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pH controlled adsorption of water-soluble ruthenium clusters onto carbon nanotubes and nanofibers surfaces

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Calculus S1: Adsorption of the cluster precursors **$[Ru_3(CO)_9(PTA)_3]$** onto carbon nanofibers.

Crystal parameters that can be found in [1] were used for this calculus. The computer program Mercury was used to assess distances within the crystal lattice. The triangular cluster can be viewed as a sphere of a given diameter. As our purpose is to stick this cluster onto a surface, we simplify this sphere as a 2D square (as the void between the circles cannot in principle be filled).

As we work principally in acidic water, one of PTA ligands is protonated and the maximum diameter seen with Mercury is 13.78 Å. No coordinated solvent is taken into account as it is difficult to know exactly what and how many solvent molecules there will be in a solvatation layer in solution.

Length of square side $a = 13.78 * 10^{-10}\ m$

Surface of the square $S = a^2 = 1.90 *\ 10^{-18}\ m^2$

If we take the LHT, that have a specific surface of $35\ m^2/g$ (see below)

With one g of LHT, we can place $\frac{35\ m^2}{1.90 * 10^{-18}\ m^2} = 1.84 * 10^{19}$ molecules of clusters onto the surface,

which corresponds to $3.06 * 10^{-5}$ mol of cluster.

The MM of $[Ru_3(CO)_9(PTA)_3]$ is $1026.78\ g/mol$,

so it corresponds to 0.0093 g of ruthenium,

which would give a catalyst with 0.92 wt. % of ruthenium.

If we take the LHT-OX, that have a specific area of $26\ m^2/g$ (see below), this would give a catalyst with 0.68 wt. % Ru.

To be certain to avoid the situation where everything is adsorbed at any pH, because of all the interactions that are not of coulombic nature, we choose to be in excess of cluster and engage amounts corresponding to 3 wt. % ruthenium. Like this a 100 % adsorption should never occur and the effect of the pH should be more precisely seen.

Calculus S2: Adsorption of the cluster precursors **[$Ru_5C(CO)_{10}(PTA)_5$]** onto carbon nanofibers.

As a single crystal analysis of [$Ru_5C(CO)_{10}(PTA)_5$] could not be done, data was taken from compound [$Ru_5C(CO)_{13}(PTA)_2$] [2]. Here also this sphere is approximated to a 2D square with a maximum side of 12.14 Å, which is the maximum length between the ligands (with one PTA that is protonated) taken from Mercury. No coordination solvent is taken into account either.

Length of square side $a = 12.14 * 10^{-10}\ m$

Surface of the square $S = a^2 = 1.47 * 10^{-18}\ m^2$

If we take the LHT, that have a specific surface of $35\ m^2/g$ (see below)

with one g of LHT, we can place $\frac{35\ m^2}{1.47 * 10^{-18}\ m^2} = 2.37 * 10^{19}$ molecules of clusters onto the surface,

which corresponds to $3.94 * 10^{-5}$ mol of cluster.

The MM of [$Ru_5C(CO)_{10}(PTA)_5$] is $1583.21\ g/mol$,

so it corresponds to 0.0200 g of ruthenium,

which would give a catalyst with 1.95 wt. % of ruthenium.

If we take the LHT-OX, that have a specific area of $26\ m^2/g$ (see below), this would give a catalyst with 1.46 wt. % Ru.

In order to be in a situation where the cluster is in excess, we choose to test the impregnation with 5 wt. % of ruthenium. Here also, a 100 % adsorption should never occur and the effect of the pH should be more precisely seen.

Calculus S3: Estimation of the number of ruthenium atoms comprised in a single nanoparticle

The calculus is greatly inspired by [3], where authors also estimated the number of ruthenium atoms inside a particle. Detailed data can be found in the Electronic Supplementary Information of this publication.

In the case of catalyst Ru5P/LHT activated at 350 °C, we observed small nanoparticles of 2 nm with a very narrow particle size distribution. Hence the following considerations to estimate the number of Ru atoms in each NP can be made.

The average diameter of a particle is approximately 2 nm, as seen by TEM.

The radius of 1 Ru nanoparticle: r_{particle} = 1 nm.

The volume of 1 Ru nanoparticle: $V_{\text{particle}} = \frac{4}{3}\ x\ \frac{22}{7}\ x\ (1)^3\ nm^3 = 4{,}19\ nm^3$.

It is safe to assume that there is also free space inside the particle. However this free space will not be taken into account here as we wish only to have an estimation of the number of ruthenium atoms. So we suppose here that the particle is composed only of ruthenium and that there is no free space.

We know that the atomic radius of 1 Ru atom: r_{atom} = 0.134 nm (from [3]).

The volume of 1 Ru atom: $V_{\text{atom}} = \frac{4}{3}\ x\ \frac{22}{7}\ x\ (0{,}134)^3\ nm^3 = 0{,}01\ nm^3$.

The number of Ru atom in a Ru particle: number $= \frac{4{,}19\ nm^3}{0{,}01\ nm^3} = 419\ atoms\ of\ Ru.$

We can therefore conclude that there are approximatively 400 atoms of ruthenium in each of the particles of catalyst Ru5P/LHT.

Table S1: Physisorption data of the nanocarbons used.

Carbon	S_{BET} (m²/g)	V_{pore} (cm³/g)	D_{pore} (nm)
LHT	35	0.18	26
LHT-OX	26	0.08	13
PS-OX	43	0.19	26
CNT	305	1.45	17

Table S2: Catalytic results in the hydrogenation of lactose after 1 h.

Sample	Ru (wt.%)	$X_{Lactose}$ (%)	Y_{LAH} (%)	S_{LAH} (%)	TOF[a] (s^{-1})
Blank	NA	23.7	0	0	NA
LHT-OX	NA	22.6	0	0	NA
Ru5/LHT	2.15	33.9	13.4	39.5	0.0066
Ru5/LHT-OX	1.79	37.1	7.9	21.2	0.0087
Ru5/LHT-OX[b]	1.79	26.9	8.1	30.0	0.0064

[a] $TOF = \frac{mol\ \ lactose\ converted}{mol\ Ru\ x\ time\ (s)}$

[b] Recyclability test

Figure S1: PZC determination of the CNT by mass titration (▲ pHi = 4.6 and ○ pHi = 10.4).

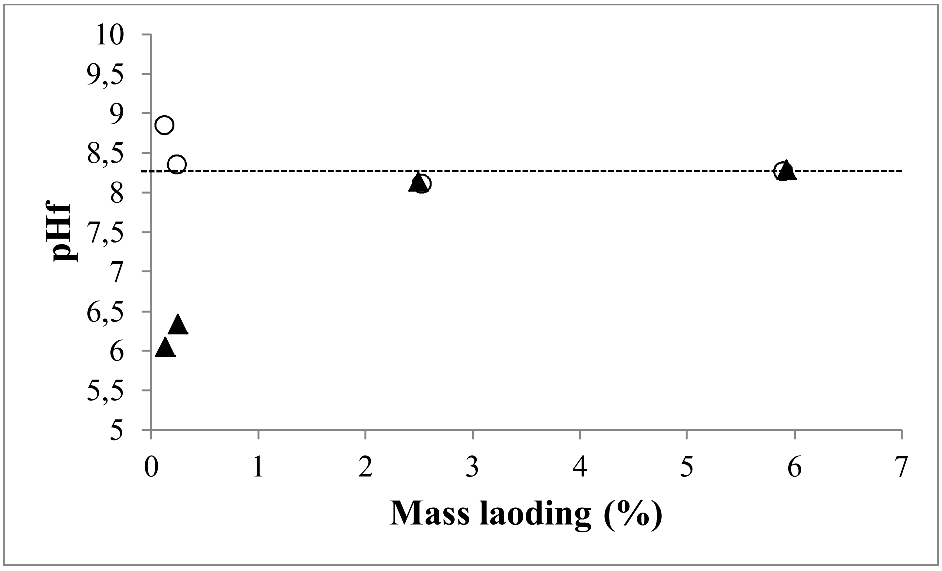


Figure S2: PZC determination of the LHT-OX by mass titration (▲ pHi = 5.1 and ○ pHi = 10.9).

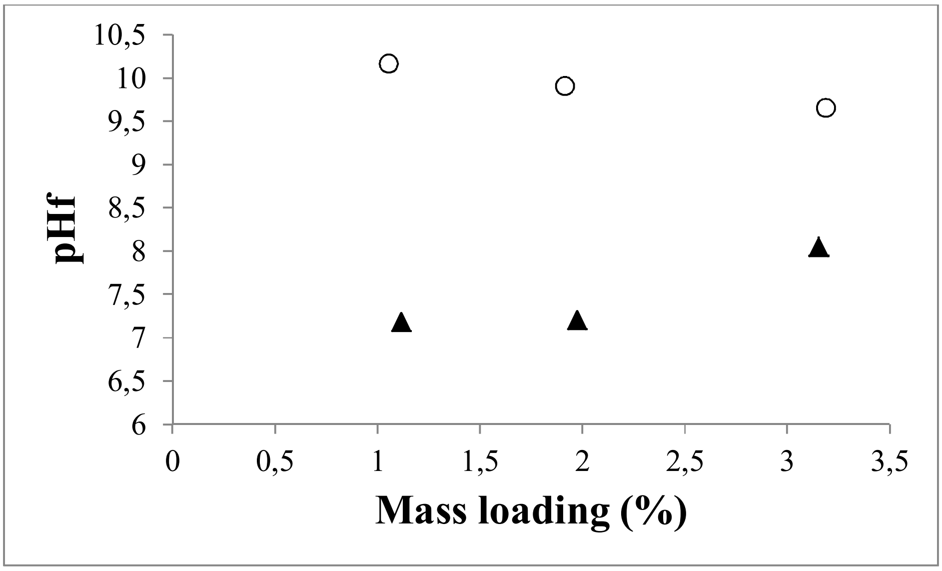


Figure S3: XPS C_{1s} photopeak and its decomposition for carbons LHT (upper left), LHT-OX (upper right), PS-OX (bottom left) and CNT (bottom right).

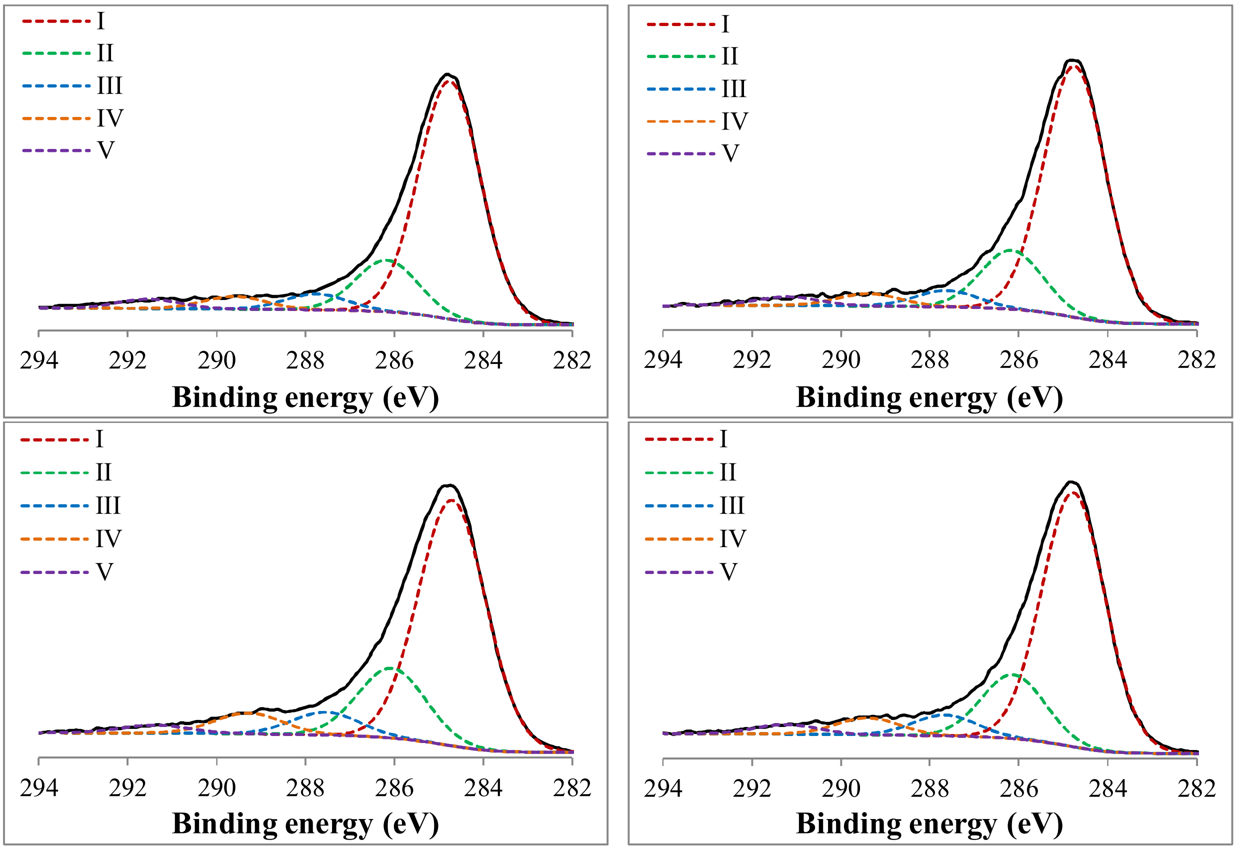


Figure S4: XPS O_{1s} photopeak for carbons LHT (upper left), LHT-OX (upper right), PS-OX (bottom left) and CNT (bottom right).

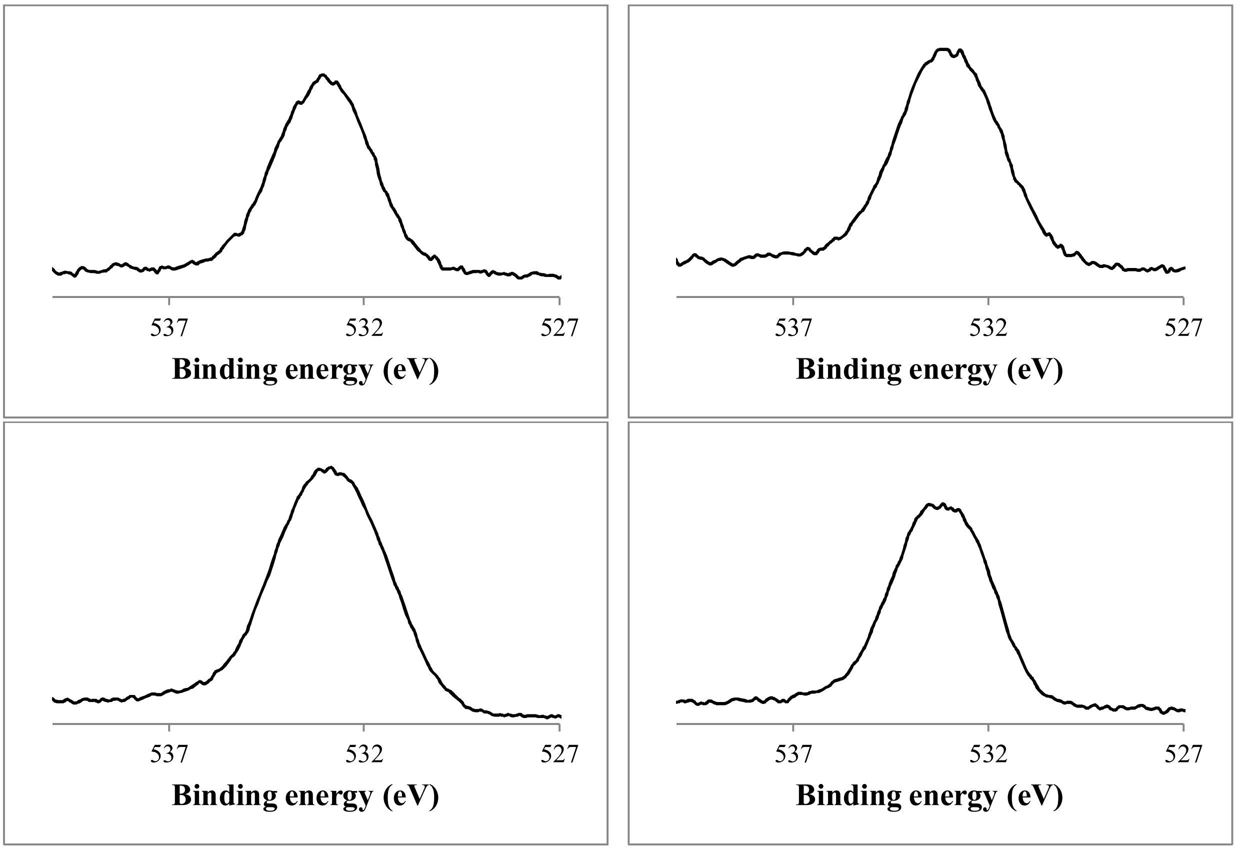


Figure S5: XPS N_{1s} photopeak for carbons LHT (upper left), LHT-OX (upper right), PS-OX (bottom left) and CNT (bottom right).

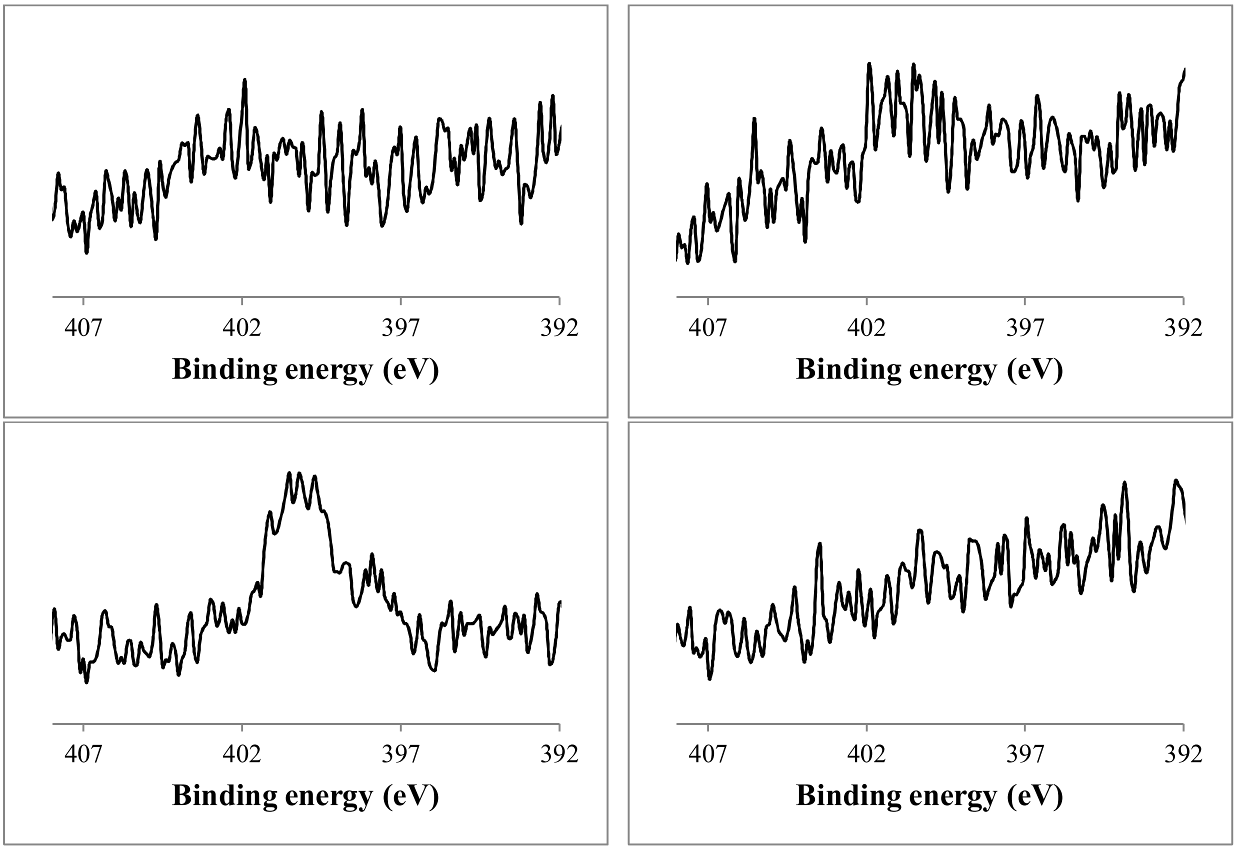


Figure S6: Titration of a solution of $[Ru_5C(CO)_{10}(PTA)_5]$ with NaOH, when HCl is present.

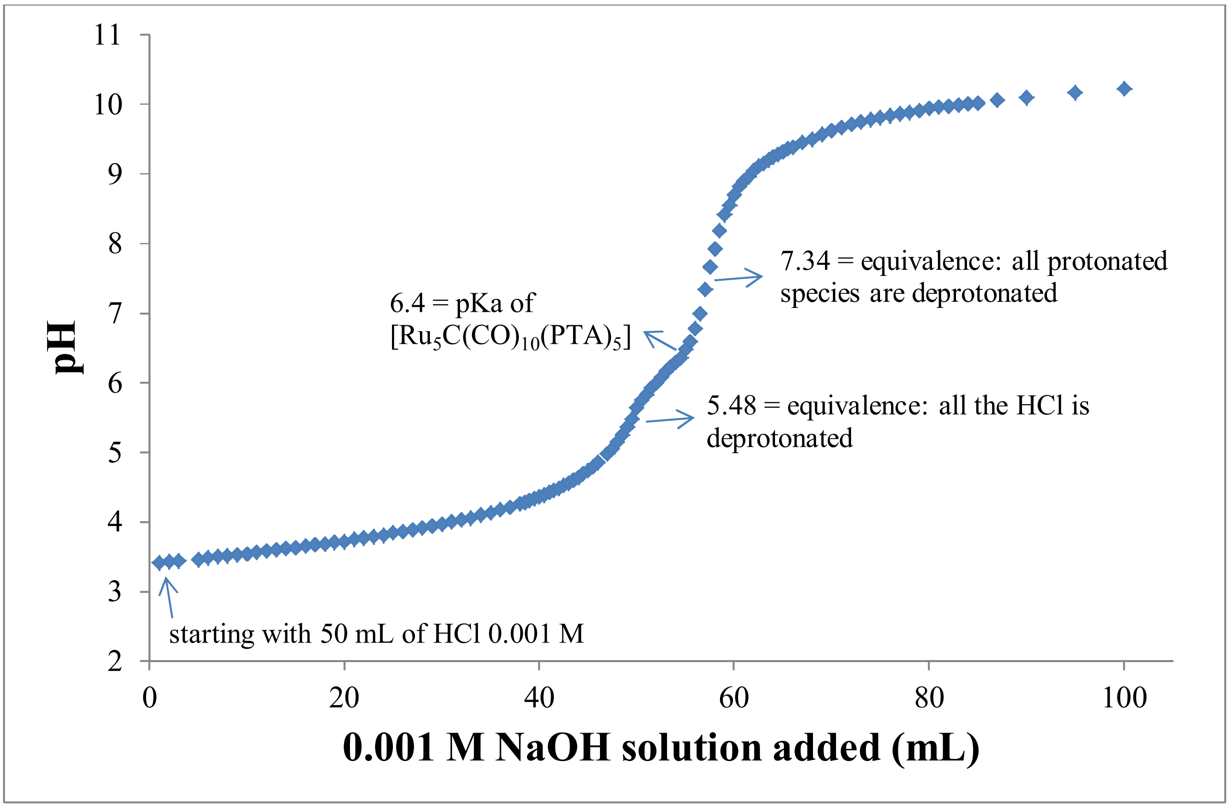


Figure S7: Titration of a solution of [$Ru_5C(CO)_{10}(PTA)_5$] with NaOH.

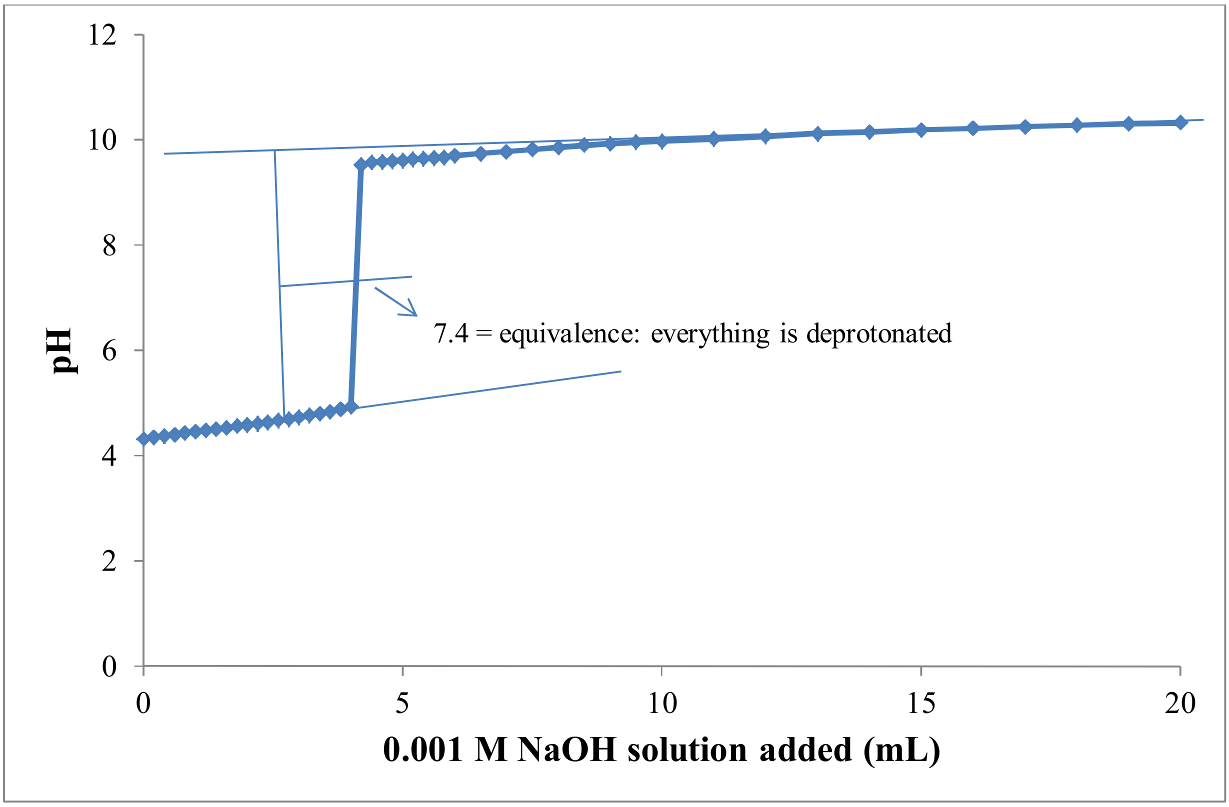


Figure S8: ^{1}H NMR monitoring of the reaction between [$Ru_5C(CO)_{10}(PTA)_5$] and benzene in D_2O – benzene alone (blue), after 4 h (green), after 24 h (red).

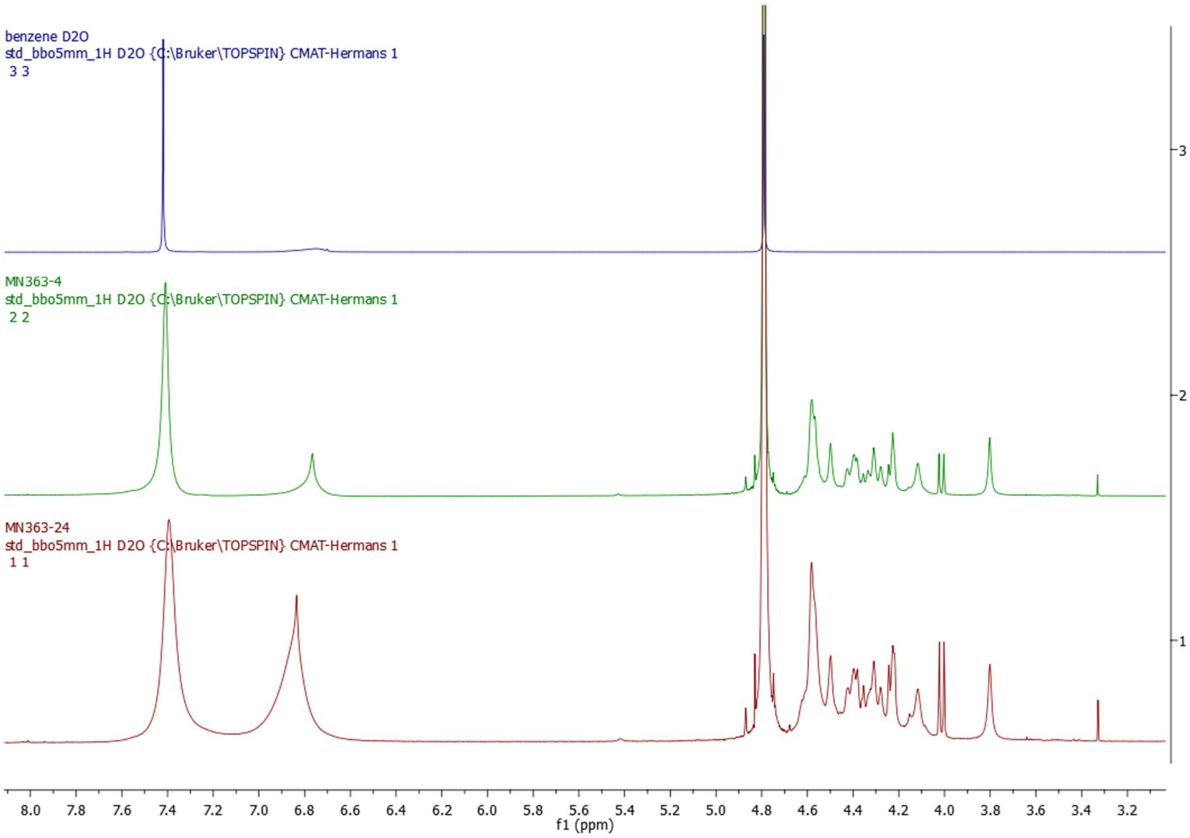


Figure S9: Mass spectrum of (a) intact cluster [$Ru_5C(CO)_{10}(PTA)_5$] (above) and of the reaction between [$Ru_5C(CO)_{10}(PTA)_5$] and benzene (below).

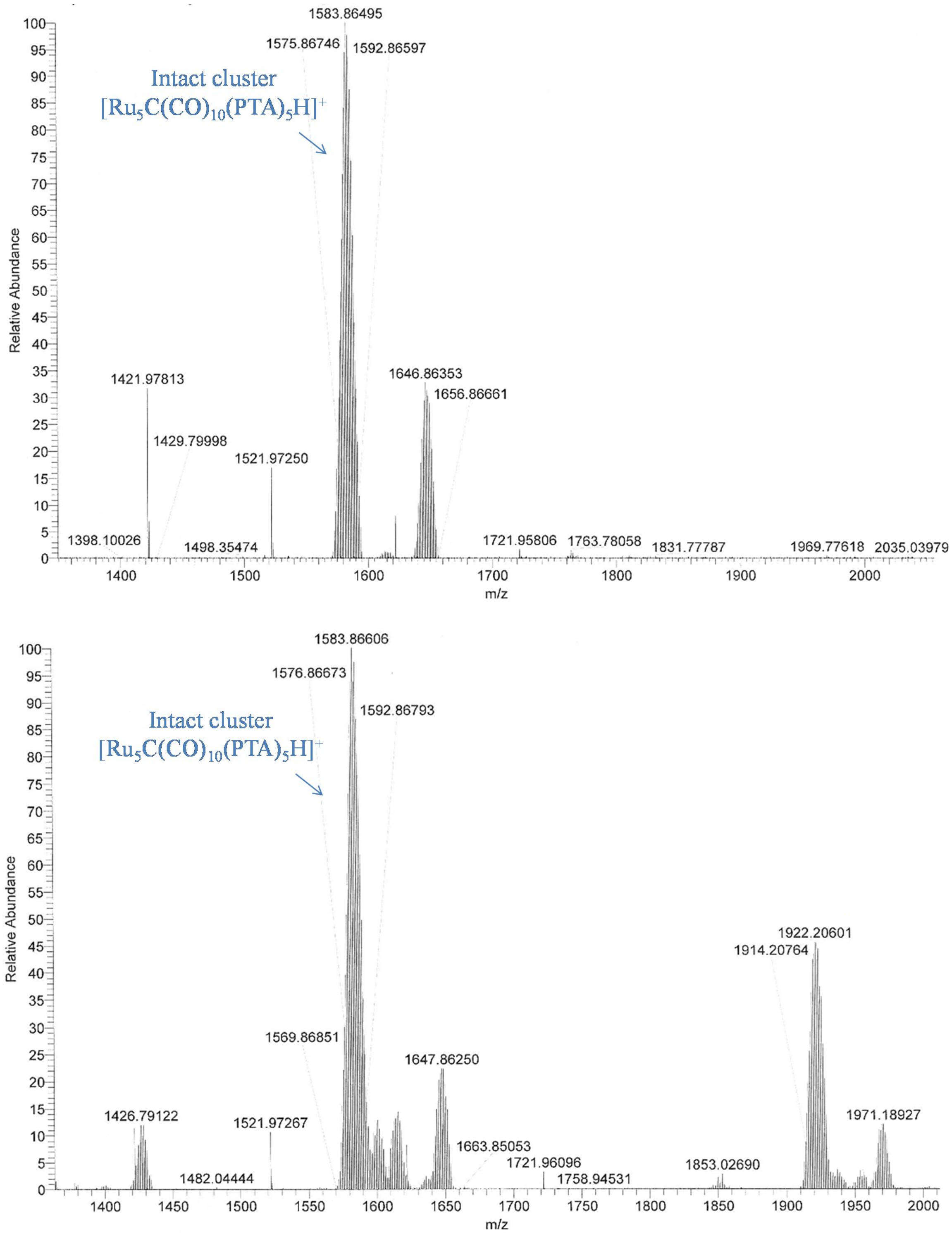


Figure S10: TGA analysis of [$Ru_5C(CO)_{10}(PTA)_5$].

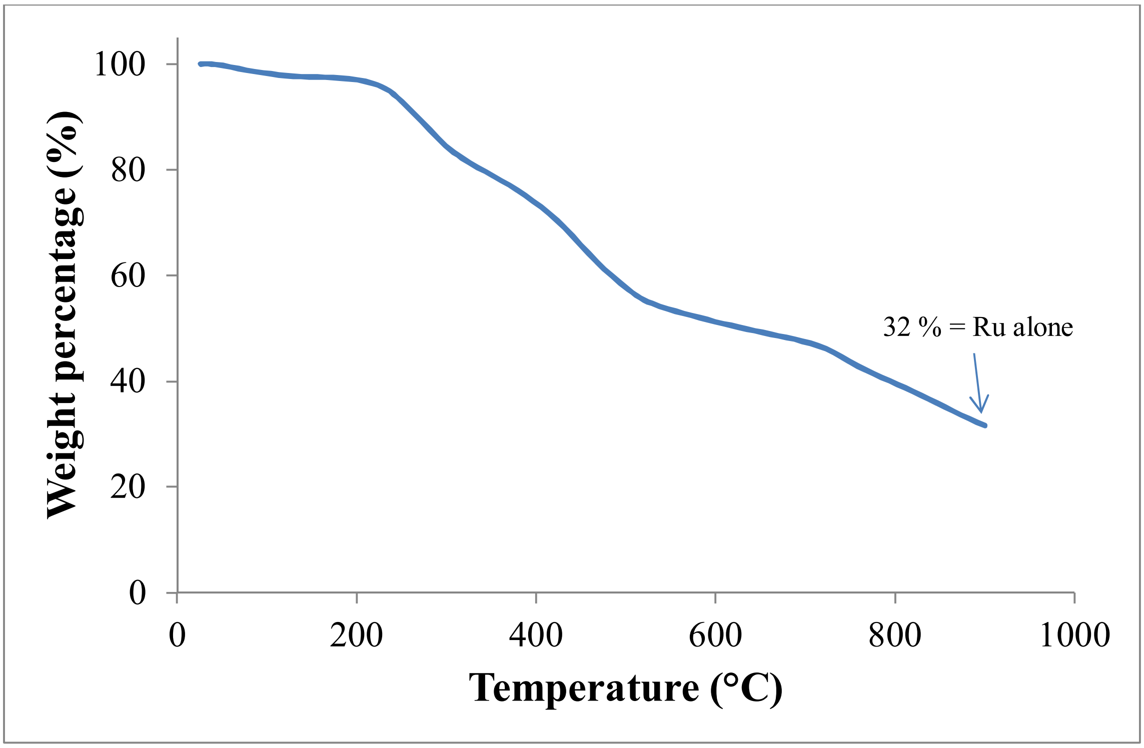


Figure S11: TGA analysis of [$Ru_3(CO)_9(PTA)_3$].

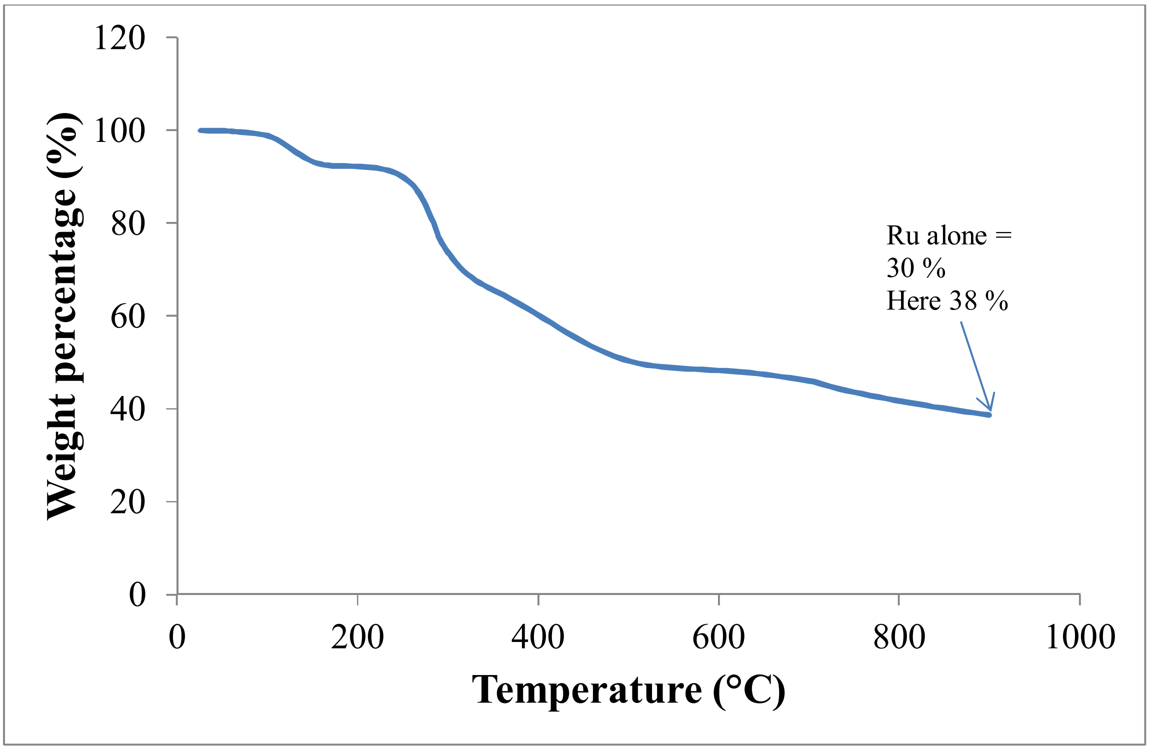


Figure S12: Nanoparticle size distribution of sample Ru5P/CNT activated at 900 °C.

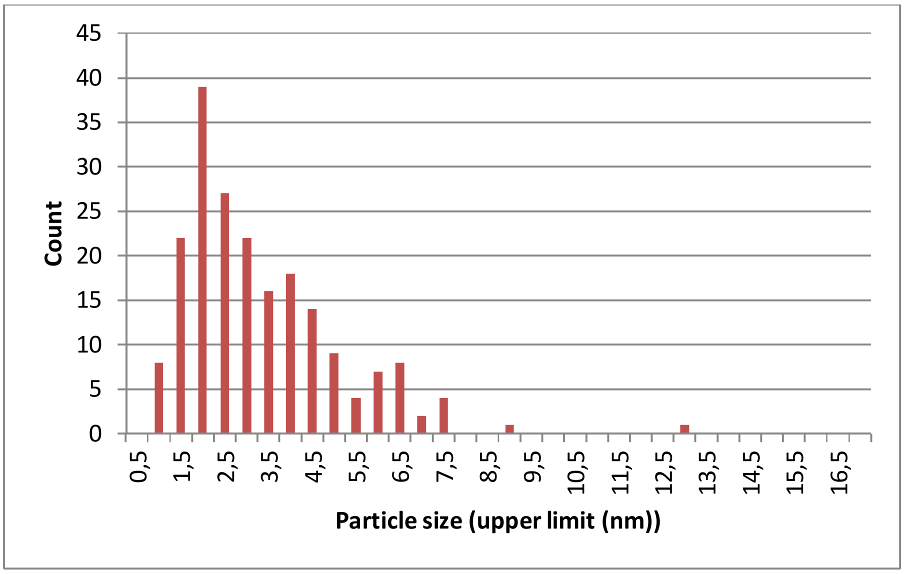


Figure S13: Additional TEM image of sample Ru5P/LHT, where nanoparticles are clearly abundant on wrinkled portions of the fibers.

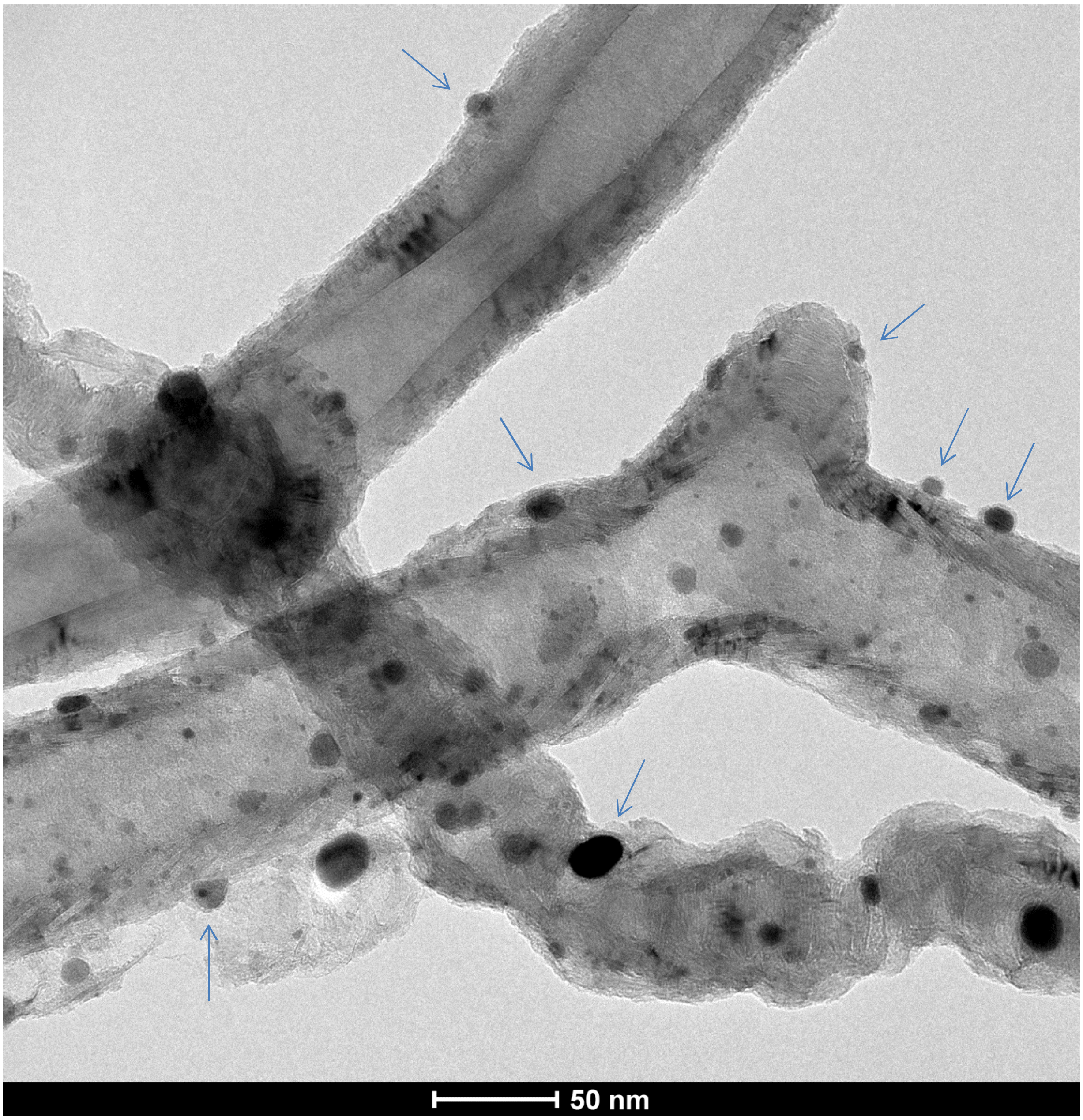


Figure S14: Additional TEM image of sample Ru5P/CNT that displays walls aligned in parallel to the axis of the tube.

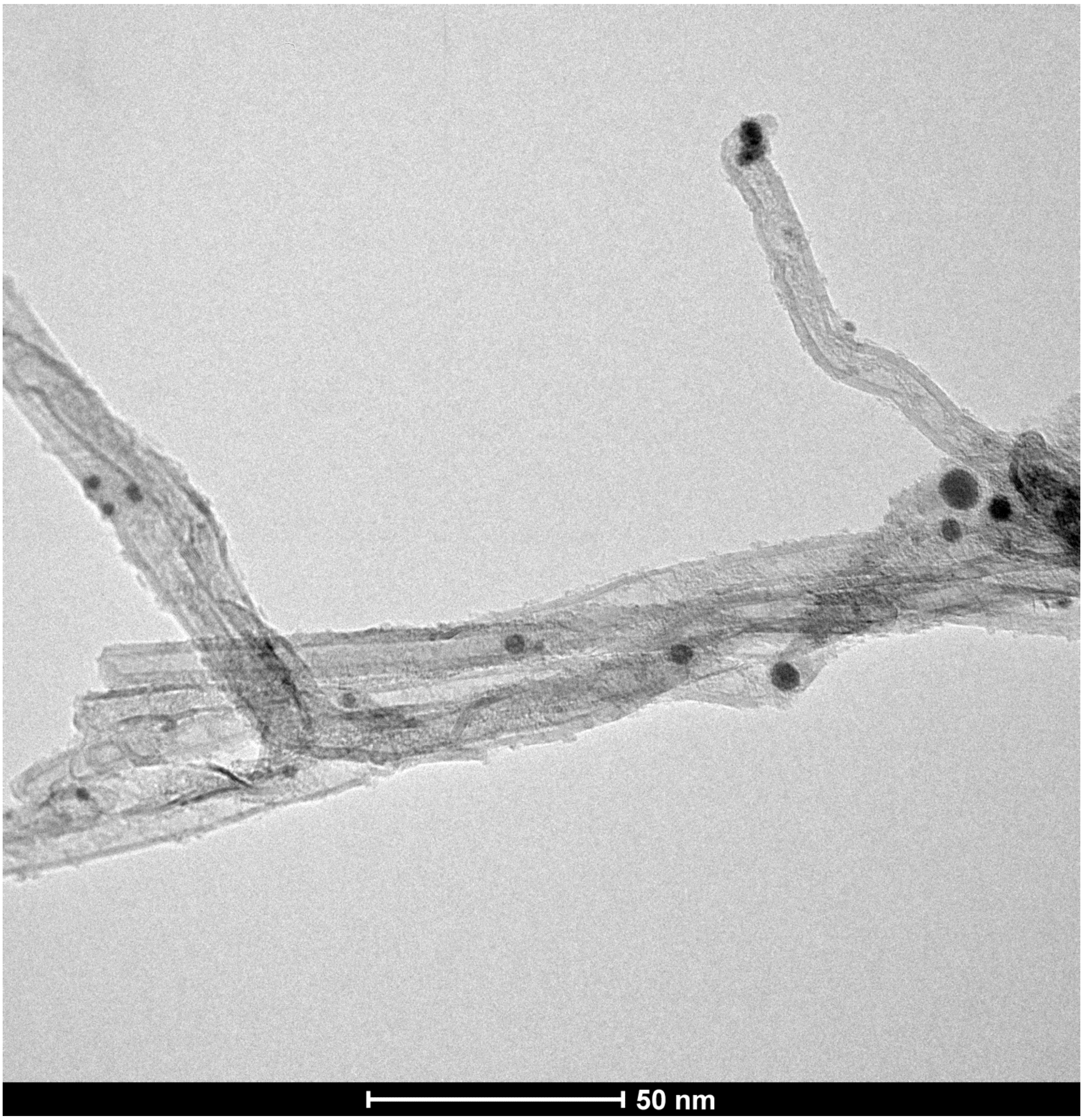


Figure S15: Lactose hydrogenation reaction showing all the by-products that can be formed.

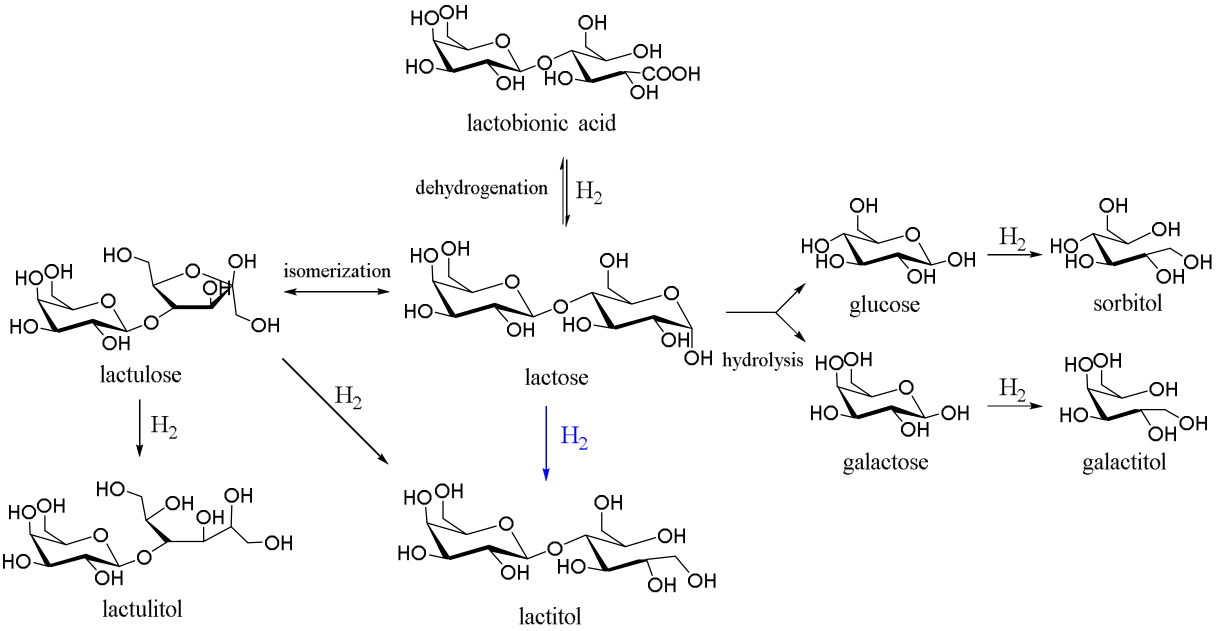


Figure S16: Lactose conversion in function of the time for the 2 tested catalysts.

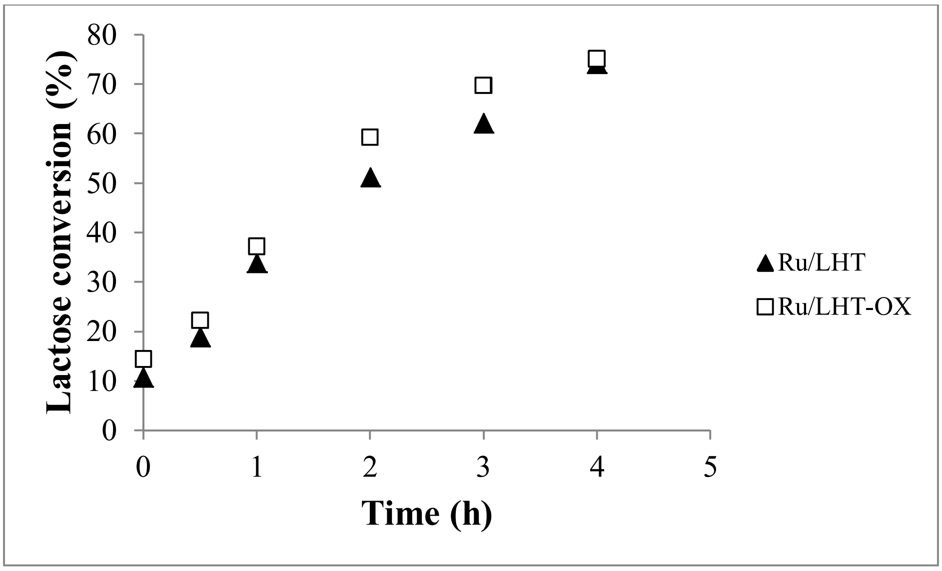


Figure S17: Lactitol selectivity in function of the time for the 2 tested catalysts.

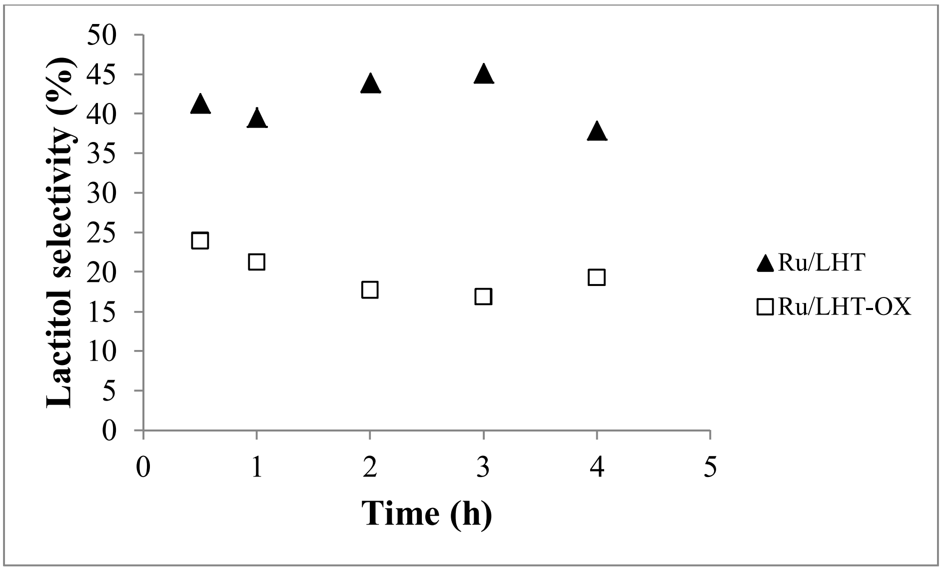


Figure S18: Lactitol yield in function of the time for the 2 tested catalysts.

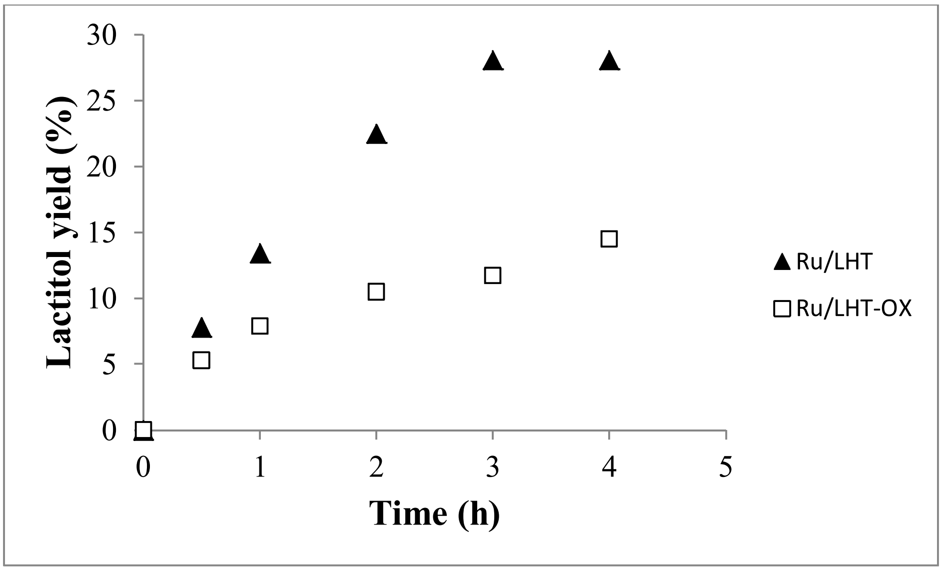


Figure S19: Lactulose yield in function of the time for the 2 tested catalysts.

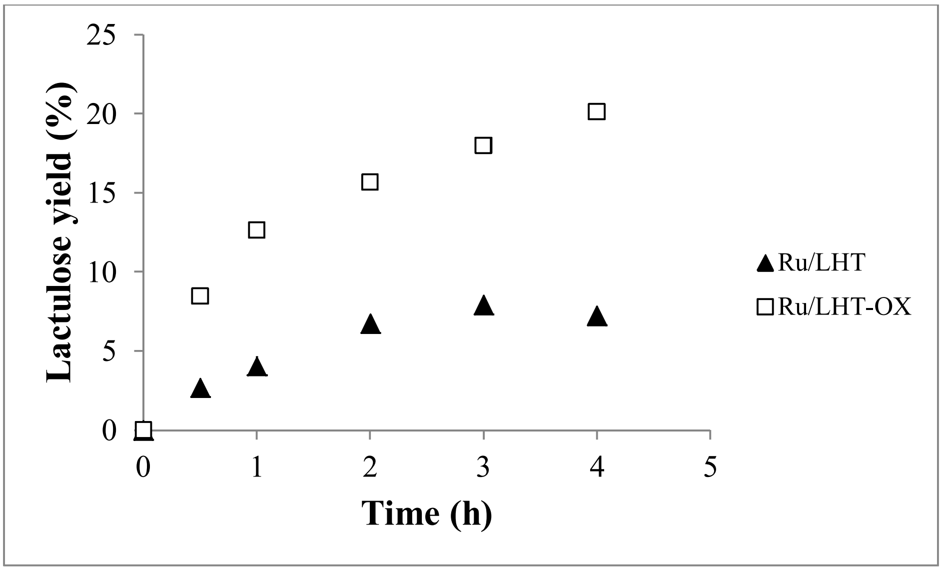
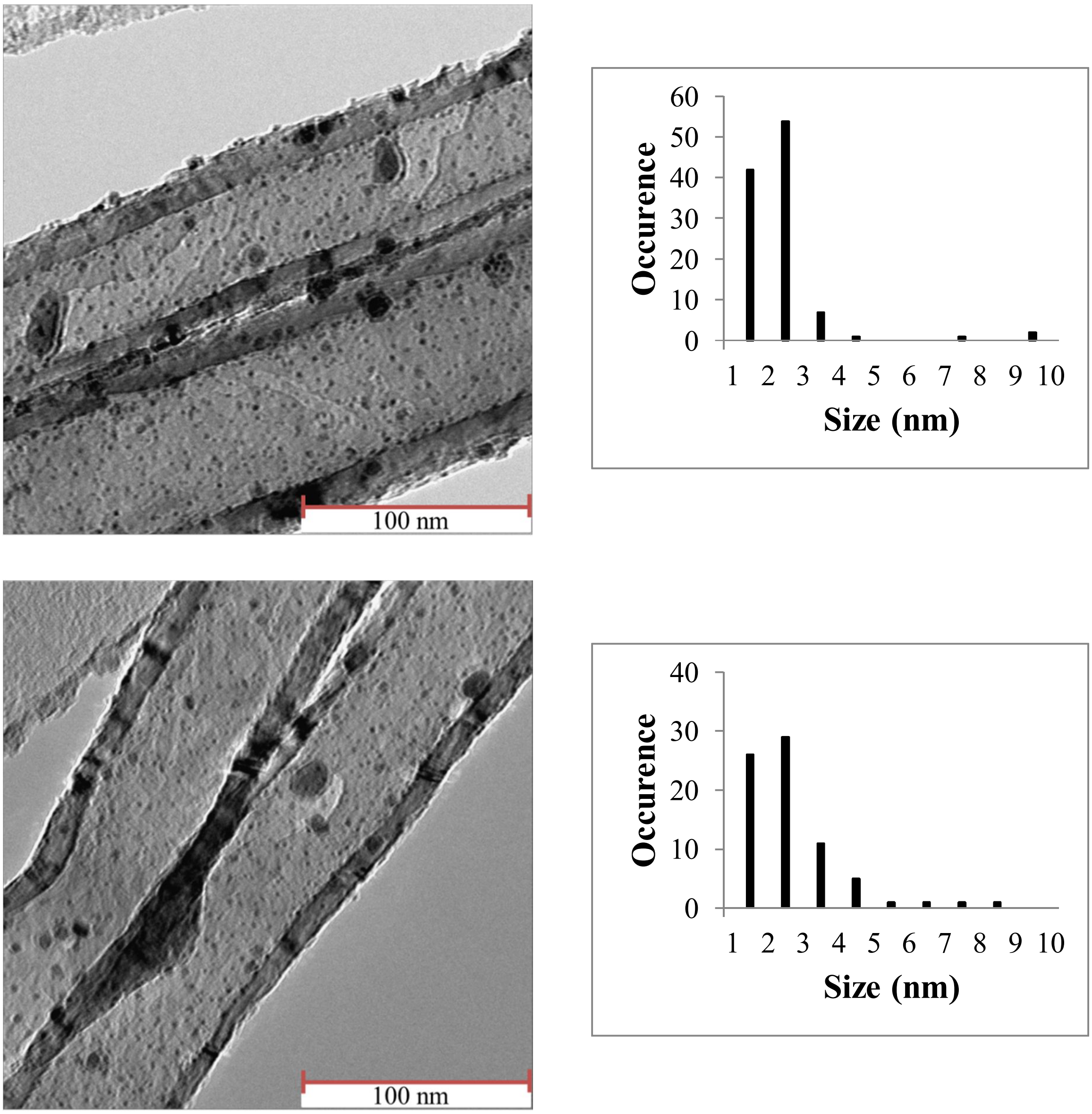


Figure S20: TEM images of the catalysts used in the hydrogenation tests prepared with $[Ru_5C(CO)_{10}(PTA)_5]$ onto LHT (above) and LHT-OX (below) with their particle size distribution.



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[2] N. Mager, K. Robeyns, S. Hermans, J. Organomet. Chem. 794 (2015) 48–58.

[3] S. Agarwal, N.J. Ganguli, RSC Adv. 4 (2014) 11893–11898.