

Supporting Information

Rh nanoparticles confined in triphenylphosphine oxide-functionalized core-crosslinked micelles with a polyanionic shell: synthesis, characterization, and application in aqueous biphasic hydrogenation

Chantal J. Abou-Fayssal,^{a,b} Leonhard Schill,^b Rinaldo Poli,^{*b,c} Anders Riisager,^{*a} Eric Manoury^{*b}, Karine Philippot^{*b}

^a *Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Technical University of Denmark, Kemitorvet, Building 207, 2800 Kgs. Lyngby, Denmark.*

^b *CNRS, LCC (Laboratoire de Chimie de Coordination), Université de Toulouse, UPS, INPT, 205 route de Narbonne, BP 44099, F-31077 Toulouse Cedex 4, France.*

^c *Institut Universitaire de France, 1, rue Descartes, 75231 Paris Cedex 05, France.*

Calculation of catalyst activity

The catalyst activity is expressed as turnover frequency (TOF) and calculated as mole of substrate converted per mole of Rh in the catalyst per hour (assuming all Rh atoms are active). The corrected TOF (cTOF) is based on the surface Rh atoms, as calculated from Eq. 1-5.

The moles of surface Rh atoms ($n_{Rh, surface}$) were obtained considering spherical NPs having a closed-packed structure (fcc), the radius of the sphere being the average measured from the TEM images, and a Rh atom diameter (D_{Rh}) of 0.27 nm.

$$N_{Rh, surface} = \frac{N_{Rh, shell}}{N_{Rh, total}} = \frac{(N_{calc} \times V_{Rh, shell})/V_{Rh, cell}}{(N_{calc} \times V_{Rh, total})/V_{Rh, cell}} = \frac{V_{Rh, shell}}{V_{Rh, total}} = \frac{V_{Rh, total} - V_{Rh, cc}}{V_{Rh, total}} \quad (1)$$

$$V_{Rh, total} = \frac{4}{3}\pi R_{RhNP}^3 \quad (2)$$

$$V_{Rh, core} = \frac{4}{3}\pi (R_{RhNP} - D_{Rh})^3 \quad (3)$$

$$n_{Rh, surface} = 0.44 \times n_{Rh, total} \quad (4)$$

$$cTOF = \frac{n_{substrate\ converted}}{n_{Rh, surface} \times time} \quad (5)$$

Supplementary Figures

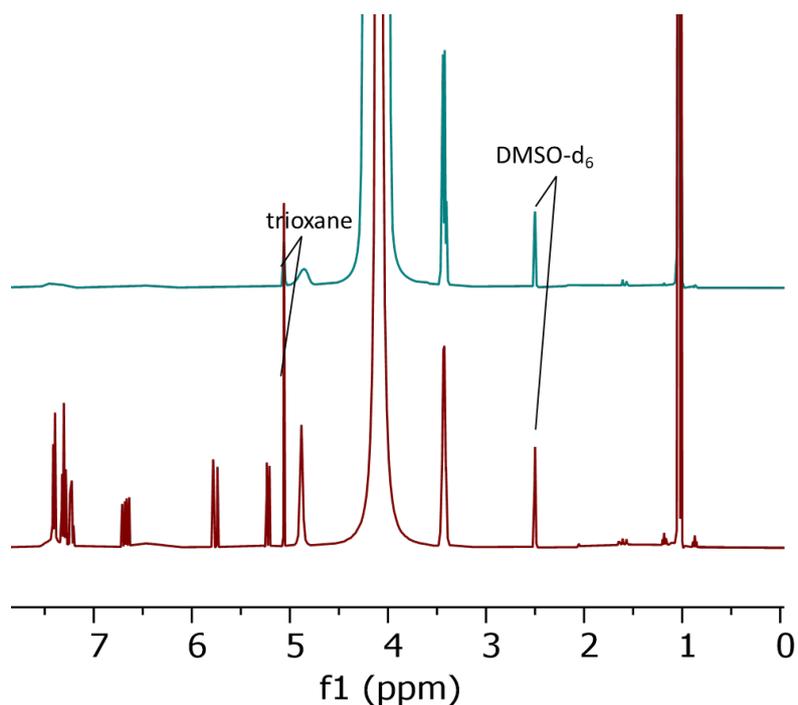


Figure S1. ¹H NMR spectrum recorded during the formation of R₀-(SS⁻Na⁺)₁₄₀-*b*-St₅₀-*b*-(St_{0.9}-*co*-SDPPO_{0.1})₃₀₀-SC(S)SnPr (TPPO@CCM-A) at t = 0 (red) and t = 4.5 h (blue) by diluting an aliquot of the reaction mixture in DMSO-d₆.

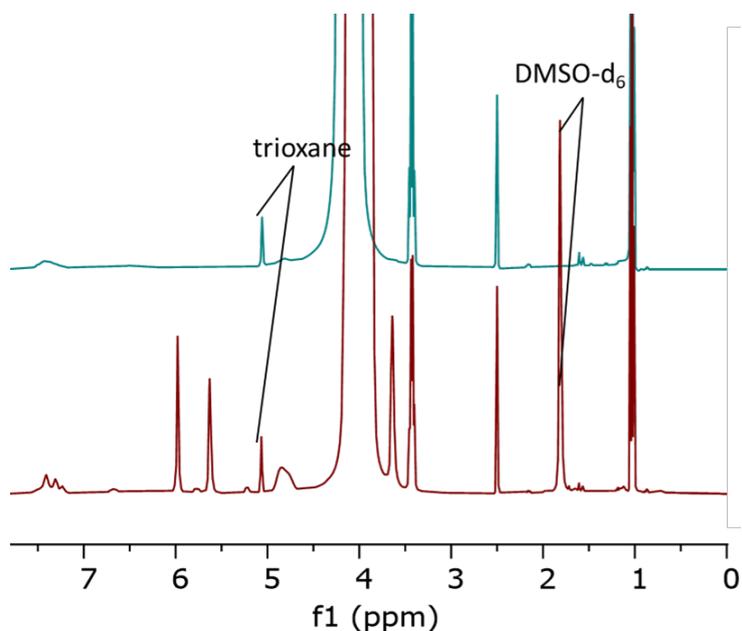


Figure S2. ¹H NMR spectrum recorded during the formation R₀-(SS⁻Na⁺)₁₄₀-*b*-St₅₀-*b*-(St_{0.9}-*co*-SDPPO_{0.1})₃₀₀-*b*-(St_{0.9}-*co*-DEGDMA_{0.1})₁₅₀-SC(S)SnPr at t = 0 (red) and t = 4.5 h (blue) by diluting an aliquot of the reaction mixture in DMSO-d₆.

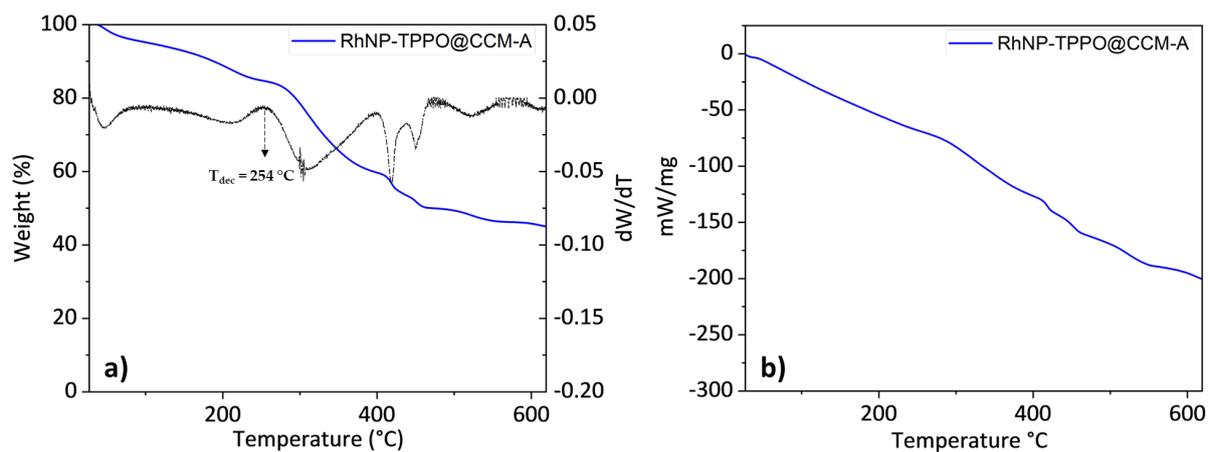


Figure S3. (a) TGA and (b) DSC profiles of RhNP-TPPO@CCM-A.

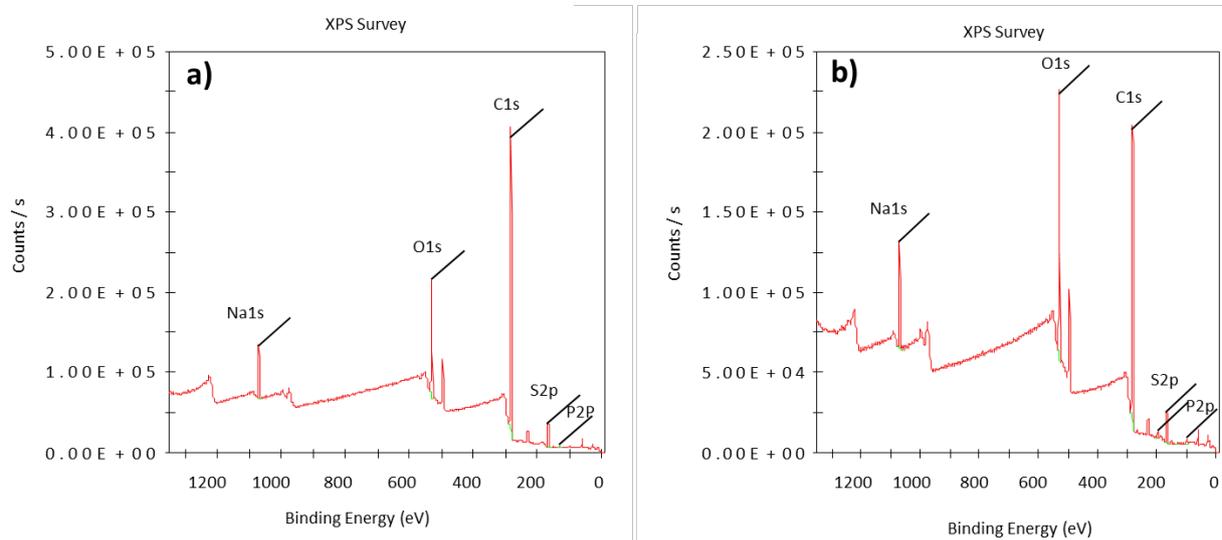


Figure S4. XPS survey spectra of a) TPPO@CCM-A and b) RhNP-TPPO@CCM-A.

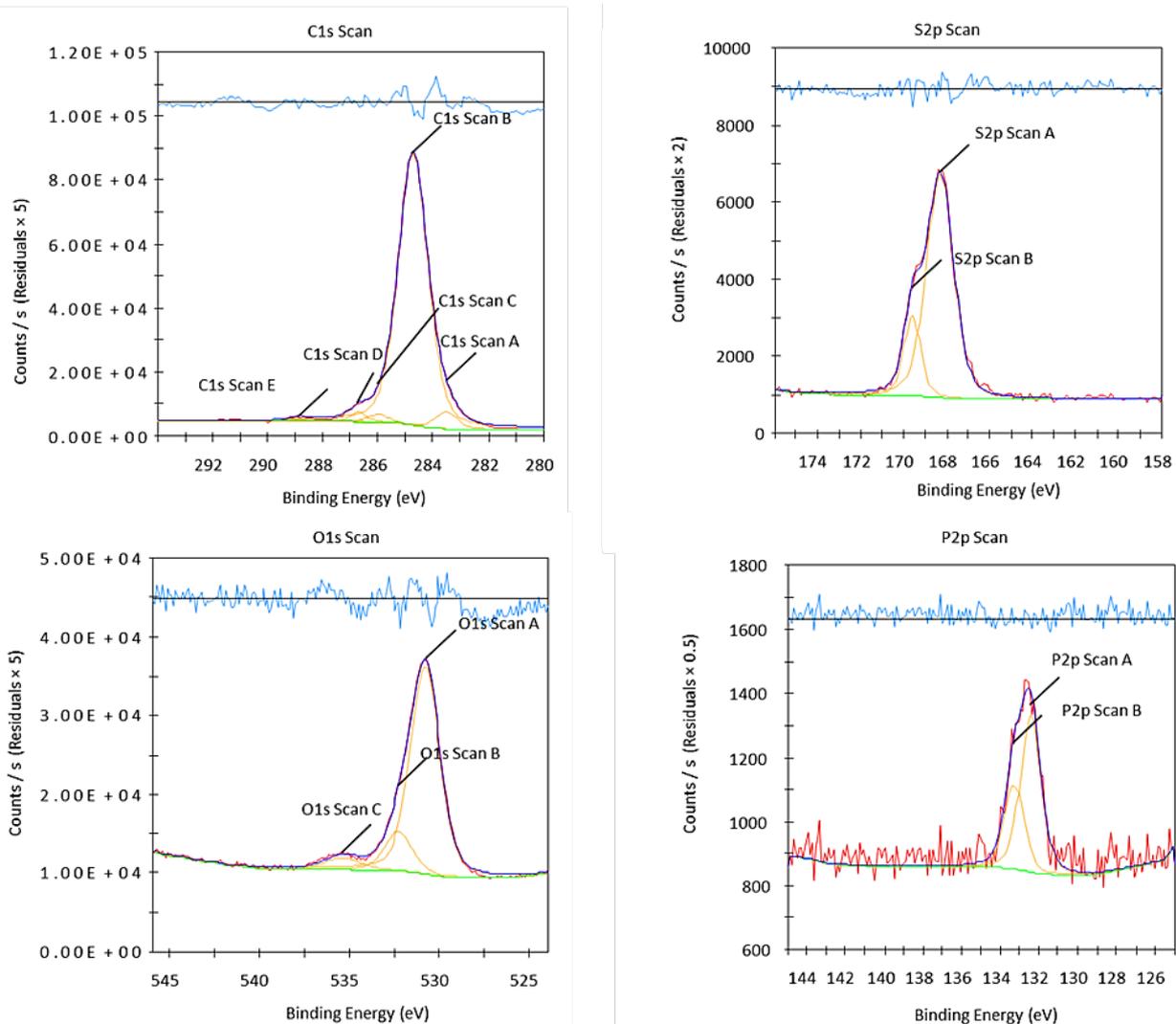


Figure S5. High-resolution XPS scan spectra of TPPO@CCM-A.

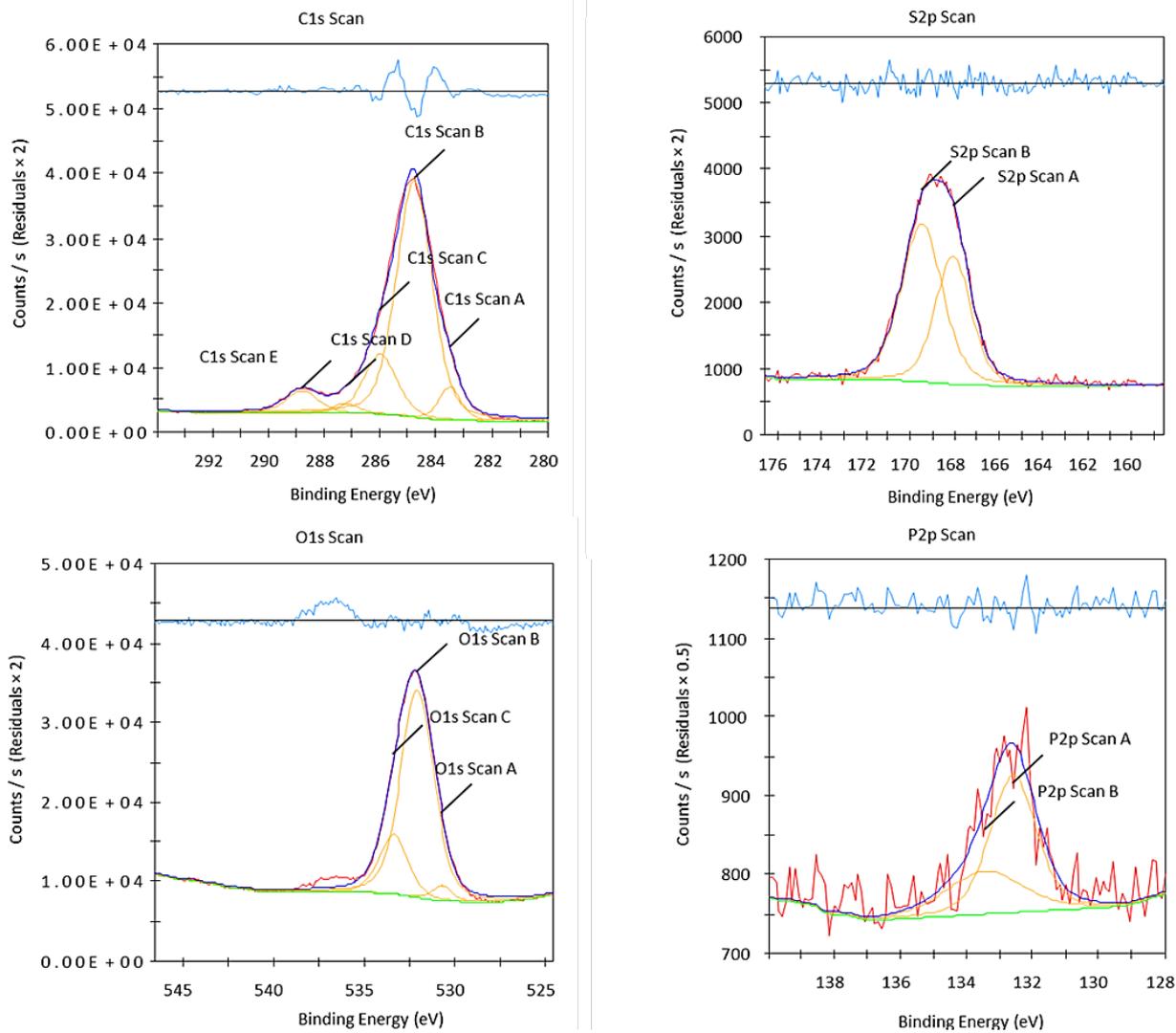


Figure S6. High-resolution XPS scan spectra of RhNP-TPPO@CCM-A.

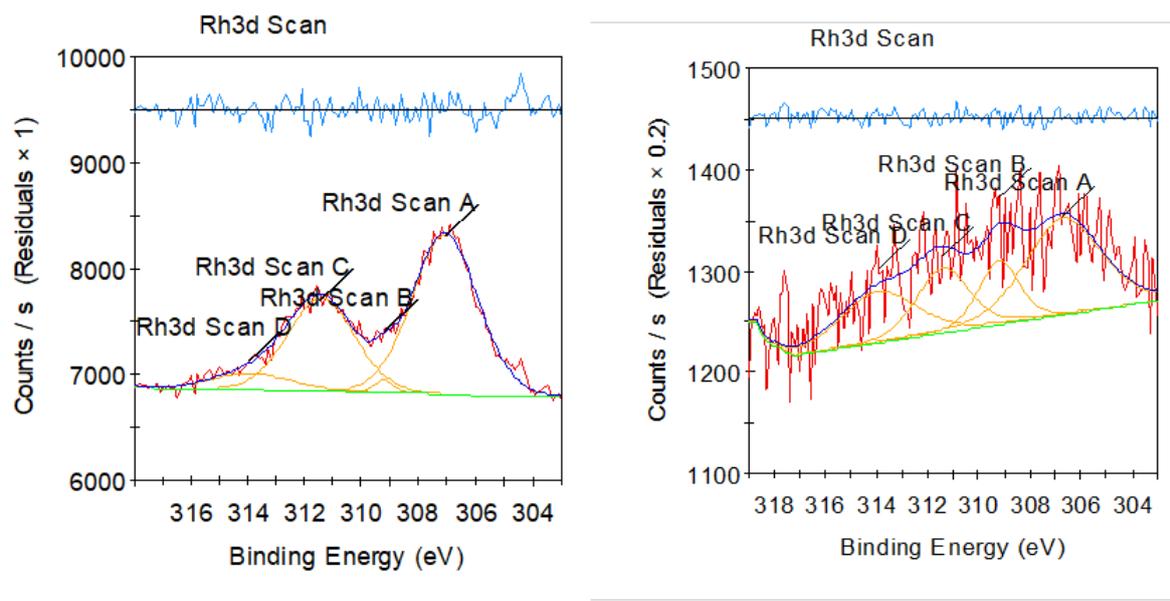


Figure S7. High-resolution XPS scan spectra of RhNP-TPPO (left) and RhNP-TPPO@CCM-A (right).

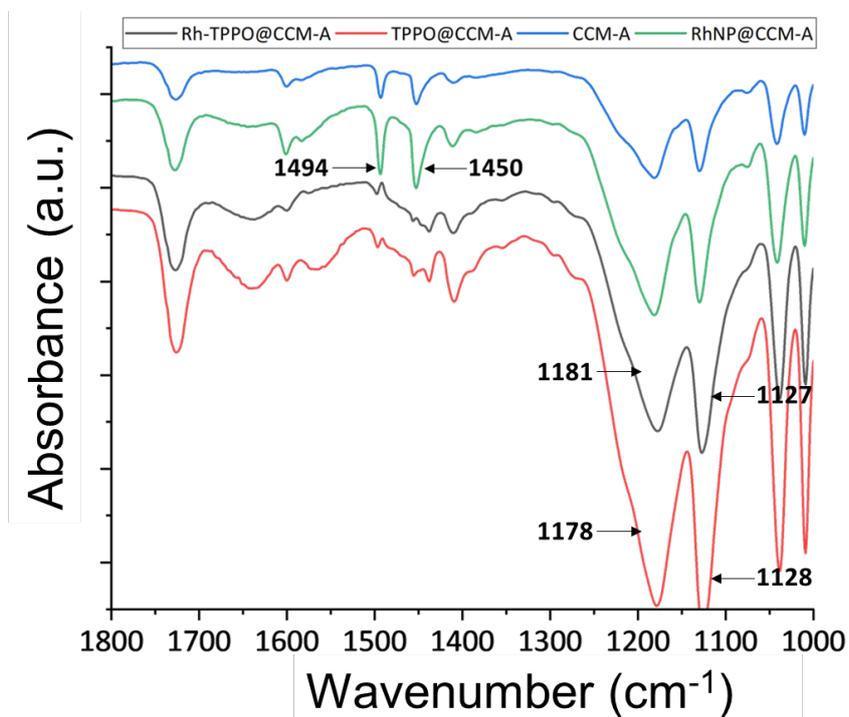


Figure S8. ATR-FTIR spectra of RhNP-TPPO@CCM-A (black), TPPO@CCM-A (red), CCM-A (blue) and RhNP@CCM-A (green) in the absorption range of 1800-1000 cm⁻¹.

1.

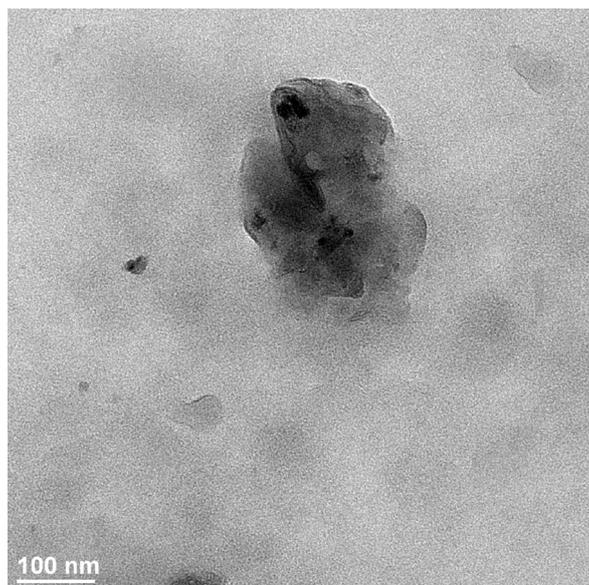


Figure S9. TEM image of one-pot synthesized RhNP@CCM-A.

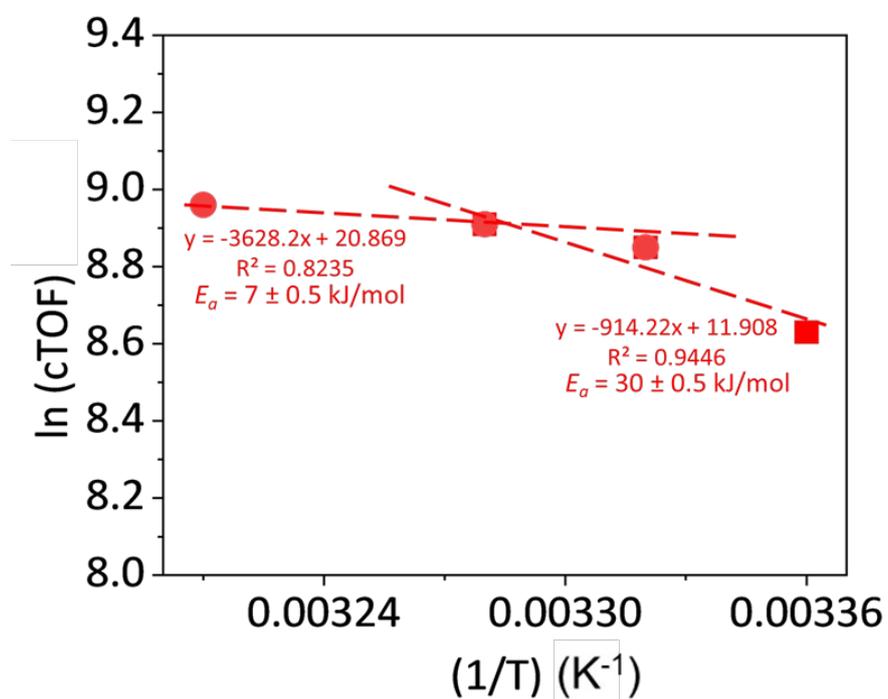


Figure S10. Arrhenius plot for the hydrogenation of styrene using RhNPs-TPPO@CCM-A latex. Reaction conditions: Styrene/Rh = 5000/1, 20 bar H₂, 0.25 h, 1200 rpm.

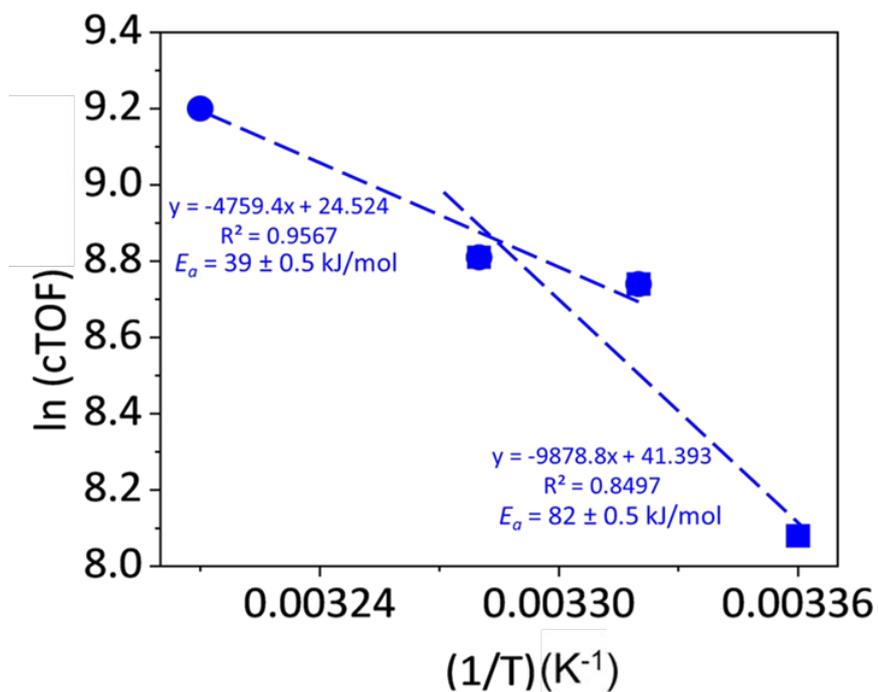


Figure S11. Arrhenius plot for the hydrogenation of styrene using RhNPs-TPPO@CCM-A latex. Reaction conditions: Styrene/Rh = 2000/1, 20 bar H₂, 0.25 h, 1200 rpm.

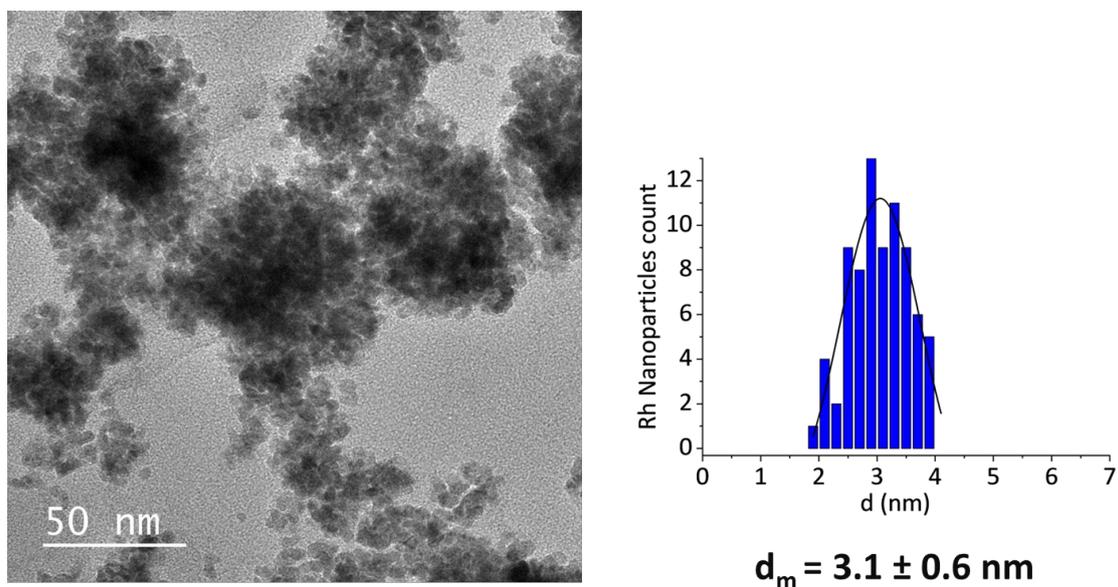


Figure S12. TEM image of RhNP-TPPO@CCM-A after the fifth reaction run and the corresponding size distribution of RhNPs ($d_m = 3.1 \pm 0.6 \text{ nm}$).

Supplementary Tables

Table S1. Binding energies (eV) of the chemical states of the C, S, and O atoms in TPPO@CCM-A and RhNP-TPPO@CCM-A.

Atom	Binding Energy TPPO@CCM-A (eV)	FWHM (eV)	Atomic ratio (%)	Binding Energy RhNP- TPPO@CCM-A (eV)	FWHM (eV)	Atomic ratio (%)	ΔE (eV) ^a
C 1s	283.5	1.1	12.3	282.9	2.0	3.9	0.6
Scan A							
C 1s	284.7	1.5	78.7	284.9	1.9	39.5	0.2
Scan B							
C 1s	286.0	1.4	8.3	286.5	1.4	3.4	0.5
Scan C							
C 1s	287.1	0.8	0.6	287.2	1.4	0.8	0.1
Scan D							
C 1s	289.7	1.3	0.0	288.9	1.3	4.1	0.8
Scan E							
S 2p	168.4	2.3	95.7	168.4	2.1	50.3	0.0
Scan A							
S 2p	169.9	0.9	4.3	169.2	3.1	49.7	0.7
Scan B							
P 2p	132.4	1.3	66.2	132.6	1.7	66.4	0.2
Scan A							
P 2p	133.3	1.2	33.8	133.4	2.8	33.6	0.1
Scan B							
O 1s	530.9	1.7	45.2	531.7	1.7	53.7	0.8
Scan A							
O 1s	532.1	2.0	49.9	533.1	1.9	44.1	1.0
Scan B							
O 1s	535.7	2.0	4.8	536.1	2.0	2.2	0.4
Scan C							

^a $\Delta E = |\text{Binding energy (TPPO@CCM-A)} - \text{binding energy (RhNP-TPPO@CCM-A)}|$.

Table S2. Binding energies (eV) of the chemical states of the Rh atoms in RhNP@TPPO^a and RhNP-TPPO@CCM-A.

Atom	Binding Energy RhNP@TPPO (eV)	FWHM (eV)	Atomic ratio (%)	Binding Energy RhNP-TPPO@CCM-A (eV)	FWHM (eV)	Atomic ratio (%)	ΔE (eV) ^b
Rh 3d	306.7	3.4	64.7	306.7	3.5	64.7	0
Scan A							
Rh 3d	309.2	1.2	1.7	309.2	1.9	1.7	0
Scan B							
Rh 3d	311.4	2.7	32.3	311.4	2.4	32.3	0
Scan C							
Rh 3d	313.9	1.2	1.4	313.9	3.5	1.3	0
Scan D							

^a Reaction conditions for the synthesis of RhNP@TPPO: [Rh(COD)(μ -Cl)]₂/TPPO = 1/4 , 1200 rpm, 20 bar of H₂, 60 °C, 20 h. ^b ΔE = |Binding energy (RhNP@TPPO) – binding energy (RhNP-TPPO@CCM-A)|.

Table S3. Binding energies (eV) of the chemical states of the C, S, and O atoms in CCM-A and RhNP@CCM-A.

Atom	Binding Energy CCM-A (eV)	FWHM (eV)	Atomic ratio (%)	Binding Energy RhNP- TPPO@CCM-A (eV)	FWHM (eV)	Atomic ratio (%)	ΔE (eV) ^a
C 1s	283.5	1.0	10.8	282.5	1.5	41.4	1.0
Scan A							
C 1s	284.6	1.6	52.4	284.7	1.5	47.8	0.1
Scan B							
C 1s	286.0	1.4	34.4	286.0	1.3	10.1	0.0
Scan C							
C 1s	287.3	0.9	2.3	287.3	0.5	0.1	0.0
Scan D							
C 1s	288.5	2.0	0.0	288.9	0.5	0.1	0.4
Scan E							
S2p	167.6	1.6	16.4	166.2	2.0	17.9	1.4
Scan A							
S2p	169.2	3.1	83.5	168.7	2.5	82.1	0.5
Scan B							
O1s	531.2	2.0	39.7	529.3	1.7	71.8	1.9
Scan A							
O1s	532.7	2.0	46.8	530.7	2.0	18.5	2.0
Scan B							
O1s	534.4	2.0	13.6	534.4	2.0	9.6	0.0
Scan C							

^a $\Delta E = |\text{Binding energy (TPPO@CCM-A)} - \text{binding energy (RhNP-TPPO@CCM-A)}|$.

Table S4. ICP-MS data for the leaching of Rh metal after each catalytic run with diethyl ether used as the washing solvent between recycles.

Run no.	¹⁰³ Rh (LR) ^a	IF cor RSD ^b	[Rh] (ppt)	[Rh] (ppm)	Σ[Rh] (ppm)	[Rh] _{initial} (ppm)	RhNPs leached (mol %) ^c
1	717366.0	0.78	51.6462	0.52			
2	1100850.1	1.52	79.2549	0.79			
3	678649.8	1.03	48.8589	0.49	3.1	161	1.93
4	788315.9	1.34	56.7542	0.57			
5	1013990.8	0.83	73.0015	0.73			

^a Low Resolution (LR). ^b Relative standard deviation (RSD) was calculated for all the runs separately. ^c Rh (mol%) cumulative loss.

Table S5. Binding energies (eV) of the chemical states of the C, S, and O atoms in RhNP-TPPO@CCM-A and RhNP@CCM-A.

Atom	Binding Energy RhNP@CCM-A (eV)	FWHM (eV)	Atomic ratio (%)	Binding Energy RhNP- TPPO@CCM-A (eV)	FWHM (eV)	Atomic ratio (%)	ΔE (eV) ^a
C 1s	282.5	1.5	41.4	283.0	2.0	3.9	0.5
Scan A							
C 1s	284.7	1.5	47.8	285.0	1.9	39.4	0.3
Scan B							
C 1s	286.0	1.3	10.1	286.5	1.4	3.4	0.5
Scan C							
C 1s	287.3	0.5	0.1	287.2	1.4	0.8	0.1
Scan D							
C 1s	288.9	0.5	0.1	289.0	1.3	4.1	0.1
Scan E							
S2p	166.2	2.0	17.9	168.4	2.1	50.3	2.2
Scan A							
S2p	168.7	2.5	82.1	169.2	3.1	49.7	0.5
Scan B							
O1s	529.3	1.7	71.8	531.7	1.7	53.7	2.4
Scan A							
O1s	530.7	2.0	18.5	533.1	1.9	44.1	2.4
Scan B							
O1s	534.4	2.0	9.6	536.1	2.0	2.2	1.7
Scan C							

^a $\Delta E = |\text{Binding energy (TPPO@CCM-A)} - \text{binding energy (RhNP-TPPO@CCM-A)}|$.