

Supramolecular shuttle and protective agent: a multiple role of methylated cyclodextrins in the chemoselective hydrogenation of benzene derivatives with ruthenium nanoparticles.

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Supplementary data

General

Randomly methylated β -cyclodextrin (Me- β -CD (1.8)) was purchased from Aldrich Chemicals. Randomly methylated α -cyclodextrin (Me- α -CD) and randomly methylated γ -cyclodextrin (Me- γ -CD) were prepared by adapting a procedure reported by Y. Kenichi et *al.* [Y. Kenechi, M. Atsushi, T. Yukio, S. Mitsukatsu, Y. Yoshiaki, I. Tomoyuki, JP pat. 8333406, 1996]. These cyclodextrins were partially methylated. Methylation occurred at positions 2, 3, or 6 and 1.8 OH groups per glucopyranose unit were statistically modified. The randomly methylated β -cyclodextrin with an average substitution degree of 0.7 was kindly providing by Roquette (Me- β -CD (0.7)). Methylation occurred mainly at positions 2 and statistically 0.7 OH groups per glucopyranose unit were modified.

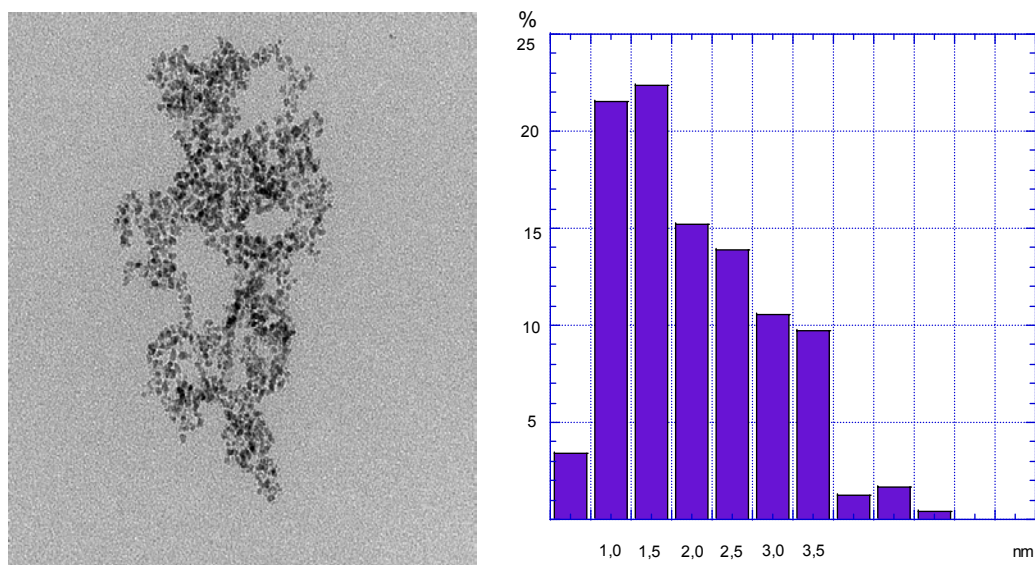
Synthesis of ruthenium(0) nanoparticles stabilized with cyclodextrins: In aqueous solution (5 mL) of the precursor RuCl_3 (3 mg, 1.44×10^{-5} mol) was added to an aqueous solution (3 mL) of cyclodextrin (1.44×10^{-4} mol). The solution was stirred for 30 mn. Then, sodium borohydride (1.37 mg, 3.6×10^{-5} mol) in 2 mL of water was added all at once under vigorous stirring at room temperature. The solution was stirred for 24 hours at room temperature before use.

General procedure for Hydrogenation: 10 mL of the previously prepared aqueous suspension of Ru(0) were introduced in a 50mL flask. The appropriate substrate (1.44×10^{-3}

mol) of substrate was added. The reaction mixture was stirred vigorously, at room temperature under 1 bar of H₂ until the reaction was finished. The reaction was monitored by the volume of hydrogen consumed and gas chromatographic analysis

TEM analysis

The transmission electronic microscopic studies were conducted using a FEI Technai G2 Sphera at 200 kV (cathode LaB6). Samples were prepared by a dropwise addition of the stabilized ruthenium nanoparticles in water onto a copper sample mesh covered with carbon. The colloidal dispersion was partially removed after 1 min using cellulose before transferring to the microscope. The picture is obtained at X 80.000 with a video GATAN USC1000 (CCD detector 2048X2048) and associated software DIGITAL Micrograph. Measurement of about 240 particles was made with program SCION Image (NIH) and was analyzed with KaleidaGraph program providing the histograms of the nanoparticles size distribution.



Spatial organization of the stabilized aqueous suspension of ruthenium nanoparticles. The average particle size was about 1.5nm with 70% of the nanoparticles between 1 and 2.5nm.