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Multigram scale-up of the selective hydrogenation of α-pinene with ruthenium nanoparticles in water

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ABSTRACT:

This paper presents the successful use of ruthenium nanoparticles, stabilized in water by ammonium surfactants, in the selective hydrogenation of α-pinene and the first industrially reported scale-up of this catalyst on a multigram-scale. After designing the nanocatalyst at the lab scale, operational parameters (substrate/metal ratio, pressure and temperature) were identified and optimized in the scale-up. The α-pinene hydrogenation process was operated with a 200 g batch, under 30 bar H_2 and at 110°C, with a complete conversion and a selectivity of 98% into *cis*-pinane within 4 h. The catalyst was easily recycled through a liquid-liquid biphasic approach for 5 reaction cycles to achieve a total turnover number (TTON) of 14000.

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KEYWORDS:

Ruthenium - Nanoparticles – Hydrogenation – α-pinene – Water – Scale-up

INTRODUCTION

Among cyclic monoterpenes, α-pinene constitutes a worldwide available and cheap chemically attractive platform molecule, predominantly present in turpentine with a production of 360,000 tons per year in 2015,[1] or as co-product of the paper industry.[2] Moreover, an enhanced production could be expected in the future decades owing to the implementation of wood-fueled biorefineries.[1] Considering the abundance of α-pinene in turpentine (60 to 85%), the upgrading of this cheap molecule into valuable chemicals represents a wise and relevant strategy.[3]

Among the valorization reactions,[4] the hydrogenation of α-pinene remains of great interest, affording either *cis* or *trans*-pinane (Figure 1), a key intermediate for the production of valuable fragrances or pharmaceuticals, such as rose musk, linalyl acetate or vitamin E.[5] The *cis* diastereoisomer, which is predominantly obtained during the hydrogenation reaction owing to the presence of the encumbered gem dimethyl bridge,[6] presents a higher reactional activity and thus is highly desirable to produce these intermediates. Therefore, there is still a need to develop scalable catalytic routes with a reduced environmental footprint and an economically viable cost for the industrial production of this valuable *cis*-enriched isomer.

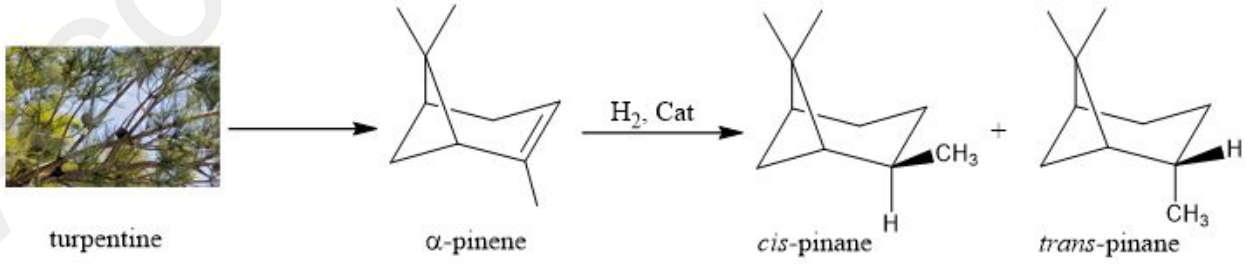

Figure 1. Hydrogenation of α-pinene to *cis* and *trans*-pinanes

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Evidently, many strategies involving mostly heterogeneous catalysts have been developed to selectively reduce α-pinene to *cis*-pinane, combined with a good reusability,[4] including nickel,[78] ruthenium,[9] palladium[10-11] on different supports. However, these processes still suffer from drastic reaction conditions, with selectivities often inferior to 90%, and are performed in organic solvents, mainly alcohols, with some additives such as NaOCl or cupric chloride salts to improve their performances.[12]

Recently, aqueous suspensions of metal nanoparticles have proved to be relevant catalysts for various applications, owing to their unique properties, affording original surface reactivities associated with a potential recycling under a liquid-liquid biphasic approach.[13] In the literature, ruthenium nanoparticles have been reported for the selective hydrogenation of α-pinene to *cis*-pinane, stabilized in water with various capping agents such as vitamin E TPGS,[14] polymers,[15-18] or cyclodextrins.[19] Some nanocatalysts, gathered in Table 1, allowed to achieve quite good catalytic performances, and proved to be reusable. However, only low scale (m < 2g of substrate) and high catalyst loading have been explored.

Table 1. Overview of the recent applications of ruthenium nanoparticles for α-pinene hydrogenation

Entry	Catalyst	Reaction conditions	Substrate amount (g)	S/M	Conv. (%)	Selectivity (%)	Number of recycling runs (TTON)
1[14]	Ru NPs / TPGS-1000	5 bar H_2, 50°C, 1.5 h	0.27	200	99.7	98.8	10 (2000)
2[16]	Ru NPs / F127 copolymers	3 bar H_2, 40°C, 3 h	0.27	200	91.3	99.0	7 (1400)
3[15]	Ru NPs / P123	7 bar H_2, 40°C, 2 h	0.27	200	99.9	98.9	8 (1600)
4[17]	Ru NPs / PVA	20 bar H_2, 70°C, 3 h	1.36	1000	99.9	98.9	8 (8000)
5[18]	Ru NPs / cellulose	15 bar H_2, 75°C, 5 h	0.68	800	80.0	100.0	7 (5600)

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In this paper, we describe the use of easy-to-prepare ruthenium nanoparticles, stabilized in water by ammonium surfactants, for the industrially scaled selective hydrogenation of α-pinene in neat water. In a first step, an efficient nanocatalyst was designed at the lab-scale through an evaluation of various reducing agents, the screening of stabilizing agents and the optimization of the water amount. The obtained nanoparticles were fully characterized through adapted physico-chemical techniques. Therefore, the multigram scale-up of the biphasic liquid-liquid α-pinene hydrogenation was a good opportunity to evaluate the potential of aqueous suspensions of metallic nanoparticles for future industrial applications.

EXPERIMENTAL SECTION

Starting Materials

Ruthenium (III) chloride hydrate $RuCl_3 \cdot 3H_2O$, and sodium borohydride $NaBH_4$ were purchased from Acros Organics. Cetyltrimethylammonium chloride (CTACl), aqueous solution (30% wt) of *N*,*N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium dihydrogen phosphate ($HEA16H_2PO_4$) were purchased from Aldrich and were used without further purification. Other *N,N*-dimethyl-*N*-hexadecyl-*N*-(2-hydroxyalkyl)ammonium salts were synthesized according to already reported procedures: HEA16Cl,[20] HEA16Br,[20] $HEA16BF_4$,[20] $HEA16HCO_3$,[20] HPA16Cl,[21] HBA16Cl,[21] THEA16Cl.[22] α-pinene (purety 96%) was provided by Dérivés Résiniques et Terpéniques company (Castets, France). For lab experiments, water was distilled twice before use. For industrial experiments, tap water was used.

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Equipments

For experiments carried out at lab-scale, stainless steel pressure reactor used was one from Parr Instrument Company (maximal pressure (PS) = 200 bar, maximal temperature (TS) = -15 °C-350 °C, internal diameter (Di) = 3.3 cm, height (h) = 5.5cm) equipped with a glass cell (V = 50 mL), a magnetic stirring and a heating plate. For experiments carried out on larger scale on DRT site, pressure reactor from Parr (V = 1.2 L, PU = 350 bar, TU = -10°C to 350°C, Di = 8.3 cm, h = 24.9 cm) was used, equipped with a heating jacket and a hollow shaft mechanical stirrer.

Zeta potential analysis

Zeta potential measurements were performed by laser Doppler electrophoresis, with Zetasizer Nano ZS90 equipment. Catalytic suspensions of ruthenium(0) were diluted to reach a metal concentration of 7.6×10^{-4} mol.L^{-1}. Analyses were performed in a cell (DTS1070, 150 µL) at 20 °C. The data was processed by the Zetasizer software.

Static multiple light scattering – Turbiscan technology

Static multiple light scattering analyses were carried out with the Turbiscan Lab technology (Formulaction, Toulouse, France). This apparatus is constituted of a near infrared light source (wavelength ¼ 880 nm), and two synchronized detectors, which all move vertically alongside the cylindrical glass sample cell. The light source head scans the entire height of the sample (up to 55 mm), and the detectors acquire transmission and backscattering data every 40 µm. The measured photon fluxes are calibrated with a non-absorbing scattering standard (calibrated polystyrene latex beads) and a transmittance standard (silicon oil). The temperature of the

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apparatus was regulated at 25.0 ± 0.1 °C. The nanoparticle suspensions were studied without any dilution and for each one of them a scan was carried out every 4 h, along 7 days.

TEM experiments

Transmission electron microscopy (TEM) images were recorded with a JEOL TEM 100CXII electron microscope operated at an acceleration voltage of 100 kV, with a KeenView camera and the ITEM software (1376x1032 px).The samples were prepared by the addition of a drop of the colloidal suspension on a copper grid coated with a porous carbon film. The size distributions for spherical particles were determined measuring 250 particles, through a manual analysis of enlarged micrographs with ImageJ software and using Microsoft Excel to generate histograms of the statistical distribution and a mean diameter. High resolution TEM analysis was carried out on a JEOL JEM 2010 UHR electron microscope with lanthanum hexaboride source (LaB6), using CDD camera (Gatan Orius SC1000) and ITEM software (4008 x 2672 pixels).

GC-FID analysis

Gas chromatography was performed using a Trace GC Ultra (Thermo Scientific) apparatus with a FID detector, equipped with a Thermo Fisher HP5-MS capillary column (30 m, 0.25 i.d., 0.5 f.t.) Parameters were as follows: temperature was increased from 120 °C to 160 °C at 5 °C/min (maintained 2 min) and then from 160 °C to 220 °C with a ramp of 20 °C/min (maintained 3 min). Injector temperature, 250 °C; detector temperature, 250 °C; injection volume 1 µL, split flow : 16 mL/min, carrier gas (He) 0.8 mL/min. The final chromatogram was recorded and treated using ChromQuest software. Products identification was performed by comparison of their retention

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times with commercial products. Reaction rate and selectivity were determined by standard calibration with *n*-dodecane as internal standard.

pH measurements

pH measurements were performed on the suspension with a Mettler Toledo pH meter without any dilution.

Synthesis of ammonium-stabilized Ru(0) suspension – Reduction by $NaBH_4$

To an aqueous solution (5 mL) of a chosen quaternary ammonium salt (2 equiv., 7.6×10^{-5} mol) was added 1 mL an aqueous solution of sodium borohydride (2.5 equiv., 9.5×10^{-5} mol). Then, this solution was quickly added under vigorous stirring to an aqueous solution (4 mL) of the ruthenium (III) chloride hydrate $RuCl_3{\cdot}3H_2O$ (1 equiv., 3.8×10^{-5} mol) to obtain a colloidal suspension of Ru (0). The reduction occurred instantaneously and was manifested by a color change from brown to black. The suspension was kept under stirring 12 h before use.

Synthesis of ammonium-stabilized Ru(0) suspension – Reduction by H_2

An aqueous solution (5 mL) of a chosen quaternary ammonium salt (2 equiv., 7.6×10^{-5} mol) was added to an aqueous solution (5 mL) of the metallic precursor $RuCl_3{\cdot}3{\cdot}H_2O$ (1 equiv., 3.8×10^{-5} mol). This mixture was then introduced in an autoclave under 10 bar H_2 and 50 °C, during 12 h, to afford a colloidal suspension of Ru(0). The reduction was manifested by a color change from brown to black.

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Catalytic experiments (50 mL reactor)

In a 50 mL pressure reactor, 10 mL of a catalytic suspension (0.038 mmol of ruthenium) and α-pinene (3.8 mmol, 0.52 g) were introduced. The autoclave was purged with H_2 and pressurized to the given pressure. The reaction was kept at room temperature, under magnetic stirring during the desired reaction time. At the end of the reaction, the reaction products were extracted with diethyl ether (3 × 10 mL) and analyzed by GC-FID.

Catalytic experiments (1.2 L reactor)

Specified amounts of ruthenium trichloride hydrate $RuCl_3 \cdot 3H_2O$, stabilizer, water and α-pinene were introduced in a 1.2 L pressure reactor. The autoclave was purged with H_2 and pressurized to a given pressure. The reactor could be heated thanks to a water jacket. The reaction was conducted under mechanical stirring with hydrogen circulation thanks to a hollow shaft. At the end of the reaction, the final products were obtained through simple decantation and the supernatant was analyzed by GC-FID.

Recycling procedure (1.2 L reactor)

The hydrogenation reaction was carried out as mentioned above. When complete conversion was reached and after decantation, the organic phase was purged through a pipe and a new batch of substrate was introduced within the reactor. A new reaction cycle could be conducted. This operation was repeated up to five times.

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RESULTS AND DISCUSSION

Lab-scale optimization

In an initial set of experiments, the best catalytic system in terms of stability and catalytic performances was defined on a laboratory-scale.

First, ruthenium nanoparticles were synthesized through a bottom-up method, by chemical reduction of the ruthenium(III) chloride hydrate ($RuCl_3 \bullet 3H_2O$) in the presence of *N*,*N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium chloride (HEA16Cl) as protecting agent with a molar ratio of 2 according to previous results.[23] First, two reduction approaches were evaluated, using either sodium borohydride ($NaBH_4$) as a well-known reducing agent (Entry 1, Table 2) for the reduction of metal salts, or dihydrogen (H_2) as a clean and green agent,[24] classically used for organometallic precursors (Entry 2, Table 2).[25]

Both colloidal suspensions were characterized by transmission electron microscopy (TEM) to determine the morphology and the size of the particles, as well as by high resolution transmission electron microscopy (HR-TEM) to better understand the sample atomic structure (Figure 2). The nanoparticles obtained through the reduction by hydride salts ($NaBH_4$) were spherical, presenting an average diameter of about 1.75 nm and a narrow size distribution (Figure 2a and 2b), while rods with sizes between 2 and 6 nm were observed for those obtained under dihydrogen (Figure 2c and 2d). Moreover, in both cases, the zeta potential values, measured by electrophoretic light scattering, showed positive values, superior to +30 mV, evidencing highly stable suspensions probably due to the significant electrostatic repulsion (Table 2).[26]

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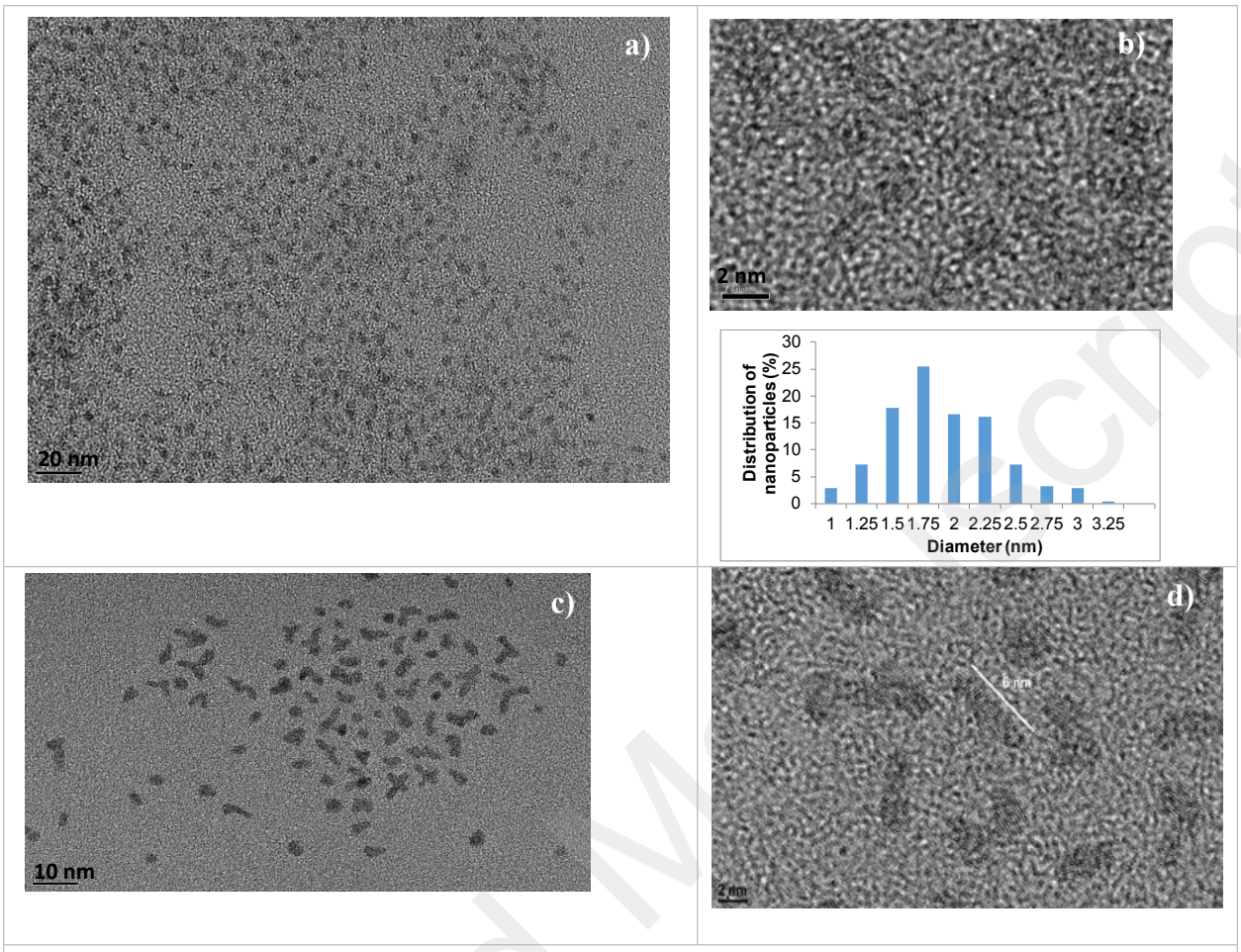

Figure 2. TEM (on the left) and HR-TEM images (on the right) of a) Ru NPs reduced by $NaBH_4$ *(magnification ×120000, scale bar 20 nm),* b) Ru NPs reduced by $NaBH_4$ *(magnification ×600000, scale bar 2 nm)* with size distribution, c) Ru NPs reduced by H_2 *(magnification ×200000, scale bar 10 nm)* and d) Ru NPs reduced by H_2 *(magnification ×600000, scale bar 2 nm)*

Both nanocatalysts were evaluated in the hydrogenation of α-pinene under 10 bar H_2, at room temperature, in water (Table 2). Whatever the catalyst was, a high level of selectivity was achieved. However, the suspension prepared with dihydrogen (H_2) displayed better kinetics, with a 96% conversion in 1h (Entry 2), compared to 84% with the catalyst synthesized with sodium borohydride (Entry 1). Moreover, dihydrogen was a more appropriate reducing agent for industrial scale-up operations.

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Table 2. Hydrogenation of α-pinene. Choice of the reducing agents for the preparation of Ru(0) nanoparticles[a]

Entry	Reducing agent	NP morphology[b]	NP size[b](nm)	pH	ζ[c](mV)	Conv.[d] (%)	Selectivity[d] (%)
1	$NaBH_4$	Spheres	1.75	2.1	+ 52	84	98
2	H_2	Rods	2-6	1.7	+ 57	96	99

[a] Reaction conditions: Ru (3.8×10^{-5} mol, 0.01 equiv.), HEA16Cl (7.6×10^{-5} mol, 0.02 equiv.), α-pinene (0.5 g, 3.8×10^{-3} mol, 1 equiv.), 10 bar H_2, H_2O (10 mL), r.t., 1 h. [b] Observed by TEM. [c] Measured by electrophoretic light scattering [d] Determined by Gas Chromatography.

The physico-chemical stability of the suspension was also studied using Turbiscan technology (Formulaction, France), based on the transmitted and backscattered laser light through the sample. This unusual technology enables to detect destabilization phenomena, such as reversible particle migration (sedimentation or creaming), or size variation (coalescence or flocculation).[27-28] Both solutions reduced either by sodium borohydride (Suspension 1) or dihydrogen (Suspension 2) were scanned from the bottom (0 nm) to the top of the sample (40 mm) at different time intervals during 7 days (Figure 3). An increase in the backscattered signal was observed on the top of the vial for the suspension 1 (Figure 3a, $NaBH_4$), evidencing a destabilization by creaming, and on the bottom of the sample for the suspension 2 (Figure 3b, H_2), indicating sedimentation. The kinetics of destabilization (Turbiscan stability index (TSI) measurements along time expressed in days) proved that the Ru@HEA16Cl nanoparticle suspension obtained with H_2 had a better stability in time (TSI variations < |0.15|) than the other one (TSI variations > |1.1|) (Figure 3c). However, in both cases, TSI values remained low and destabilization phenomena were almost negligible, evidencing a good stability of both suspensions. In the following experiments, dihydrogen was chosen as an eco-responsible and easy-to-use reducing agent at industrial scale, as well as a suitable reagent for one-pot synthesis.

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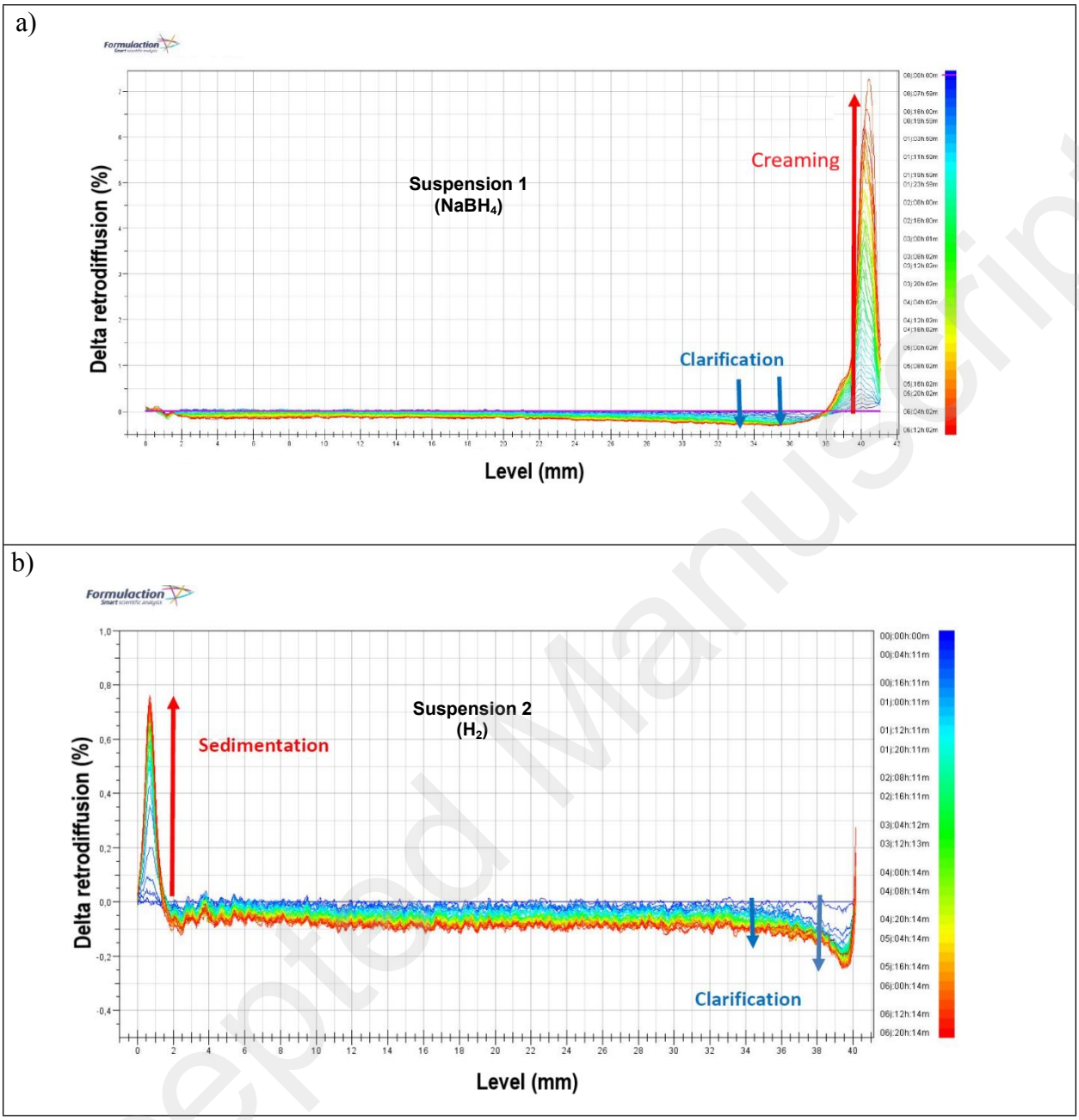

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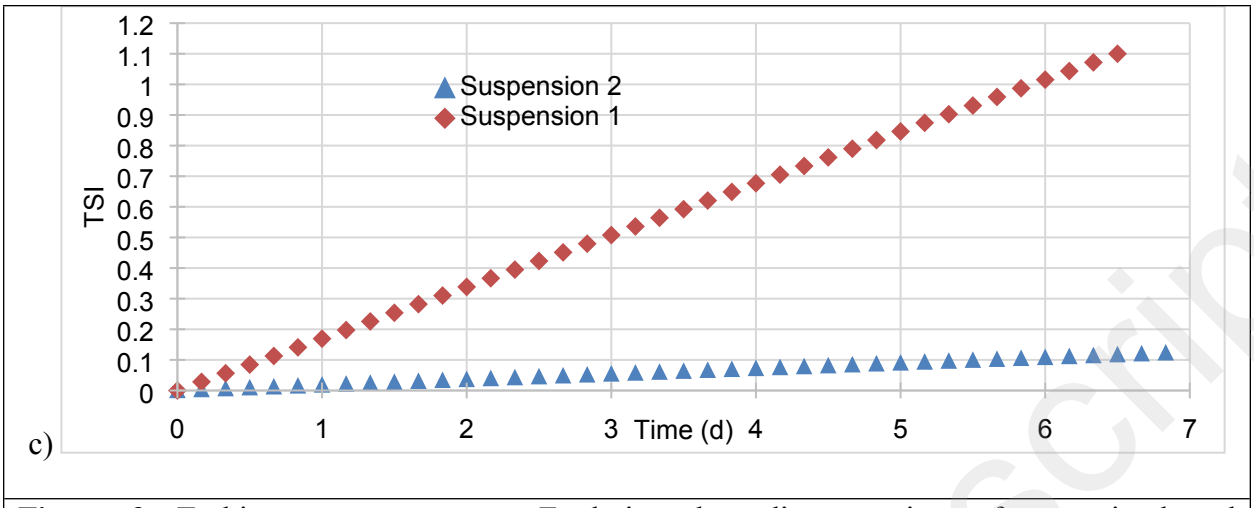

Figure 3. Turbiscan measurements. Evolution depending on time of transmitted and backscattered signals (Delta Retrodiffusion) depending on the sample level in mm (25°C) a) For suspension 1 ($NaBH_4$), b) For suspension 2 (H_2) and c) Turbiscan Stability Index (TSI) depending on time (day)

Secondly, the influence of various water-soluble capping agents for the ruthenium nanospecies on the catalytic performances was investigated. This choice remains crucial to insure relevant catalytic performances in the nanometer-sized micelles,[29] as well as to maintain the catalyst within the aqueous media. Several ammonium surfactants, that possess a highly hydrophilic mono- or poly-hydroxylated polar head combined with a lipophilic sixteen-carbon chain, with diverse counter-ions, were used as capping agents of ruthenium nanoparticles and evaluated in the selective hydrogenation of α-pinene at 10 bar H_2 and room temperature in water. The results are gathered in Figure 4 and compared to the commercial CTACl surfactant.

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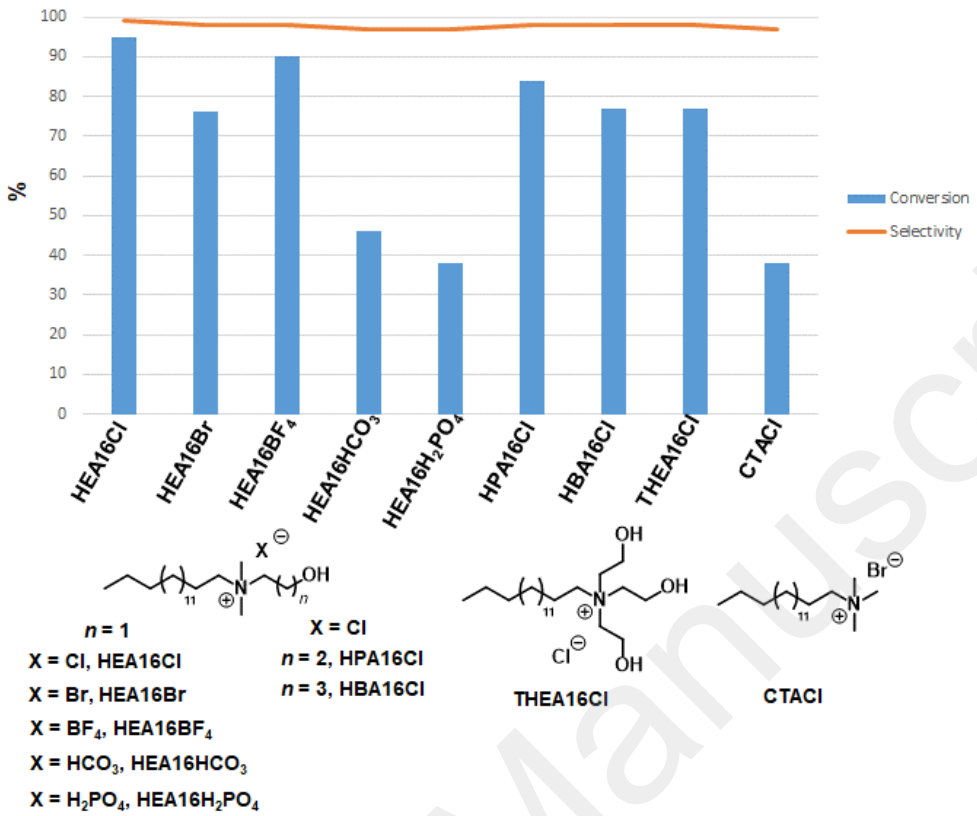

Figure 4. Screening of various surfactants on the catalytic performances in α-pinene hydrogenation. Reaction conditions: Ru@capping agent (3.8×10^{-5} mol, 0.01 equiv.), capping agent (7.6×10^{-5} mol, 0.02 equiv.), α-pinene (0.5 g, 3.8×10^{-3} mol, 1 equiv.), 10 bar H_2, H_2O (10 mL), r.t., 1 h

First, in most of the cases, compared to the usual CTACl surfactant that led to only 38% conversion, the hydroxylated surfactants afforded an increased conversion up to 95%. These improved catalytic performances could be attributed to an enhanced water-solubility of the surfactant owing to the hydroxyl function, thus potentially affording a better colloidal protection. Moreover, free micelles of surfactants could improve the solubility of the organic substrate within the aqueous phase, thus enhancing the reaction rate.[20, 30] In the HEA family, the screening of various counter-ions was performed, showing an effect of this parameter on the catalytic activity, in the following order: Cl > BF_4 > Br > HCO_3 > H_2PO_4. These results could be attributed to the

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steric hindrance of the adsorbed anion at the metal surface, thus hampering the substrate access to the active species,[31] as well as the coordination strength.[32]

To conclude, best results were achieved with HEA16Cl, with 95% conversion and 99% selectivity into the targeted *cis*-pinane. This surfactant possesses a head group of smaller size, and consequently a lower molecular area A. This parameter, defined as the area occupied by the surfactant molecules at the interface, is directly influenced by the steric hindrance of the polar head. Moreover, the HEA16Cl capping agent also displays a higher critical packing parameter (CPP) which indicates a flexible bilayer organization of the micelles and might improve its ability as transfer agent between phases.[33]

Finally, the amount of water used in the catalytic reaction was identified as a potential problematic operational parameter in the scale-up, in order to limit the wastewater flow. The concentration of ruthenium in water was increased gradually from 3.8 mM to 12.7 mM, with a constant HEA16Cl/Ru molar ratio of 2 (Table 3, entries 1-3), by decreasing the amount of water. Whatever the amount of water was, similar hydrogenation performances were observed with conversion up to 88% and a selectivity of 99% for higher metal concentration (Entry 3). To meet the requirement of an industrial process, the ruthenium concentration was fixed at 12.7 mM for the following scale-up.

Table 3. Hydrogenation of α-pinene. Influence of the water amount[a]

Entry	Ruthenium concentration ($mmol.L^{-1}$)	Water amount (g)	Conversion[b] (%)	Selectivity[b] (%)
1	3.8	10	84	98
2	7.6	5	86	98
3	12.7	3	88	99

[a] Reaction conditions: Ru (3.8×10^{-5} mol, 0.01 equiv.), HEA16Cl (7.6×10^{-5} mol, 0.02 equiv.) α-pinene (0.5g, 3.8×10^{-3} mol, 1 equiv.), 10 bar H_2, H_2O, r.t., 1 h. [b] Determined by Gas Chromatography

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Scale-up experiments

Based on these encouraging results, the hydrogenation of α-pinene, catalyzed by the Ru@HEA16Cl catalyst, was performed from 100 to 600 gram scale, using the facilities of the DRT plant. The experiments were conducted in a 1.2 L-reactor, equipped with mechanical stirring and a heating jacket. Moreover, the procedure was simplified, since all the reagents (metallic precursor, surfactant, water and substrate) were simultaneously introduced in the reactor and directly placed under dihydrogen. Thus, the Ru@HEA16Cl nanoparticles were synthesized *in situ* and controlled by TEM after a catalytic hydrogenation of α-pinene (Figure 5). They were rather spherical with an average diameter of 2.3 ± 0.5 nm, and no agglomeration phenomenon was observed after this catalytic reaction.

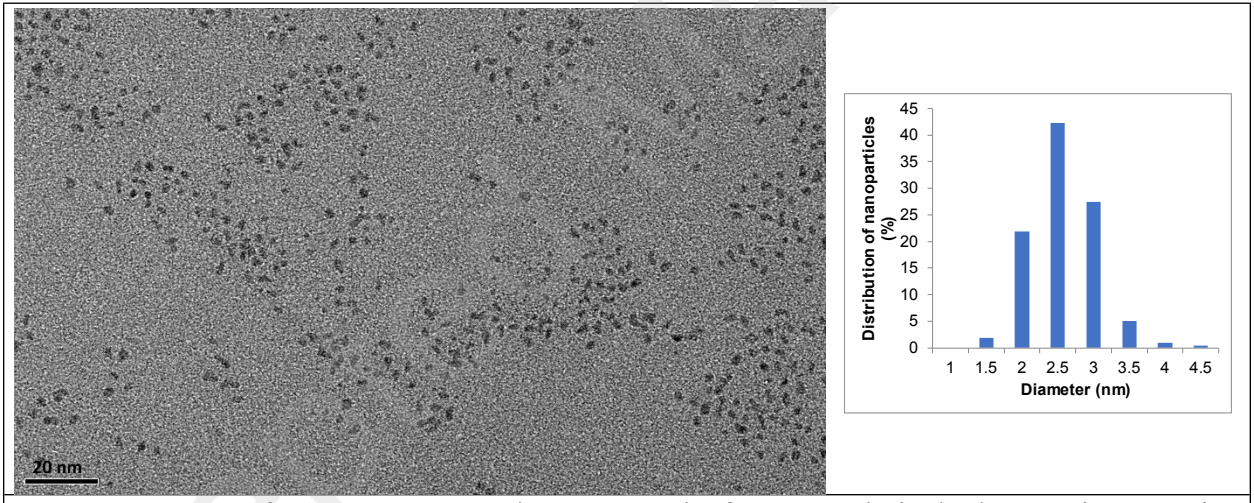

Figure 5. TEM of Ru NPs prepared *in situ* and after a catalytic hydrogenation reaction *(magnification x100000, scale bar 20 nm)* with size distribution.

The hydrogenation of α-pinene was carried out using the optimized Ru@HEA16Cl catalyst with a metal concentration in water of 12.7 mmol.L^{-1}, under 10 bar H_2 and at room temperature, with various substrate/metal ratios. The results are gathered in Table 4.

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Table 4. Scale-up of α-pinene hydrogenation. Catalyst loading[a]

Entry	Substrate/Metal ratio	Pinene amount (g)	Water amount (g)	t (h)	Conversion[c] (%)	Selectivity[c] (%)
1[b]	100	0.5	3	1	88	99
2	100	108	600	5	> 99	99
3	1000	108	60	6.5	96	99
4	3000	648	120	7	21	98
5	10000	270	15	5.5	4	99

[a] Reaction conditions: Ru (12.7 mmol.L^{-1} in water), HEA16Cl (2 equiv./metal) α-pinene (purety 96%), 10 bar H_2, H_2O, 50 °C. [b] Reaction conducted at r.t. [c] Determined by Gas Chromatography

First, while maintaining the same substrate/metal molar ratio and a substrate/water molar ratio of 0.2, a scale-up from 500 mg (Entry 1, 50 mL reactor) to 100 g (Entry 2, 1.2 L reactor) of α-pinene proved to be feasible by adjusting the process temperature at 50 °C and the reaction time from 1 to 5 h, with a complete conversion and a selectivity of 99% in *cis*-pinane. In a second set of experiments, the catalyst loading, which constitutes a crucial deciding factor in terms of economic profitability, was assessed to meet industrial requirements (Entries 2-5). Lowering the catalyst loading by increasing the substrate/metal molar ratio from 100 to 1000, while maintaining the α-pinene amount, afforded *cis*-pinane with a 96% conversion and an excellent selectivity of 99% after 6.5 h (Entry 3). However, increasing the α-pinene amount, while decreasing the catalyst loading, led to slower reaction kinetics with quite low conversions (inferior to 21%) but 99% of selectivity. These results could be attributed to an increased organic phase (composed of pure α-pinene) compared to the aqueous phase, thus slowing the mass transfer of the substrate at the metal surface. To improve the performances of the Ru@HEA16Cl nanocatalyst, the operational conditions, such as the temperature and the pressure, were investigated at a relevant substrate/metal ratio of 3000 (Figure 6).

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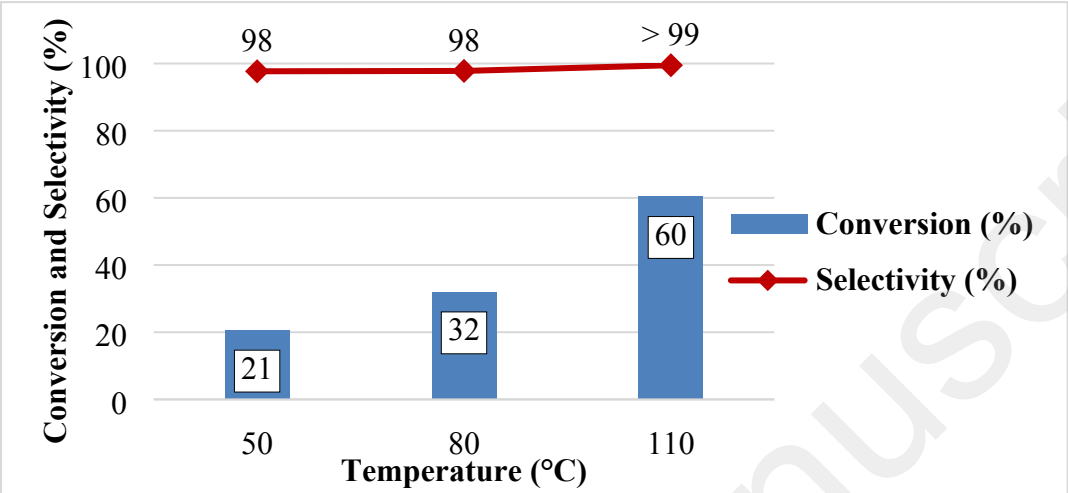
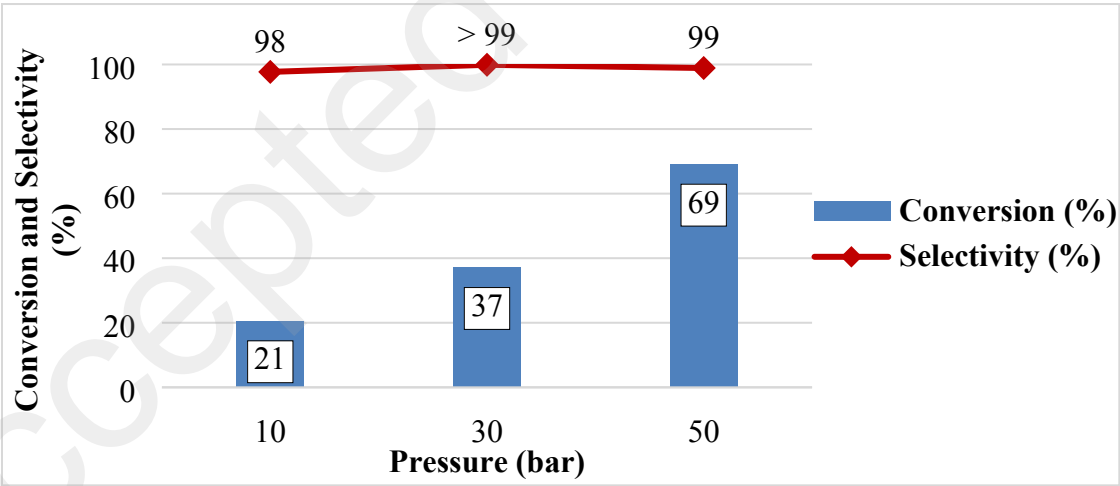
Figure 6. Optimization of the reaction parameters of the α-pinene hydrogenation with Ru@HEA16Cl nanocatalyst

a) Influence of the temperature under 10 bar H_2[a]



[a] Reaction conditions : α-pinene (4.57 mol, 648 g), $RuCl_3 \cdot 3H_2O$ (1.5×10^{-3} mol, 0.372 g), HEA16Cl (3×10^{-3} mol, 1.04 g), H_2O (120 g), S/M = 3000, 1000 rpm, 10 bar of H_2, 7h. Conversion and selectivity determined by Gas Chromatography

b) Influence of the pressure under 50°C



[a] Reaction conditions : α-pinene (3.81 mol, 540 g.), $RuCl_3 \cdot 3H_2O$ (1.3×10^{-3} mol, 0.310 g), HEA16Cl (2.5×10^{-3} mol, 0.866 g), H_2O (100 g), S/M = 3000, 1000 rpm, 50°C, 7h. Conversion and selectivity determined by Gas Chromatography

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At a pressure of 10 bar H_2, an increase in the temperature of the α-pinene hydrogenation from 50 to 110°C led to higher conversions at the same reaction time, affording *cis*-pinane with a 60% conversion in 7 h while maintaining an excellent selectivity superior to 99%. However, at this temperature, a slight agglomeration of the nanoparticles could be observed, considering metal nanoparticles dispersed in water as a metastable system.[34] At a temperature of 50°C, higher conversions up to 69% in 7 h could be achieved while increasing the pressure up to 50 bar H_2, with a relevant selectivity (>99%) in the *cis*-diastereoisomer. Since both parameters have a beneficial effect on the catalytic activity, the reaction was finally carried out at 110°C and 30 bar of H_2, leading to a complete conversion in 4.5 h with a 99% selectivity for a 540 g α-pinene batch.

Finally, based on these optimized reaction conditions (110°C, 30 bar H_2, substrate/metal ratio of 3000), recycling experiments were also conducted on a 200 g α-pinene batch (Figure 7). At the end of the reaction, the *cis*-pinane was separated from the catalyst phase through a simple decantation and recovered through the sampling valve. And then, a new batch of substrate was introduced within the aqueous suspension of ruthenium nanoparticles and hydrogenated under the optimized reaction conditions. During the second run, similar catalytic performances were achieved with a 97% conversion and a 97% selectivity in 4 h. In the third cycle, a drop in the conversion was observed but only by extending the reaction time to 9 h, a complete conversion was restored with a 95% selectivity for the following runs. This activity loss, which could have been hidden at high metal loadings,[35] could be attributed to a visual slow agglomeration of surfactant-stabilized nanoparticles between cycles decreasing the specific metal area, probably due to high process temperature used. Therefore, in this industrial-scaled approach, the deactivation of the catalyst by a chemical poison has been discarded.

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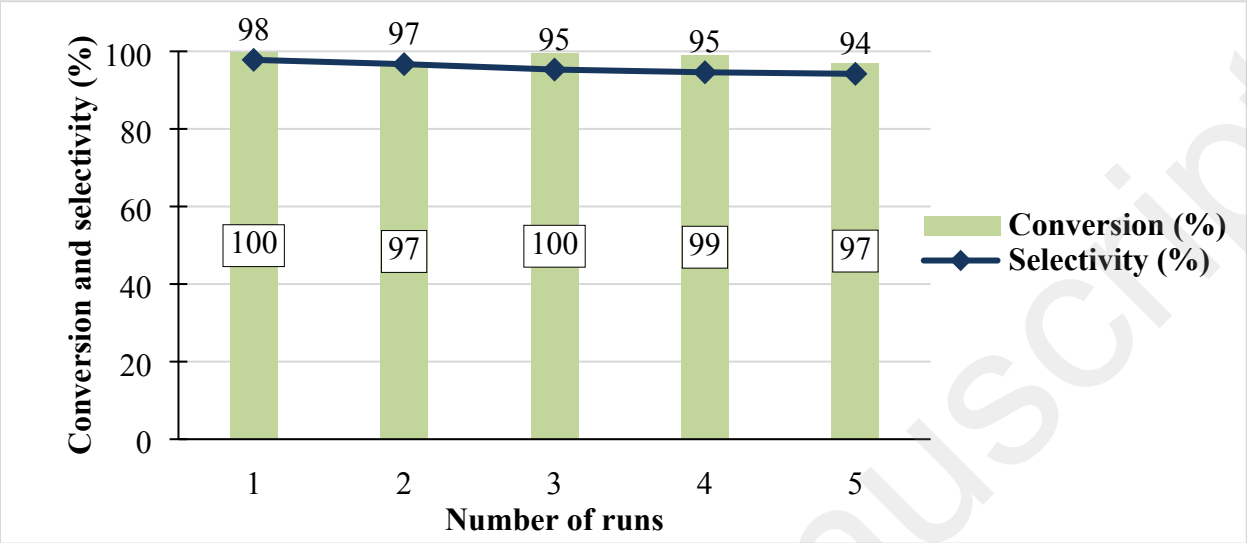
Figure 7. Recycling runs



Reaction conditions: α–pinene (1.52 mol, 216 g), $RuCl_3 \cdot 3H_2O$ (0.51×10^{-3} mol, 0.124 g), HEA16Cl (1×10^{-3} mol, 0.352 g), H_2O (40 g), S/M = 3000, w =1000 rpm, 30 bar H_2, 110°C, 4 h (runs 1 and 2) and 9 h (runs 3-5) Conversion and selectivity determined by Gas Chromatography

Finally, the productivity of this catalytic system could be measured in term of turnover number (TON) defined as mole of desired product formed per mole of metal catalyst. Based on the total α-pinene transformed, a total turnover number (TTON) of 14000 was achieved after five runs. To our knowledge, this value constitutes the best result defined in the literature (related to Table 1).

CONCLUSION

In summary, this study confirmed the potential of ruthenium nanoparticles stabilized in water by ammonium surfactants as an efficient catalyst for the selective hydrogenation of biosourced α-pinene into *cis*-pinane. Ruthenium nanoparticles were easily prepared *in situ* by chemical reduction under green and clean dihydrogen, in water as an inexpensive and environmentally benign solvent. Suitably designed with HEA16Cl surfactant, these nanoparticles proved to be

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active, with complete conversion in 2 h, and selective under mild conditions (10 bar of H_2, room temperature). This process was scalable, showing good catalytic performances, in regards to the more efficient stirring of the pilot scale compared to the lab-scale. On a 540 g batch, α-pinene was totally transformed in 4h30 under 30 bar of H_2 and at 110°C, with a very low catalyst loading (0.033 mol%) maintaining excellent selectivity towards *cis*-pinane (> 99%). Through a biphasic liquid-liquid approach, the catalyst could be easily separated from the product by a simple decantation and recycled over several runs. These relevant results provide significant benefits in terms of yield, cost and environmental footprint and afford good prospects for industrial applications in the hydrogenation of hydrophobic alkenes.

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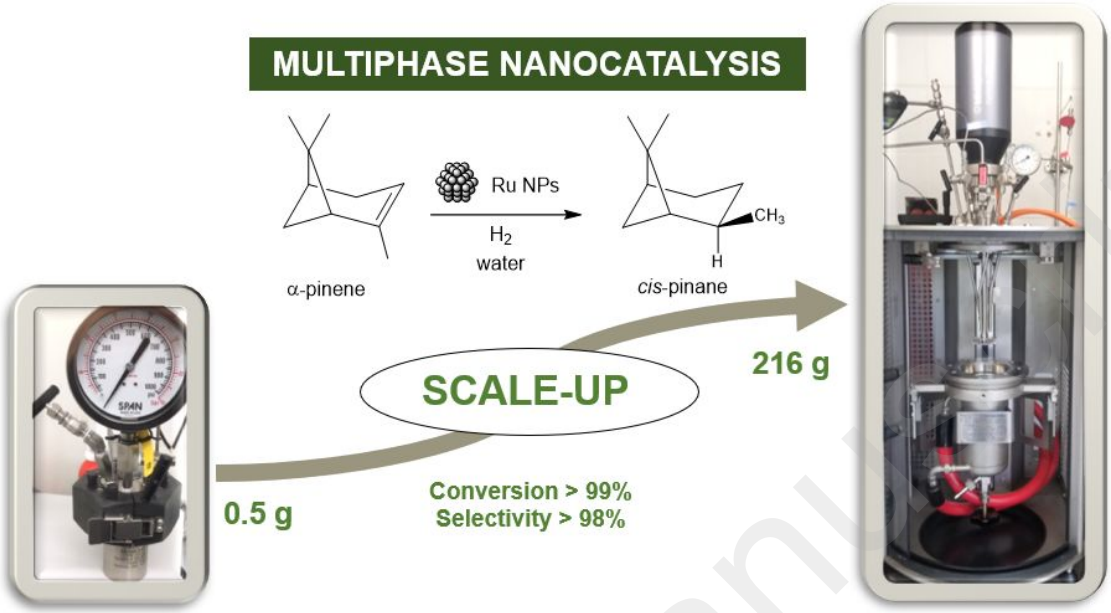
Graphical abstract



Synopsis

The selective hydrogenation of α-pinene into *cis*-pinane was industrially scaled-up, using reusable aqueous suspensions of ruthenium(0) nanoparticles, stabilized with an ammonium surfactant.

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