Supporting information for

Cyclodextrins as growth controlling agents for enhancing the catalytic activity of PVP-stabilized Ru(0) nanoparticles

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General

Ruthenium chloride hydrate (40-43% of Ru), sodium borohydride, PVP-K30 (MW = 58 000) were obtained from Acros Organics and Aldrich Chemicals and were used without further purification. Furfural was purchased from Aldrich Chemicals and purified by distillation under reduced pressure. Randomly methylated β-cyclodextrin (RaMe-β-CD), α-CD and γ–CD were purchased from Wacker Chemie AG whereas β-CD was purchased from Roquette Frères. Randomly methylated α-cyclodextrin (RaMe-α-CD) and randomly methylated γ-cyclodextrin (RaMe-γ-CD) were prepared by adapting a procedure reported by Kenichi et *al*. [Y. Kenichi, M. Atsushi, T. Yukio, S. Mitsukatsu, Y. Yoshiaki, I. Tomoyuki, JP Patent, 8333406, 1996].

Synthesis of the PVP-stabilized Ru(0) NPs in colloidal suspensions

In a typical experiment, the colloidal suspension was prepared as follows at ambient temperature. 35.2 mg (3.0×10^{-4} mol, 8 equiv.) of PVP-K30 and the desired quantity of cyclodextrin were dissolved in 5 mL of deionized water under vigorous stirring during 24 hours. 9.3 mg (3.8×10^{-5} mol, 1 equiv.) of $RuCl_3$ were dispersed in 5 mL of deionized water. The both solutions were mixed together under vigorous stirring during 30 minutes, then 21.6 mg (5.7×10^{-4} mol, 15 equiv.) of $NaBH_4$ previously

dissolved in a minimum of water (3 drops) were quickly added to the mixture. The resulting colloidal suspension was kept under vigorous stirring for 24 hours in order to check that there is no agglomeration of the metallic particles before the beginning of the catalytic test.

General procedure for hydrogenation

The stainless steel autoclave was charged with 10 mL of the colloidal suspension of PVP-stabilized Ru(0) NPs. 182.5 mg of furfural (1.9×10^{-3} mol, 50 equiv.) was added into the autoclave and hydrogen was introduced at constant pressure up to 10 bars. The mixture was heated to 30°C and stirred at 750 rpm. The reaction was monitored by the volume of consumed H_2 and by analyzing aliquots of the reaction mixture using a Shimadzu GC-17A gas chromatograph, equipped with a methyl silicone capillary column (30 m × 0.32 mm) and a flame ionization detector.

For the recycling procedure, after complete conversion of furfural, the products were extracted by liquid-liquid extraction and decantation with diethyl ether until complete elimination of organic products from the aqueous phase. After elimination of the organic phase under vacuum, the colloidal suspension was reloaded with furfural and dihydrogen and reused in hydrogenation in the autoclave as described above.

TEM analysis

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 ca. 225 particles found in arbitrarily chosen area of the images using the SCION Image software.

DLS analysis

DLS studies were conducted on aqueous solutions of cyclodextrins alone or in a mixture with PVP 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 analyses the scattered light at an angle of 173° by utilizing a non-invasive backscatter technique. Cells, syringes and filters were washed at least ten times with deionized water. The samples were prepared at the desired concentration and were kept under vigorous stirring during 24 h before analysis. Then, the samples were filtered through a sterile 0.22 µm filter. A total of 20 scans, each with a period of 50 s, was accumulated for each sample. All samples were analyzed in triplicate using the the DTS Software from Malvern Instruments to acquire the correlogram (correlation function versus time). For each analysis, it was checked that the intercept values deduced from the autocorrelation functions were in a range between 0.8 and 1. Note that, the area of the peak for large particles is much larger than the peak for the small particles. The intensity of scattering of a particle is assumed to be proportional to the sixth power of its diameter.

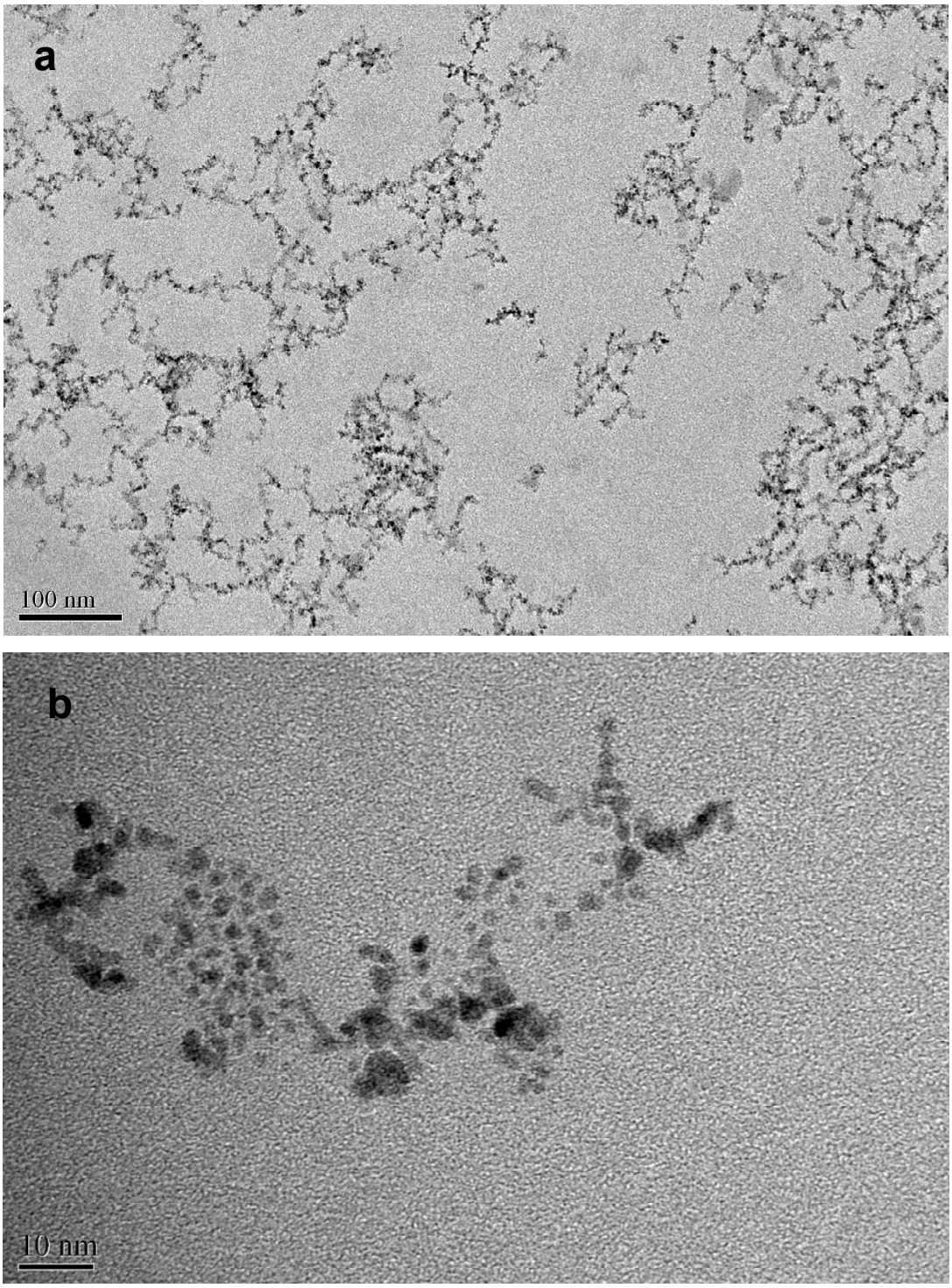


Fig S1 TEM micrographs of Ru(0) colloidal suspension stabilized by PVP:RaMe-β-CD mixture in a ratio 8:2 at low (a) and high (b) magnification.

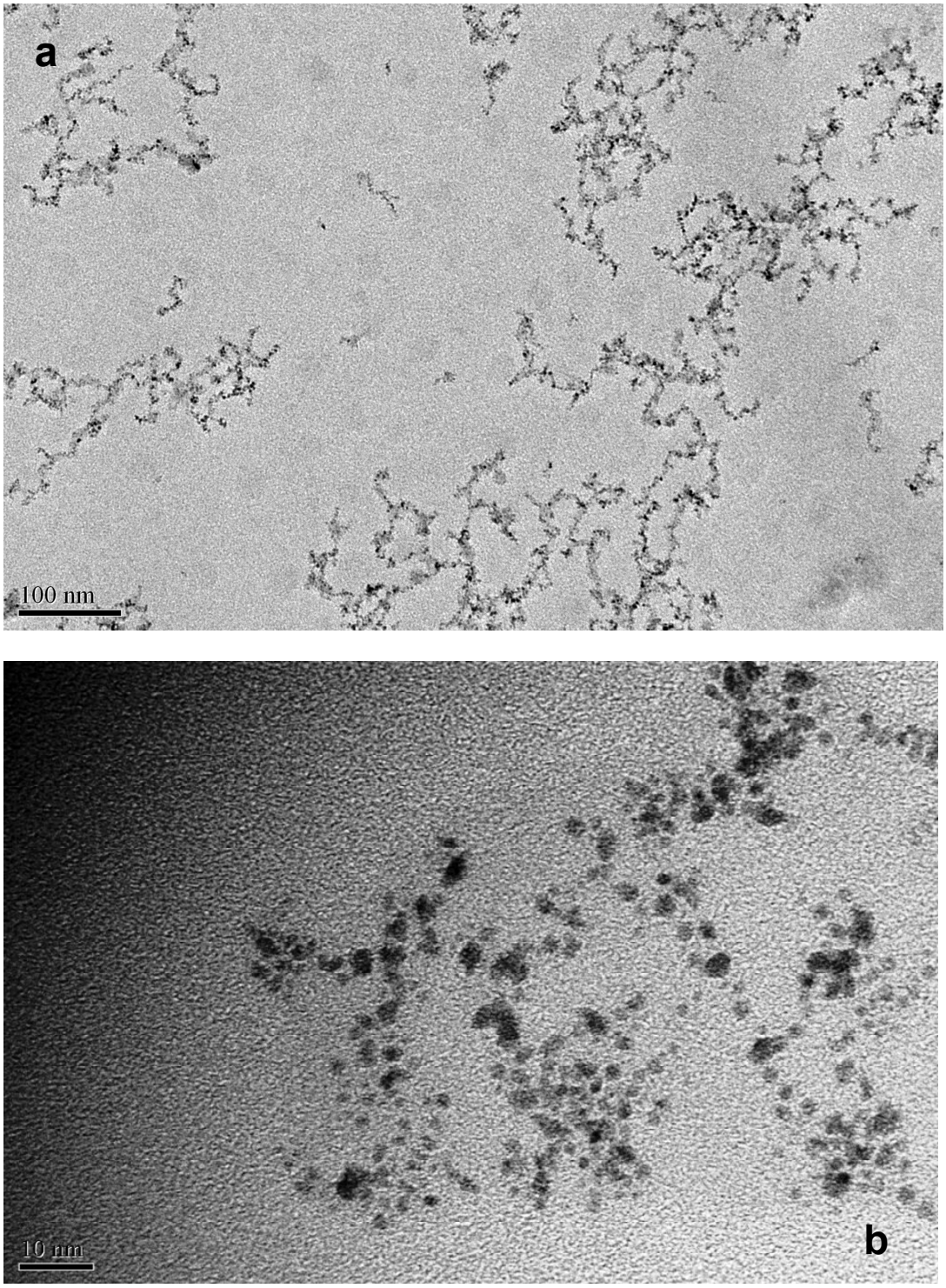


Fig S2 TEM micrographs of Ru(0) colloidal suspension stabilized by PVP:RaMe-γ-CD mixture in a ratio 8:2 at low (a) and high (b) magnification.

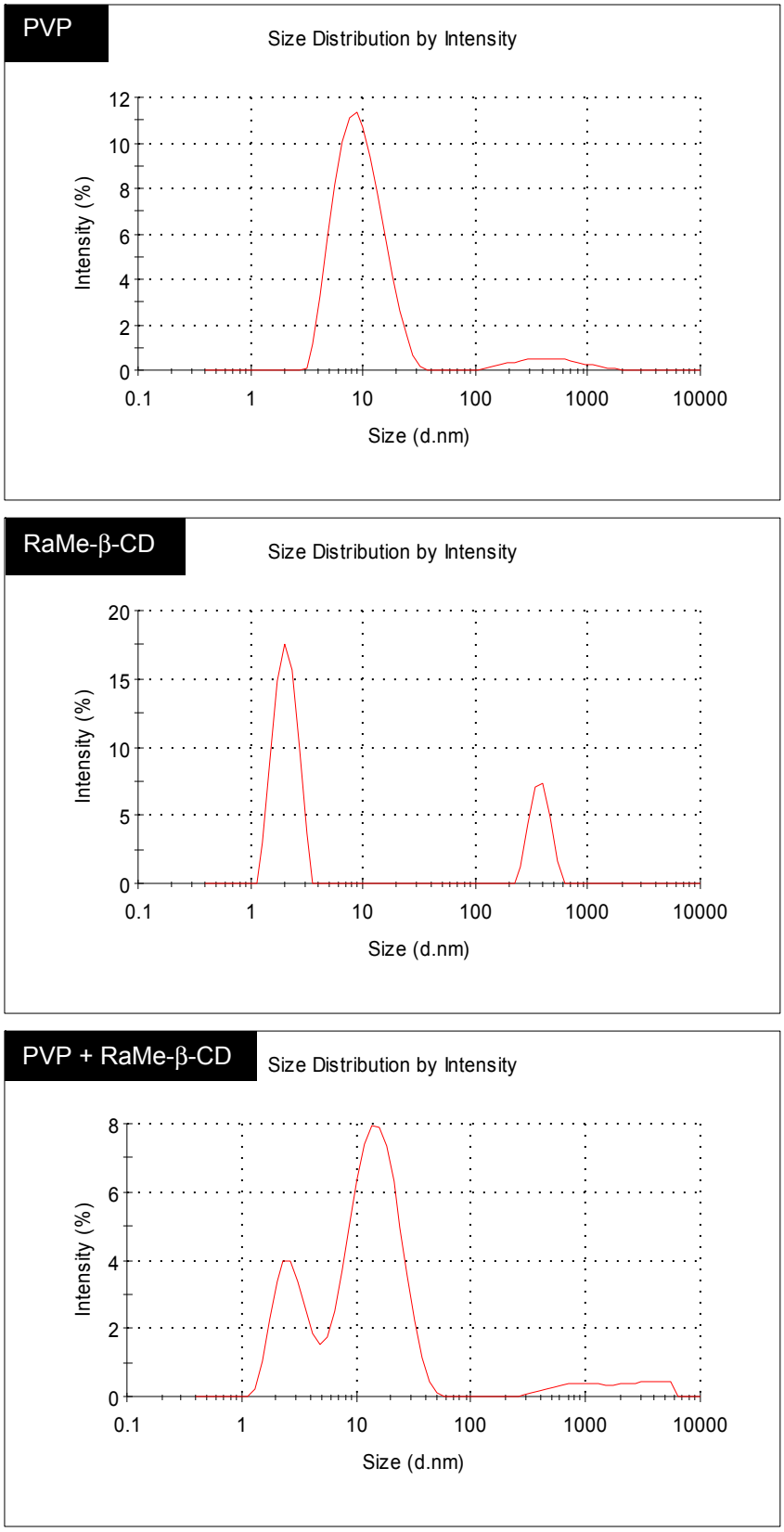


Fig. S3 Size distributions obtained by DLS measurements performed on an aqueous solution of PVP (50 mM), RaMe-β-CD (50 mM), and a mixture of PVP:RaMe-β-CD with a ratio of 8:2 (200 mM:50 mM)

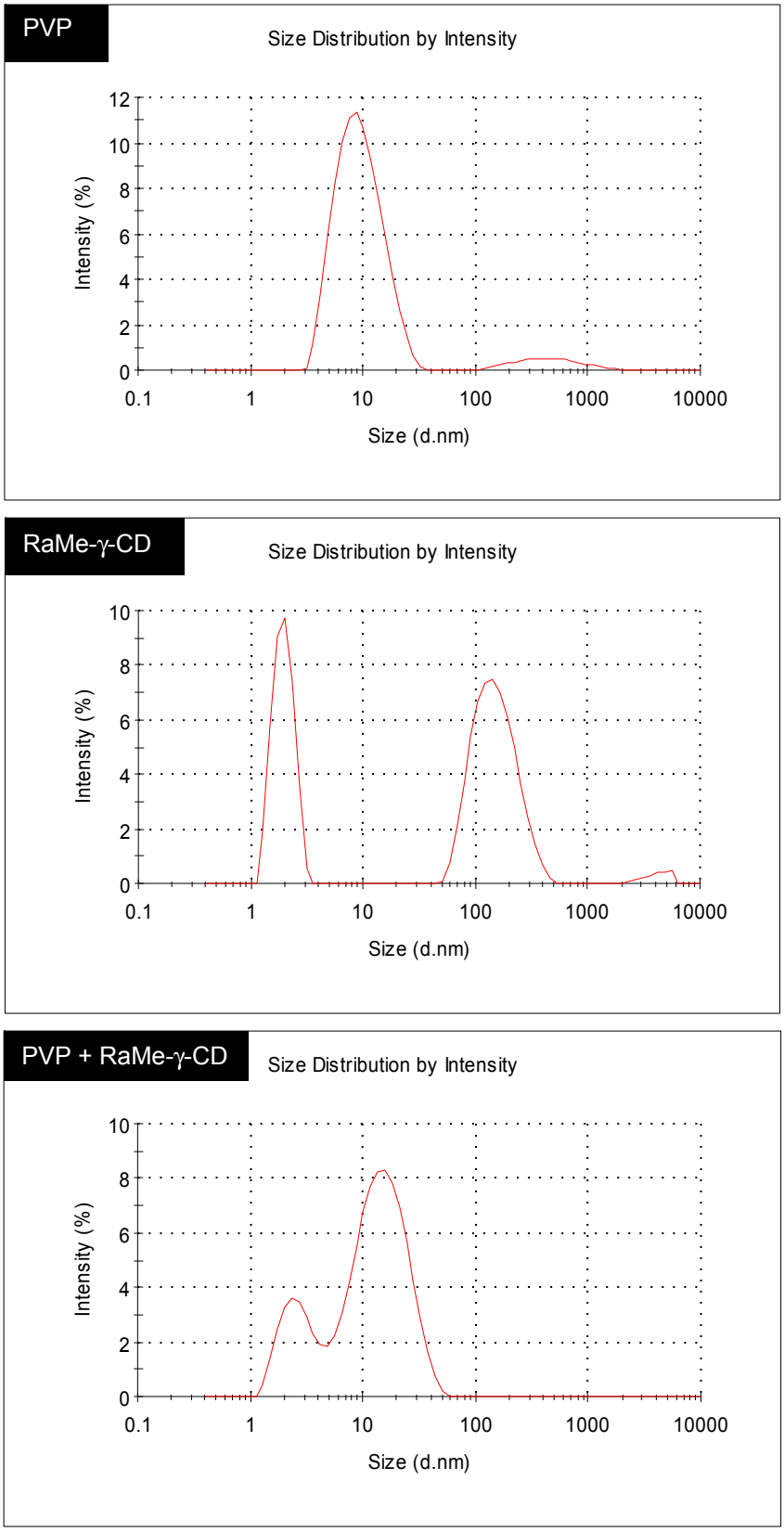


Fig. S4 Size distributions obtained by DLS measurements performed on an aqueous solution of PVP (50 mM), RaMe-γ-CD (50 mM), and a mixture of PVP:RaMe-γ-CD with a ratio of 8:2 (200 mM:50 mM).

DLS analysis

Complementary information has been provided by Dynamic Light Scattering (DLS) measurements performed on aqueous solutions of methylated cyclodextrin, alone or in a mixture with PVP. Thus, it is observed that PVP has a particle size distribution centred at about 10 nm and this value does not seem to be influenced by the addition of oligosaccharide. By contrast, we have found that the state of aggregation of CD in aqueous solution is deeply disturbed by the presence of the polymer. With the mixtures of PVP with RaMe-β-CD and RaMe-γ-CD, the intensity of the band characteristic of the large aggregates (200-400 nm) decreases to the benefit of a new band in the range of 1-3 nm, which is associated to the formation of small assemblies containing 2 or 3 cyclodextrin units. Note that a similar tendency has been also observed in the case of native cyclodextrins (α-CD and γ-CD).

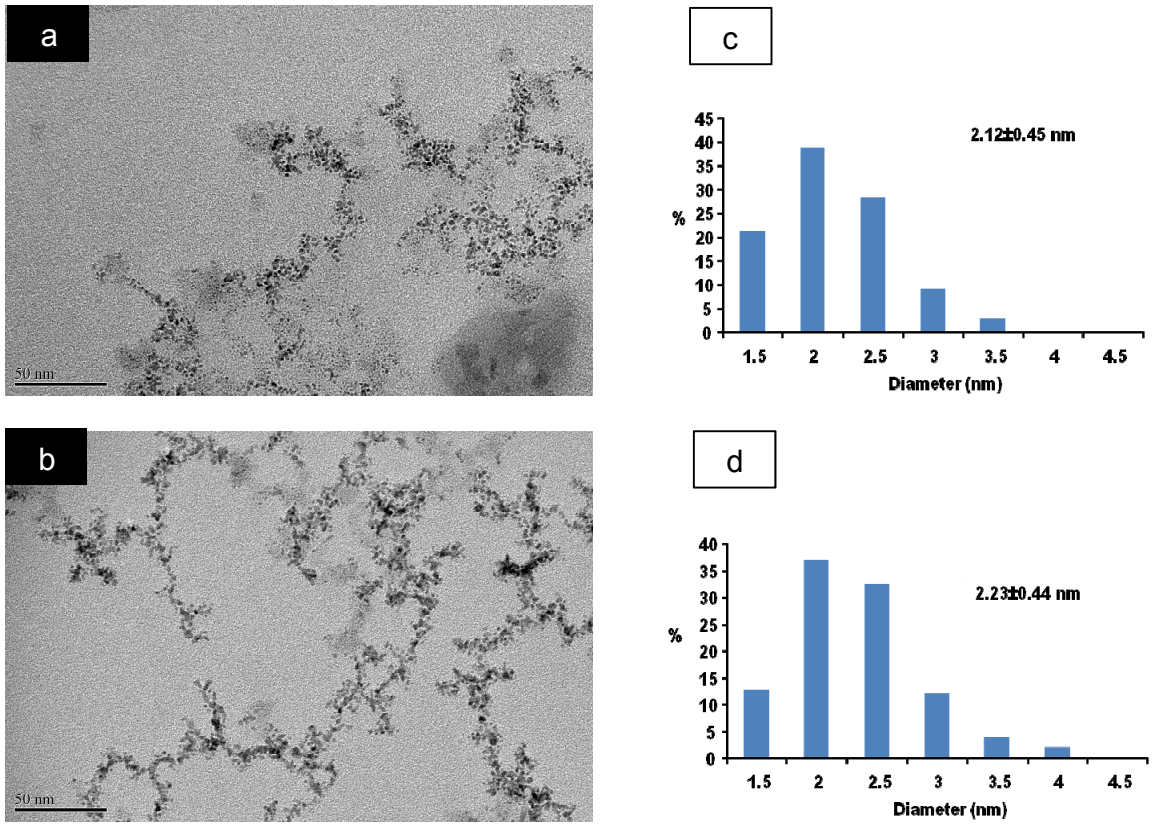
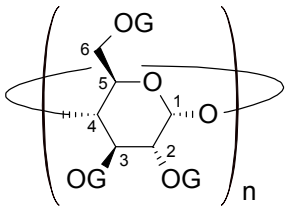


Fig. S5 TEM micrographs (a, b) and size distributions (c, d) of Ru(0) colloidal suspensions prepared from mixtures of PVP and RaMe-β-CD (a,c) and PVP and RaMe-γ-CD (b,d) in a ratio 8:2 and recovered after one catalytic run.

Table S1 Chemical structure and characteristic of the cyclodextrin derivatives



G : H or R

Abbreviation	n	Substituent R	Carbons bearing the OR group	Number of R groups per CD	Molecular weight ($g\ mol^{-1}$)
α-CD	6	(-)	(-)	0	972
γ–CD	8	(-)	(-)	0	1297
RaMe-α-CD	6	CH_3	2, 3 and 6	10.8	1127
RaMe-β-CD	7	CH_3	2, 3 and 6	12.6	1314
RaMe-γ-CD	8	CH_3	2, 3 and 6	14.4	1502

Table S2 Influence of the ratio PVP:Ru on the stability of PVP stabilized Ru(0) NPs and their catalytic performance in the hydrogenation of furfural

PVP: Ru	Stability of the colloidal suspension	Conversion (%)	Selectivity (%)	
			FA	THFA
2:1	No	n.d. [a]	/	/
4:1	No	n.d. [a]	/	/
6:1	No	n.d. [a]	/	/
8:1	Yes	30	94	6
15:1	Yes	20	95	5
30:1	Yes	16	97	3

Reaction conditions: Ru(0) (3.8×10^{-5} mol), PVP-K30 (3.0×10^{-4} mol), Substrate:Ru (mol/mol) = 50, H_2O (12 mL), H_2 (1.0 MPa), stirring rate (750 rpm), 30°C, 1.5 h.

[a] Non determined