Supporting information for

Ruthenium-containing β-cyclodextrin polymer globules for the catalytic hydrogenation of biomass-derived furanic compounds

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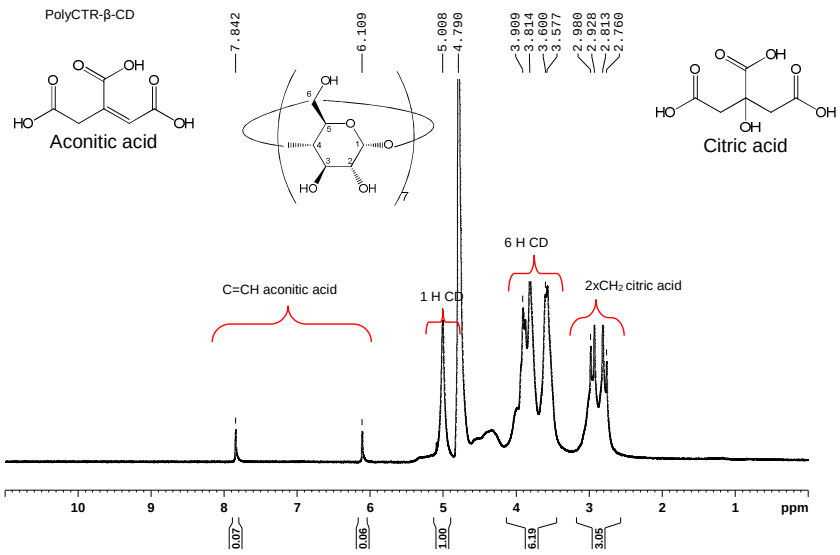
Method for determining the β-cyclodextrin content in Poly(CTR-β-CD)



The number of citric acid and aconitic acid molecules per cyclodextrin unit has to be calculated as follows :

✓ *Ratio citric acid/CD :*

$$\frac{(CH_2)\text{ citric acid integral} \times H_1\text{ CD number}}{H(CH_2)\text{ citric acid number} \times H_1\text{ CD integral}}$$

Numerical application: (3.05×7) / (4×1) = **5.34**

✓ *ratio aconitic acid/CD :*

$$\frac{(CH=)\text{aconitic acid integral} \times H_1\text{ CD number}}{(CH=)\text{aconitic acid number} \times H_1\text{ CD integral}}$$

Numerical application: (0.13×7) / (1×1) = **0.91**

✓*Then the weight percent of a compound i can be determined from the general formula:*

$$\frac{\text{ratio (specie i/CD)} \times M_i}{\Sigma\,(\text{ratio}_i \times M_i)}$$

Numerical application for β-CD: 1135/(5.34×192+ 0.91×174 + 1×1135) = **49 wt. %**

where 1135, 192 and 174 are the molar masses (g mol^{-1}) of β-CD, citric acid and aconitic acid respectively.

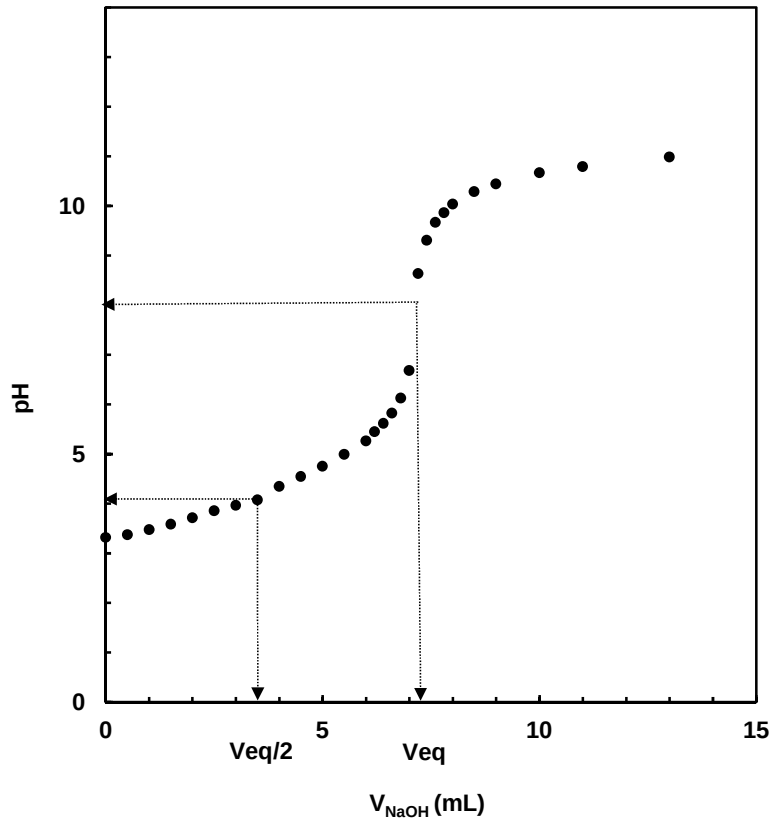


Fig. S1 Acid-base titration curve of poly(CTR-β-CD). *Experimental procedure:* 50 mg of poly(CTR-β-CD) are dissolved in 100 mL of a 0.1 M NaCl solution. The resulting solution is titrated by a 0.05 M NaOH solution. The equivalent volume Veq is determined by the derivative curve dpH/dV. The pH value at Veq/2 gives a mean pKa value of 4.1 for the poly(CTR-β-CD).

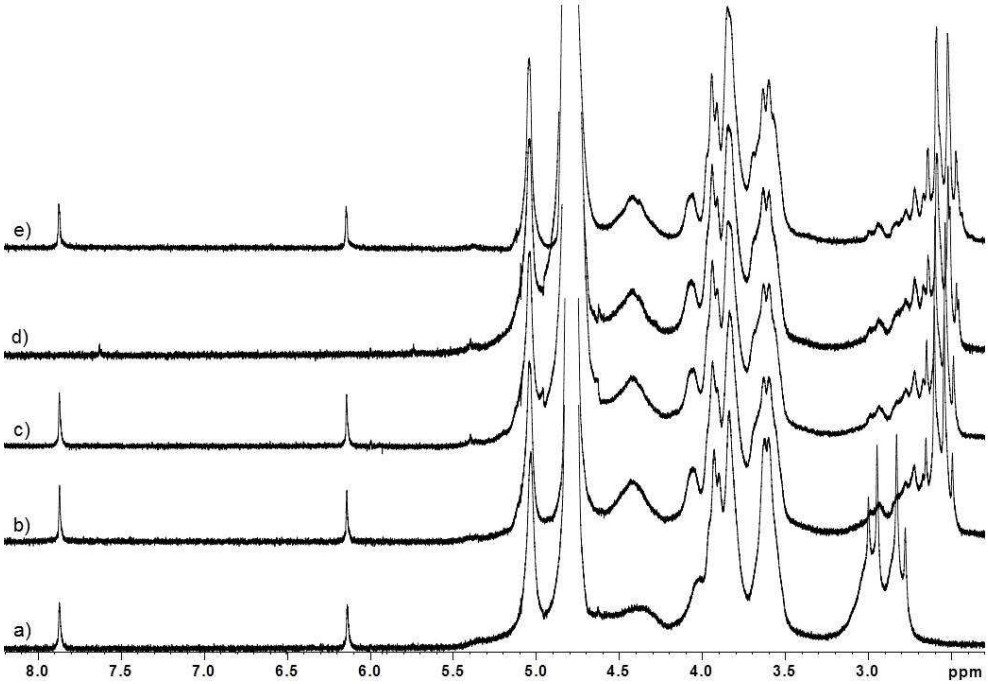


Fig. S2 ^{1}H NMR analysis in D_2O of poly(CTR-β-CD) after addition of the different reactants used for the synthesis of Ru(0) NPs: (a) Pristine poly(CTR-β-CD); (b) poly(CTR-β-CD) with $NaHCO_3$; (c) poly(CTR-β-CD) with $NaHCO_3$ and $Ru(NO)(NO_3)_3$; (d) poly(CTR-β-CD) with $NaHCO_3$, $Ru(NO)(NO_3)_3$ and $NaBH_4$ and (e) poly(CTR-β-CD) with $NaHCO_3$ and $NaBH_4$ (no metal)

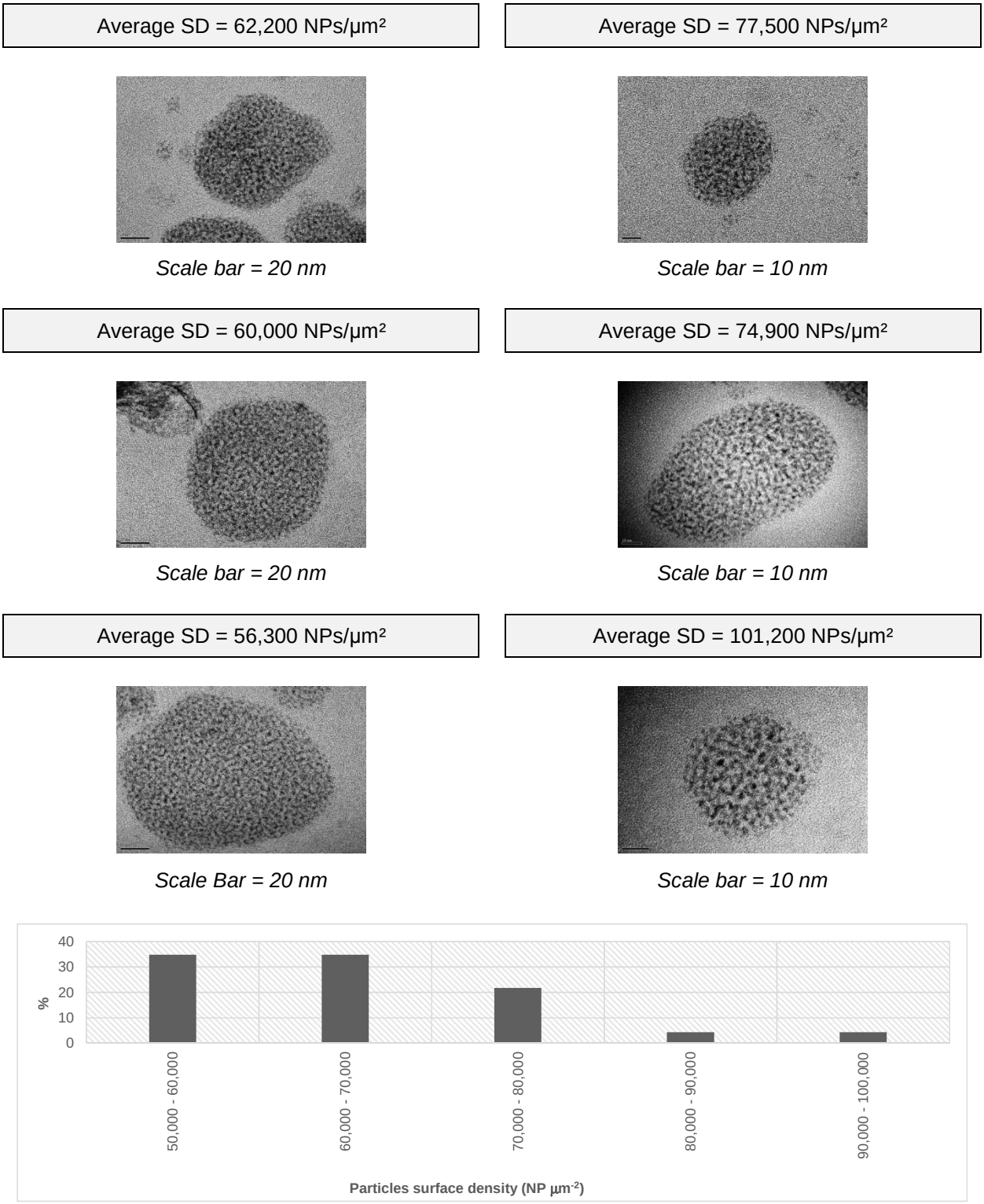


Fig. S3 Representative TEM micrographs showing ruthenium-containing poly(CTR-β-CD) spherical superstructures with the corresponding Ru(0) nanoparticles surface density. The normalized histogram of the distribution was constructed from the counting of ca. 600 particles selected from 23 regions with surface areas of 300 to 400 nm^2.

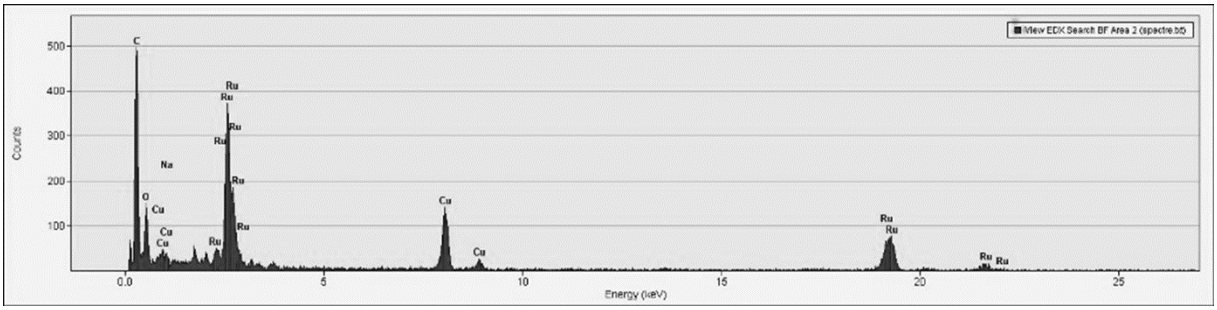
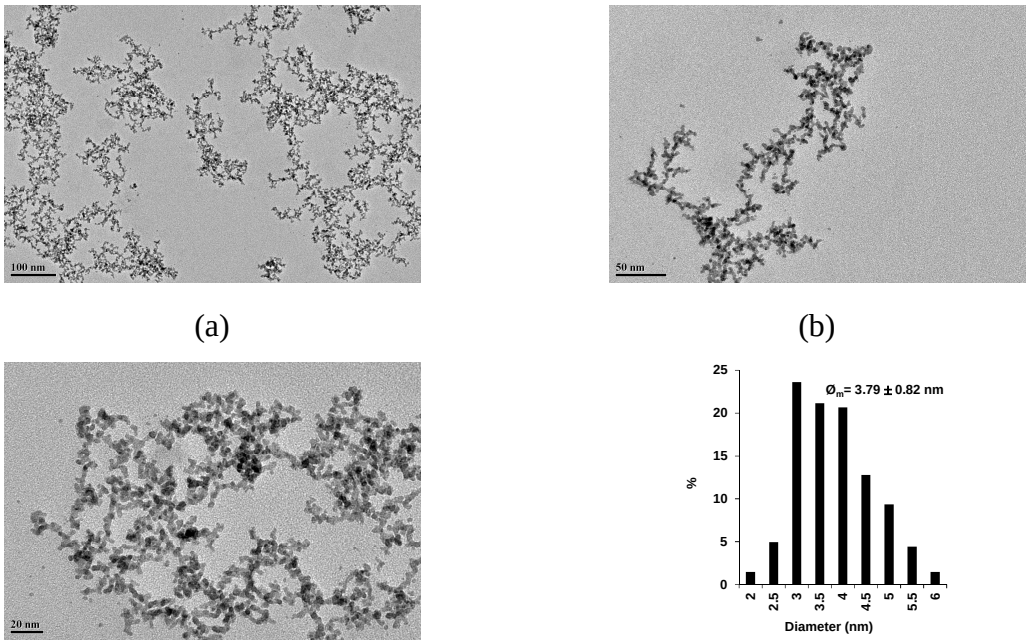


Fig. S4 EDS spectrum of poly(CTR-β-CD) Ru(0) NPs in a selected region area.



(a) (b)

(c) (d)

Fig. S5 TEM characterization of the poly(CTR-MaltoD) Ru(0) NPs at different magnifications: (a) 1ow-magnification image; (b) medium-magnification image; (c) high-magnification image and (d) corresponding particle size distribution obtained from the measurement of ca. 200 particles.

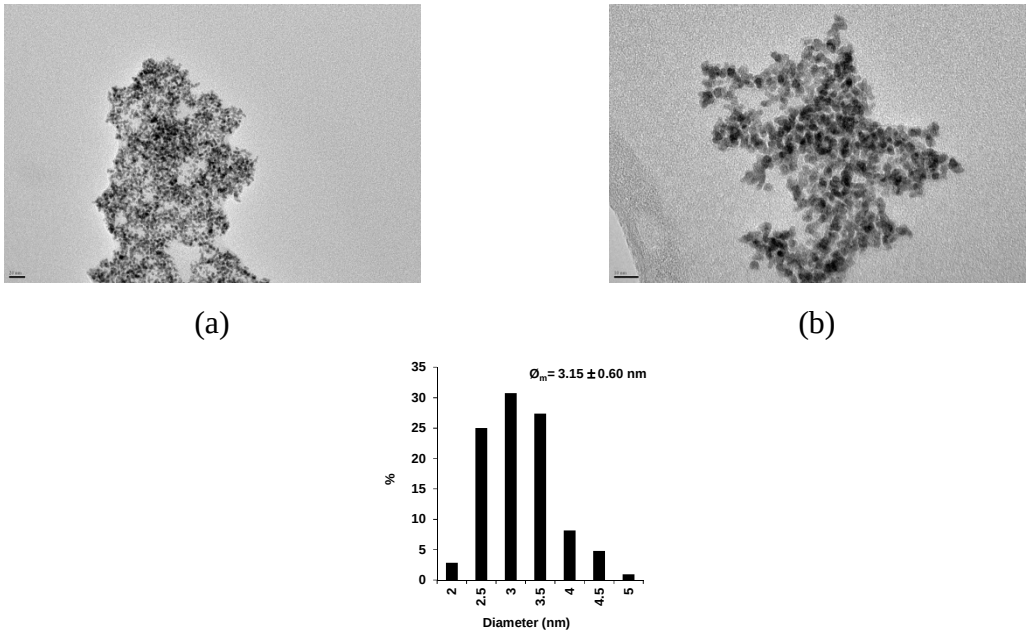


Fig. S6 TEM characterization of the CTR-stabilized Ru(0) NPs at different magnifications: (a) medium-magnification image; (b) high-magnification image and (c) corresponding particle size distribution obtained from the measurement of ca. 200 particles.

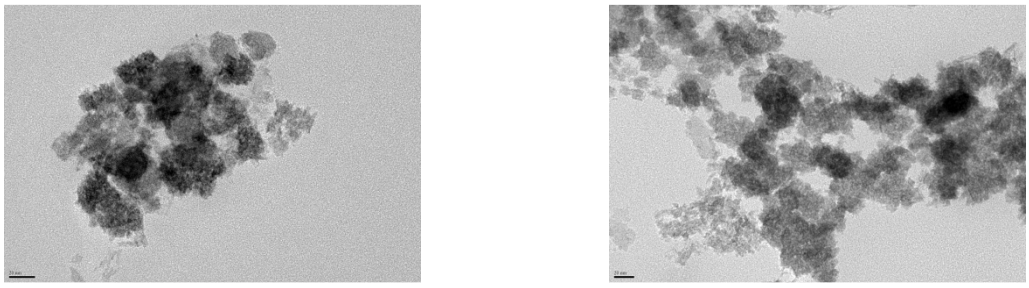


Fig. S7 TEM characterization of the PM(CTR+β-CD) Ru(0) particles synthesized from the mixture of citric acid and β-CD (weight ratio of 1:1) as stabilizing agent.

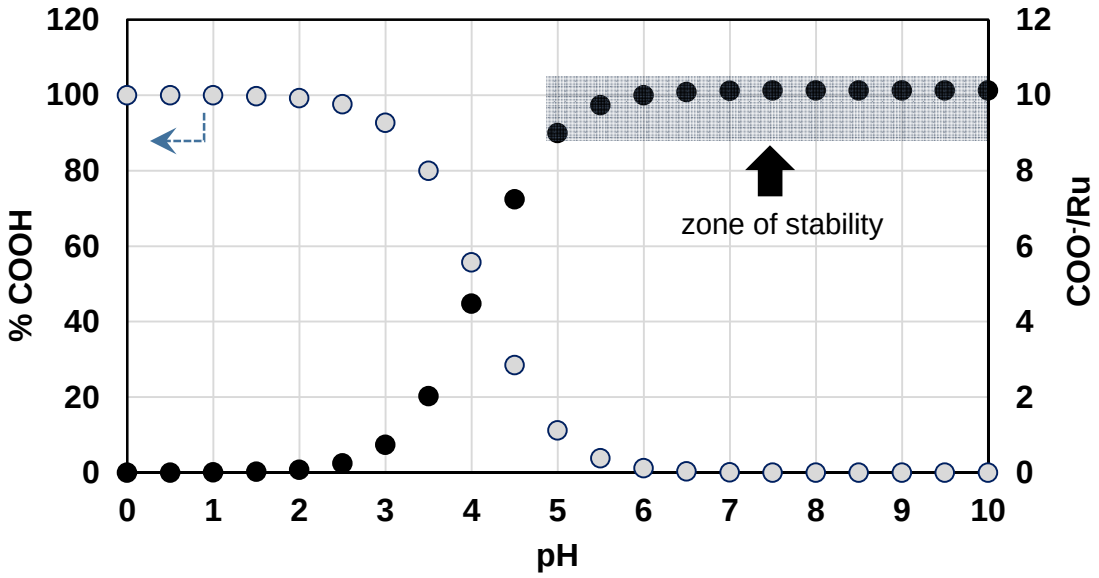


Fig. S8 Plots of the distribution of carboxylic acid groups and ratio of carboxylate to ruthenium *vs* the pH of the aqueous suspension made of poly(CTR-β-CD) Ru(0) NPs.

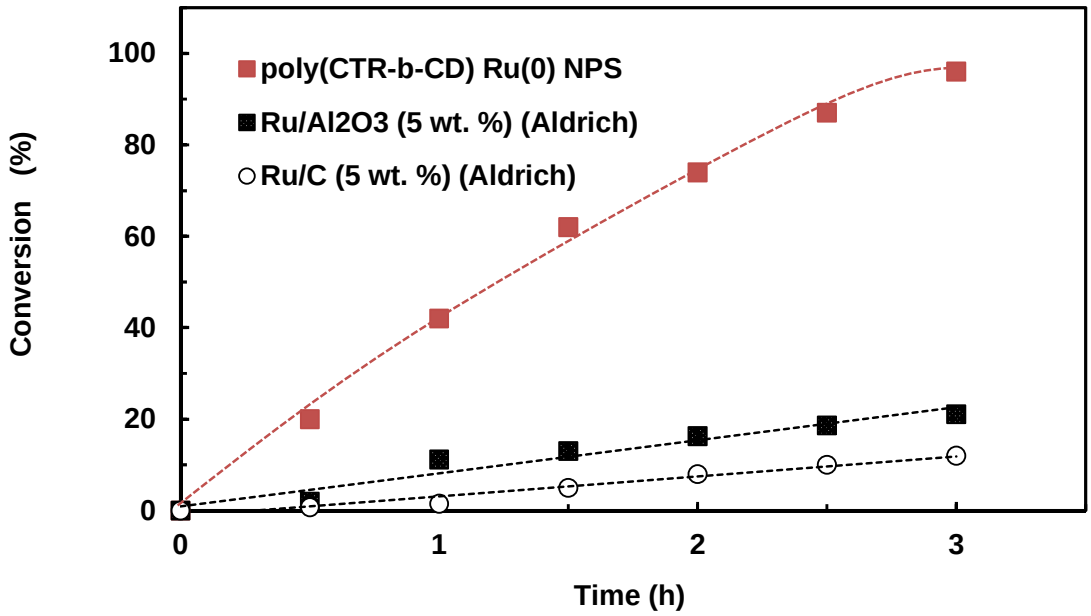


Fig S9 Conversion of 2-furaldehyde as a function of time over different ruthenium catalytic systems: polyCTR-β-CD Ru(0) NPs (■) Ru/Al_2O_3 (80 mg) (■) and Ru/C (80 mg) (○). Reaction conditions: Ru (40 μmol, 1 equiv.), 2-furaldehyde (2 mmol, 50 equiv), H_2 (1.0 MPa), solvent (H_2O, 12 mL), stirring rate (1400 rpm), temperature (303 K), reaction time (3 h).

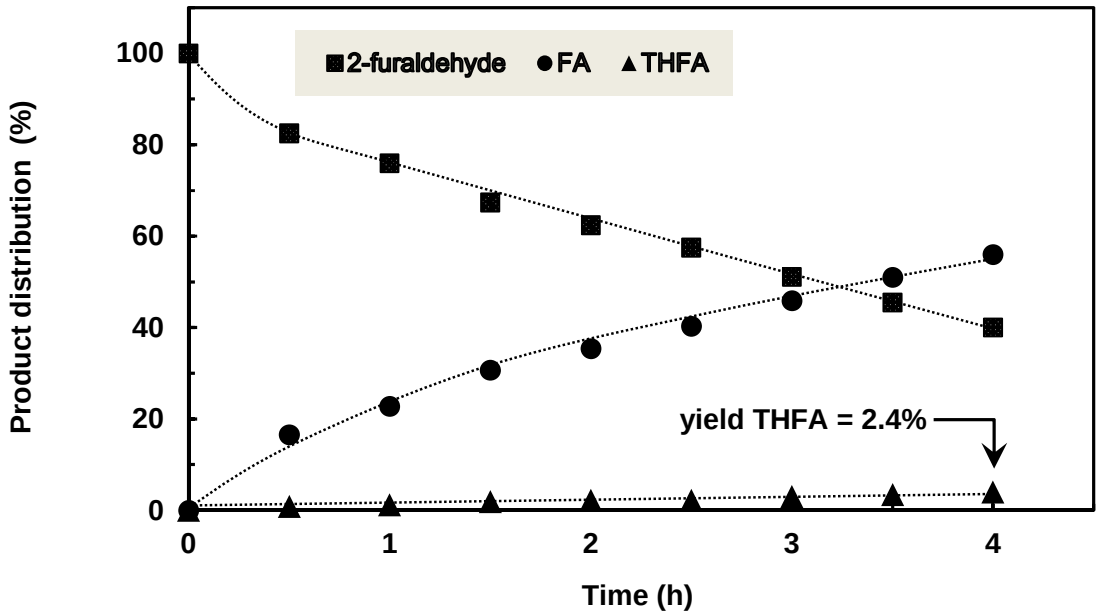


Fig. S10 Reaction profile for the hydrogenation of 2-furaldehyde over CTR-β-CD Ru(0) NPs at 30°C and under 1 MPa H_2: 2-furaldehyde (■), furfuryl alcohol (●) and tetrahydrofurfuryl alcohol (▲).

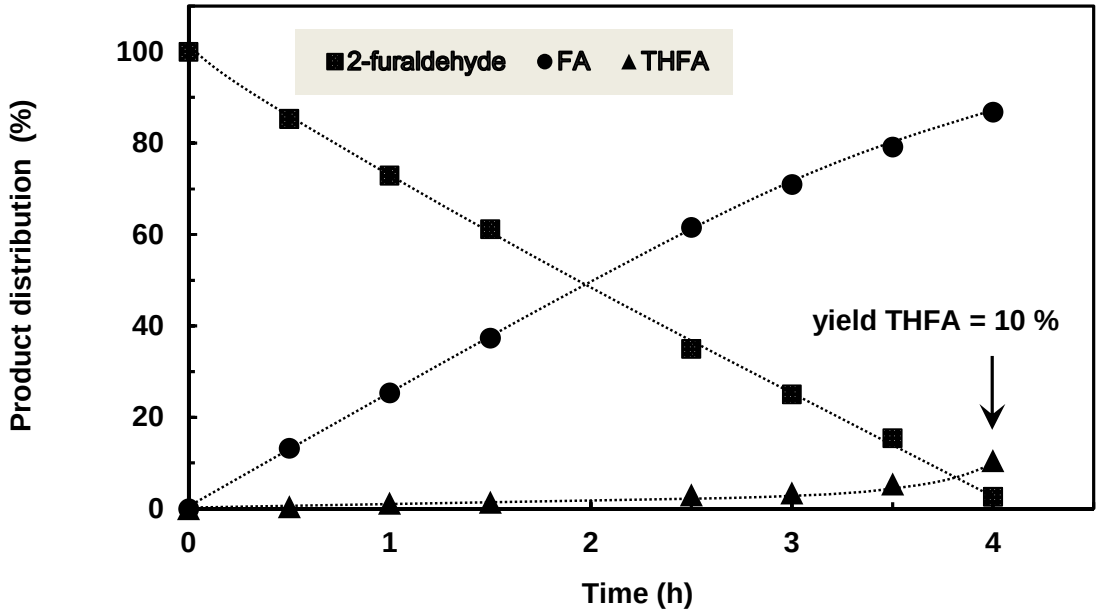
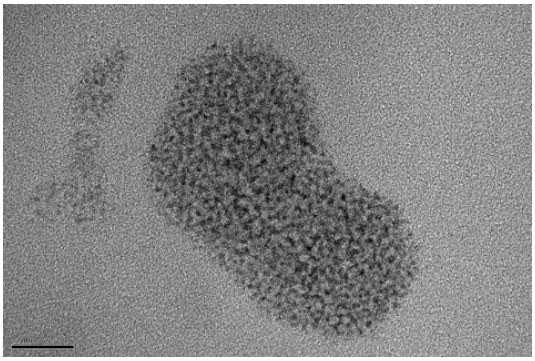


Fig. S11 Reaction profile for the hydrogenation of 2-furaldehyde over PM(CTR+β-CD) Ru(0) NPs at 30°C and under 1 MPa H_2: 2-furaldehyde (■), furfuryl alcohol (●) and tetrahydrofurfuryl alcohol (▲).



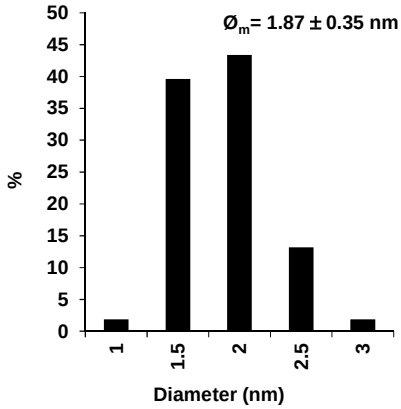


Fig. S12 TEM characterization of the poly(CTR-β-CD) Ru(0) NPs recovered at the end of the hydrogenation reaction of 2-furaldehyde (reaction time 4 h.).

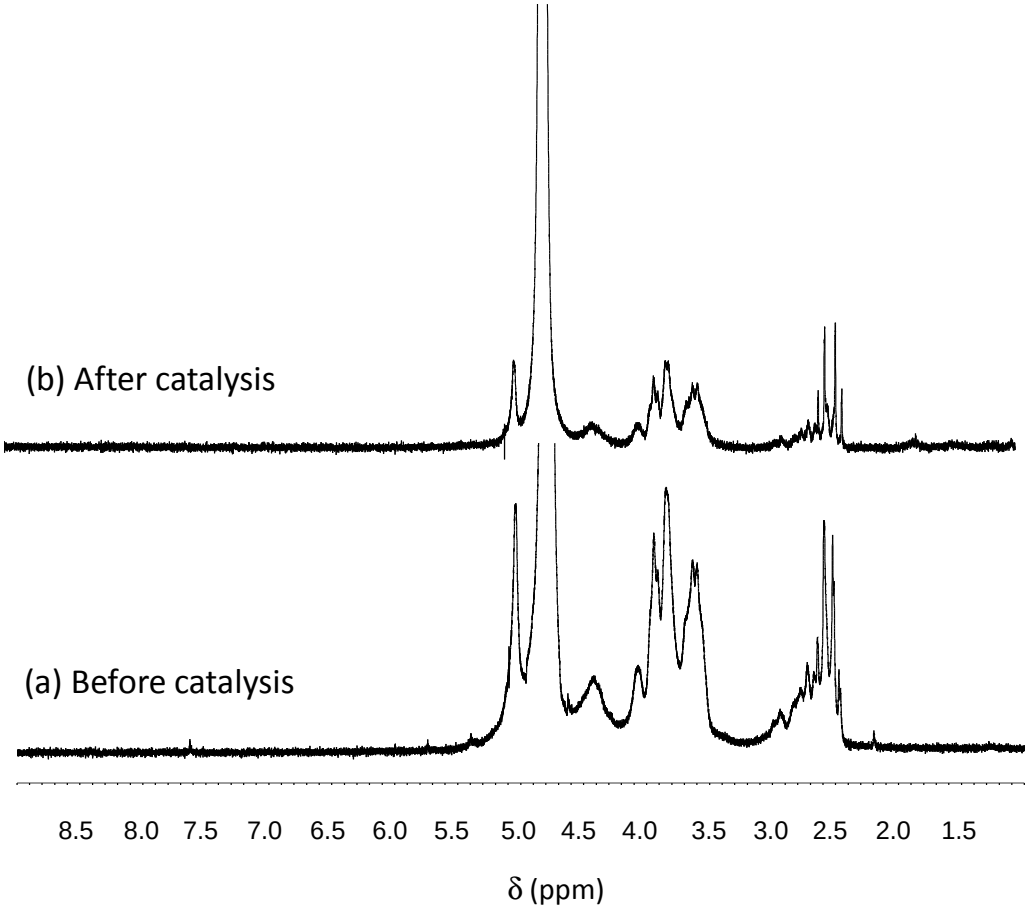


Fig. S13 (a) ^{1}H NMR spectrum of poly(CTR-β-CD) Ru(0) NPs dispersed in D_2O (before catalysis) (b) ^{1}H NMR analysis of poly(CTR-β-CD) Ru(0) NPs recovered at the end of the hydrogenation reaction of 2-furaldehyde (303 K, 10 bar H_2, reaction time 4 h.), extraction of the organic product with $CDCl_3$ followed by its evaporation (35°C, water pump) and re-dissolution in D_2O (after catalysis).