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DOI: 10.1039/C7CY01687E

Journal Name

ARTICLE

Acid-tolerant cyclodextrin based ruthenium nanoparticles for the hydrogenation of unsaturated compounds in water

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Sébastien Noël,[a] Dolorès Bourbiaux,[a] Nicolas Tabary,[b] Anne Ponchel,[a] Bernard Martel,[b] Eric Monflier[a] and Bastien Léger*[a]

A water-soluble β-cyclodextrin polymer synthesized by crosslinking β-cyclodextrin with epichlorohydrin and glycidyltrimethylammonium chloride allowed the stabilization of ruthenium nanoparticles in basic aqueous medium but also in acidic medium. The aqueous ruthenium colloidal suspensions obtained with this polymer were active as catalysts for the hydrogenation of a large variety of unsaturated compounds including aromatic or fatty acids. The recycling of this catalytic system was attested through ten consecutive runs without loss of stability and activity, demonstrating its robustness.

Introduction

Solvent dispersed metal nanoparticles (NPs) have received a great attention for the twenty past years in a wide range of applications such as catalysis.[1-3] Contrary to the supported and the bulky versions, these systems provide a high surface area of catalytically active metal thanks to a large fraction of surface-exposed metal atoms and high number of edges and defects. Nevertheless, the major drawback of these solvent dispersed nanoparticles is their tendency to aggregate, leading with time to a metal sedimentation and preventing any catalyst recovery. An effective way to overcome this problem is to stabilize the nanoparticles by utilizing capping agents soluble in the solvent medium (e.g. surfactants,[4] ligands,[5] or polymers[6]). While providing long-term stability, the choice of the capping agent is critical as it helps in controlling the size and shape of the particles as well as the accessibility of surface active sites to the reactants.

Among the capping agents, cyclodextrins that are cyclic oligosaccharides composed of six (α-), seven (β-) or eight (γ-) α-D-glucopyranose units connected by α-(1,4)-linkage have proven to be effective stabilizers of metal NPs in water and have demonstrated their potential for aqueous phase catalysis, such as for the hydrogenation of petro and biosourced substrates.[7,8]

More and more sophisticated cyclodextrin-assisted synthesis of NPs have been developed over the last ten years, ranging from using cyclodextrins (CDs) in the molecular form to covalently linked in a polymer network.[9-14] Thus, we have recently reported that a 3D-polymer of β-CD synthesized by crosslinking β-CD with citric acid (polyCTR-β-CD) allowed not only the stabilization of size-controlled ruthenium NPs from $Ru(NO)(NO_3)_3$ but also their confinement within discrete microcapsules.[15] This result reflects the important role played by the association of different stabilizing effects (*i.e.* cross-linked chains, β-CD structure, ionizable -COOH groups). Tested in the hydrogenation of furan-derived compounds (*i.e.* 2-furaldehyde and furylacrolein), these embedded Ru NPs were shown to be highly active, stable and recyclable nano-sized catalysts, as compared to other control colloidal systems using standard stabilizers such as PVP.[12] Nevertheless, the major shortcoming of poly(CTR-β-CD) is related to the fact that the stability of the resulting Ru colloids was pH-dependent, with a marked reduction in stability when the pH was decreased from basic to acidic values due to the protonation of the carboxylate functions. To overcome this problem, the use of a β-CD polymer containing tetraalkylammonium groups has been considered. Indeed, it is well known that the tetraalkylammonium salts can stabilize catalytically active metal nanoparticles in water[4,16] and are tolerant to acidic medium.

We hereby report that a water-soluble β-cyclodextrin polymer (polyEPG-β-CD) synthesized by crosslinking β-CD with epichlorohydrin (EP) and glycidyltrimethylammonium chloride (GTMAC) can efficiently stabilize ruthenium nanoparticles in basic aqueous medium but also in acidic medium. Furthermore, these ruthenium nanoparticles exhibit high stability and catalytic activity for hydrogenation of a wide range of unsaturated compounds such as higher olefins, styrene and furan or fatty acid derivatives. The possibility to recycle the catalytic suspension will also be discussed using 1-tetradecence as substrate.

[a] Univ. Artois, CNRS, Centrale Lille, ENSCL, Univ. Lille, UMR 8181, Unité de Catalyse et de Chimie du Solide (UCCS), F-62300 Lens, France.
E-mail : bastien.leger@univ-artois.fr
[b] Univ. Lille, CNRS, ENSCL, UMR 8207, Unité Matériaux et Transformations, F-59000 Lille, France.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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Materials and methods

Reagents

Native β-cyclodextrin, abbreviated as β-CD, was kindly supplied by Roquette Frères (Lestrem, France). All chemicals were purchased from Aldrich Chemicals or Acros Organics and were used without further purification. Ruthenium nitrosyl nitrate (1.5 wt% of Ru solution) was supplied by Strem Chemicals.

Characterization techniques

Transmission Electron Microscopy (TEM) was performed on a Tecnai microscope (200 kV). A drop of the colloidal suspension was deposited onto a carbon coated copper grid. Metal particle size distributions have been determined from the measurement of around 200 particles found in arbitrarily chosen area of the images using the program SCION Image. Dynamic Light Scattering (DLS) studies were conducted in aqueous solutions at a controlled temperature (25 ± 0.1 °C) using a Malvern Zetasizer Nano ZS equipment. The Zetasizer Nano ZS apparatus uses a 632.8 nm helium-neon laser and analyzes the scattered light at an angle of 173° by utilizing a non-invasive backscatter technique. All samples were analyzed in triplicate using the DTS Software from Malvern Instruments to acquire the correlogram (correlation function versus time). Thermogravimetric measurements (TG) were performed using a simultaneous TGA/DSC 3+ instrument from Mettler Toledo coupled with a computer having the STARe Software. Approximately, 15 mg of sample was heated in an open 70 µL alumina crucible from 40 to 800 °C (10 °C.min^{-1}) under air with a flow of 20 mL.min^{-1}. ^{1}H spectra were recorded at 300.13 MHz on a Bruker Avance DPX300 spectrometer. D_2O (isotopic purities) were purchased from Euriso-Top. Fourier Transform InfraRed spectroscopy (FTIR) experiments were carried out in the 4000–400 cm^{-1} region with a spectral resolution of 2 cm^{-1} on a Shimadzu IR Prestige-21 spectrometer equipped with a PIKE MIRacle diamond crystal.

Synthesis of the cationic water soluble polymer of β-CD

The synthesis protocol has already been described in a previous publication.[17] A typical synthesis for a molar ratio β-CD:EP:GTMAC 1:10:10 (hereafter reported as polyEPG-β-CD) is described below : in a 100 mL double necked round bottom flask, 5 g (4.4 mmol) of β-CD was dissolved in 8 mL of NaOH solution (22 %(w/v) in water) under magnetic stirring at 600 rpm at room temperature for 24 h. Then 7.40 mL (44 mmol, 10 molar equivalents with respect to β-CD) of the GTMAC solution (90 %(w/v) in water) and 3.45 mL (44 mmol, 10 molar equivalents with respect to β-CD) of EP were rapidly added. The resulting solution was heated to 60 °C during 3 hours. After the reaction time, the reaction was stopped by addition of 20 mL of acetone. Then, acetone was eliminated after decantation. 20 mL of distilled water were added to the aqueous phase that was then neutralized with HCl (6 M) and was heated to 50 °C overnight. At this step, the obtained solution was filtrated to get rid of the insoluble part, if necessary. Then, filtrate was dialyzed for 72 h against distilled water (Spectra/Por 1, molecular weight cut-off 6–8 kDa) in order to only collect a purified high molecular weight fraction. The polymer samples were finally isolated by freeze-drying.

Synthesis of the polyEPG-β-CD-stabilized Ru NPs in colloidal suspensions

In a typical experiment, the colloidal suspension was prepared as follows at ambient temperature. 235 mg of polymer (0.4 mmol of ammonium group) were dissolved in 5 mL of HPLC water. Besides this solution, 269 mg (40 µmol, 10 molar equivalents with respect to ruthenium) of a ruthenium nitrosyl nitrate solution were diluted in 3 mL of water and were added to the previous solution. The mixture is kept under constant stirring at room temperature for 30 minutes before the addition of 4 mL (0.4 mmol, 10 molar equivalents with respect to ruthenium) of a 0.1 M sodium borohydride solution. The color of the reaction medium changes upon addition of $NaBH_4$ from orange to dark brown due to the reduction of Ru(III) to Ru(0). The resulting colloidal dispersion is visually stable for months and no sedimentation is observed.

Catalytic test

All hydrogenation experiments have been performed using a stainless steel autoclave Parker-Autoclave Engineers containing a glass vessel which was charged with 12 mL of standard ruthenium colloidal suspension and the substrate (2.0 mmol, 50 eq.). Hydrogen was fed to the system at constant pressure up to 10 bar. The mixture was heated up to 30 °C with a thermostated oil bath and stirred at 1000 rpm. The reaction was monitored by analyzing an aliquot of the reaction mixture after 1.5 h of reaction with a Varian 3900 gas chromatograph, equipped with a CP-Sil-5B (30 m × 0,25 mm x 0,25 µm) and a flame ionization detector using decane or dodecane as external standard. For the carboxylic acid based compounds, a Shimadzu GC-17A gas chromatograph Shimadzu GC-2010 Plus equipped with a capillary column in polyethylene glycol (30 m x 0,25 mm x 0,25 µm) and a flame ionization detector using decane as external standard.

Results and Discussion

Synthesis and characterization of Ru NPs

The water-soluble polyEPG-β-CD polymer was synthesized by crosslinking β-CD with EP in the presence of GTMAC in alkaline conditions according to the following molar ratios: β-CD:EP:GTMAC = 1:10:10.[17] After washing and neutralization of excess NaOH, the water-soluble fraction is dialyzed against water (6,000-8,000 Da cellulosic membranes) and lyophilized in order to obtain a white powder. Fig. 1 depicts the principle

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of the synthesis of polyEPG-β-CD. The average molecular weight based on gel permeation chromatogram analysis is Mw = 22000 g.mol^{-1} with a polydispersity index of 1.2 while the weight percentage of β-CD incorporated in the polymer determined by ^{1}H NMR analysis is estimated to be 51 wt% corresponding to 0.45 mmol per gram of polymer. Analysis of the ^{1}H NMR spectrum also allows to determine precisely the amount of ammonium groups bound to the polymer, *i.e.* 1.7 mmol per gram of polymer (26 wt%).

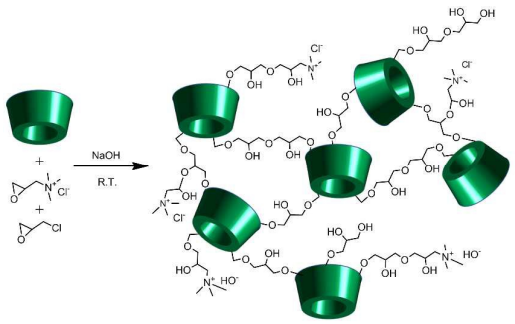

Fig. 1. Synthesis of polyEPG-β-CD polymer from β-CD, EP and GTMAC.

Concerning the synthesis of Ru_polyEPG-β-CD, the procedure is very similar to that previous reported for poly(CTR-β-CD) protected Ru NPs, with the difference that there is no preliminary step of deprotonation because of the absence of carboxylic groups in polyEPG-β-CD.[15] In short, the synthesis involves a one-step reduction between the ruthenium (III) salt and sodium borohydride, in the presence of a controlled amount of polyEPG-β-CD (10 molar equivalents of ammonium group per ruthenium). Several analyses were performed in order to characterize the ruthenium NPs in the liquid phase or in the solid state (after lyophilization of the colloidal suspension). First, we have checked that the polymer structure was not deeply modified after the reduction step, compared to that of the pristine polyEPG-β-CD.

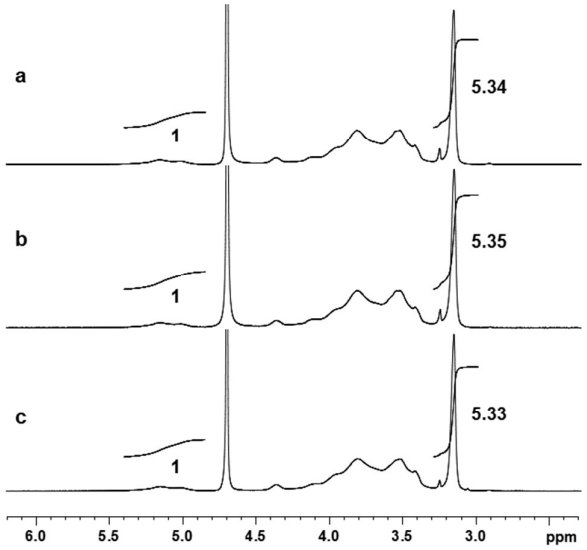

Fig. 2. ^{1}H NMR analysis in D_2O of (a) polyEPG-β-CD; (b) polyEPG-β-CD with $Ru(NO)(NO_3)_3$; (c) Ru_polyEPG-β-CD.

In this context, ^{1}H NMR experiments were carried out in D_2O in the presence of samples of polyEPG-β-CD recovered by lyophilization at different stages of the preparation (i.e. after successive addition of $Ru(NO)(NO_3)_3$ and $NaBH_4$). The ^{1}H NMR spectra are given in Fig. 2, and these analyses did not reveal any significant change in the 3.0 - 5.5 ppm region of the spectra. Additionally, no change of integrated ratio between the signals at 3.15 ppm (ascribed to the methyl protons of the alkyl ammonium groups) and 5.15 ppm (proton H_1 of the cyclodextrin) was observed, suggesting there was no appreciable C-O or C-N cleavages in the polymer structure during the nanoparticles synthesis.

Further evidence for the stability of the polymer structure was provided by ATR-FTIR spectroscopy. Fig. 3 plots the ATR-FTIR spectra of polyEPG-β-CD lyophilized samples with the ruthenium nitrosyl nitrate salt (before and after performing the reduction step). The spectra measured on the control samples, *i.e.* pristine polyEPG-β-CD and $Ru(NO)(NO_3)_3$ are included for comparison.

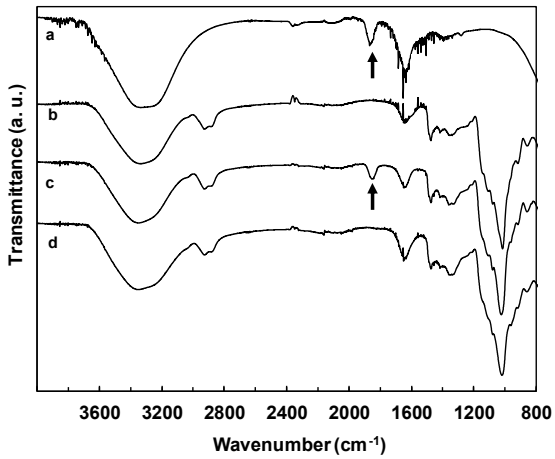

Fig. 3. FTIR analysis of (a) $Ru(NO)(NO_3)_3$; (b) polyEPG-β-CD; (c) polyEPG-β-CD with $Ru(NO)(NO_3)_3$; (d) Ru_polyEPG-β-CD.

In contrast with the spectrum of $Ru(NO)(NO_3)_3$ that exhibited no marked bands in the 800-1300 cm^{-1} region (spectrum a), the ATR-FTIR spectrum of polyEPG-β-CD (spectrum b) showed the presence of β-CD units, as evidenced by the bands ascribed to vibrational modes of the glucosyl units [930, 990, 1020, 1075 and 1150 cm^{-1} for β-CD].[18,19] Note that the CH_3 and CH_2 groups gave rise to characteristic C-H stretching bands in the range of wavenumber 3020-2840 cm^{-1} (asymmetric and symmetric C-H stretching vibrations) while the OH stretching band formed a broad structureless envelope. When $Ru(NO)(NO_3)_3$ was added to polyEPG-β-CD, without or with $NaBH_4$ (spectra c and d, respectively), most of these spectral features were retained, suggesting again that the polymer chains did not collapse during the synthesis of Ru NPs. The

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only significant difference, which was found in the corresponding spectrum of Ru_polyEPG-β-CD, was the disappearance of the band positioned at 1854 cm^{-1} assigned to N-O vibration modes in $Ru(NO)(NO_3)_3$ species (see arrow in Fig. 3), and this can be interpreted by the reduction of ruthenium metal ions Ru^{3+} into Ru(0).[20,21] XPS analysis was performed in order to have indication in oxidation state of Ru. Ru_polyEPG-β-CD colloidal suspension was recovered by lyophilization in order to obtain a well-dispersed powder. This powder was analyzed by X-ray photoelectron spectroscopy. Unfortunately, the Ru concentration was too low (0.8 w.t.%) and consequently, it was impossible to get any Ru signal (Fig. S1 in the ESI).

Additional thermogravimetric experiments were performed to evaluate the impact of Ru NPs on the thermal behavior of polyEPG-β-CD. The TG profiles of polyEPG-β-CD and Ru_polyEPG-β-CD carried out in air are shown in Fig. 4. The first weight loss below 200 °C was associated with the removal of physically and chemically adsorbed water within the polymer network, and no significant difference was found between the two samples. A rapid weight loss occurred between 260 and 400 °C in the case of the pristine polyEPG-β-CD (curve a) and this temperature range is typical for the decomposition of cyclodextrins in samples.[17,22] Then decomposition proceeded more slowly up to 670 °C where the polymer was totally degraded (100 % weight loss). In the presence of Ru NPs, a similar behavior was observed (curve b), although the decomposition started earlier (220 against 260 °C) and ended earlier (550 °C against 670 °C), with a total weight loss of 87 %. The slight modification of the thermal degradation was explained by the presence of ruthenium and/or ruthenium oxide particles in close contact with the organic material, which accelerated the decomposition through metal-catalyzed oxidation.[23] Note also that the experimental weight loss is in good agreement with that expected by assuming the complete degradation in air of the polyEPG-β-CD protected Ru NPs into ruthenium oxide RuO_2 with sodium metaborate $NaBO_2$ as non-volatile residues (88 %). Indeed, the remaining borate species are known to be thermally stable even at temperatures as high as 800 °C and could originate from the hydrolysis of the reducing agent ($NaBH_4$) used during the NPs synthesis.[24]

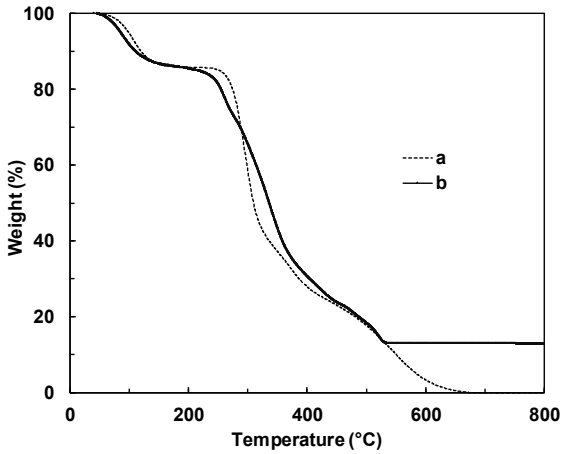

Fig. 4. Thermogravimetric analysis in air of the following lyophilized materials: (a) polyEPG-β-CD; (b) Ru_polyEPG-β-CD.

The morphology of Ru NPs stabilized by polyEPG-β-CD was examined using two complementary techniques, *i.e.* TEM and DLS analyses (Fig. 5 and Fig. S2 in the ESI). Since the stability of the colloidal dispersion can be altered by the pH changes,[15] the measurements were performed at different pH values (10, 7 and 4) adjusted or not, using concentrated hydrochloric acid (1M). It is worth mentioning that the equilibrium pH of the colloidal suspension was close to 10 at the end of the synthesis (*i.e.* after $NaBH_4$ addition). At this pH, according to the transmission electron micrograph and size distribution, we observed that the ruthenium NPs (3.8 nm ± 0.9 nm) were assembled into worm-like structure (Fig. 5-a). The DLS size distribution plot showed that Ru_polyEPG-β-CD formed large objects with a size distribution ranging from 10 to 100 nm and hydrodynamic size of ca. 40 nm, suggesting that the nano-sized Ru NPs were embedded in the 3D-cross linked polymer core. Moreover, crystalline domains are shown in Fig. S3-a (in the ESI) with the presence of distinct lattice planes, which can be further analyzed by reduced Fast Fourier Transform (FFT)-derived diffraction patterns (Fig. S3-b in the ESI). The FFT-derived diffraction pattern indicates that the diffraction spot could be identified as ruthenium nanocrystals with a hexagonal close-packed structure, based on the reflection from the (101) planes having a typical d-spacing of 0.20 nm. Noteworthy, the addition of hydrochloric acid to the colloidal suspension up to a pH 4 did not affect to a great extent the size and polydispersity of the Ru particles. Indeed, TEM investigations at pH 7 and 4 confirmed that narrowly distributed ruthenium nanoparticles were achieved in the range of 2 to 6 nm. The shape of the superstructures looked very similar to the equilibrium shape of polyEPG-β-CD Ru NPs (pH 10), showing the presence of small worm-like microdomains with random orientations (Fig. 5-b and 5-c). No variation of the hydrodynamic diameter compared to that measured at pH 10 was also noticed, confirming that in the range of pH 4-10 the aggregation state of polyEPG-β-CD was not pH-dependent. It is worth mentioning that these results on the chemical stability of the colloidal system through TEM and DLS measurements are also in agreement with those measured by FTIR and ^1H NMR analyses, which showed no noticeable effects before and after addition of HCl (Fig. S4 and Fig. S5 in the ESI). Taken together, the above characterizations show that polyEPG-β-CD is a robust candidate for stabilizing water-dispersed ruthenium nanoparticles, with the capacity to resist to pH values as low as 4. The latter aspect is of particular interest for developing catalytic reactions with acid compounds.

Hydrogenation of 1-tetradecene in aqueous media (model reaction)

The catalytic activity of the ruthenium colloidal suspension stabilized by polyEPG-β-CD was first evaluated in the aqueous biphasic hydrogenation of 1-tetradecene, chosen as a model of highly hydrophobic substrate. Catalytic tests were performed

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at 30 °C under 10 bar of hydrogen with a substrate/metal ratio of 50 (Table 1). The reaction kinetic was monitored by gas chromatography. For comparison, a number of control experiments were also carried out in the same reaction conditions using different types of stabilizing agents, such as β-CD alone, polyCTR-β-CD (polymer formed by the crosslinking of β-CD with citric acid)[15] or the commonly utilized polymer polyvinylpyrrolidone (PVP).

In all cases, it is worth noting that the amounts of ruthenium metal and $NaBH_4$ were exactly the same as those used for the

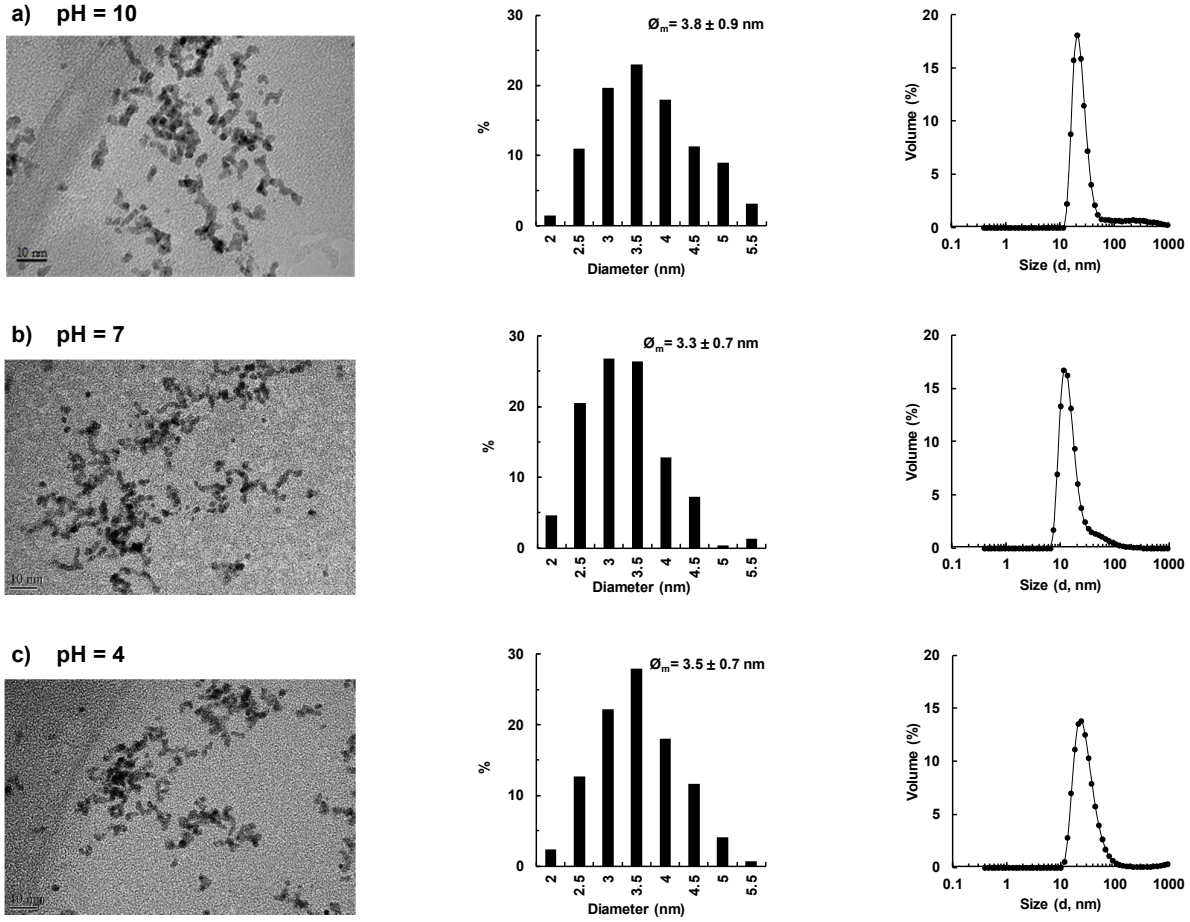

Fig. 5. Transmission electron micrographs, size distributions and hydrodynamic diameters based on volume distribution by DLS experiments of Ru_polyEPG-β-CD for several pH values (a) pH = 10; (b) pH = 7; (c) pH = 4.

synthesis of Ru_polyEPG-β-CD. However, in order to fully evaluate the effect of the covalent structure of polyEPG-β-CD and the contribution of its multiple functional groups (*i.e.* cross-linked chains, β-CD cavities and ammonium groups), several other control syntheses of Ru NPs were conducted by varying the combination of building blocks during the cross-linking procedure. One of the control, denoted as Ru_HEP-HG-β-CD, consisted in ruthenium NPs stabilized by a simple physical mixture of β-CD, glycerol (hydrolyzed epichlorohydrin, HEP) and 2,3-dihydroxypropyl trimethylammonium chloride (hydrolyzed GTMAC, HG). Another control, denoted as Ru_polyEPG-MD, where ruthenium NPs were stabilized by a polymer analogue to polyEPG-β-CD, in which the cyclic oligosaccharide was replaced by maltodextrin (a linear oligosaccharide with approximately 7 glucose units). The last control, denoted as Ru_polyEP-β-CD, corresponded to Ru NPs stabilized by an ammonium-free cross-linked polymer prepared in similar conditions as those of polyEPG-β-CD, except that no GTMAC was introduced during the crosslinking step. When comparing the conversion of 1-tetradecene over the different samples after 1.5 h, it is apparent that the ruthenium nanoparticles stabilized with the cross-linked polyEPG-β-CD polymer showed the highest activity, with 66 % 1-tetradecene conversion, tetradecane being the only product observed (Entry 1). It can be seen that the ruthenium nanoparticles synthesized in presence of the physical mixture

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Table 1. Hydrogenation of 1-tetradecene in presence of Ru NPs[a]

Entry	Stabilizer	Conv. [%][b]	NPs stability	
			Before catalysis	After catalysis
1	polyEPG-β-CD	66	Yes	Yes
2	HEP-HG-β-CD[c]	-	No	-
3	β-CD[d]	12	Yes	No
4	polyCTR-β-CD[e]	13	Yes	No
5	PVP[f]	8	Yes	No
6	polyEP-β-CD[g]	32	Yes	Yes
7	polyEPG-MD[h]	19	Yes	Yes
8	polyEPG-β-CD[i]	10	Yes	Yes

[a] Reaction conditions: Ru (40 μmol), polyEPG-β-CD (235.5 mg. 400 μmol in ammonium group), 1-tetradecene (2 mmol), hydrogen pressure (10 bar), temperature (30 °C), stirring rate (1000 rpm), 12 mL water, reaction time (1.5 h). [b] Conversion determined by GC analysis. [c] Prepared by mixing β-CD, hydrolysed epichlorohydrin and hydrolysed glycidyltrimethylammonium chloride. [d] 113 mg of β-CD (2.5 molar equiv). [e] 100 mg of polyCTR-β-CD. [f] 235 mg of PVP K-30 (M_W = 58000 g.mol^{-1}). [g] 235 mg of polyEP-β-CD (controlled non-cationic polymer prepared in the same conditions as those of polyEPG-β-CD, but without addition of glycidyltrimethylammonium chloride. [h] 235 mg of polyEPG-MD (controlled polymer prepared in the same conditions as those of polyEPG-β-CD by replacing β-CD with maltodextrin). [i] Adamantanol test (32.1 mg of 1-Adamantol, 2 molar equivalents towards β-CD units in polyEPG-β-CD, added in the solution 24 h after the reduction step. The resulting mixture is tested in catalysis additional 24 hours).

HEP-HG-β-CD did not appear as a valuable stabilizing agent since a metal sedimentation occurred immediately after the addition of the $NaBH_4$ reducing agent (Entry 2). In the case of colloidal suspensions stabilized by either molecular β-CD (Entry 3), polyCTR-β-CD (Entry 4) or a standard stabilizer such as PVP (Entry 5), we observed that the resulting Ru NPs were unstable and precipitated during the reaction, leading to moderate conversions (less than 13 %) and thereby compromising the reusability of the catalytic systems. In contrast, the use of the two other dextran polymers cross-linked by epoxy ring opening through epichlorohydrin appeared to be efficient to produce stable Ru colloidal suspension. In line with what was already observed for polyEPG-β-CD, the ruthenium metal NPs protected by polyEP-β-CD or polyEPG-MD remained stable in solution and showed no trace of aggregation or aging of the particles. However, it can be seen that the two latter systems were much less active than the corresponding polyEPG-β-CD, achieving 32 % (Entry 6) and 19 % (Entry 7) 1-tetradecene conversion. The contrasting activity displayed by polyEPG-β-CD and polyEPG-MD, with a drop in conversion of 47 %, were assumed to result from the presence of a large amount of β-CD units (51 wt%) within the polymer network, capable of forming inclusion complexes with the hydrophobic substrate close to the metal surface. This suggested that the covalently linked β-CD were available for mass transfer and facilitated the hydrogenation of long alkyl chain substrates such as 1-tetradecene, with the water-dispersible nanocatalyst.

This mass transfer property of CDs has been successfully exploited in transition metal catalysis under aqueous biphasic conditions and has been extensively reported in the literature.[25,26] In our case, the involvement of a molecular recognition process between 1-tetradecene and the β-CD on Ru_polyEPG-β-CD has been confirmed by a test carried out in the presence of 1-adamantanol as a competitive guest molecule. Indeed, it is well-known that adamantane derivatives possess a very high affinity for the β-CD cavity with high association constant (for instance K = 1520 M^{-1} for 1-adamantanol)[27] and can act as a guest competitor with respect to the substrate.[28] Practically, 1-adamantanol was introduced at the end of the synthesis of Ru NPs (after the 24 h-period of stabilization). Then the resulting suspension was stirred for a further 24 h before proceeding to the catalytic test with 1-tetradecene as model substrate. Thus, in the presence of an excess of competitor (2 equiv.), it can be noticed that the catalytic activity sharply decreased from 66% to only 10% (Entry 8), providing evidence that the β-CD units acted as a molecular receptor capable of bringing the substrate closer to the catalytically active surface during the catalytic process.

Meanwhile, a clear enhancement of the activity was also noticed when ammonium cations were present. For example, when comparing the catalytic performance of Ru NPs protected by polyEP-β-CD (without ammonium) and polyEPG-β-CD (with ammonium), the 1-tetradecene conversion increased from 32 % to 66 %, irrespective of the incorporation rate of β-CD in the polymer (estimated to be higher by about 10 wt. % in polyEP-β-CD compared to polyEPG-β-CD).

The high stability and high activity found on polyEPG-β-CD Ru NPs can be explained by the combined action of steric (hydroxyalkyl chains, β-CD units) and electrostatic (alkyl ammonium groups) held together by the polymer backbone. In addition, the presence of the CD moieties influenced the hydrogenation performances not only by its capping property, but also by facilitating the meeting between the substrate and the catalyst though molecular recognition.

Hydrogenation of alkenes, aromatic derivatives and phenylacetylene in aqueous media

In order to extend the scope of this catalytic system, the aqueous phase hydrogenation of various unsaturated compounds was investigated under the same experimental conditions as those previously used for 1-tetradecene (T = 30 °C, P_{H2} = 10 bar and t = 1.5 h) (Table 2). It is worth noting that the Ru colloidal suspensions remained stable during catalysis. In the case of long-chain alkenes (from n = 10 to n = 16) with terminal double bonds, we observed that the catalytic activity decreased with increasing the length of the alkyl chain. For example, the hydrogenation with 1-decene and 1-dodecene allowed reaching complete conversions (Entries 1 and 2) against only 34 % conversion for 1-hexadecene (Entry 4). Similar results were already observed in CD-assisted aqueous biphasic catalysis using water-dispersed metal NPs[26] or water-soluble organometallic complexes.[29] This trend was generally ascribed as a consequence of increasing mass transfer limitations with increasing the length of the alkyl chain. When using aromatic substrates such as styrene, the conversion was complete after 1.5 h reaction time, with the formation of 100%

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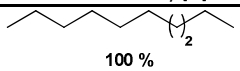
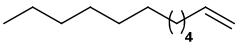
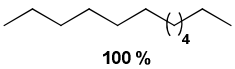
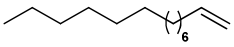
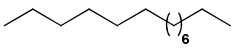
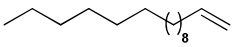
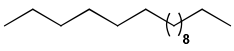
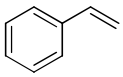
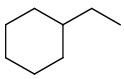
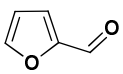
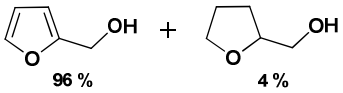
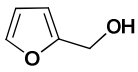
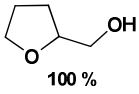
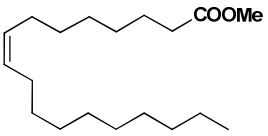
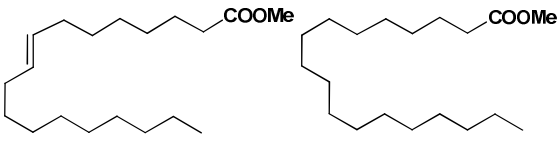
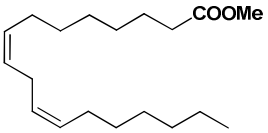
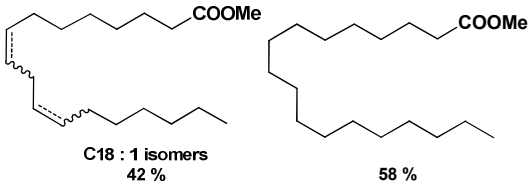
ethylcyclohexane (Entry 5). PolyEPG-β-CD Ru NPs were also proved to be efficient in the hydrogenation of furfural (Entry 6) and furfuryl alcohol (Entry 7) selected as model compounds of biomass-derived-feedstocks (furan derivatives can be produced in large amounts from plant materials rich in pentosans).[30] A better conversion was achieved with furfuryl alcohol (100 %) than with furfural (52 %). This catalytic activity gave rise to comparable performances as those obtained with the Ru_polyCTR-β-CD catalyst.[15] Indeed, the TOF were equal to 18 h^{-1} and 20 h^{-1} for the hydrogenation of furfural respectively with Ru_polyEPG-β-CD and Ru_polyCTR-β-CD under the same experimental conditions. Hydrogenation of unsaturated Fatty Acid Methyl Esters (FAMEs) was also examined. Note that to ensure the complete solubilization of reactants and products (saturated fatty compounds tend to be solids at room temperature), we used ethyl acetate as co-solubilizing solvent (water/ethyl acetate (vol./vol.) = 2:1). With methyl oleate (C18:1, *cis*-9), Ru_polyEPG-β-CD proved to be efficient for hydrogenating the olefinic C=C bond and producing the fully saturated methyl stearate (C18:0). The conversion of methyl oleate was rather similar to that measured with 1-hexadecene (28 % *vs*. 34 %), despite a slightly altered selectivity (86 %). Indeed, a small amount of the *trans* isomer, *i.e.* methyl elaidate (C18:1, *trans*-9), could be detected in these conditions (Entry 8). An even more complex distribution of products was obtained in the case of methyl linoleate (C18:2). Ru_polyEPG-β-CD afforded a selectivity in the saturated ester C18:0 of 58 % at 37 % conversion and the remaining 42 % were the partially hydrogenated products (C18:1, *cis*/*trans*-9 and *cis*/*trans*-12) (Entry 9).

Table 2. Hydrogenation of long-chain alkenes and arenes in presence of Ru_polyEPG-β-CD[a]

Entry	Substrate	Conversion [%][b]	Product selectivity [%][b]
1		100	 100 %
2		100	 100 %
3		66	 100 %
4		34	 100 %
5		100	 100 %
6		52	 96 % 4 %
7		100	 100 %
8[c]		28	 14 % 86 %
9[c]		37	 C18 : 1 isomers 42 % 58 %

[a] Reaction conditions: catalyst (40 μmol), polyEPG-β-CD (235.5 mg. 400 μmol in ammonium group), substrate (2 mmol), hydrogen pressure (10 bar), temperature (30°C), stirring rate (1000 rpm), 12 mL water, reaction time (1.5 h). [b] Conversions and selectivities were determined by GC analysis. [c] Same reaction conditions as those described in footnote [a] except that ethyl acetate (6 mL) was used as co-solvent.

The hydrogenation of phenylacetylene by Ru_polyEPG-β-CD was also considered. The influence of different parameters such as hydrogen pressure and temperature on the hydrogenation of phenylacetylene with PolyEPG-β-CD Ru NPs

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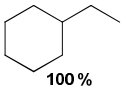
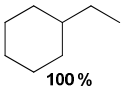
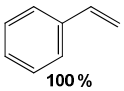
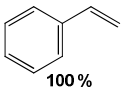
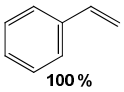
was studied (Table 3). Under the same experimental conditions as previously described (T = 30 °C, P_{H2} = 10 bar), phenylacetylene was completely converted into ethylcyclohexane within 30 min (Entry 1). The kinetic curve (Fig. S6 in the ESI) clearly shows that the highest amount of styrene was obtained after 10 min. But for longer reaction time, only ethylcyclohexane was obtained as final product. If the hydrogen pressure was decreased down to 5 bar, the same conversion was obtained within 1 h (Entry 2) and the highest amount of styrene was obtained at 20 min (Fig. S7 in the ESI). If the catalytic reaction was performed under atmospheric pressure and at 30°C, the conversion was very low even after 4 h but the only final product was styrene (Entry 3). Because of this interesting result in terms of selectivity, the temperature was increased to 50°C and in this case, phenylacetylene was completely converted into styrene within 20 h (Fig. S8 in the ESI) without any loss of stability of the colloidal suspension during the catalytic test (Entry 5).

Table 3. Influence of hydrogen pressure and temperature on the hydrogenation of phenylacetylene in presence of Ru_polyEPG-β-CD[a]

Entry	Hydrogen pressure (Bar)	Temperature (°C)	Reaction time (h)	Conversion [%][b]	Product selectivity [%][b]
1	10	30	0.5	100	 100 %
2	5	30	1	100	 100 %
3	1	30	4	2	 100 %
4	1	50	4	14	 100 %
5	1	50	20	100	 100 %

[a] Reaction conditions: ruthenium (40 μmol), polyEPG-β-CD (235.5 mg. 400 μmol in ammonium group), phenylacetylene (2 mmol), stirring rate (1000 rpm), 12 mL water. [b] Conversions and selectivities were determined by GC analysis.

The use of solvent dispersed ruthenium nanoparticles for the semi-hydrogenation of alkynes has already been reported by the team of Wang.[31] In this case, ruthenium nanoparticles were not dispersed in aqueous phase but in PEG_{2000} in presence of toluene and *n*-heptane. Considering a phenylacetylene/Ru molar ratio of 1000, 98% of phenylacetylene were converted within 11 h with a selectivity in styrene of 92% but under harsher experimental conditions, *i.e.* 20 bar H_2 and 100 °C. Consequently, our catalytic result is the first result concerning the catalytic hydrogenation of phenylacetylene using solvent dispersed ruthenium nanoparticles in aqueous phase with such a good selectivity into styrene under mild experimental conditions. It should be noticed that a Ru_PVP colloidal suspension as control catalyst was synthesized and used for the catalytic hydrogenation of phenylacetylene under 1 bar of H_2 and at 50°C. The colloidal suspension was unstable during the catalytic test. It clearly shows the robustness of Ru_polyEPG-β-CD catalyst and that polyEPG-β-CD is an efficient protective agent of Ru NPs.

The novel water-dispersible polyEPG-β-CD Ru catalytic system was also found to be active for the aqueous-phase hydrogenation of several unsaturated substrates bearing a carboxylic acid group. However, as some substrates and hydrogenated products were not miscible and could be solid in the studied experimental conditions, *i.e.* 10 bar H_2 and 30 °C, catalytic experiments were performed using ethyl acetate as co- solubilizing solvent. The results are gathered in Table 4. However before going into the detail, it is important to note that preliminary hydrogenation tests carried out with fatty acids, *i.e.* oleic acid and linoleic acid, showed that polyEPG-β-

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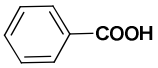
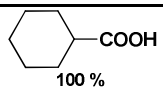
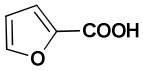
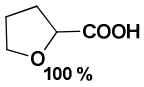
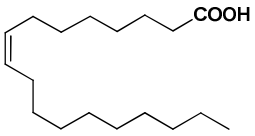
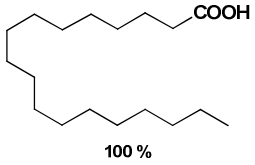
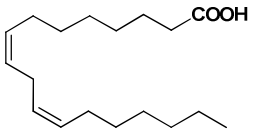
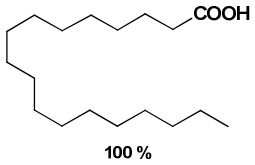
CD Ru NPs did not remained stable during catalysis and underwent demixing. Indeed, the runs with oleic acid and linoleic acid afforded a spontaneous transfer of the ruthenium NPs at the interface between the two phases (Fig. 6-a). This behavior can be explained by the pH value of the colloidal suspension after synthesis (pH 10), which is high enough to deprotonate the carboxylic acid in fatty acids and form organosoluble carboxylate with highly strong metal coordination properties.[28] To maintain the nanoparticles in the aqueous organic phase and avoid any demixing phenomenon, the Ru_polyEPG-β-CD colloidal suspensions were acidified to pH in the range of ~ 3.5-4 with a few drops of hydrochloric acid (1M) before use. In these pH conditions, the dissociation of the carboxylic acid groups was negligible and the resulting Ru NPs colloidal dispersions remained stable during the catalytic runs irrespective of the nature of the acid substrate (Fig. 6-b). The less ionic the substrate is, the better is the immobilization of the metal NPs in the aqueous phase.

Table 4. Hydrogenation of alkene and arene based carboxylic acids in presence of Ru_polyEPG-β-CD under acidic conditions.[a]

Entry	Substrate	Conversion [%][b]	Product selectivity [%][b]
1		71	
2		67	
3		100	
4		100	

[a] Reaction conditions: catalyst (40 μmol), polyEPG-β-CD (400 μmol), substrate (2 mmol), hydrogen pressure (10 bar), temperature (30 °C), stirring rate (1000 rpm), 12 mL water, 6 mL ethyl acetate, reaction time (1.5 h). [b] Conversions and selectivities were calculated by GC analysis.

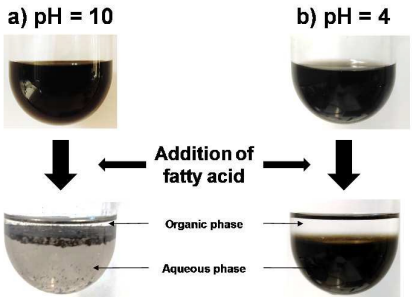


Fig. 6. Photographs of the polyEPG-β-CD Ru system after the addition of a 0.33 M solution of fatty acid (linoleic or oleic) in ethyl acetate at different initial pH a) pH = 10; b) pH = 4.

Hydrogenation of an aromatic substrate, such as benzoic acid yielded 71% conversion within 1.5 h, with the exclusive formation of cyclohexanecarboxylic acid (Entry 1). We observed that 2-furoic acid followed a similar trend as a 67 % conversion was obtained after 1.5 h with 100 % selectivity to the saturated tetrahydro-2-furoic acid (Entry 2). These sets of experiments tend to indicate that the aromatic rings of benzoic and furoic acids were harder to reduce than those of styrene and furfuryl alcohol. Noteworthy is the observation that, in the same experimental conditions, the conversions were complete when using unsaturated fatty acids as substrates. Thus, hydrogenation of oleic acid (C18:1, *cis*-9) and linoleic acid (C18:2, *cis*-6 and *cis*-9) afforded respectively yields in the fully saturated stearic acid (C18:0) of 100 % after only 1.5 h reaction time (Entries 3 and 4). In both cases, no partially hydrogenated products could be detected in these conditions, indicating that the internal C=C double bonds are sufficiently reactive and accessible to undergo hydrogenation in aqueous media.

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Recycling experiments

The reusability of polyEPG-β-CD Ru NPs was further investigated using 1-tetradecene as substrate (Fig. 7).

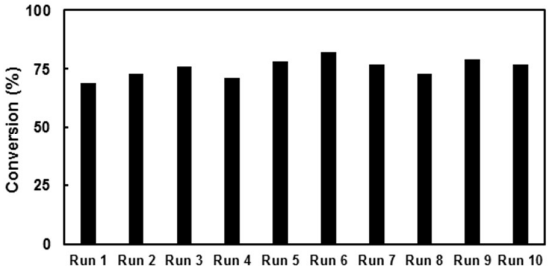

Fig. 7. Reusability of Ru_polyEPG-β-CD in the hydrogenation of 1-tetradecene. Reaction conditions: Ru (40 μmol), 1-tetradecene (2 mmol), hydrogen pressure (10 bar), temperature (30 °C), stirring rate (1000 rpm), water (12 mL), reaction time (1.5 h).

In short, after the first run carried out with the fresh Ru NPs achieving 66 % conversion within 1.5 h (Table 2, Entry 3), the aqueous suspension was extracted with diethyl ether until complete elimination of organic products. After decantation and diethyl ether removal, the aqueous suspension was reloaded with 1-tetradecene

and dihydrogen and reused in the autoclave in the same conditions (10 bar H_2, 30 °C, 1.5 h).

As evidenced by Fig. 7, the catalytically active Ru NPs could be recycled and reused at least for 10 consecutive runs without any loss of activity. Interestingly, the stability of the polyEPG-β-CD Ru system has been further confirmed by TEM measurements carried out after the 1st, 3rd, 5th and 10th run (Fig. 8). The images taken on the recycled catalysts after these different runs showed in all cases narrow particle size distributions centered with mean diameters ranging from 3.3 to 3.7 nm. In addition, the shape of assemblies of polyEPG-β-CD-protected Ru NPs was very similar to that of pristine polyEPG-β-CD, suggesting the worm-like structures could be readily retained even after the 10th run. In addition, the latter results provided strong evidence of the robustness and ease of handling of this novel polyEPG-β-CD Ru system.

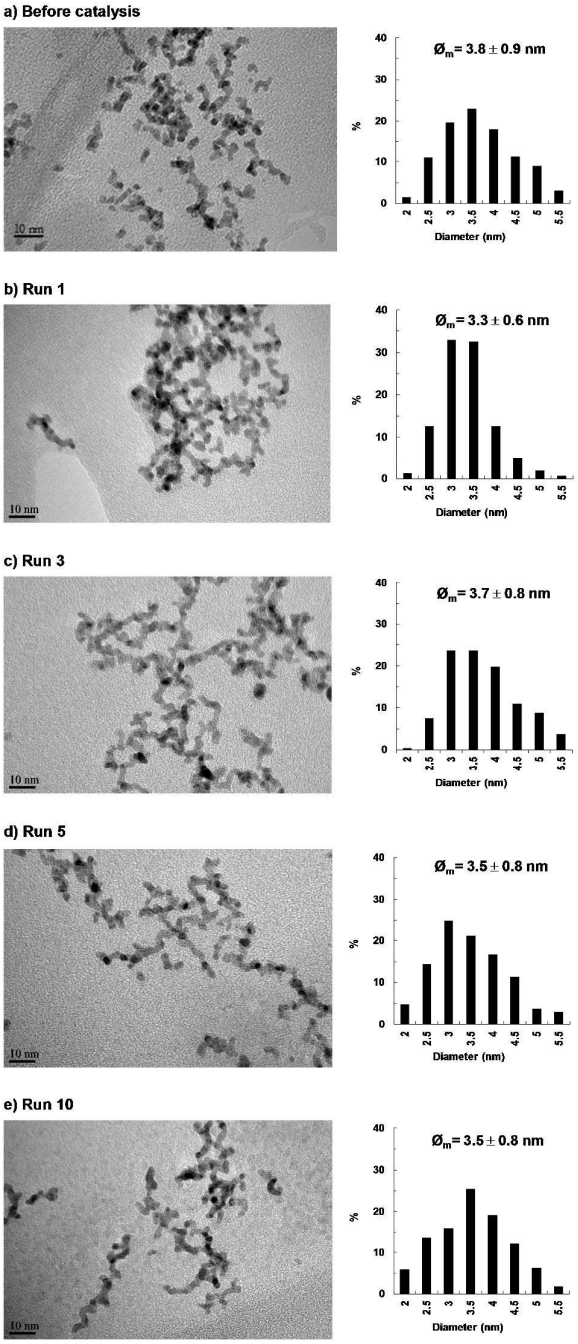

Fig. 8. Transmission electron micrographs and corresponding size distributions of the recycled Ru_polyEPG-β-CD catalyst collected before catalysis (a) and after the runs 1 (b), 3 (c), 5 (d) and 10 (e).

Conclusions

In this paper, we showed that a cationic β-cyclodextrin polymer synthesized by crosslinking β-CD with epichlorohydrin and glycidyltrimethylammonium chloride is a candidate of choice for the synthesis of catalytically active ruthenium nanoparticles for hydrogenation of various organic compounds in water. The chemical reduction of Ru (III) species by sodium borohydride provided stable colloidal suspensions of polyEPG-β-CD Ru NPs organized into small worm-like micro domains of size-controlled nanoparticles (3.8 nm) with narrow size

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distributions. The physical features of the colloidal suspensions remained practically unaffected by the pH change (from pH 10 down to pH 4). The beneficial impact of the different interactions (steric-type, electrostatic-type and host-guest-type) within this novel polymer of β-CD was demonstrated in the model reaction of 1-tetradecene. The positive results were successfully extended to a wide range of substrates (long-alkyl chain olefins, aromatics and FAMEs) as well as derivatives bearing carboxylic acid substituents. This catalytic system could be readily recycled and reused for several runs, demonstrating its high resistance against aggregation and deactivation during catalysis. These results open up promising perspectives for the hydrogenation of even more sophisticated substrates, such as lignin derivatives or bio-oils.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Chevreul Institute (FR 2638), Ministère de l'Enseignement Supérieur et de la Recherche, Région Nord – Pas de Calais and FEDER are acknowledged for supporting and funding partially this work. The TEM and XPS facilities in Lille (France) are supported by the Conseil Régional du Nord-Pas de Calais, and the European Regional Development Fund (ERDF). The authors are grateful to Dr. Nicolas Kania (UCCS, University of Artois) for technical assistance in FTIR and TGA measurements. The authors are grateful to Dr. Ahmed Addad (UMET, University of Lille 1) for technical assistance in TEM measurements and to M. Trentesaux ans Dr. P. Simon for XPS analysis.

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View Article Online
DOI: 10.1039/C7CY01687E

Ru NPs, stabilized by a water soluble cationic β-cyclodextrin polymer, proved to be efficient for the hydrogenation of acid substrates.