

Supplementary Materials

In Situ Ruthenium Catalyst Modification for the Conversion of Furfural to 1,2-Pentanediol

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Fraction of surface atoms

The number of Ru atoms in *hcp* cell (N) is 6. Ru atom radius (R_{Ru}) is 0.214 nm. The volume of Ru cell is 0.0817 nm³. R_{NP} represents the radius of a NP, determined using TEM images.

The volume of all Ru atoms on the shell of NP: $V_{shell} = V_{total} - V_{core} = 4/3\pi R_{NP}^3 - 4/3\pi(R_{NP} - R_{Ru})^3$, V_{total} meaning the volume of one Ru nanoparticle, V_{core} presenting the volume of NP excluded the one outer layer of atoms.

The numbers of metal atoms on the shell $N_{shell} = N * V_{shell} / 0.0817$.

The number of total Ru atoms $N_{total} = N * V_{total} / 0.0817$.

The percentage of Ru atoms on the surface of NP = $N_{shell} / N_{total} * 100\%$.

Taking into consideration these calculations for a 1.6 nm Ru NP the % of Ru surface atoms is 61.

Arblaster, J. W., Crystallographic properties of ruthenium. *Platinum Met. Rev.* **2013**, *57*, 127-136.

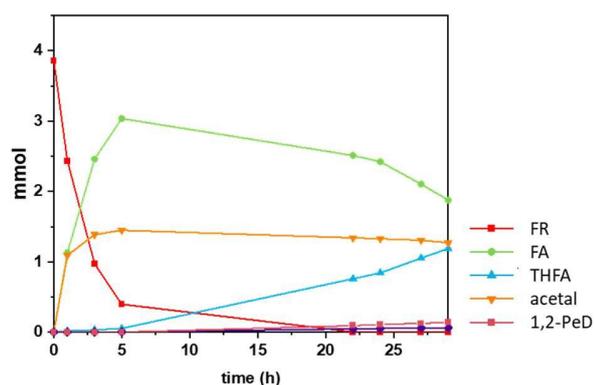


Figure S1. Time-concentration curve for furfural hydrogenation using Ru/PVP as catalyst. Furfural (red curve), furfuryl alcohol (green curve), tetrahydrofurfuryl alcohol (blue curve), acetal (orange curve), 1,2-pentanediol (pink curve). Reaction conditions: 2×10^{-2} mmol of Ru, 4 mmol of FA, 0.5 mmol of dodecane (internal standard), 20 bar of H_2 , 125°C, 15 mL of 1-propanol. Quantities of products and reagents were determined by GC using an internal standard technique.

M. Cardona-Farreny, P. Lecante, J. Esvan, C. Dinoi, I. Del Rosal, R. Poteau, K. Philippot, M.R. Axet, Bimetallic RuNi nanoparticles as catalysts for upgrading biomass: metal dilution and solvent effects on selectivity shifts, *Green Chem.*, 23 (2021) 8480-8500.

Table S1. Size before and after the hydrogenation of furfural in 1-PrOH using Ru/PVP nanocatalyst in situ modified.

Entry	Catalyst	Size before reaction (nm) ^a	Size after reaction (nm) ^a	Leaching (%) ^b
1	Ru/PVP		1.6 ± 0.3	0.8
2	Ru/PVP + HDA		1.5 ± 0.3	1.6
3	Ru/PVP + TMP	1.6 ± 0.3	1.6 ± 0.4	3.0
4	Ru/PVP + TBA		1.4 ± 0.4	1.3
5	Ru/PVP + PN		1.6 ± 0.4	0.1
6	Ru/PVP + NHC		1.7 ± 0.4	2.9

^aMean values of nanoparticle size determined from TEM images by considering at least 200 particles.

^bDetermined by ICP analysis.

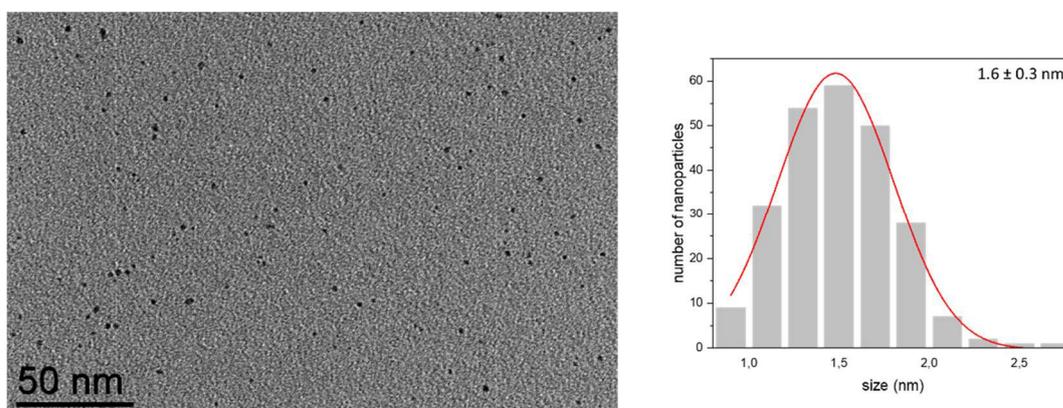


Figure S2. TEM image of Ru/PVP (scale bar 50 nm) together with the respective size histogram.

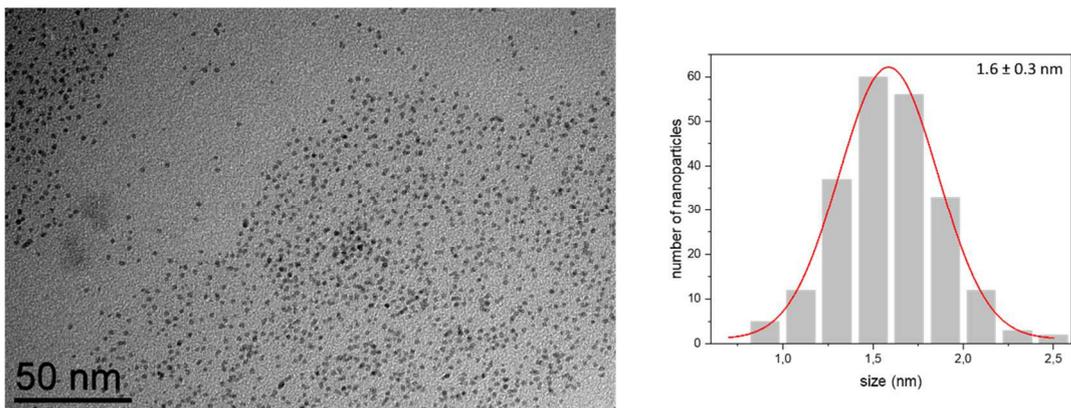


Figure S3. TEM image of Ru/PVP after the hydrogenation of furfural in 1-PrOH at 20 bar of H₂ pressure (scale bar 50 nm) together with the respective size histogram.

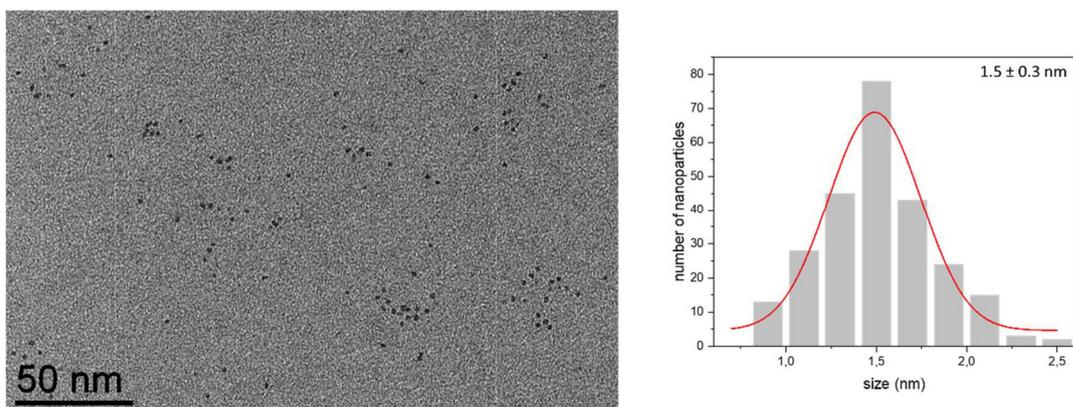


Figure S4. TEM image of Ru/PVP after the hydrogenation of furfural in 1-PrOH at 20 bar of H₂ pressure in the presence of HDA (scale bar 50 nm) together with the respective size histogram.

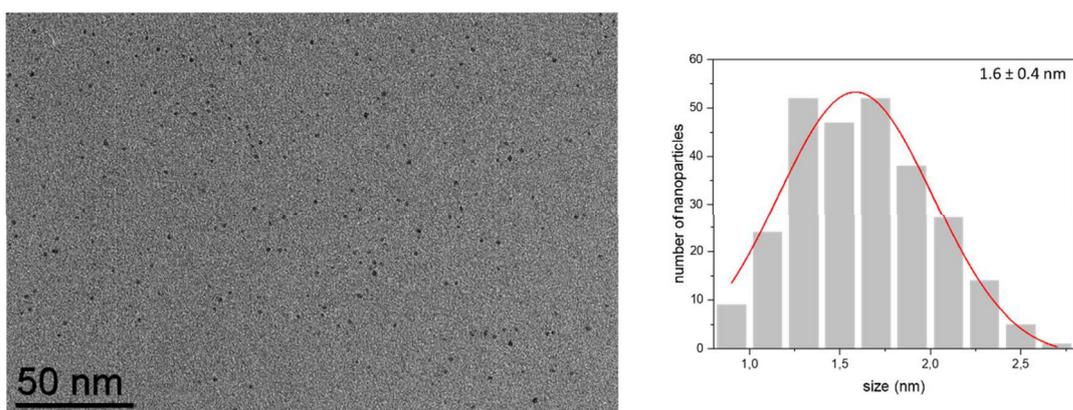


Figure S5. TEM image of Ru/PVP after the hydrogenation of furfural in 1-PrOH at 20 bar of H₂ pressure in the presence of TMP (scale bar 50 nm) together with the respective size histogram.

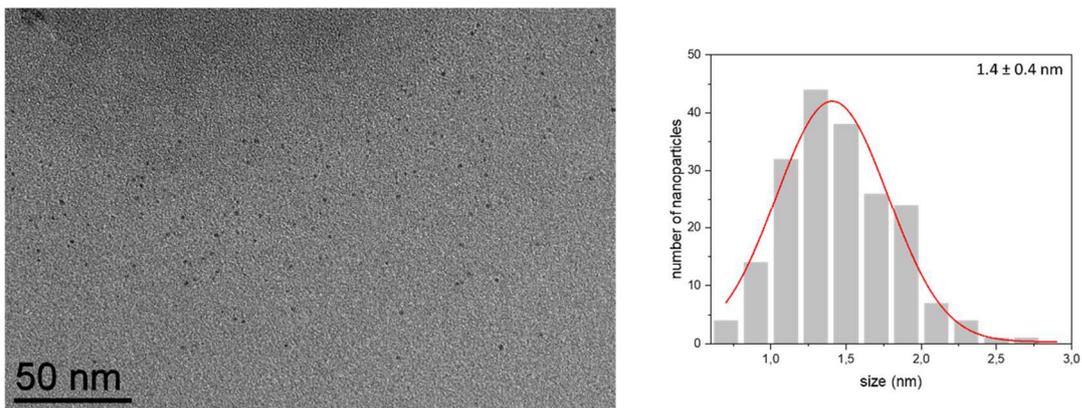


Figure S6. TEM image of Ru/PVP after the hydrogenation of furfural in 1-PrOH at 20 bar of H₂ pressure in the presence of TBA (scale bar 50 nm) together with the respective size histogram.

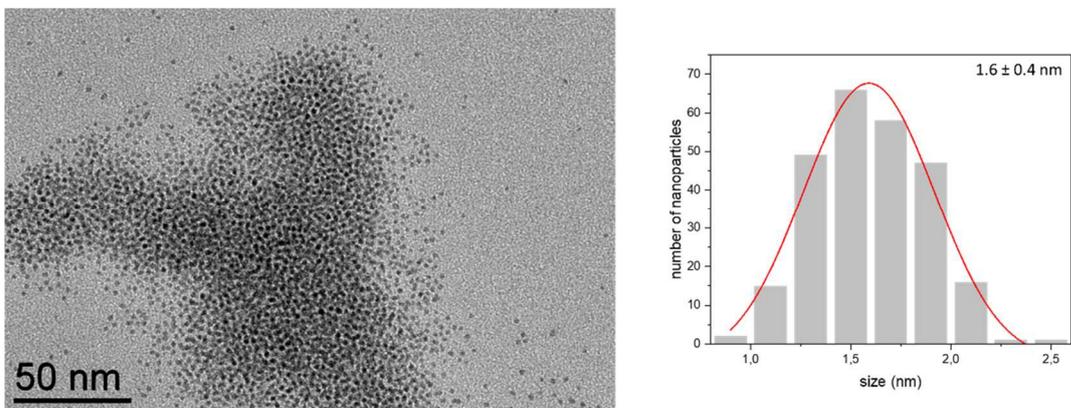


Figure S7. TEM image of Ru/PVP after the hydrogenation of furfural in 1-PrOH at 20 bar of H₂ pressure in the presence of PN (scale bar 50 nm) together with the respective size histogram.

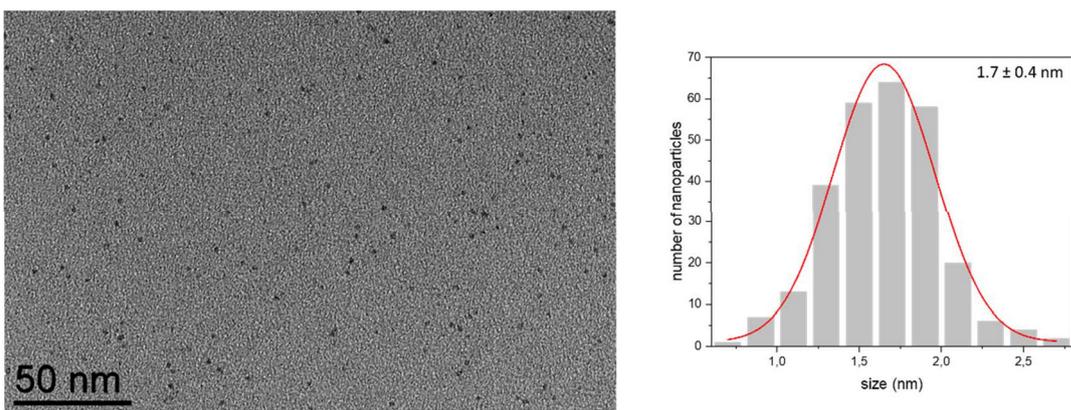


Figure S8. TEM image of Ru/PVP after the hydrogenation of furfural in 1-PrOH at 20 bar of H₂ pressure in the presence of NHC (scale bar 50 nm) together with the respective size histogram.