Selective Hydrogenation of α-Pinene to Cis-pinane over Ru Nanocatalysts in Aqueous Micellar Nanoreactors

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Supporting Information

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S1. Experimental

S1.1 Materials

α-Pinene (purity: 97%) was supplied by Jiangxi Hessence (China) Chemicals Co. Ltd. $RuCl_3$, $PdCl_2$, $RhCl_3$ and $PtCl_4$ were supplied by CIVI-Chem (China) Industrial Corporation. Pd/C (10% Pd) was purchased from Aladdin (China) Industrial Corporation. Ethyl acetate (purity: AR) was purchased from Sinopharm (China) Chemical Reagent Co. Ltd. TPGS-1000 was purchased from Aladdin (China) Industrial Corporation. 0.5% TPGS-1000/H_2O (weight ratio) solution was prepared by dissolving 0.5 g TPGS-750-M in 100 g water. TPGS-750-M and SPGS-550-M (2% W/W solution in water) was purchased from Sigma-Aldrich (Shanghai) Trading Co. Ltd. H_2 (purity≥99.9%) was supplied by Qingdao (China) Heli Co. Ltd. Water was double distilled and deionized before use. Other reagents were of analytical-grade purity and without further purification.

S1.2 Preparation of Ru(0) nanoparticles

In a typical experiment, 2 mL 0.5% TPGS-1000/ H_2O (weight ratio) and 2.0 mg $RuCl_3$ were placed in a stainless steel reactor. The mixture was stirred for 10 min at 25 °C. The reactor was then sealed, and purged with H_2 to remove air. Subsequently, the reactor was pressurized to 0.5 MPa H_2, and placed in a 50 °C water bath. After stirring for 1 h, the reactor was cooled to ambient temperature and vented. A homogeneous dark solution of the catalyst was obtained and could be used directly for the hydrogenation of α-pinene. We measured the valence state of the obtained Ru(0) nanoparticles, with the results indicating that Ru(III) was reduced to Ru(0) (Fig S1). Pd(0), Rh(0) and Pt(0) nanoparticles were prepared using the same procedure, and their metal precursors were $PdCl_2$, $RhCl_3$ and $PtCl_4$, respectively. Their TEM images and XRD spectra were shown in Fig S2.

S1.3 Hydrogenation of α-pinene

In a typical experiment, 0.2730 g of α-pinene was added to the catalytic system as described in section S1.2. The reactor was sealed and purged with H_2 to remove air. Then the reactor was pressurized to 0.5 MPa H_2 and placed in a 50 °C water bath, the mixture was stirred for 1.5 h. After the reaction, the remaining products were isolated by liquid-liquid extraction with *ethyl acetate* (5 × 0.5 mL). The *ethyl acetate* layer was then removed via syringe, and the combined extracts were analyzed using gas chromatography (GC). For the recycling procedure, a small aliquot was removed using a pipette from the reaction mixture after the final extraction to ensure the product and any starting materials were removed as completely as possible. Without the addition of fresh surfactant or $RuCl_3$ and Na_2CO_3, the α-pinene (0.2730 g) charged into the autoclave with the remaining aqueous solution for subsequent recycling.

S1.4 Characterization methods

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 catalyst 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). The amount of Ru leaching during the reaction was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Prodigy XP, Leeman). The mean diameter of the micelles containing Ru nanoparticles was determined by dynamic light scattering (DLS, Nano ZS90, Malvern). The structure of the obtained metal nanoparticls was determined by X-ray diffraction (XRD, Enraf Noius CAD4). The conversion and selectivity were measured in a gas chromatography (GC, GC9790, Fuli) equipped with a flame ionization detector (FID) detector and an OV 1701 (50 m, 0.25 mm i.d.) column. The zeta potential of the micelles containing Ru nanoparticles was characterized by a Zetasizer Nano ZS90 instrument (pH=4.0, 25 °C).

S2. XPS Measurement

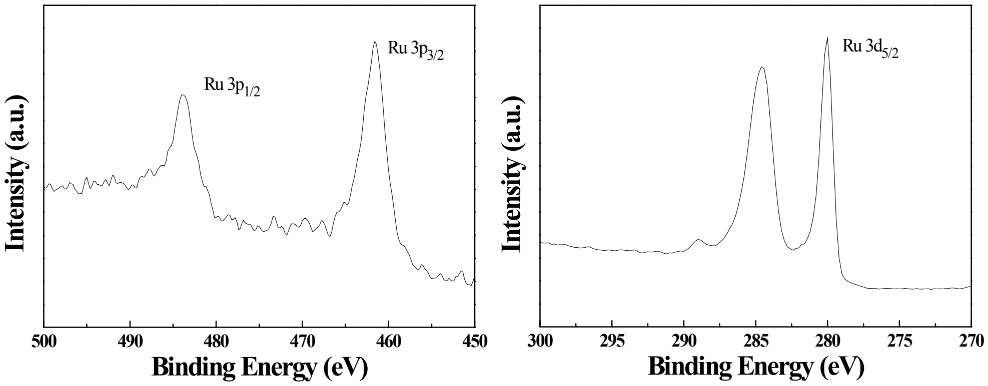
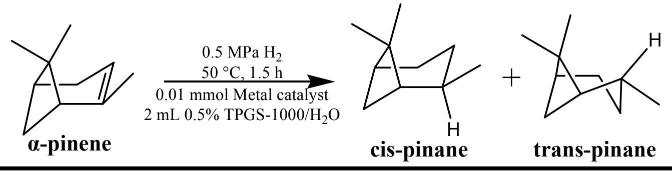


Fig. S1 XPS spectra of Ru nanoparticles

S3. Impact of various metal precursors

Table S1 Impact of nano-metals on the conversion of α-pinene



Metal	Average Diameter (nm) [a]	Structure [b]	Conv. (%) [c]	Select. (%) [d]	TOF (h^{-1}) [e]	d%	Atomic radius (nm)	Lattice constant (nm)	Electronic configuration
Ru(0)	2.47 ± 0.07	*hcp*	61.3	99.2	81.7	50	0.134	0.271	$4d^75s^1$
Rh(0)	2.64 ± 0.14	*fcc*	67.0	96.1	89.3	50	0.134	0.380	$4d^85s^1$
Pd(0)	2.57 ± 0.06	*fcc*	59.2	92.1	78.9	46	0.137	0.389	$4d^{10}$
Pt(0)	2.23 ± 0.05	*fcc*	65.3	94.5	87.1	44	0.138	0.392	$5d^96s^1$

[a] Measured using TEM, The results represent error margin of 95% confidential intervals. [b] Measured using XRD. The images of TEM and XRD were presented in Fig. S2. [c] Determined by GC. [d] Selectivity: The percentage of cis-pinane in the

product. ^{e} Turnover frequency defined as number of mol of converted substrate per mol of catalyst per hour.

S4. TEM Measurement and XRD measurement

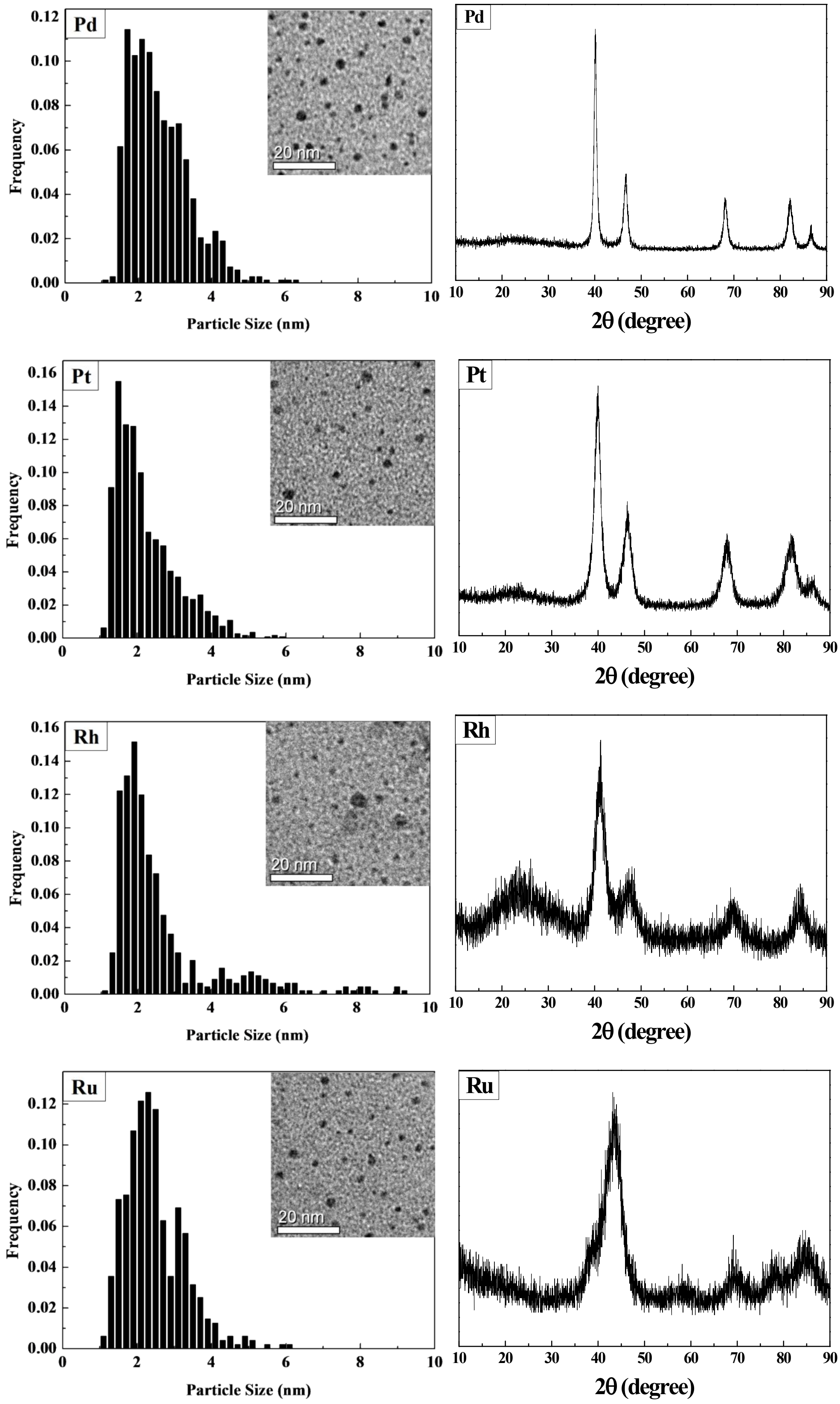


Fig. S2 XRD spectra, TEM images and particle size distributions in various nanoparticles

S5. TEM images and particle size distributions

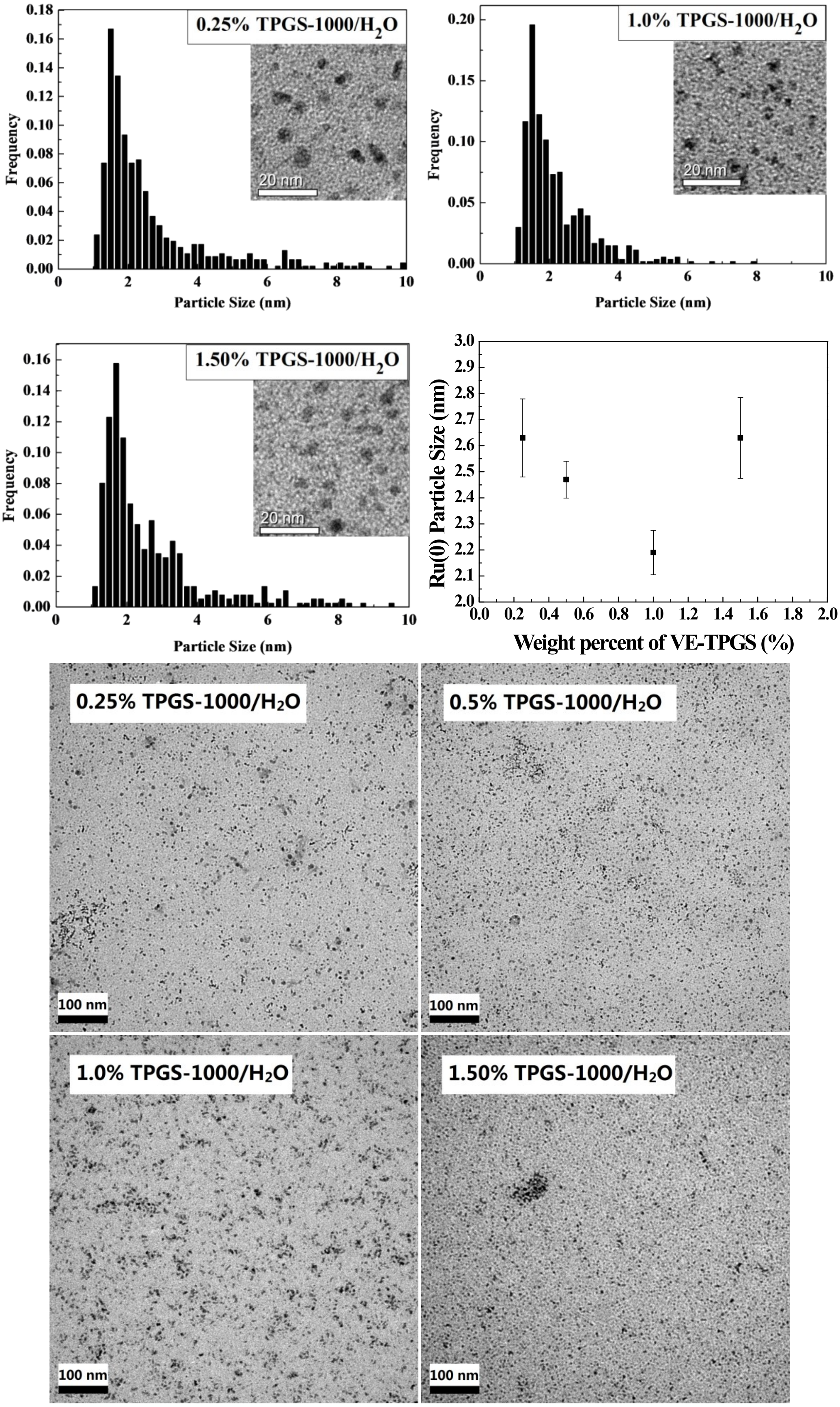


Fig. S3 TEM images and particle size distributions of Ru(0) in various weight percent of TPGS-1000. The error bars represent error margin of 95% confidential intervals.

S6. Appearance of the reaction

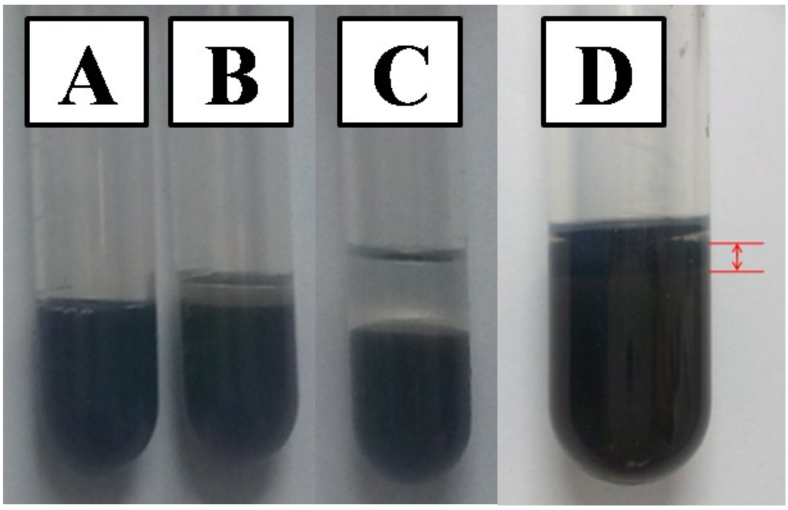


Fig. S4 Photographs of catalyst Ru(0) under the reaction conditions. A) Ru(0) nanoparticles in 0.5% TPGS-1000 solution. B) After reaction completion. C) Extraction with *ethyl acetate*. D) After reaction completion (without Na_2CO_3). Ru(0) nanoparticles were aggregated into clumps on the upper of the aqueous phase.

S7. CLSM Images

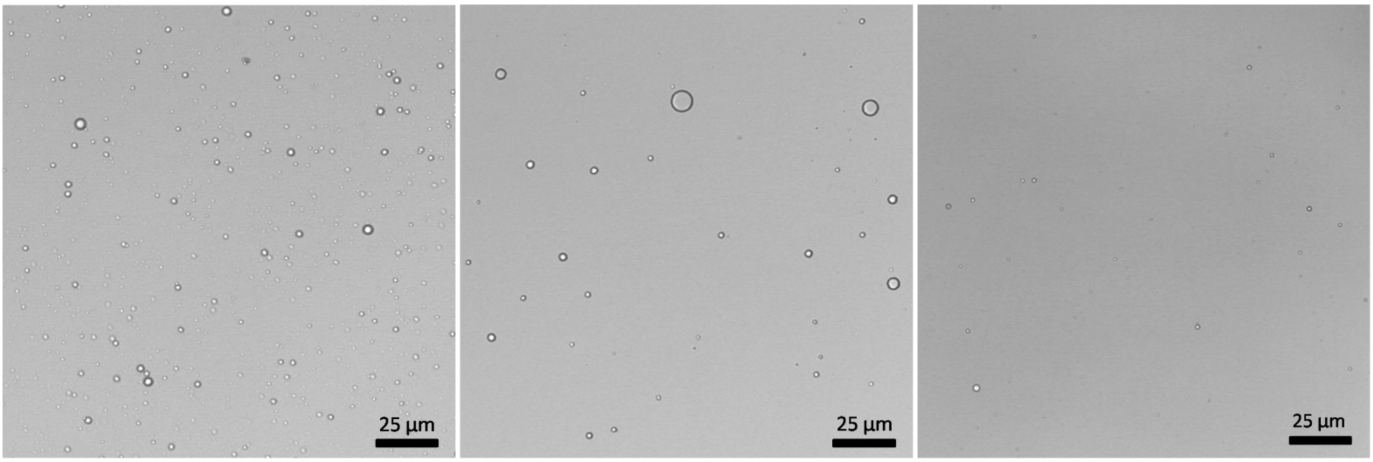
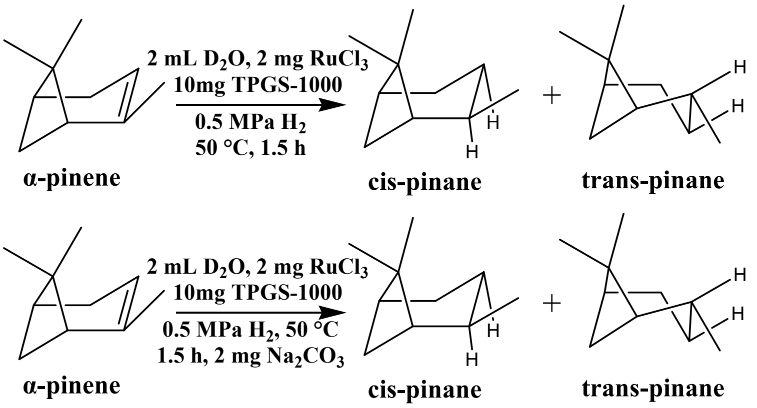


Fig. S5 Images of α-pinene dispersed in the catalyst phase under the reaction conditions. Left) Added Na_2CO_3 in the hydrogenation reaction, α-pinene dispersed evenly in the semi-homogeneous catalyst. Medially) Without Na_2CO_3 in the hydrogenation reaction. Right) The catalyst phase after extraction with *ethyl acetate*.

S8. Hydrogenation of α-pinene over Ru(0) nanoparticles in D_2O



Scheme S1 Hydrogenation of α-pinene over Ru(0) nanoparticles in D_2O

S9. Additional data

Table S2 The data of contrast experiments under some special conditions [a]

Entry	Ru(0) (mmol)	Na_2CO_3 (mg)	H_2O (mL) [b]	*n*-Heptane (mL) [b]	Ethyl acetate (mL) [b]	H_2 (MPa)	Temperature (°C)	Time (h)	Conv. (%) [c]	Select. (%) [d]
1	0.01	2.0	1	0	0	0.5	50	1.5	98.9	98.7
2	0.01	2.0	0	1	0	0.5	50	1.5	61.8	98.1
3	0.01	2.0	0	0	1	0.5	50	1.5	99.1	98.7
4	0	2.0	0	0	0	0.5	50	1.5	0	-
5	0	2.0	0	0	1	0.5	50	1.5	0	-
6 [e]	0.01	2.0	0	0	0	0.5 (N_2)	50	1.5	0	-
7 [e]	0.01	2.0	0	0	1	0.5 (N_2)	50	1.5	0	-
8	0.01	2.0	0	0	0	0.5	50	1.4	98.0	98.6
9	0.01	2.0	0	0	0	0.5	45	1.5	95.2	98.7
10	0.01	2.0	0	0	0	0.4	50	1.5	97.3	98.5

[a] Reaction conditions: substrate (2 mmol), catalyst (0.01mmol). 2 mL TPGS-1000/H_2O (0.5%) [b] Placed in the reactor with α-pinene. [c] Determined by GC. [d] Selectivity: The percentage of cis-pinane in the product. [e] H_2 was replaced with N_2.

When 1.0 mL excess water (entry 1) or ethyl acetate (entry 3) was added to the prepared catalytic system, the conversion of α-pinene decreased slightly. But the conversion decreased 37.9% with 1.0 mL excess n-heptane (entry 2) was added. These results indicate that n-heptane affected the catalytic activity. So we chose ethyl acetate as the extraction. We also draw the conclusion that Ru(0) was the sole catalyst (entries 4,5). The aqueous medium and ethyl acetate played no role in providing H_2 (entries 6,7), suggesting that the both hydrogen atoms took place in the lipophilic core between the metal and the hydrogen-containing micelles. Experiment results (entries 8,9,10) showed that reaction conditions were not necessary to increased or decreased.