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# Anionic Amphiphilic Cyclodextrins bearing Oleic Grafts for the Stabilization of Ruthenium Nanoparticles Efficient in Aqueous Catalytic Hydrogenation

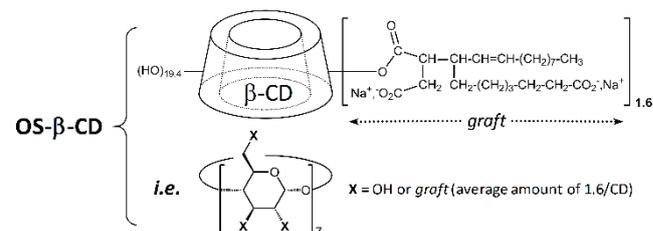
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**Abstract:** Oleic succinyl  $\beta$ -cyclodextrin was proved to be efficient for the stabilization of ruthenium nanoparticles (NPs) in aqueous medium. These NPs were characterized by FTIR spectroscopy and transition electron microscopy (TEM). The catalytic activity of these NPs was evaluated in the aqueous hydrogenation of petrosourced and biosourced unsaturated compounds such as benzene and furfural derivatives. The catalytic system can be easily recycled and reused up to nine runs without any loss of activity and selectivity, demonstrating its robustness.

Transition metal nanoparticles (NPs) are widely used in the field of catalysis. <sup>[1-3]</sup> This kind of catalytic system provides high active surface area and can be dispersed in water by using capping agents. <sup>[4]</sup> Among the described water-soluble capping agents, cyclodextrins (CDs) are efficient biosourced molecules. CDs are water-soluble chemical receptors consisting of six ( $\alpha$ -CD), seven ( $\beta$ -CD) or eight ( $\gamma$ -CD) 1,4-linked  $\alpha$ -D-glucopyranose units. <sup>[5]</sup> CDs are able not only to include organic substrates into their hydrophobic cavity but CDs can also interact with the metallic nanoparticles surfaces. They have been employed under various forms and environments such as free form (native or modified CD), inclusion complex form with appropriate guests molecules (ionic surfactants, phosphanes), or in combination with polymer matrices (physically or chemically incorporated). <sup>[6]</sup> In this context, easy accessible oleic succinyl-cyclodextrins were considered as eco-compatible capping agents. <sup>[7]</sup> Indeed, CDs and oleic acid derivatives are industrially produced from renewable resources. In addition, this kind of structure contains different functional moieties such as carboxylate function, oleic succinyl chain and CD ring which could favor both electrostatic and steric stabilizations of NPs in water. The presence of the hydrophobic cavity of the CD could also promote the meeting between hydrophobic substrate and NPs. In this communication, we report that oleic succinyl- $\beta$ -cyclodextrin (OS- $\beta$ -CD) (Scheme 1) was efficient to stabilize ruthenium nanoparticles. These NPs were characterized by FTIR spectroscopy and transition electron microscopy (TEM). The catalytic activity of these NPs was evaluated in the aqueous hydrogenation of petrosourced (alkyl olefins and benzene derivatives) and biosourced unsaturated compounds (furfural derivatives, methyl oleate and citronellal).

The recyclability of the catalytic system was also evaluated in the case of furfuryl alcohol as substrate.

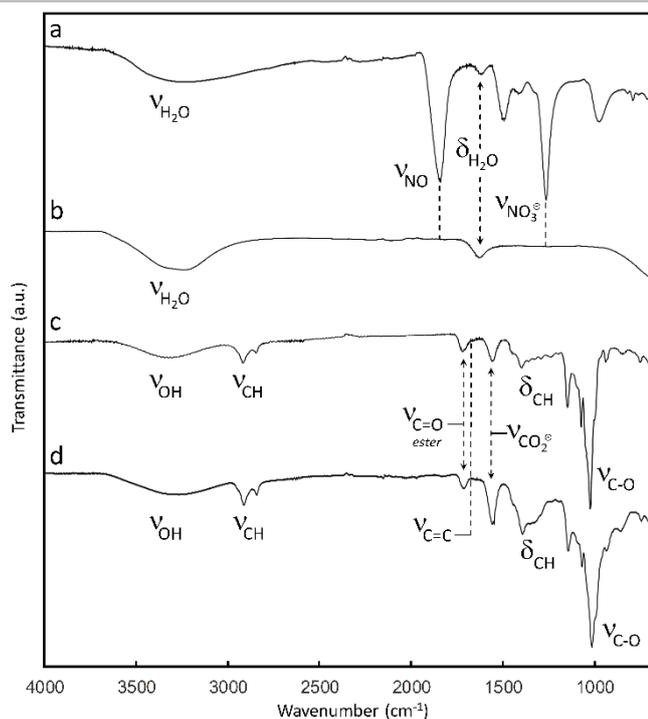
The synthesis of OS- $\beta$ -CD was carried out in two steps according to a previously described method. <sup>[7]</sup> Briefly, the first step consists in the alkenylation of maleic anhydride by oleic acid to produce an oleic succinic anhydride (OSA). The second step involves the grafting of the OSA on  $\beta$ -CD followed by a treatment with an aqueous sodium hydroxide solution to give the carboxylate functions. The degree of substitution is equal to 1.6, i.e. 1.6 hydroxyl group on 21 was functionalized by the oleic-succinyl group. In Scheme 1, in order to simplify this representation, only one kind of graft was presented, among the two possible, knowing that each hydroxyl groups of the  $\beta$ -CD can react with one or the other carbonyl group of the succinic anhydride. The water-solubility and the critical aggregation concentration of OS- $\beta$ -CD were equal to 286 g.L<sup>-1</sup> and 170 mg.L<sup>-1</sup>, respectively (at 20°C).



**Scheme 1.** Schematic representation of OS- $\beta$ -CD.

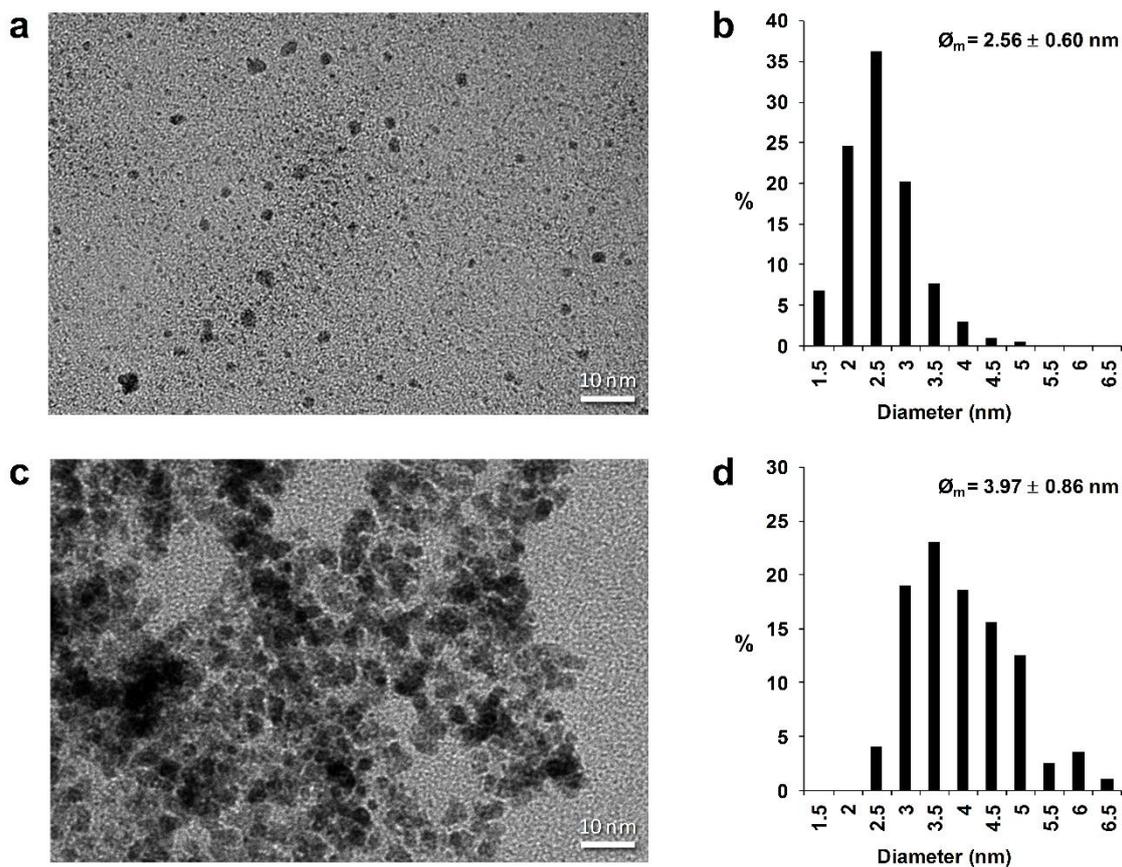
For the synthesis of ruthenium nanoparticles stabilized by OS- $\beta$ -CD (Ru\_OS- $\beta$ -CD NPs), the ruthenium salt Ru(NO)(NO<sub>3</sub>)<sub>3</sub> (1 equiv.) and OS- $\beta$ -CD (3 equiv.) were solubilized in water and stirred for 30 min at room temperature before addition of sodium borohydride (10 equiv.) as a reducing agent. Note that the 3 equivalents of OS- $\beta$ -CD corresponds to almost 5 equivalents of oleic graft and therefore to 10 equivalents of carboxylate functions with respect to ruthenium. The color of the aqueous solution changed from orange to dark brown once sodium borohydride was added, illustrating the reduction of Ru(III) and the formation of Ru NPs. The resulting colloidal suspension was kept under stirring 18 h to permit the total transformation of NaBH<sub>4</sub> excess into sodium metaborate (NaBO<sub>2</sub>) by hydrolysis. An interaction of NaBO<sub>2</sub> with the metal nanoparticles is possible. The reduction of the metal precursor has been studied by ATR-FTIR spectroscopy. Fig. 1 plots the ATR-FTIR spectra of lyophilized samples corresponding to ruthenium nitrosyl nitrate (Fig. 1a), ruthenium nitrosyl nitrate after the addition of sodium borohydride (Fig. 1b), OS- $\beta$ -CD (Fig. 1c) and Ru\_OS- $\beta$ -CD NPs (Fig. 1d).

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**Figure 1.** ATR-FTIR spectra of (a) Ru(NO)(NO<sub>3</sub>)<sub>3</sub>; (b) Ru(NO)(NO<sub>3</sub>)<sub>3</sub> + NaBH<sub>4</sub>; (c) OS-β-CD and (d) Ru\_OS-β-CD NPs.

The spectrum of Ru(NO)(NO<sub>3</sub>)<sub>3</sub> showed absorption bands at 1270 and 1840 cm<sup>-1</sup> corresponding respectively to the nitrate (ν<sub>NO<sub>3</sub><sup>-</sup></sub>) and nitrosyl (ν<sub>NO</sub>) stretching bands (Fig. 1a). After addition of NaBH<sub>4</sub> to a Ru(NO)(NO<sub>3</sub>)<sub>3</sub> aqueous solution and stirring at room temperature during 18h, the bands at 1270 and 1840 cm<sup>-1</sup>, related to NO<sub>3</sub><sup>-</sup> and NO moieties, disappear in the corresponding spectrum (Fig. 1b). This modification can be explained by the simultaneous reduction of Ru(III) and NO<sub>3</sub><sup>-</sup>, followed by NO leaching.<sup>[8]</sup> However, it should be noticed that in this case, no stable NPs were formed since a sedimentation of black ruthenium in water was observed. In Figure 1c, OS-β-CD IR spectrum reveals bands coming from the vibrational modes of the glucosyl units carbon-oxygen single bonds [930-1150 cm<sup>-1</sup>]. Stretching bands characteristic of carboxylate anionic groups [1550 cm<sup>-1</sup>] and of carbonyl group of the ester moiety [1740 cm<sup>-1</sup>] are also clearly observed, together with a very weak signal due to the carbon-carbon double bond of the graft [around 1680 cm<sup>-1</sup>]. At higher wavenumbers, stretching bands of C-H bonds [2800-3020 cm<sup>-1</sup>] and of the hydroxyl groups [3300 cm<sup>-1</sup>] are also present. The spectrum of Ru\_OS-β-CD NPs also shows the disappearance of nitrate and nitrosyl bands due to the reduction of the metallic precursor into NPs (Compare Fig. 1d to Fig. 1a). Moreover, no modification of the spectral features of the OS-β-CD was observed, proving that its structure was not modified during the synthesis of the NPs.



**Figure 2.** a) TEM image at a magnification of  $\times 200\,000$  and b) size distribution of Ru\_OS-β-CD NPs ; c) TEM image at a magnification of  $\times 200\,000$  and d) size distribution of Ru\_β-CD NPs.

Ru\_OS- $\beta$ -CD NPs were also characterized by transmission electron microscopy (TEM). The TEM image revealed no aggregation of metal nanoparticles. Ru\_OS- $\beta$ -CD NPs were homogeneously dispersed with a narrow size distribution centered at  $2.56 \pm 0.60$  nm with 80% of the NPs having a diameter between 2 and 3 nm (Fig. 2a and 2b). The zeta potential of Ru\_OS- $\beta$ -CD NPs was measured and equal to  $-41$  mV. This value was in good agreement with zeta potential values measured for NPs stabilized in the presence of carboxylate functions (between  $-40$  mV and  $-60$  mV).<sup>[9]</sup> This value is also in correlation with good stability of the colloidal suspension in the aqueous phase. As a control, Ru\_ $\beta$ -CD NPs have been synthesized from Ru(NO)(NO<sub>3</sub>)<sub>3</sub> and native  $\beta$ -CD to study the influence of the grafting on the cyclodextrin backbone on the dispersion and the size of the Ru NPs. The TEM image of Ru\_ $\beta$ -CD NPs (Fig. 2c and 2d) clearly shows that metal nanoparticles are organized into non-ordered superstructures with a mean diameter of  $3.97 \pm 0.86$  nm. This kind of organization has also been reported in the literature for Ru NPs stabilized with methylated cyclodextrins.<sup>[10]</sup> Moreover, the size distribution is less narrow in the case of Ru\_ $\beta$ -CD NPs than in the case of Ru\_OS- $\beta$ -CD NPs and two different populations can be distinguished, one centered on 3.5 nm and another one centered on 6 nm. This TEM study proves the beneficial effect of the grafting of the oleic unit on  $\beta$ -CD on the size and the dispersion of Ru NPs in the aqueous phase.

The catalytic activity of the Ru\_OS- $\beta$ -CD NPs was first evaluated in the aqueous hydrogenation of styrene as model substrate for control experiments. The catalytic experiments were performed at a temperature of 30°C, under a hydrogen pressure of 10 bar and with a styrene/ruthenium molar ratio equal to 100. Some control experiments were done under the same reaction conditions always considering the same amount of ruthenium salt and NaBH<sub>4</sub> as described for the Ru\_OS- $\beta$ -CD NPs synthesis. More precisely, Ru colloidal suspensions stabilized either by oleic acid sodium salt,  $\beta$ -CD alone or by an oleic acid sodium salt/ $\beta$ -CD physical mixture have been synthesized and tested.

**Table 1.** Hydrogenation of styrene in the presence of Ru NPs<sup>[a]</sup>

Entry	Stabilizer	Time (min)	Conv. (%) <sup>[b]</sup>	NP Stability	
				Before catalysis	After catalysis
1	(-)	360	<1	No	No
2	Oleic acid sodium salt <sup>[c]</sup>	360	<1	No	No
3	$\beta$ -CD <sup>[d]</sup>	60	100 <sup>[g]</sup>	Yes	No
4	Oleic acid sodium salt + $\beta$ -CD <sup>[e]</sup>	60	<1	No	No
5	OS- $\beta$ -CD <sup>[f]</sup>	60	100 <sup>[g]</sup>	Yes	Yes

<sup>[a]</sup> Reaction conditions: Ru ( $1 \times 10^{-5}$  mol), Styrene ( $1 \times 10^{-3}$  mol), hydrogen pressure (10 bar), temperature (30 °C), stirring rate (750 rpm), 12 mL water. <sup>[b]</sup> Conversion of styrene determined by GC analysis with external standard (decane). <sup>[c]</sup> Oleic acid sodium salt ( $5 \times 10^{-5}$  mol). <sup>[d]</sup>  $\beta$ -CD ( $3 \times 10^{-5}$  mol). <sup>[e]</sup> Prepared by mixing  $\beta$ -CD ( $3 \times 10^{-5}$  mol) and oleic acid sodium salt ( $5 \times 10^{-5}$  mol). <sup>[f]</sup> OS- $\beta$ -CD ( $3 \times 10^{-5}$  mol). <sup>[g]</sup> yield of 100% in ethylcyclohexane.

Without stabilizer or in the presence of oleic acid sodium salt, the conversion of styrene was non-significant (Table 1; entries 1 and

2). This could be explained by a lack of stability before the catalytic test. In the case of  $\beta$ -CD alone as protective agent, the styrene was completely converted into ethylcyclohexane within 1h (Table 1, entry 3). However, the Ru NPs were unstable and precipitated during the reaction. The experiment performed in the presence of a physical mixture of oleic acid sodium salt and  $\beta$ -CD gave no conversion and the catalytic system became unstable during the hydrogenation (Table 1, entry 4). The experiment performed in the presence of OS- $\beta$ -CD as stabilizer led to a total conversion of styrene into ethylcyclohexane within 1h and with a colloidal suspension perfectly stable at the end of the reaction (Table 1, entry 5). Thanks to a kinetic monitoring, it should be noticed that styrene was completely converted into ethylcyclohexane within two successive reaction steps (see Supporting Information). It means hydrogenation of styrene into ethylbenzene followed by ethylbenzene into ethylcyclohexane. This last experiment undoubtedly showed that the catalytic system based on Ru\_OS- $\beta$ -CD NPs was efficient and stable. As the oleic arm of OS- $\beta$ -CD contains a carbon-carbon double bond, the stability of OS- $\beta$ -CD has been evaluated during the catalytic experiment. It is important to underline that after 18h at 30°C under 10 bar of hydrogen pressure, the carbon-carbon double bond of the graft was not reduced as evidenced by NMR experiments (see Supporting Information).

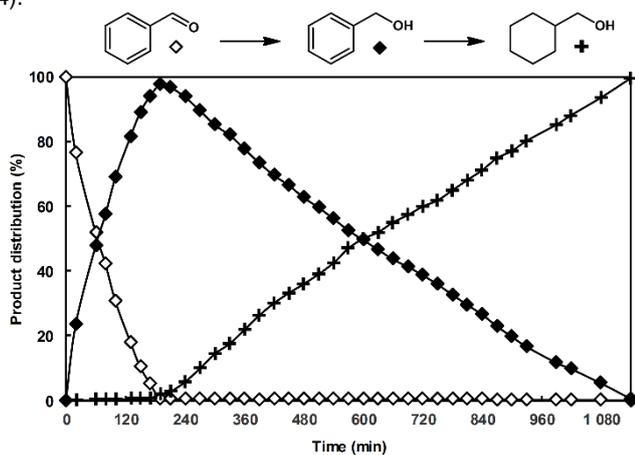
**Table 2.** Hydrogenation of various substrates in presence of Ru\_OS- $\beta$ -CD NPs<sup>[a]</sup>

Entry	Substrate	Products	Time (min) <sup>[b]</sup>
1	1-Octene	Octane	220
2	1-Decene	Decane	640
3	1-Tetradecene	Tetradecane	3800
4	Anisole	Methoxycyclohexane	80
5	Styrene	Ethylcyclohexane	60
6	Allylbenzene	Propylcyclohexane	150
7	Benzaldehyde	Hydroxymethylcyclohexane	1140
8	Benzyl alcohol	Hydroxymethylcyclohexane	780
9	Methyl oleate	Methyl stearate	nd
10	Citronellal	3,7-dimethyloctan-1-ol	270
11	Furfural	Tetrahydrofurfuryl alcohol	840
12	Furfuryl alcohol	Tetrahydrofurfuryl alcohol	255

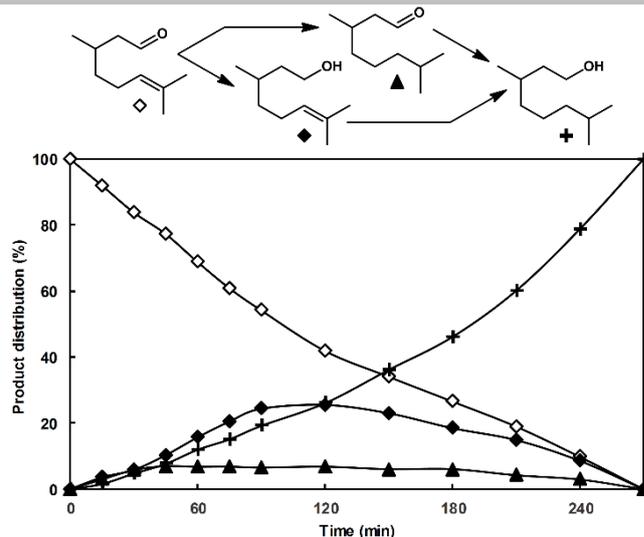
<sup>[a]</sup> Reaction conditions: Ru ( $1 \times 10^{-5}$  mol), OS- $\beta$ -CD ( $3 \times 10^{-5}$  mol), substrate ( $1 \times 10^{-3}$  mol), hydrogen pressure (10 bar), temperature (30 °C), stirring rate (750 rpm), 12 mL water; <sup>[b]</sup> Time to get the final product with a yield of 100% determined by GC analysis with external standard (decane, except dodecane for 1-decene).

To extend this catalytic study, the hydrogenation of other substrates was investigated. All the catalytic results are summarized in table 2 and the final products correspond to the fully saturated substrates. In the case of alkenes with terminal double bonds, the reaction time significantly increased with the alkyl chain length (Table 2, entries 1-3). This tendency was

already described in the case of the aqueous hydrogenation of terminal olefins catalyzed by metallic NPs assisted by CDs.<sup>[11]</sup> In the presence of Ru\_OS- $\beta$ -CD NPs, anisole, styrene, allylbenzene, benzaldehyde and benzyl alcohol were completely converted into their fully saturated equivalent after 80, 60, 150, 1140 and 780 minutes, respectively (Table 2, entries 4-8). For styrene, allylbenzene and benzaldehyde, the reduction took place in two consecutive steps. The C=C (vinyl or allyl) or C=O bond were firstly reduced followed by the reduction of the aromatic ring. As an example, the figure 3 depicted the reaction profile of the hydrogenation of benzaldehyde. This profile illustrates the sequential nature of the reaction as benzaldehyde was firstly hydrogenated into benzyl alcohol (99% of yield into 170 minutes), which is subsequently hydrogenated into hydroxymethylcyclohexane (100% of yield into 1140 minutes). In the case of benzaldehyde and benzyl alcohol, the catalytic activities were very low compared to other aromatic substrates (Table 2, compare entries 4-6 to 7-8). The reaction profiles relative to styrene and allylbenzene were presented in the Supporting Information. The efficiency of these NPs was also evaluated on substrates issued from biomass. The catalytic system based on Ru\_OS- $\beta$ -CD NPs was inefficient for the reduction of methyl oleate (Table 2, entry 9). This result is in accordance with the fact that the carbon-carbon double bond of OS- $\beta$ -CD oleic arm was not reduced under these reaction conditions. The reduction of ( $\pm$ ) citronellal, a monoterpene present in the citronella oil, was also considered. Citronellal can be reduced into citronellol, 3,7-dimethyloctan-1-al and 3,7-dimethyloctan-1-ol (the fully saturated product). Contrary to the previous examples, the different steps of reduction took place simultaneously and maximum yields of citronellol and 3,7-dimethyloctan-1-al were reached after 90 minutes (25% and 7%, respectively). Then, the both percentages decreased and 3,7-dimethyloctan-1-ol was mainly produced (Fig. 4).

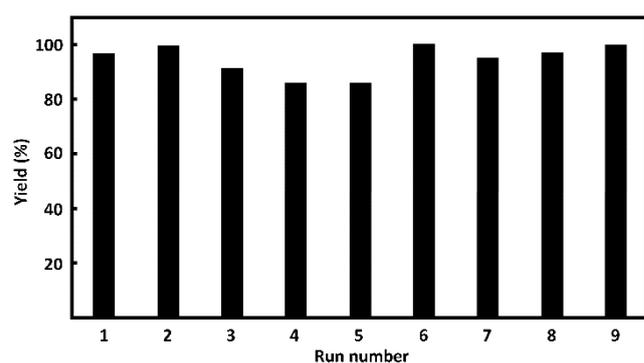


**Figure 3.** Reaction profile for the hydrogenation of benzaldehyde using Ru\_OS- $\beta$ -CD NPs. Reaction conditions: Ru ( $1 \times 10^{-5}$  mol), OS- $\beta$ -CD ( $3 \times 10^{-5}$  mol), substrate ( $1 \times 10^{-3}$  mol), hydrogen pressure (10 bar), temperature (30 °C), stirring rate (750 rpm), 12 mL water.



**Figure 4.** Reaction profile for the hydrogenation of citronellal using Ru\_OS- $\beta$ -CD NPs. Reaction conditions: Ru ( $1 \times 10^{-5}$  mol), OS- $\beta$ -CD ( $3 \times 10^{-5}$  mol), substrate ( $1 \times 10^{-3}$  mol), hydrogen pressure (10 bar), temperature (30 °C), stirring rate (750 rpm), 12 mL water.

The hydrogenation of furfural and furfuryl alcohol (produced from plant materials rich in pentosans) was also evaluated. The catalytic activity was better in the case of furfuryl alcohol than furfural (Table 2, entries 11 and 12). This behaviour has already been described and seems logical since in the case of furfural, the carbonyl double bond has to be also reduced. From a kinetic monitoring point of view, the hydrogenation of furfural into tetrahydrofurfuryl alcohol takes place in two consecutive steps (furfural into furfuryl alcohol and then furfuryl alcohol into tetrahydrofurfuryl alcohol; see Supporting Information). This reaction pathway has also been previously reported in the literature in the case of Ru NPs stabilized by an anionic cyclodextrin polymer.<sup>[6b]</sup>



**Figure 5.** Reusability of the catalytic system Ru\_OS- $\beta$ -CD NPs in the hydrogenation of furfuryl alcohol. Reaction conditions: Ru ( $1 \times 10^{-5}$  mol), OS- $\beta$ -CD ( $3 \times 10^{-5}$  mol), furfuryl alcohol ( $0.5 \times 10^{-3}$  mol), hydrogen pressure (40 bar), temperature (30 °C), stirring rate (750 rpm), 12 mL water, 30 min. Yield in tetrahydrofurfuryl alcohol determined by GC analysis with external standard (decane).

The recyclability of the catalytic system was also investigated by reusing the aqueous catalytic phase for successive furfuryl alcohol hydrogenation runs (Fig. 5). In this case, the furfuryl

alcohol /ruthenium molar ratio is equal to 50 and the hydrogen pressure to 40 bar in order to reduce the reaction time. After the first run (30 min), the product of the reaction was extracted with chloroform. Although the OS- $\beta$ -CD concentration was 25 times higher than its critical aggregation concentration, no formation of emulsion was observed. This point is essential to facilitate an easy separation between the aqueous and the organic phases. After decantation and chloroform removal, the aqueous suspension was reloaded with furfuryl alcohol and dihydrogen in the autoclave and reused under the same experimental conditions. The Ru\_OS- $\beta$ -CD NPs can be recycled and reused for at least 9 consecutive runs with similar yields (between 85–100 %) without any loss of the stability of the colloidal suspension. The stability of Ru\_OS- $\beta$ -CD NPs was confirmed by TEM experiments performed after the ninth run. The TEM image revealed that NPs were still homogeneously dispersed with a slightly larger size distribution centered at  $3.43 \pm 0.62$  nm (compared to  $2.56 \pm 0.60$  nm before catalysis experiment) and with 75% of the NPs with size ranging from 2 to 3.5 nm (see Supporting Information). Additionally, other experiments were performed to check the absence of ruthenium in the extracted organic phase. To this end, the organic phase extracted from the first and the ninth runs were reused at 30°C under 40 bar of H<sub>2</sub> with fresh furfuryl alcohol. After 3 hours, the analysis of organic phase by GC indicated no conversion of the fresh furfuryl alcohol in the both cases. This absence of conversion showed that no leaching of active ruthenium nanoparticles in the organic phase occurred during the extraction step. These results are very impressive since up to now only a CD/polymer combination could allow such a good stability and good recyclability of a nanoheterogeneous catalytic system.<sup>[6c,11]</sup> Indeed, in the case of Ru NPs stabilized by a free form CD (methylated  $\beta$ -CD), a destabilization of the catalytic system, was observed after the fifth recycling run.<sup>[10b]</sup>

In conclusion, we showed that oleic succinyl- $\beta$ -cyclodextrin was efficient for the synthesis of catalytically active ruthenium nanoparticles. The TEM image revealed that Ru\_OS- $\beta$ -CD NPs were homogeneously dispersed with a narrow size distribution centered on 2.56 nm. These NPs were efficient for the hydrogenation of olefins, aromatic and biosourced substrates. In the case of furfuryl alcohol, the catalytic system can be easily recycled and reused for several consecutive runs demonstrating the robustness of this catalytic system. These preliminary results are very promising since this is the first free form CD able to efficiently stabilize Ru NPs during recycling experiments. So, this easily synthesized oleic succinyl- $\beta$ -cyclodextrin could find other applications by varying the nature of the transition metal or considering another catalytic reaction.

## Experimental Section

### Chemicals and reagents

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

### Characterization techniques

Transmission Electron Microscopy (TEM) was performed on a Tecnai microscope (200 kV). The sample into powder was deposited onto the carbon coated copper grid. All the TEM images are gathered in Supporting Information. Metal particle size distributions have been determined from the measurement of 199 particles for Ru\_OS- $\beta$ -CD NPs, 174 particles for Ru\_OS- $\beta$ -CD NPs after the ninth catalytic run and 207 particles for Ru\_ $\beta$ -CD NPs. The nanoparticles were found in arbitrarily chosen area of the images using the program ImageJ software. Zeta potential measurements were carried out in water suspension using a Malvern Zetasizer Nano ZS at a controlled temperature ( $25 \pm 0.1^\circ\text{C}$ ). The  $\xi$ -potential corresponds to the potential difference between the dispersion medium and the electrical double layer of the fluid attached to the dispersed particles. The measurements are based on a Laser Doppler electrophoretic mobility of the heterogeneous catalyst via the Helmholtz-Smoluchowski equation  $\xi = (\eta/\epsilon)\mu_e$ , where  $\mu_e$  is defined as the ratio between the velocity of the heterogeneous catalyst and the magnitude under the applied electric field,  $\eta$  is the viscosity of the suspending liquid and  $\epsilon$  stands for the dielectric conductivity of water. The heterogeneous catalysts were analyzed without any previous treatment. All the samples were analyzed in triplicate using the DTS Software from Malvern Instruments to acquire the phase plot and the zeta potential distribution. Fourier transform infrared spectroscopy (FTIR) experiments were carried out in the  $4000\text{--}400\text{ cm}^{-1}$  region with a spectral resolution of  $2\text{ cm}^{-1}$  using a Shimadzu IR Prestige-21 spectrometer equipped with a PIKE MIRacle diamond crystal. The samples were always prepared as follow : inorganic salts, organic compounds were dissolved in HPLC water. To get a final volume for each sample of 12 mL, the required volume of water is added. The solutions or dispersions were kept under vigorous stirring during 18 hours and then lyophilized. The dried samples were finally analyzed by FTIR spectroscopy.

### Synthesis of Ru\_OS- $\beta$ -CD NPs

In a typical experiment, the colloidal suspension was prepared as follows at ambient temperature. 50.5 mg of the OS- $\beta$ -CD (30  $\mu\text{mol}$ , 3 molar equivalents with respect to ruthenium) were dissolved in 5 mL of HPLC water. Besides this solution, 66.8 mg (10  $\mu\text{mol}$ ) of a 1.5 wt% ruthenium nitrosyl nitrate solution (10  $\mu\text{mol}$  of Ru) were diluted in 3 mL of water which was added to the previous solution. The mixture was kept under constant stirring at room temperature for 30 minutes before the addition of 4 mL of 0.025 M sodium borohydride solution (0.1 mmol, 10 molar equivalents with respect to ruthenium). The color of the reaction medium changed upon addition of NaBH<sub>4</sub> from orange to dark brown due to the reduction of Ru(III). The resulting colloidal suspension was kept under stirring 18 h before their utilization for the catalytic test to permit the total transformation of NaBH<sub>4</sub> excess into NaBO<sub>2</sub> by hydrolysis. The final suspension 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 desired substrate amount. Hydrogen was fed to the system at constant pressure up to the desired pressure. The mixture was heated up to 30 °C with a thermostated oil bath and stirred at 750 rpm. Conversions and selectivities were determined by GC analysis using the calibration method with an external standard.

### Recyclability study

The recycling experiments have been performed using furfuryl alcohol as substrate. At the end of the reaction, all organic compounds were extracted using chloroform. After decantation and chloroform removal, the aqueous phase containing the catalyst was reused for another run by reloading with furfuryl alcohol and fed with hydrogen.

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**Keywords:** • Cyclodextrins • Hydrogenation • Metal nanoparticles • Oleic acid • Supramolecular catalysis

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