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

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S1. Details of UV-Vis absorption spectra

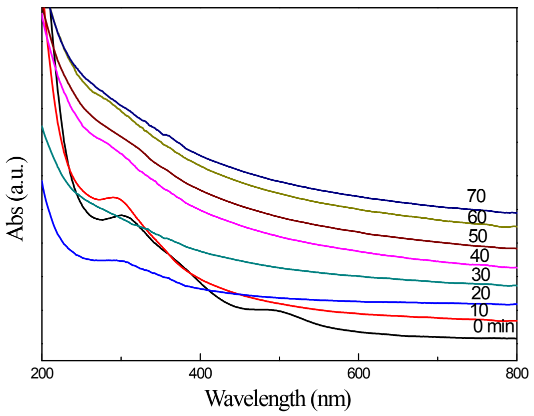

Fig. S1 UV-Vis absorption spectra of the reduction of $RuCl_3$

Reaction conditions: P = 0.5 MPa, T = 40 °C, water = 2 mL, m_{P123} = 30 mg, $RuCl_3$ =0.01 mmol.

The UV-Vis absorption spectra in the aqueous solution had a wavelength of 200-800 nm. As shown in Fig. S1, before heating, the absorption peaks at 320 nm and 510 nm represent Ru (III) species.[1] The absorption peak at 510 nm disappeared immediately after heating. However, the peak at 380 nm decreased slowly and gradually shifted to a short wavelength. This result implies that the Ru (III) species was gradually reduced to the corresponding zero-valent metal during this reduction process. After about 60 min, the absorption peak at 380 nm disappearedcompletely,[2] indicating that Ru^{3+} was reduced completely to Ru^0. The spectrum of the fully reduced solution displayed strong scattering absorption at wavelengths of 200-800 nm, confirming the formation of P123-Ru micellar nanoparticles.

S2. Details of XPS spectra

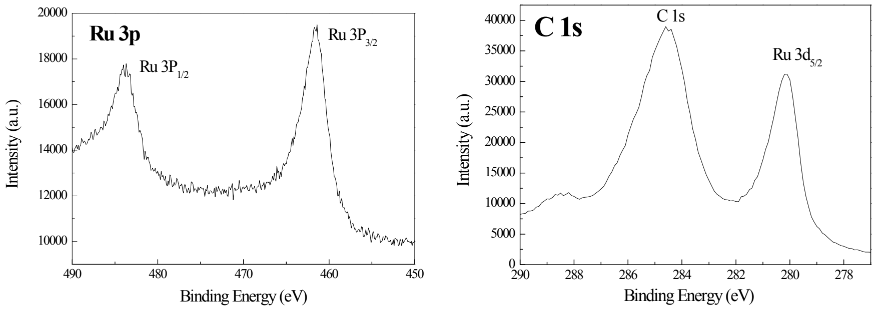

Fig.S2 XPS spectra of Ru nanoparticles stabilized by P123 micelles

Fig. S2 shows the XPS spectra of the Ru nanoparticles. The binding energies of Ru 3p1/2, Ru 3p3/2, and 3d5/2 in the micelles were found to be 484.4 eV, 461.6 eV, and 280.1 eV, respectively, which is concordant with the respective values for bulk Ru metals at 484.1eV, 462.0eV, and 280.2eV.[3] These results demonstrate that Ru (III) was reduced to zero-valence metallic Ru. It should be noted that although the RuO_2 was not detected by UV–Vis spectra characterization, the XPS results indicate that a few atomic layers of Ru (III) species existed on the surface of Ru nanoparticles likely owing to the exposure of Ru nanoparticles in air during the specimen preparation.

S3. Hydrogenation of α-pinene under various surfactants

Table S1. Hydrogenation of α-pinene under various surfactants

Entry	Metal	Reaction medium	Surfactant	Cis-Pinane (%)	Trans-Pinane (%)	Conversion (%)	Selectivity (%)
1	$RuCl_3$	-	-	1.3	0.3	1.6	81.3
2	$RuCl_3$	H_2O	-	53.8	1.4	55.2	97.5
3	Pd/C	-	-	46.7	6.1	52.8	88.5
4	Pd/C	H_2O	-	70.0	8.1	78.1	89.6
5	$RuCl_3$	H_2O	P123 (MW:5800)	88.9	1.4	90.3	98.4
6	$RuCl_3$	H_2O	PSS (MW:8000)	80.5	1.4	81.9	98.3
7	$RuCl_3$	H_2O	PVP (MW:40000)[4]	79.7	1.6	81.3	98.0
8	$RuCl_3$	H_2O	PVA (MW:80000)	67.5	1.4	68.9	98.0

Entries 1-2[5] and Entries 3-4[6] without preparation of Ru nanoparticles.
Preparation of Ru nanoparticles (Entries 5-8): metal precursor: $RuCl_3$ (0.01 mmol), surfactants: 30 mg, reaction medium: water (2 mL).
Hydrogenation of α-pinene: $P = 1.0$ MPa, $T = 40$ °C, $t = 1$ h. $m_{\text{substrate}}= 2$ mmol,

As shown in Table S1, the reaction rate in water (entries2 and 4) was faster than that without water (entries1 and 3), which may be attributed to the greater diffusion of the reactants in water than that without water. This theory was explored in our previous research. We also explored the effects of several commercially available surfactants under the same conditions, which indicated that the reaction rate in an amphiphilic triblock copolymer (entry 5) was faster than that in an amphiphilic ionic polymer (entry 6) and in hydrophilic polymers (entries 7, 8).This result occurred because at a microscopic level, these copolymer-based catalysts were assembled at the interfaces of emulsion droplets and consequently acted as microreactors. Thus, they exhibited a remarkable rate of acceleration for the hydrogenation of α-pinene in water.[7]

S4. Details of TEM images of Ru nanoparticles in various reaction media

TEM micrographs of Ru nanoparticles dispersed in various reaction media are shown as black points in Fig S3. It is noteworthy that the P123-stabilizing Ru nanoparticles had average diameters of 2-5 nm. However, the stability of the Ru nanoparticles in B, C, and D in the figure, was very poor. During the preparation of these samples, the Ru nanoparticles aggregated and precipitated. For sample A, the phenomenon also appeared after a slightly longer period, which indicates that the Ru nanoparticles were protected by P123 micelles in water. Sample D indicates that ethanol destroyed the P123 micelles, which is consistent with that reported in previous research.[8]

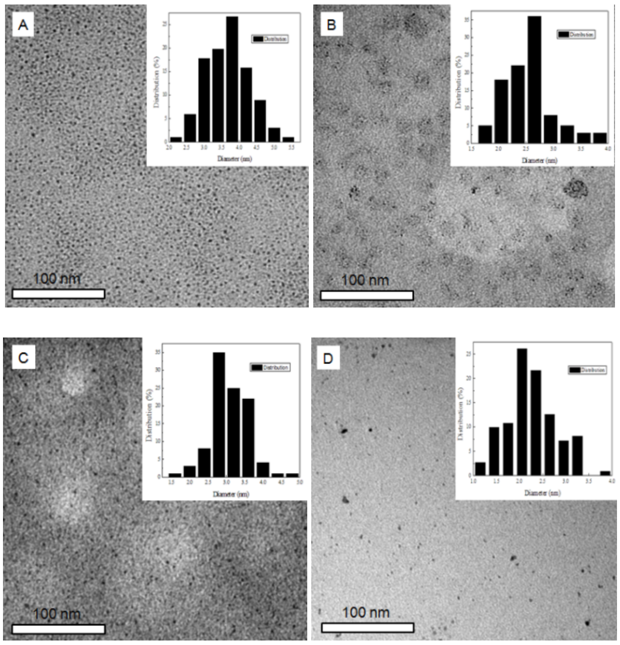

Fig S3 TEM images of Ru nanoparticles in various reaction media.
A: ethanol, B: ethyl acetate, C: methanol, D: V ethanol: V water = 1 : 1

S5. The influence of water on α-pinene hydrogenation

Table S2. The influence of various volumes of water on α-pinene hydrogenation

Volume of water (mL)	Conversion (%)	Selectivity (%)	TOF (h^{-1})
1	74.5	98.7	149.0
2	90.3	98.9	180.6
3	86.7	98.8	173.4
4	84.5	98.6	169.0

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: $RuCl_3$ (0.01 mmol), surfactants: P123 (Mw: 5800, 30 mg), reaction medium: water (2 mL)

The amount of water influence on the catalytic activity and selectivity of Ru nanoparticles was studied; the data are plotted in Table S2. When the amount of water increased from 1 mL to 2 mL, the conversion of α-pinene rose from 74.5% to 90.3%. The conversions decreased with further increases in the amount of water. Interestingly, the selectivity for cis-pinane was almost unchanged when the water amount increased from 1 mL to 4 mL.

S6. The influence of P123 concentration on α-pinene hydrogenation

We further discussed the effect of P123 concentration on the sizes of micelles and the vesicle-microreactor. As shown in Table S3, when only P123 was added to water, the average sizes of P123 micelles tended to decrease slightly with an increase in P123 concentration. When $RuCl_3$ was added to the P123 hydrosol and the Ru nanoparticles were reduced, the sizes of the

P123 micelles increased to some extent likely because Ru nanoparticles enter the interior cores of micelles and increase the micelle size. The prepared catalyst was used to catalyze the hydrogenation of α-pinene, and the catalyst-containing phase was analyzed by CLSM. Because vesicles are not as stable as the microemulsion, the results indicated a broad size distribution with diameters of about 500-900nm.Therefore, the concentration of P123 has little effect on the sizes of micelles and the vesicle-microreactor.

Table S3. The influence of P123 concentration on α-pinene hydrogenation

Concentration of P123 ($\times 10^{-3}$ mol/L)	Without $RuCl_3$ (nm) [a]	After reduction (nm) [a]	Average size of vesicles (nm) [b]	Conversion (%)	Selectivity (%)
0.43	20.8	23.9	599	76.5	98.1
0.86	20.6	24.2	638	82.1	98.4
1.29	19.8	25.7	757	83.7	98.3
1.72	19.5	23.4	664	85.9	98.6
2.16	19.0	24.1	753	89.1	98.8
2.59	19.1	23.6	695	92.8	98.9
3.02	19.0	22.8	748	92.1	98.7
3.45	18.7	23.2	746	90.4	98.7
4.31	18.7	23.3	798	81.6	98.5
5.17	18.9	23.7	714	72.3	98.4

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).
[a]: measured by DLS, [b]: measured by CLSM.

S7. The influence of stirring rate on α-pinene hydrogenation

Table S4. The influence of various stirring rate on α-pinene hydrogenation

Stirring rate (r / min)	Conversion (%)	Selectivity (%)	TOF (h^{-1})
300	55.1	98.8	110.2
400	77.5	98.8	155.0
500	90.5	98.9	181.0
600	91.0	98.9	182.0
700	91.3	98.8	182.6

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: $RuCl_3$ (0.01 mmol), surfactants: P123 (Mw: 5800, 30 mg), reaction medium: water (2 mL)

The various stirring rate influence on the catalytic activity and selectivity of Ru nanoparticles was studied; the data are plotted in Table S4. When the stirring rate increased from 300 r/min to 500 r/min, the conversion of α-pinene rose from 55.1% to 90.5%. With further increases in the stirring rate, the conversions change very little. In addition, the selectivity for cis-pinane was almost unchanged when the stirring rate increased from 300 r/min to 700 r/min.

S8. Details of TEM images of Ru nanoparticles in various recycle stages

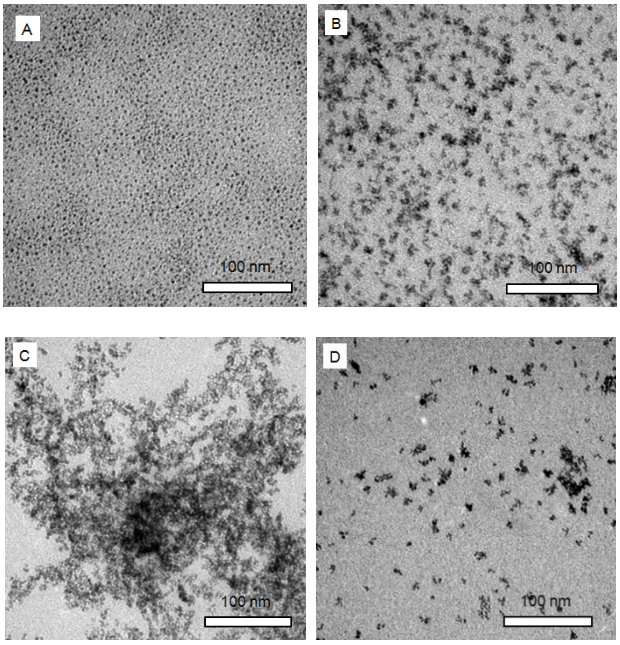

Fig S4 TEM images of Ru nanoparticles in various recycle stages
A: 1 cycle, B: 7 cycles, C: 8 cycles, D: 14 cycles

The particle size of Ru nanoparticles was almost unchanged after one cycle, and the nanoparticles displayed a homogeneous distribution similar to that before recycling. The TEM image (Fig. S4B) revealed that the particle sizes of Ru nanoparticles increased, and aggregation occurred after seven recycles. As clearly shown in Fig. S4C, the aggregation phenomenon became more substantial, and Ru particles with larger sizes were formed. Obvious aggregation was observed after 14runs (Fig. S4D).

S9. Ruthenium leaching tested by ICP

Table S5. Ruthenium leaching tested by ICP analysis

Sample	Sample volume	Concentration of Ru (ppm)	Percentage of Ru leaching (%) [b]
$RuCl_3$	2.1mg	1000	-
α-pinene	0.273g	0.09	-
P123	30mg	0	-
n-heptane	2g	0.25	-
aqua regia	5mL	0	-
after 1 cycle [a]	1.14g	4.1	0.82
after 1 cycle	1.14g	0.79	0.16
after 7 cycle	1.14g	2.1	0.42
after 8 cycle	1.14g	3.9	0.78
after 14 cycle	1.14g	5.0	1.00

A certain amount of sample was dissolved in 5mL of aqua regia. The mixture was then transferred to a 10mL volumetric flask, diluted to 10mL, and tested by ICP analysis.

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).

[a]: without P123, [b]: Ratio of the leaching of Ru and the concentration of Ru in fresh catalyst.

S10. The influence of n-heptane on α-pinene hydrogenation

Table S6. The influence of various volumes of n-heptane on α-pinene hydrogenation

Volume of n-heptane (mL)	Conversion (%)	Selectivity (%)	TOF (h^{-1})
0	99.9	98.9	99.9
0.5	93.7	98.4	93.7
1.0	86.3	98.4	86.3
1.5	81.9	98.3	81.9
2.0	75.6	98.1	75.6

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: water (2 mL)

A set of experiments was designed to explore whether the residual extractant had an influence on the activity of catalysts. The aforementioned prepared catalyst with an additional 0.5-2.0mL n-heptane was used to catalyze the hydrogenation of α-pinene under the same experimental conditions. As shown in Table S6, the additional n-heptane resulted in a gradual decreased in the conversion of α-pinene likely because organic solvents such as n-heptane destroy the structure of micelles and affect the catalytic activity.[9] In addition, hydrophobic n-heptane can enter the interior of micelles and to dilute the α-pinene in P123 micelles, which hinders the α-pinene contact with the catalyst and leads to a decrease in catalytic activity.

S11. Reproducibility of the reaction

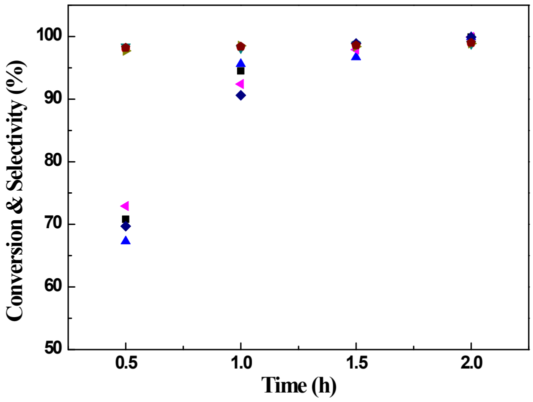

Fig. S5. Reproducibility of the reaction

Hydrogenation of α-pinene: *P* = 1.0 MPa, *T* = 40 °C, *t* = 1 h, [substrate] : [catalyst]=200 : 1, α-pinene: 2 mmol, reaction medium: water (2 mL), surfactant: P123 (30 mg), metal precursor: $RuCl_3$ (0.01 mmol).

The curves of the reaction at 40°C and1.0 MPa of H_2 were separate determined four times; the results are shown in Fig. S5. At all reaction times, the selectivity to cis-pinane was better than 98.0% in all of the repeated experiments up to complete conversion of pinene. The maximum deviation of the conversion was ±5%, which is satisfactory.

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