetheless, for the forementioned catalytic systems, the catalysts were easy to be deactivated and/or harsh reaction conditions were usually required such as high temperature and pressure.

Colloidal methods are widely applied in preparing metallic nano-catalysts, and the particle sizes and shapes can be accurately controlled [16]. Such colloids can be used directly as catalysts after dispersion in liquid reaction media [17]. During colloid preparation, many polymers acting as stabilizers have been utilized to prevent particle agglomeration and crystal growth [18–20]. With the further studies in these years, it is widely reported that stabilizers interact with the surface of nanoparticles and compete with reactant molecules for the binding sites of the catalysts [21,22]. Acting as stabilizers, some polymers can improve the catalytic efficiency as well as chemoselectivity of catalysts [23]. It is demonstrated that the particle growth is controlled by the chemical structure [24] and the concentration of the polymer stabilizers [25]. Polyvinyl alcohol (PVA), a kind of water-soluble surfactant, is an excellent stabilizer for colloid preparation. It is nontoxic, commercially available,

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Table 1
Catalytic performance of different catalysts on hydrogenation of α-pinene.

Entry	Catalyst	Conversion/%	[b]Selectivity/%	[c]TOF/h^{-1}
1	Pd/C (10 wt%)	26.4	97.3	88
2	Ru/C (5 wt%)	44.2	95.6	147
3	Ru-PVP	20.2	94.9	67
4	Ru-PSS	30.4	95.6	101
5	Ru-PEG	43.8	97.0	146
6	Ru-PVA	99.9	98.9	376
7	[a]Ru-PVA	44.3	98.4	218

Reaction conditions: $P = 2.0$ MPa, $T = 343$ K, $t = 3$ h, The molar ratio of α-pinene to Ru nanoparticles (S/C) = 1000:1.

[a] Reaction conditions: $P = 2.0$ MPa, $T = 325$ K, $t = 2$ h. S/C = 1000:1.

[b] Selectivity: calculating formula (cis-pinane selectivity%= $\frac{\text{mole of cis-pinane formed}}{\text{the total amount of the products}} \times 100\%$) was based on Ref. [15].

[c] TOF: turnover frequency measured in [mol product] per [mol metal] per h.

relatively inexpensive, and possesses good bio-compatibility [26]. Coating of particle surfaces with PVA can prevent their agglomeration, and give rise to evenly dispersed nanoparticles [27,28].

In this paper, Ru/PVA colloids were prepared using the chemical reduction method with hydrogen. Then the nanoparticulate system was applied in the hydrogenation of α-pinene. The effects of PVA molecular weight and reaction medium on the reaction were emphatically investigated. Some characterization techniques, such as transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and confocal laser scanning microscope (CLSM) were used to obtain more detailed information about the Ru nanoparticles and the reaction system in terms of size distribution and colloidal properties. Furthermore, the scheme of the formation of Ru nanoparticles and hydrogenation of α-pinene was explored. Several parameters, such as temperature, reaction time and hydrogen pressure, were also evaluated.

2. Experimental

2.1. Materials

$RuCl_3$ was purchased from Aladdin Industrial Corporation (Ru content ≥ 37.5%). 10 wt% Pd/C, 5 wt% Ru/C, $PtCl_4$, $RhCl_3$ and $PdCl_2$ were purchased from CIVI-Chem Industrial Corporation (China). α-Pinene (purity ≥ 98%) was purchased from Jiangxi Hessence Chemicals Company Limited (China). PVA (average molecular weight = 47,000-205,000) were supplied by Sigma-Aldrich Company. Poly (styrene sulfonate) (PSS, *M*w: 8000), polyvinyl pyrrolidone (PVP K15, *M*w: 10000) and polyethylene glycol (PEG, Mw: 70000) were purchased from Aladdin Industrial Corporation. Hydrogen (purity ≥ 99.9%) was purchased from Qingdao Heli Company Limited (China). All chemicals and reagents used were of analytical grade. Double distilled and deionized water was used throughout the work.

2.2. Ru-PVA colloid preparation

In a typical experiment, $RuCl_3$ (2.1 mg, 0.01 mmol), PVA (Mw: 78,000, 15 mg) and water (3.0 mL) were added into a 75 mL stainless steel autoclave equipped with a teflon liner. The mixture was stirred at ambient temperature for 2 h until PVA and $RuCl_3$ were completely dissolved in water. Then the reactor was sealed. The air in it was replaced 4 times with 1.0 MPa H_2. The mixture was reacted at 50 °C for 1 h under 0.5 MPa H_2. After the reaction was completed, the obtained dark colloid was used directly for the catalytic hydrogenation of α-pinene or other substrates without any further separation or washing.

2.3. TEM analysis

Ru particle size distribution was determined by using TEM (Hitachi-7650) that was operated at 300 kV. Typically a drop of colloidal suspension was dispersed on a copper grid covered by a carbon film and dried at ambient temperature.

2.4. XPS analysis

The XPS spectra for evaluating the surface chemical states were recorded by use of Al*Ka* (1486.7 eV) X-ray source and an Axis Ultra system (Kratos Axis Ultra DLD, UK). During the measurements, the ultimate vacuum was 1×10^{-9} Torr. The binding energies were calibrated by setting the C1 s peak at 284.60 eV. For sample preparation, the Ru nanoparticles were isolated by centrifugation in ethanol and washed with water several times followed by centrifugation at 3500 rpm over 5 min. The powder isolated was dried under reduced pressure.

2.5. Ru leaching analysis

The content of Ru nanoparticles in product phase was determined by means of inductively coupled plasma-atomic emission spectrometry (ICP-AES). The Ru leaching analysis was performed using a Prodigy XP ICP-AES instrument (Leeman, U.S.A.). The samples were digested in 5 mL aqua regia and then diluted to 10 mL before analysis.

2.6. CLSM analysis

The pictures of emulsion droplets were obtained through a TCS-SP5-II CLSM instrument (Leica, German).

2.7. Hydrogenation of α-pinene or other substrates

Hydrogenation of α-pinene or other substrates was also performed in the 75 mL stainless steel autoclave. In a typical experiment, α-pinene (1.360 g, 10 mmol) was added into the as-prepared Ru-PVA colloids as depicted in Section 2.2. The mixture reacted at 70 °C under 2.0 MPa H_2 and was stirred for 3 h. When the reaction was completed, the products were extracted using *n*-heptane before injection into a GC 9790 gas chromatograph (Fuli, China) which was equipped with an OV-1701 capillary column (50 m × 0.25 mm × 0.25 μm) and a flame ionization detector (FID). After *n*-heptane remaining in the reactor was removed, the fresh α-pinene was added into the autoclave for the next cycle.

Table 2
Effect of PVA molecular weight on hydrogenation of α-pinene.

PVA Molecular weight	Average particle size of Ru nanoparticles/nm	Conversion /%	Selectivity /%	TOF/h^{-1}
47000	4.6	44.7	98.3	505
78000	2.4	60.6	98.7	685
145000	4.3	31.9	98.1	360
205000	5.6	33.4	98.0	377

Reaction conditions: $P = 2.0$ MPa, $T = 343$ K, $t = 1$ h. S/C = 1000:1, mass of PVA: 15 mg, solvent: water (3 mL).

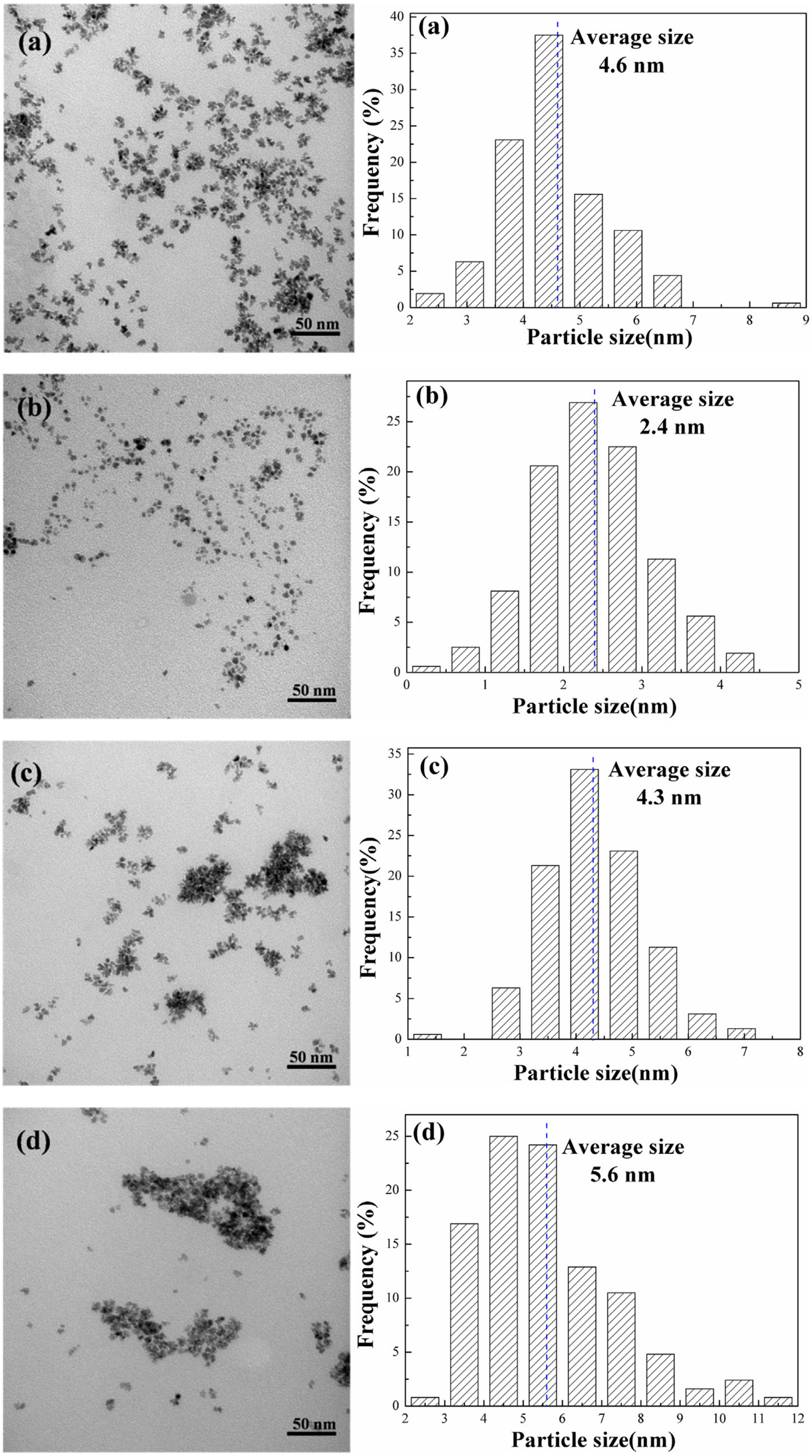


Fig. 1. The TEM images (left) and the corresponding particle size distribution histograms (right) of Ru nanoparticles stabilized by PVA with different molecular weight: (a) 47000, (b) 78000, (c) 145000, (d) 205000.

3. Results and discussions

3.1. Effects of catalysts on hydrogenation of α-pinene

Commercially available Pd/C and Ru/C were selected as the standard for the comparation on the performance of other catalysts. Three common hydrophilic polymers such as poly (styrene sulfonate) (PSS, Mw: 8000), polyvinyl pyrrolidone (PVP K15, Mw: 10000) and polyethylene glycol (PEG, Mw: 70000) were substituted for PVA as the stabilizers of Ru nanoparticles. The preparation of Ru-PSS, Ru-PVP and Ru-PEG was the same as that of Ru-PVA. The results were shown in Table 1.

It was observed that both the conversion and selectivity were superior when the hydrogenation of α-pinene was catalyzed by Ru-PVA. Although the difference in the selectivity to *cis*-pinane is not obvious, it is crucial in the perfume industry because the purity of *cis*-pinane has a direct effect on the quality of downstream products. When α-pinene hydrogenation was catalyzed by the other five catalysts (Entries 1–5), the conversion was poor instead. For Ru-PEG, serious aggregation of Ru nanoparticles after the catalytic hydrogenation of α-pinene was observed. So it indicated that Ru-PVA performed exceptionally well compared with them. When the temperature and reaction time was 325 K and 2 h, respectively, the α-pinene conversion decreased to 44.3% (Entry 7), however, the selectivity to *cis*-pinane was still as high as 98.4%. For Pd/C, Ru-PVP and Ru-PSS, we can also increase the reaction temperature and/or prolong reaction time to enhance the α-pinene conversion to 44% or so. Thus the selectivity to *cis*-pinane can be compared at identical conversion levels. Nevertheless, the selectivity for *cis*-pinane would decrease with the dramatically increasing temperature, which was much disadvantageous for the hydrogenation of α-pinene [15,29]. Compared with other PVA-stabilized metallic nanoparticles such as Rh-PVA, Pd-PVA and Pt-PVA, Ru-PVA showed the best performance. Both the conversion of α-pinene and the selectivity for *cis*-pinane were the highest (Table S1). Therefore, the above results proved that Ru-PVA had excellent catalytic performance.

3.2. Effects of PVA molecular weight on the formation of Ru nanoparticles and hydrogenation of α-pinene

The catalytic activity and selectivity of Ru nanoparticles stabilized by PVA with different molecular weight from 47000 to 205000 were investigated on hydrogenation of α-pinene. As shown in Table 2, no obvious difference in the selectivity to *cis*-pinane was observed when PVA molecular weight changed. However, the conversion increased initially and then declined with the increasing PVA molecular weight. The results may be partially related to the particle size and distribution of Ru nanoparticles. As shown in Fig. 1 (A), when PVA molecular weight was 47000, Ru nanoparticles dispersed evenly but with a larger size of 4.6 nm. It indicated that the Ru nanoparticles further grew up to larger particles when the chain length of PVA was not long enough, which decreased specific surface areas of the catalyst. As depicted in Fig. 1 (B), when PVA molecular weight was 78000, the average size of Ru nanoparticles was 2.4 nm. It was the smallest as indicated in Table 2 and Fig. 1. In addition, the size distribution of Ru nanoparticles in Fig. 1 (B) was narrower than those in the other figures. Therefore, PVA-78000 could provide optimum protection against agglomeration so that the α-pinene conversion reached a maximum, 60.6%. With PVA molecular weight further increasing, some of nanoparticles aggregated into nanoclusters as shown in Fig. 1 (C) and (D). It was because just like PVP, the higher the PVA molecular weight was, the kinetic behavior of chains was more complex in the solution [24]. Thus the closer capped Ru^{3+} within longer chains of PVA could be aggregated more easily as the Ru^{3+} were reduced and grown, which decreased the catalytic activity [30]. Besides the particle size and disdribution of Ru nanoparticles, the interaction between PVA and the surface of the nanoparticles could block some active sites and influence the catalytic performance as well [22].

Only prolonging the reaction time and other experimental conditions unchanged, we continued to explore the effect of PVA molecular weight on hydrogenation of α-pinene, and the results were described in Table S2. Ru nanoparticles had the highest catalytic activity under any circumstances when the molecular weight of PVA was 78000. Therefore, PVA with the molecular weight of 78000 was selected as the stabilizer for the following experiments.

3.3. Effects of reaction medium on the formation of Ru nanoparticles and hydrogenation of α-pinene

Four kinds of PVA-stabilized Ru nanoparticles were prepared with different solvents. Then they were applied in the hydrogenation of α-pinene and the results were shown in Table 3.

It was observed that the α-pinene conversion increased with the increase of solvent polarity, and the selectivity for *cis*-pinane all exceeded 97%. The maximum conversion could be obtained in particular with water as solvent. On the one hand, water could promote the hydrogenation of α-pinene [31]. On the other hand, it might be attributed to the hydrophilic nature of PVA and the formation of emulsion droplets during the hydrogenation of α-pinene. It can be confirmed by the following CLSM image as shown in Fig. 2. The emulsion droplets were spherical particles with a narrow size distribution, and an average size of about 1.26 μm was obtained. The emulsion reaction medium is favorable for the improvement of the mass-diffusion limitation in liquid multiphase systems that was caused by reactant molecules being located in the different phases [32]. For hydrogenation of α-pinene, although H_2 diffusion was limited because of its low concentration in the liquid phase [33], especially transport of α-pinene was improved. Each emulsion droplet could act as a microreactor. Each microreactor was capable of affording higher local concentration of α-pinene near the Ru nanoparticles, and thus exhibiting a remarkable rate acceleration for the hydrogenation of α-pinene in water. Therefore, in water medium, the Ru catalysts showed the optimum catalytic activity.

3.4. Effects of PVA concentration on hydrogenation of α-pinene

Fig. 3 shows the influence of PVA concentration on the catalytic performance of Ru nanoparticles. It was observed that the conversion of α-pinene increased when PVA concentration rose from 0 to 6.42×10^{-5} mol L^{-1}. However, with the PVA concentration further increasing, the conversion declined. On the one hand, the phenomenon was attributed to the steric stabilization of PVA [34]. The polymer chains surrounding the Ru^0 particles sterically afforded the most effective inhibition in particle nucleation and growth at PVA concentration of 6.42×10^{-5} mol L^{-1}. With further addition of PVA, the rate of nucleation decreased because the PVA chains present in the solution interfered with the formation of Ru particles [25], which to some extent resulted in the loss of catalytic activity. Moreover, when excess stabilizers were added, the number of active sites decreased because the polymer blocked part of

Table 3
Hydrogenation of α-pinene by Ru nanoparticles dispersed in different solvents.

Solvent	Conversion/%	Selectivity/%	TOF/h^{-1}
n-heptane	0	–	–
ethyl acetate	18.6	97.3	210
ethanol	21.1	97.1	238
water	60.6	98.7	685

Reaction conditions: $P = 2.0$ MPa, $T = 343$ K, $t = 1$ h. S/C = 1000:1, mass of PVA (Mw: 78000) = 15 mg, solvents: 3 mL.

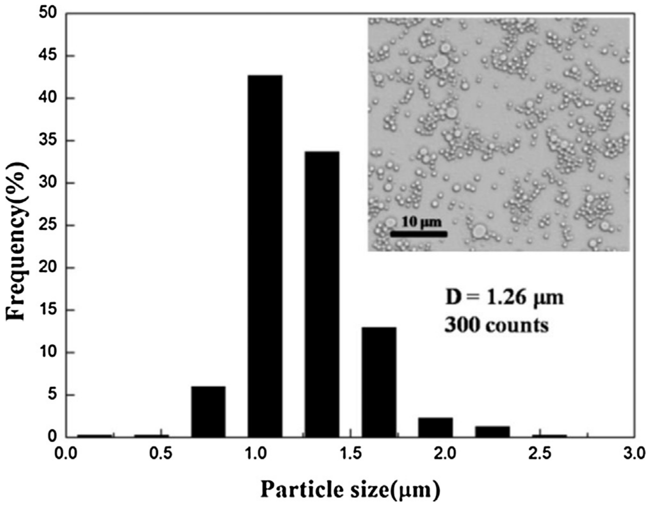


Fig. 2. Particle size distribution and CLSM image of emulsion system during the hydrogenation of α-pinene.

active sites, which was in agreement with many previous studies [22,35,36]. On the other hand, the declined reactivity when the PVA concentration exceeded a certain value might be due to a dilution effect on substrate in the emulsion droplets. Besides, it was observed that the viscosity of the solution increased, which might enhance the G-L mass transfer limitation and interfere with the contact of reactant molecules [37]. With regard to the selectivity for *cis*-pinane, the values remained nearly constant with the increase of PVA concentration as described in Fig. 3(b). So the optimal PVA concentration was 6.42×10^{-5} mol L^{-1}.

3.5. The scheme of reaction

During the formation of Ru nanoparticles, PVA can stabilize them in part by ligation of Ru surface atoms and also by physically occupying space around the nanoclusters. Thereby PVA sterically prevented the aggregation of Ru nanoparticles [19] as depicted in Fig. 4(a). The XPS spectra of Ru nanoparticles demonstrated that 88.5% Ru^{3+} was reduced to Ru^0 as shown in Fig. S1.

When the hydrogenation of α-pinene occurred with stirring, the organic phase α-pinene dispersed in the catalyst phase in the form of emulsion droplets (Fig. 2). The internal phase was separated from external phase by the droplets, which resulted in a large reaction area. At a microscopic level, the PVA-stabilized catalysts were possibly assembled at the interface of the emulsion droplets, which favored the high concentration of substrate around catalytic active sites [32]. The droplets might consequently act as microreactors and this micro-circumstance could probably promote the substrate to contact with ruthenium catalyst [38]. Moreover, the biphasic interface areas were remarkably increased by the presence of emulsion droplets, and the mass-diffusion limitation of the hydrophobic substrate with the hydrophilic catalysts was effectively diminished. The cooperative effects of the above factors would accelerate the reaction. Compared with Rh, Pd and Pt, Ru had the highest selectivity for hydrogenation of α-pinene to *cis*-pinane as shown in Table S1. The special configuration of the adsorbed PVA on Ru nanoparticles, although difficult to determine [39], probably favored the formation of *cis*-rich products. Therefore, the excellent selectivity for *cis*-pinane was obtained.

3.6. The effects of reaction conditions on α-pinene hydrogenation

Reaction temperature and hydrogen pressure were varied respectively under different reaction time. The results were reported in Fig. 5. It clearly indicated that the conversion of α-pinene increased in most cases with an increase of the temperature (Fig. 5(a)). As shown in Fig. 5(b), α-pinene conversion increased remarkably when the temperature rose from 50 °C to 70 °C. At 80 °C, the conversion was approaching 100%. However, the selectivity for *cis*-pinane slightly decreased, which was much disadvantageous for hydrogenation of α-pinene [15,29]. In addition, higher reaction temperature would increase the production cost for the factories. Therefore, 70 °C was the optimal reaction temperature. As depicted in Fig. 5(c), an increase in H_2 pressure from 1.0 MPa to 2.0 MPa resulted in a significant increase in the conversion of α-pinene. However, the conversion increased very slowly at more than 2.0 MPa. It is probably related with the steric stabilization of PVA to the Ru nanoparticles. The ligation of PVA with Ru surface atoms and the physical occupation around the nanoclusters makes the active sites of Ru nano-catalysts limited [19]. During the process of α-pinene hydrogenation, the amount of the adsorption-state hydrogen originally increased obviously with an increase in H_2 pressure. At more than 2.0 MPa, the number of the atomic hydrogen absorbed on the active sites of the Ru species nearly reached its saturation value. Therefore, the conversion increased very slowly. Considering that high pressure put forward higher demands to the industrial equipment, the optimal H_2 pressure was determined to be 2.0 MPa. It was also observed that the conversion increased as reaction time was prolonged (Fig. 5(d)). When the reaction time was 3 h, the conversion reached nearly 100% and the selectivity for *cis*-pinane was still as high as before. Based on the above

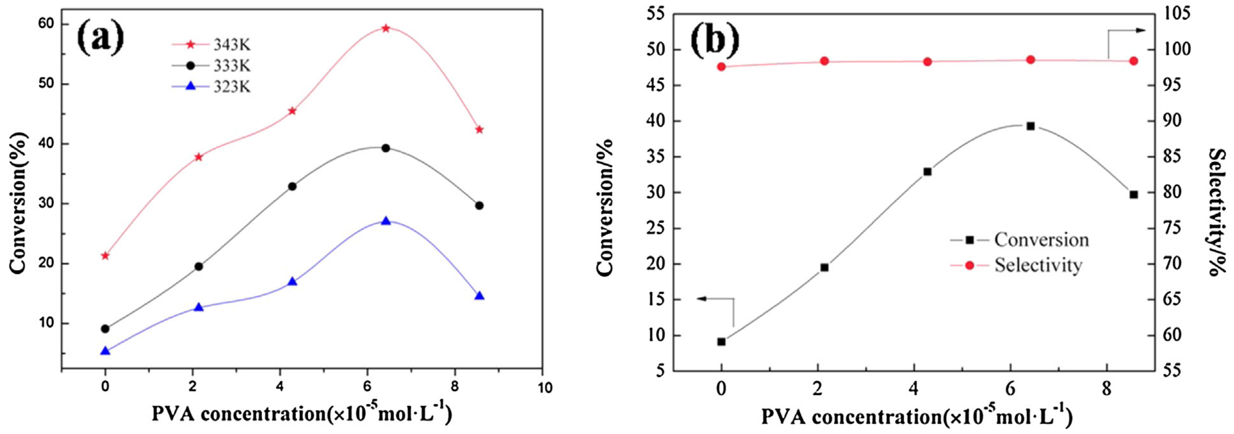


Fig. 3. The effect of PVA concentration on α-pinene hydrogenation. Reaction conditions: P = 2.0 MPa, t = 1 h, 10 mmol α-pinene, 0.01 mmol $RuCl_3$, PVA (*M*w: 78000), 3 mL water, (a) T = 323 K, 333 K, 343 K, (b) T = 333 K.

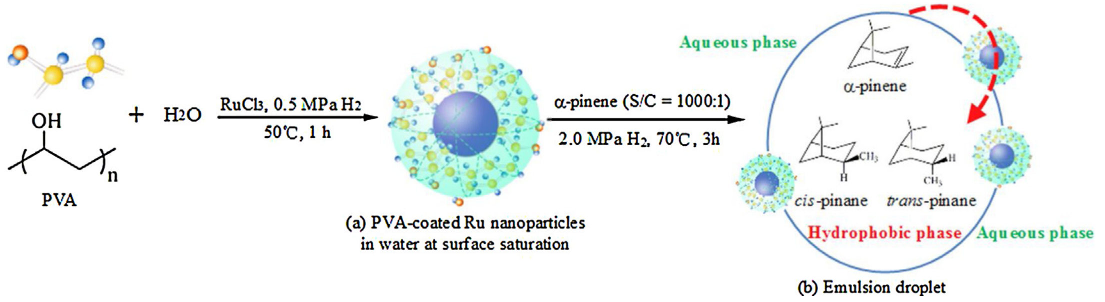


Fig. 4. Scheme on catalytic hydrogenation of α-pinene.

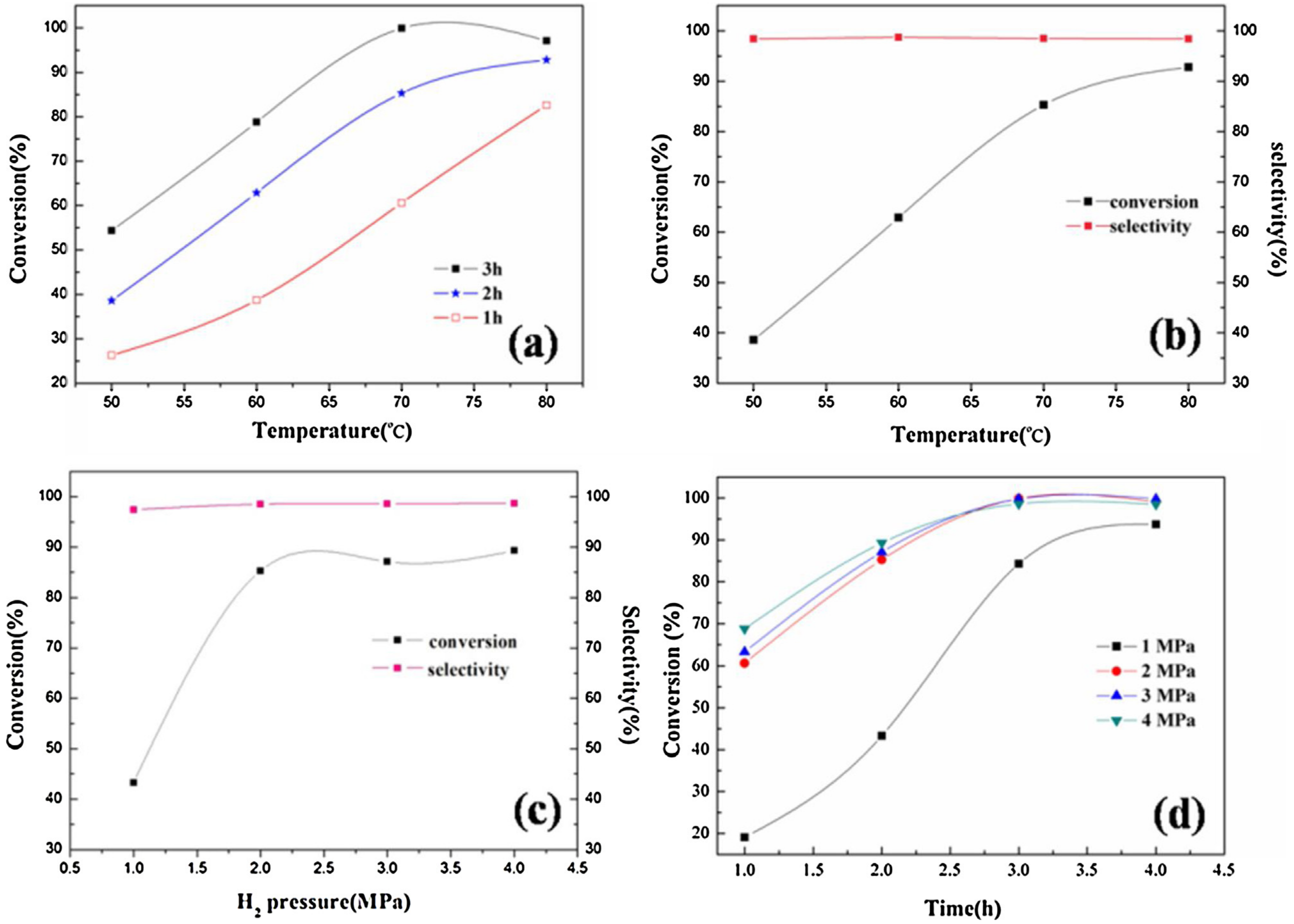


Fig. 5. Effects of reaction conditions on hydrogenation of α-pinene. Reaction conditions: S/C = 1000:1, (a) P = 2.0 MPa, T = 323–353 K, t = 1–3 h; (b) P = 2.0 MPa, T = 323–353 K, t = 2 h; (c) P = 1.0–4.0 MPa, T = 343 K, t = 2 h; (d) P = 1.0–4.0 MPa, T = 343 K, t = 1.0–4.0 h.

results, when S/C = 1000:1, the optimum reaction conditions were as follows: P = 2.0 MPa, T = 343 K, t = 3 h. Under the aforementioned conditions, the conversion of α-pinene could reach 99.9%, and the selectivity for *cis*-pinane was 98.9%, higher than the previous studies [12,15,31,40].

3.7. The reusability of the catalyst

An attractive feature of the present emulsion catalytic system lies in the easy separation of product by extraction due to the low solubility of Ru-PVA in *n*-heptane. Water-soluble catalysts in aqueous biphasic system can be easily reused [41]. A new reaction could be conducted by adding fresh α-pinene into the catalytic system after the product phase was separated from the catalyst phase. The reusability experiments of Ru-PVA catalyst started with a conversion of 90.1%. As shown in Fig. 6, it was possible to recover and reuse Ru-PVA at least eight times without significant loss in its catalytic performance. After the 8th cycle, both the conversion and selectivity remained as high as 89.8% and 98.2%, respectively. On the one hand, PVA could protect the Ru nanoparticles from poisoning and agglomerating [19]. On the other hand, it was probably due to the formation of emulsion droplets. Acting as microreactors, they could further decrease the contact of the nanoparticles and thus protect them from agglomeration. Therefore, the Ru-PVA catalyst showed good repeatability. The conversion declined gradually after eight cycles, which might be attributed to the trace loss of catalysts. ICP analysis showed that 0.90 ppm Ru nanoparticles leached into the *n*-heptane phase after the 1 st cycle. In addition, the aggregation of some nanoparticles also to some extent caused a decline in catalytic activity. However, after the 13th cycle, the conversion still

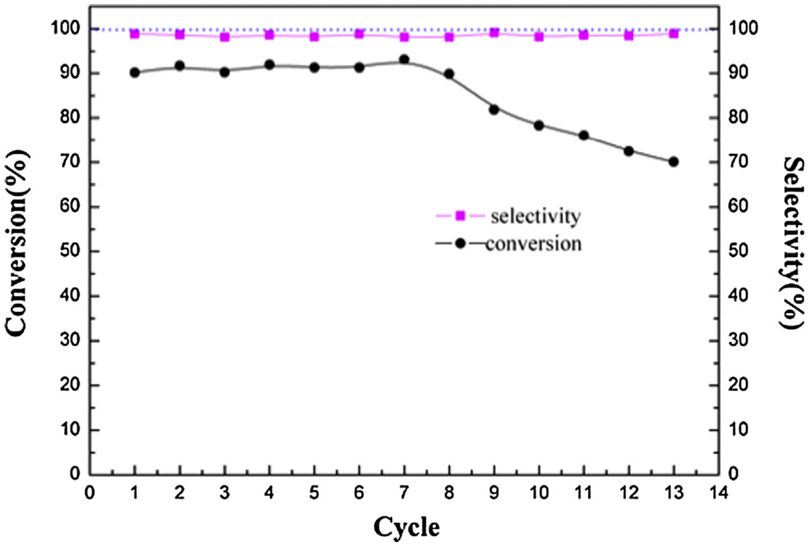
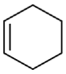
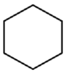
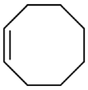
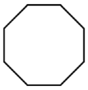
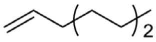
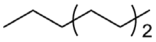
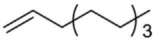
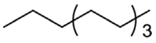
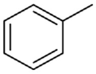
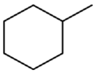
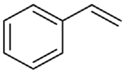
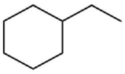


Fig. 6. The reusability of Ru-PVA catalyst. Reaction conditions: 2.0 MPa H_2, 338 K, 3 h, S/C = 1000:1.

Table 4
Hydrogenation of other substrates catalyzed by Ru-PVA colloids.

Entry	Substrate	Product	Reaction time/h	Conversion/%	TOF/h^{-1}
1			1.0	99.9	1129
2			1.5	99.9	753
3			1.5	99.9	753
4			2.0	99.7	563
5			2.0	99.9	565
6			2.0	99.8	564

Reaction conditions: *P* = 2.0 MPa, *T* = 343 K, the molar ratio of substrate to catalyst = 1000:1.

exceeded 70%. It is worth noting that the selectivity for *cis*-pinane was almost unchanged during the whole cycle process.

3.8. Hydrogenation of other substrates catalyzed by Ru-PVA colloids

In order to demonstrate the possibility for a general application of this emulsion catalytic system, a wide range of substrates were tested with Ru-PVA catalyst. The results were summarized in Table 4. To our delight, Ru nanoparticles showed high activity for either cyclenes or long chain alkenes. Particularly, Ru nanoparticles exhibited superior catalytic activity for the reduction of aromatic olefins, possibly due to the deposits of water-insoluble product as an oil on the water surface. Therefore, the products could be separated easily from the aqueous phase containing Ru nanocatalyst [42].

4. Conclusions

In summary, Ru nanoparticles with relatively small diameters and narrow size distribution were prepared by simple hydrogenation reduction of $RuCl_3$ dispersed in PVA solution. PVA-stabilized Ru nanoparticles were applied in the catalytic hydrogenation of α-pinene, showing excellent performance, especially the high selectivity to *cis*-pinane. Through steric effect, PVA could protect the Ru nanoparticles from poisoning and aggregation. Even after eight cycles, no obvious loss in both catalytic activity and selectivity was observed.

In addition, water was used as the reaction medium, and the hydrogenation process was environmentally friendly. Both the synthesis of the catalyst and the hydrogenation of α-pinene were convenient under mild conditions. Therefore, the developed catalyst system has good prospects for industrial application. Moreover, the catalyst is also efficient for the hydrogenation of other substrates, such as olefinic and aromatic compounds, which provides a promising and general strategy for the hydrogenation of other natural hydrophobic products.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.mcat.2017.10.020.

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