

# Supplementary Materials

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

Lauriane Bruna, Miquel Cardona-Farreny, Vincent Colliere, Karine Philippot and M. Rosa Axet \*

CNRS, LCC (Laboratoire de Chimie de Coordination), Université de Toulouse, UPS, INPT,  
205 route de Narbonne, CEDEX 04, 31077 Toulouse, France;  
bruna.lauriane98@gmail.com (L.B.);  
miquel.cardona@lcc-toulouse.fr (M.C.-F.); vincent.colliere@lcc-toulouse.fr (V.C.);  
karine.philippot@lcc-toulouse.fr (K.P.)  
\* Correspondence: rosa.axet@lcc-toulouse.fr

### 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 nm<sup>3</sup>.  $R_{NP}$  represents the radius of a NP, determined using TEM images.

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

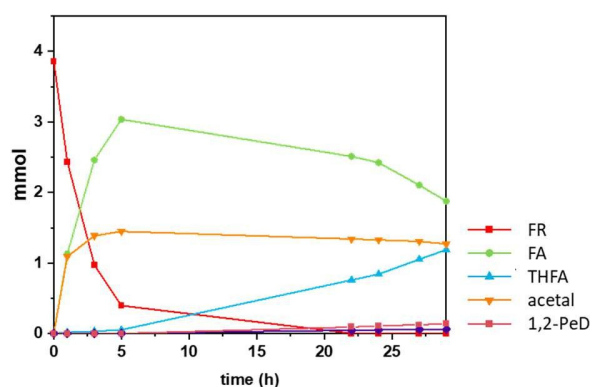
The numbers of metal atoms on the shell  $N_{shell} = N \cdot V_{shell} / 0.0817$ .

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

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

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:  $2 \times 10^{-2}$  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.

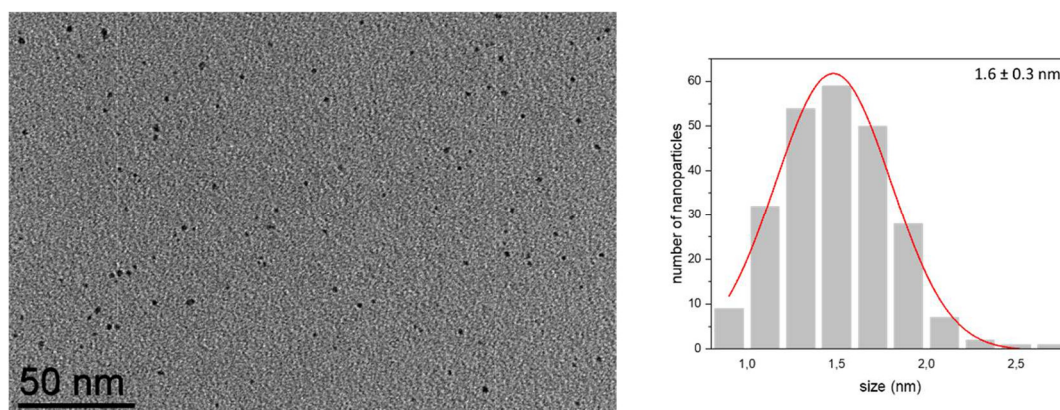
M. Cardona-Farreny, P. Lecante, J. Esvan, C. Dinoi, I. Del Rosal, R. Poteau, K. Philippot, M.R. Axet, Bimetallic RuNi nanoparticles as catalysts for upgrading biomass: metal dilution and solvent effects on selectivity shifts, *Green Chem.*, 23 (2021) 8480-8500.

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

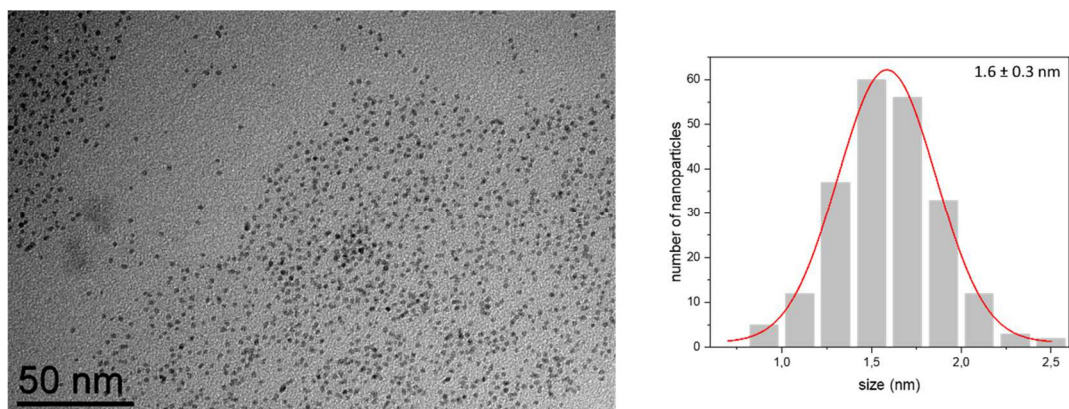
Entry	Catalyst	Size before reaction (nm) <sup>a</sup>	Size after reaction (nm) <sup>a</sup>	Leaching (%) <sup>b</sup>
1	Ru/PVP	1.6 ± 0.3	1.6 ± 0.3	0.8
2	Ru/PVP + HDA		1.5 ± 0.3	1.6
3	Ru/PVP + TMP		1.6 ± 0.4	3.0
4	Ru/PVP + TBA		1.4 ± 0.4	1.3
5	Ru/PVP + PN		1.6 ± 0.4	0.1
6	Ru/PVP + NHC		1.7 ± 0.4	2.9

<sup>a</sup>Mean values of nanoparticle size determined from TEM images by considering at least 200 particles.

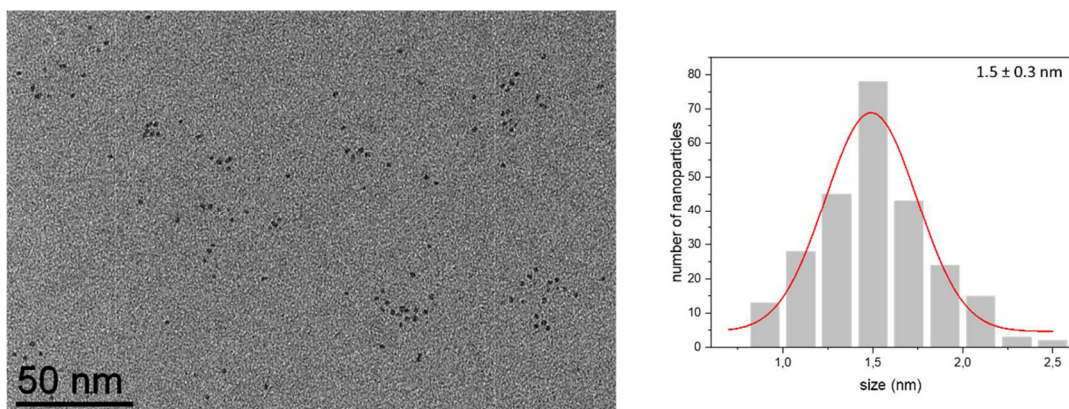
<sup>b</sup>Determined by ICP analysis.



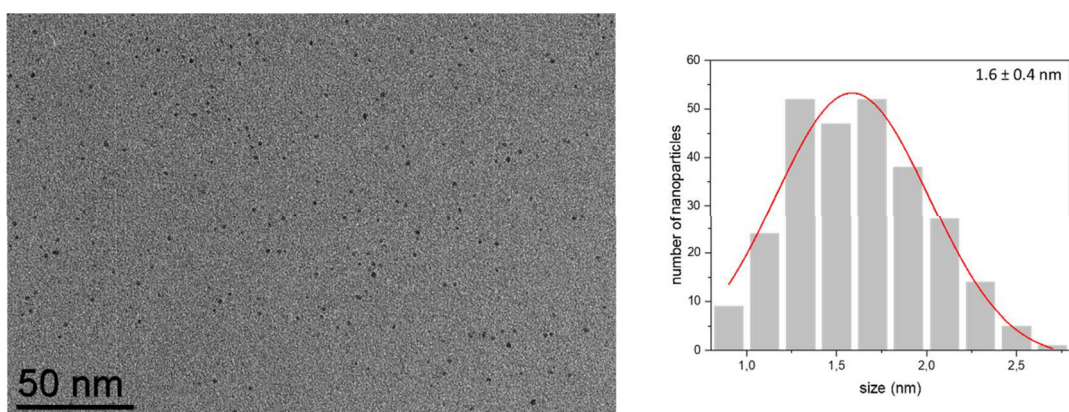
**Figure S2.** TEM image of Ru/PVP (scale bar 50 nm) together with the respective size histogram.



**Figure S3.** TEM image of Ru/PVP after the hydrogenation of furfural in 1-PrOH at 20 bar of H<sub>2</sub> pressure (scale bar 50 nm) together with the respective size histogram.

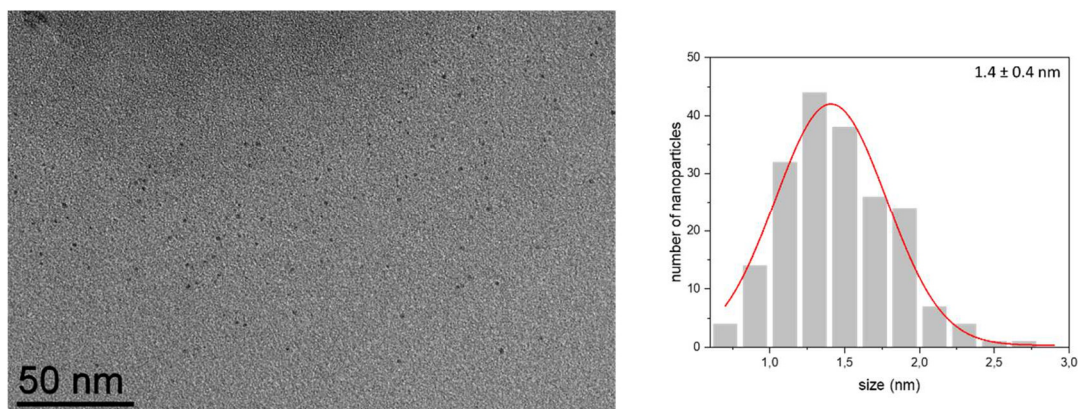


**Figure S4.** TEM image of Ru/PVP after the hydrogenation of furfural in 1-PrOH at 20 bar of H<sub>2</sub> pressure in the presence of HDA (scale bar 50 nm) together with the respective size histogram.

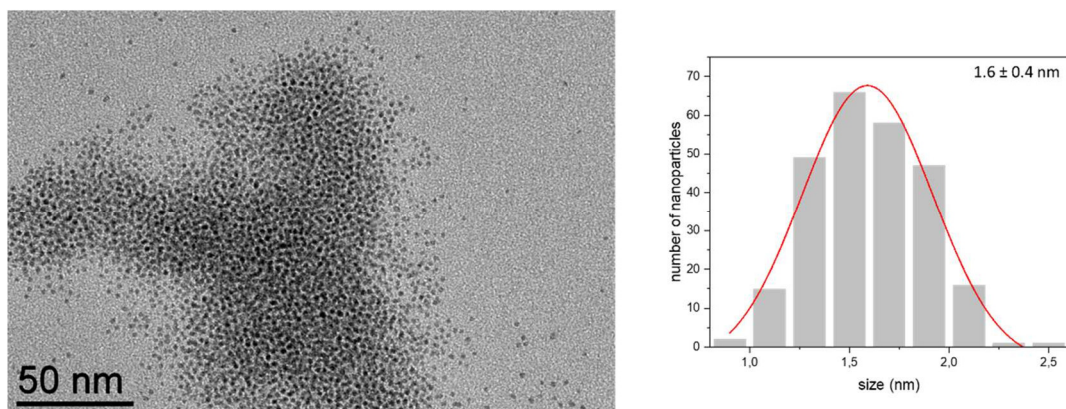


**Figure S5.** TEM image of Ru/PVP after the hydrogenation of furfural in 1-PrOH at 20 bar of H<sub>2</sub> pressure in the presence of TMP (scale bar 50 nm) together with the respective size histogram.

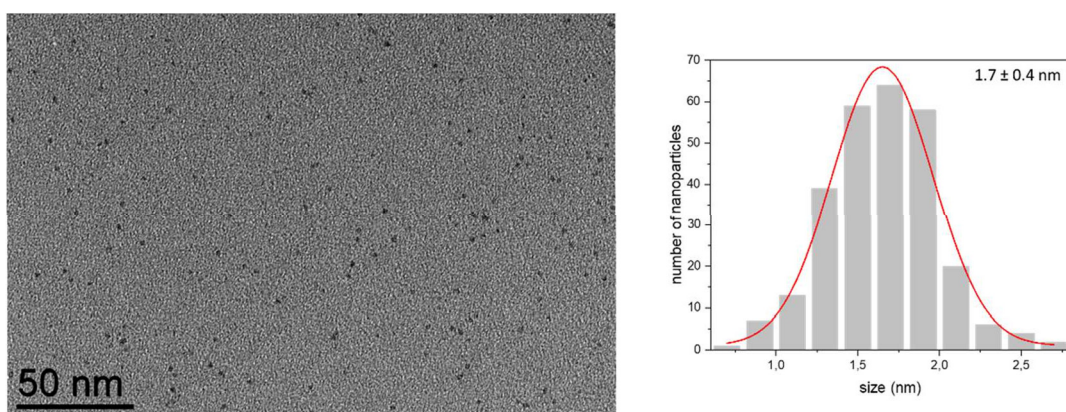




**Figure S6.** TEM image of Ru/PVP after the hydrogenation of furfural in 1-PrOH at 20 bar of H<sub>2</sub> pressure in the presence of TBA (scale bar 50 nm) together with the respective size histogram.



**Figure S7.** TEM image of Ru/PVP after the hydrogenation of furfural in 1-PrOH at 20 bar of H<sub>2</sub> 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 H<sub>2</sub> pressure in the presence of NHC (scale bar 50 nm) together with the respective size histogram.