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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).