

† Electronic Supplementary Information (ESI)

Controlling the Selectivity of Bimetallic Ruthenium-Platinum Nanoparticles Supported on N-Doped Graphene by Adjusting their Metal Composition

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1. ICP-AES

Table S1. Metal contents (wt%) and compositions (Pt:Ru molar ratio) of mono and bimetallic catalysts calculated by ICP-AES and XRF.^a

Catalizador	Metal wt %	Pt wt %	Ru wt %	Pt:Ru molar ratio (theor.)	Pt:Ru molar ratio (exp.)
Ru/NH ₂ -rGO	2.5	–	2.5	-	-
Pt ₁ Ru ₅ /NH ₂ -rGO	2.4	0.7	1.7	1:5	1:4.7
Pt ₁ Ru ₁ /NH ₂ -rGO	2.8	1.9	0.9	1:1	1:1.1
Pt ₅ Ru ₁ /NH ₂ -rGO	2.9	2.6	0.3	5:1	4.5:1
Pt/NH ₂ -rGO	2.4	2.4	–	-	-

a. Ru and Pt contents (wt%) were determined by ICP-AES and XRF, respectively.

2. HRTEM

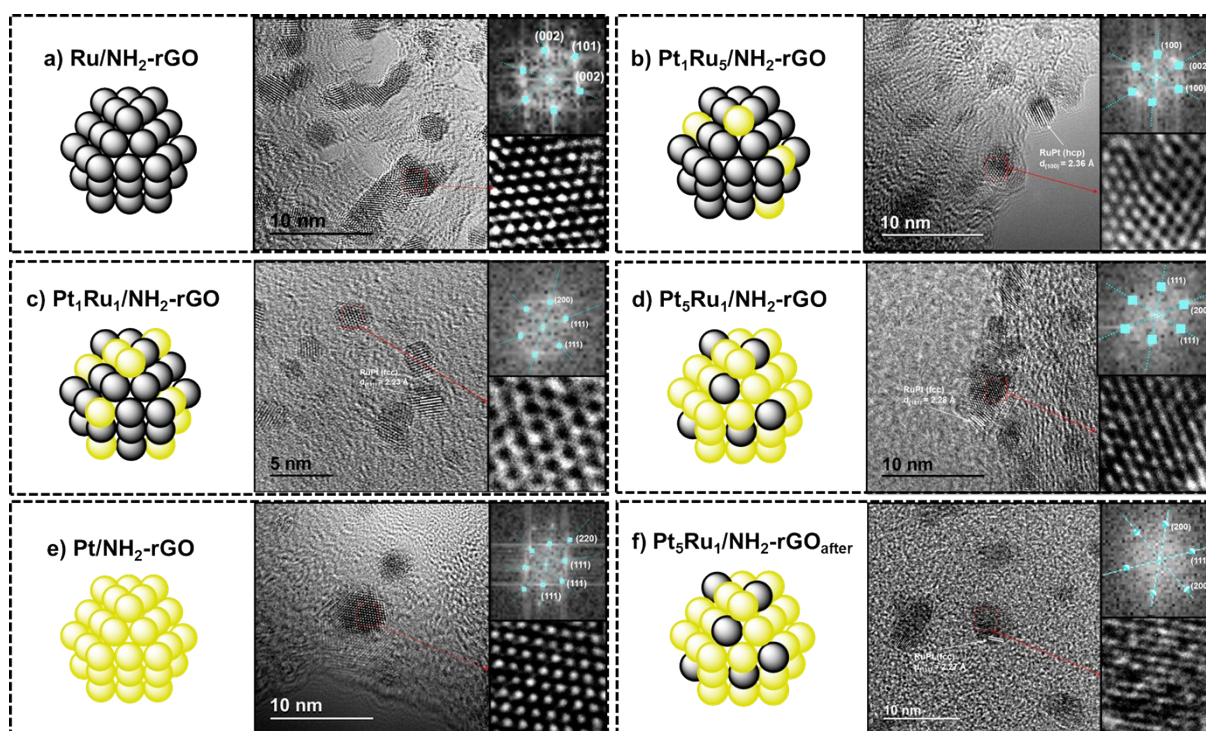
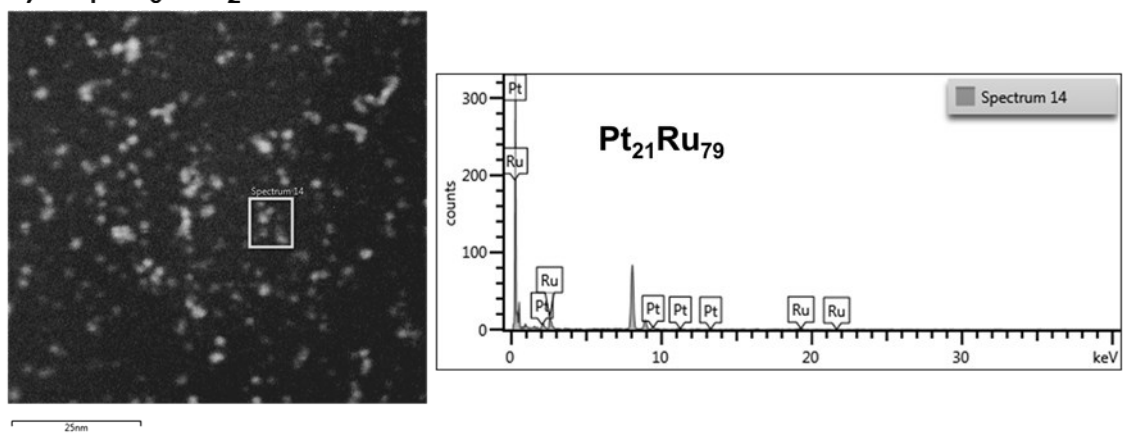


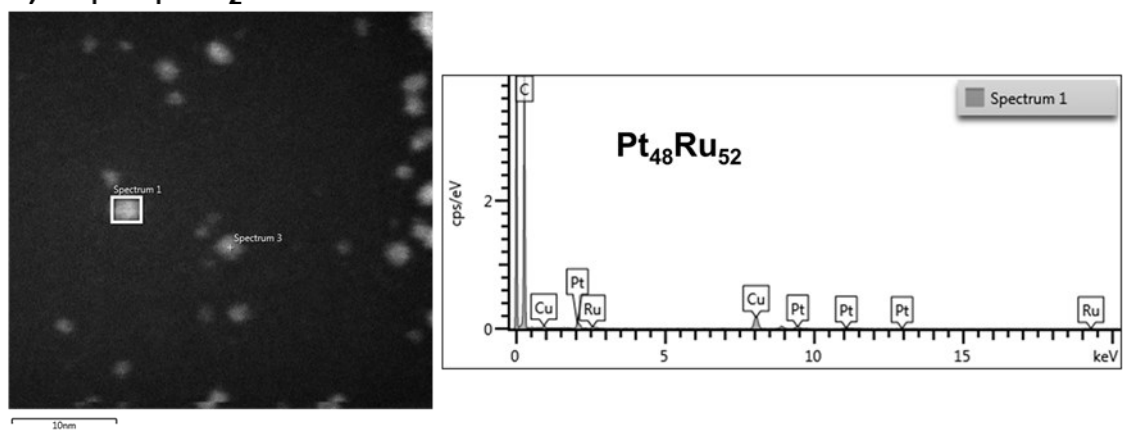
Figure S1. HRTEM micrographs (left, right bottom) and Fourier analysis (right, top) of (a) Ru/NH₂-rGO, (b) Pt₁Ru₅/NH₂-rGO (c), Pt₁Ru₁/NH₂-rGO (d) Pt₅Ru₁/NH₂-rGO, (e) Pt/NH₂-rGO and (f) Pt₅Ru₁/NH₂-rGO after catalysis.

3. HAADF-STEM

a) $\text{Pt}_1\text{Ru}_5/\text{NH}_2\text{-rGO}$



b) $\text{Pt}_1\text{Ru}_1/\text{NH}_2\text{-rGO}$



c) $\text{Pt}_5\text{Ru}_1/\text{NH}_2\text{-rGO}$

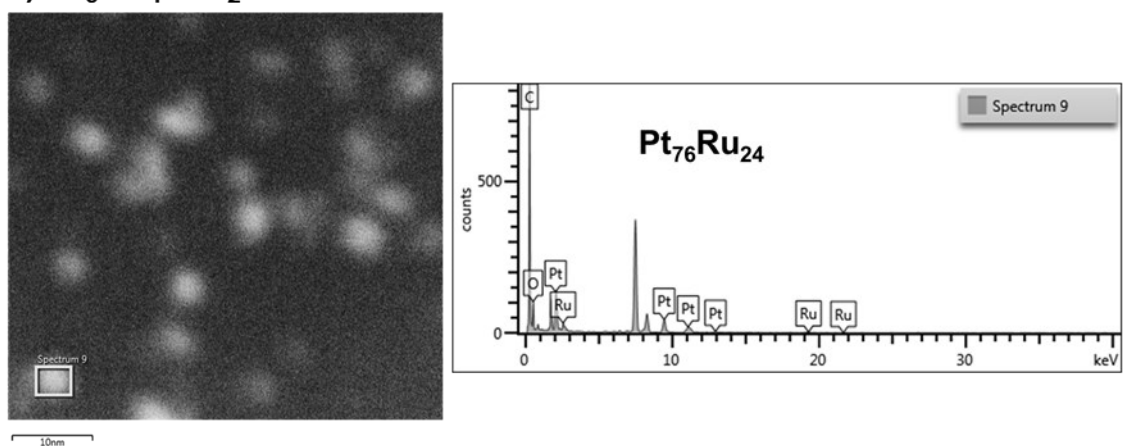


Figure S2. HAADF-STEM image (left) and relative composition of (a) $\text{Pt}_1\text{Ru}_5/\text{NH}_2\text{-rGO}$, (b) $\text{Pt}_1\text{Ru}_1/\text{NH}_2\text{-rGO}$ and (c) $\text{Pt}_5\text{Ru}_1/\text{NH}_2\text{-rGO}$ determined by EDX.

4. Raman

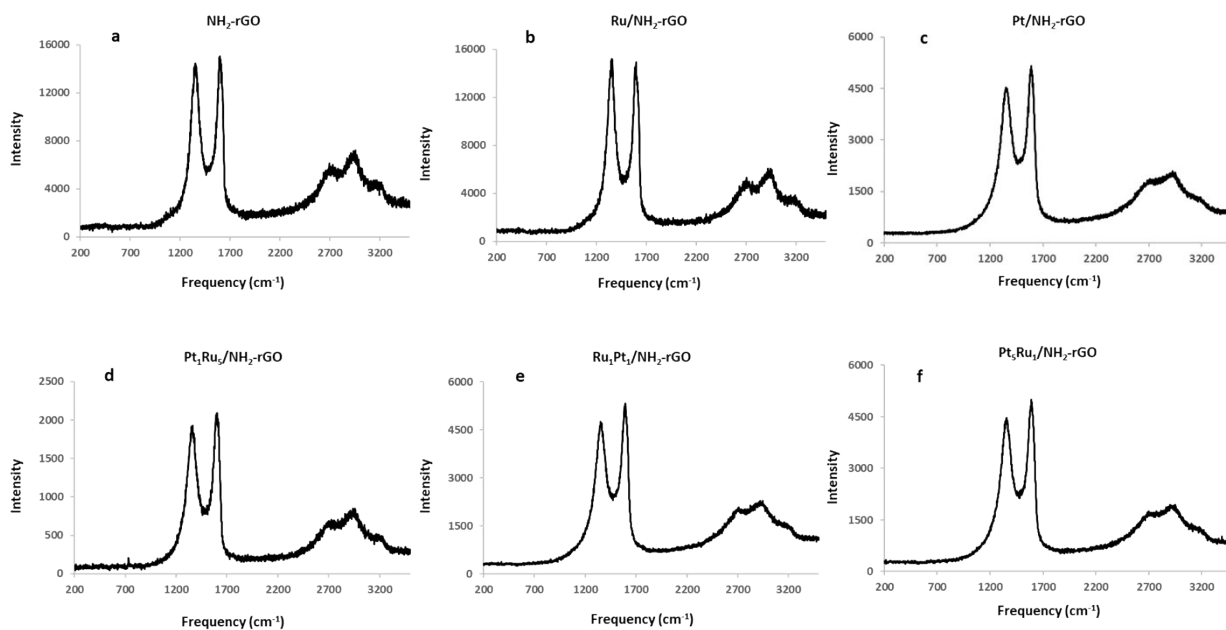


Figure S3. Raman spectrum of NH₂-rGO (a), Ru/NH₂-rGO (b), Pt/NH₂-rGO (c), Pt₁Ru₅/NH₂-rGO (d), Pt₁Ru₁/NH₂-rGO (e), Pt₅Ru₁/NH₂-rGO (f).

5. XPS

Table S2. Metal contents (wt%) and compositions (atomic % and molar ratios) of bimetallic catalysts calculated by XPS.

Catalyst	% _{at.} Pt	% _{at.} Ru	Pt:Ru molar ratio
Pt ₁ Ru ₅ /NH ₂ -rGO	28	72	1:4.3
Pt ₁ Ru ₁ /NH ₂ -rGO	56	44	1.1:1
Pt ₅ Ru ₁ /NH ₂ -rGO	78	22	4.7:1

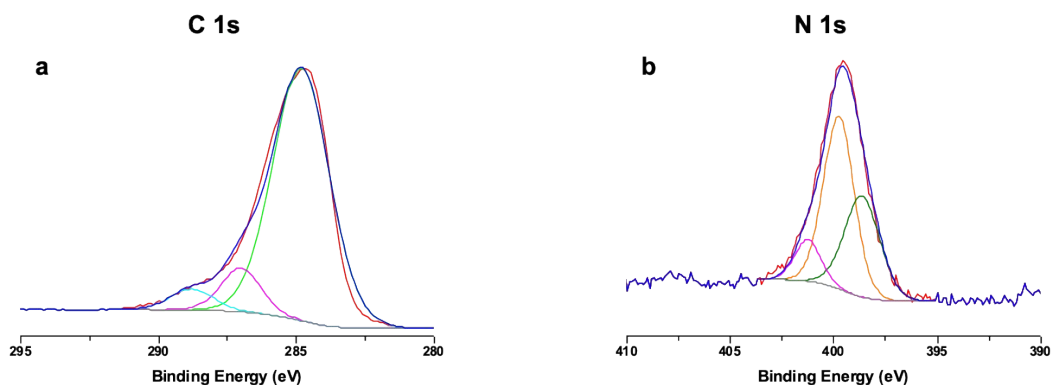


Figure S4. X-ray photoelectron spectroscopy (XPS) of the C 1s (a) and N 1s (b) signals of NH₂-rGO

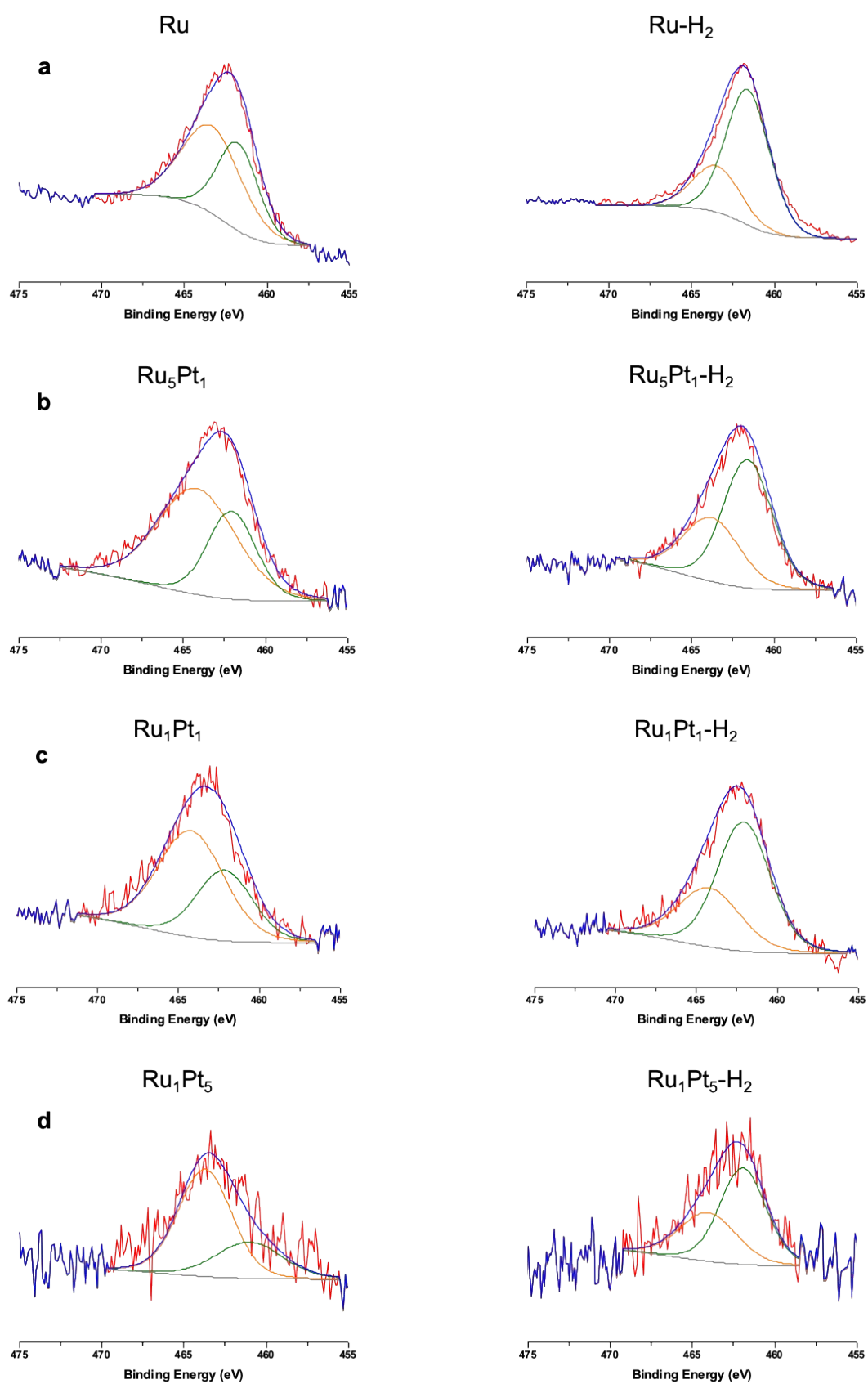


Figure S5. XPS of Ru 3p_{3/2} area of Ru/NH₂-rGO (a), Pt₁Ru₅/NH₂-rGO (b), Pt₁Ru₁/NH₂-rGO (c) and Pt₅Ru₁/NH₂-rGO (d) before (left) and after reduction conditions (right).

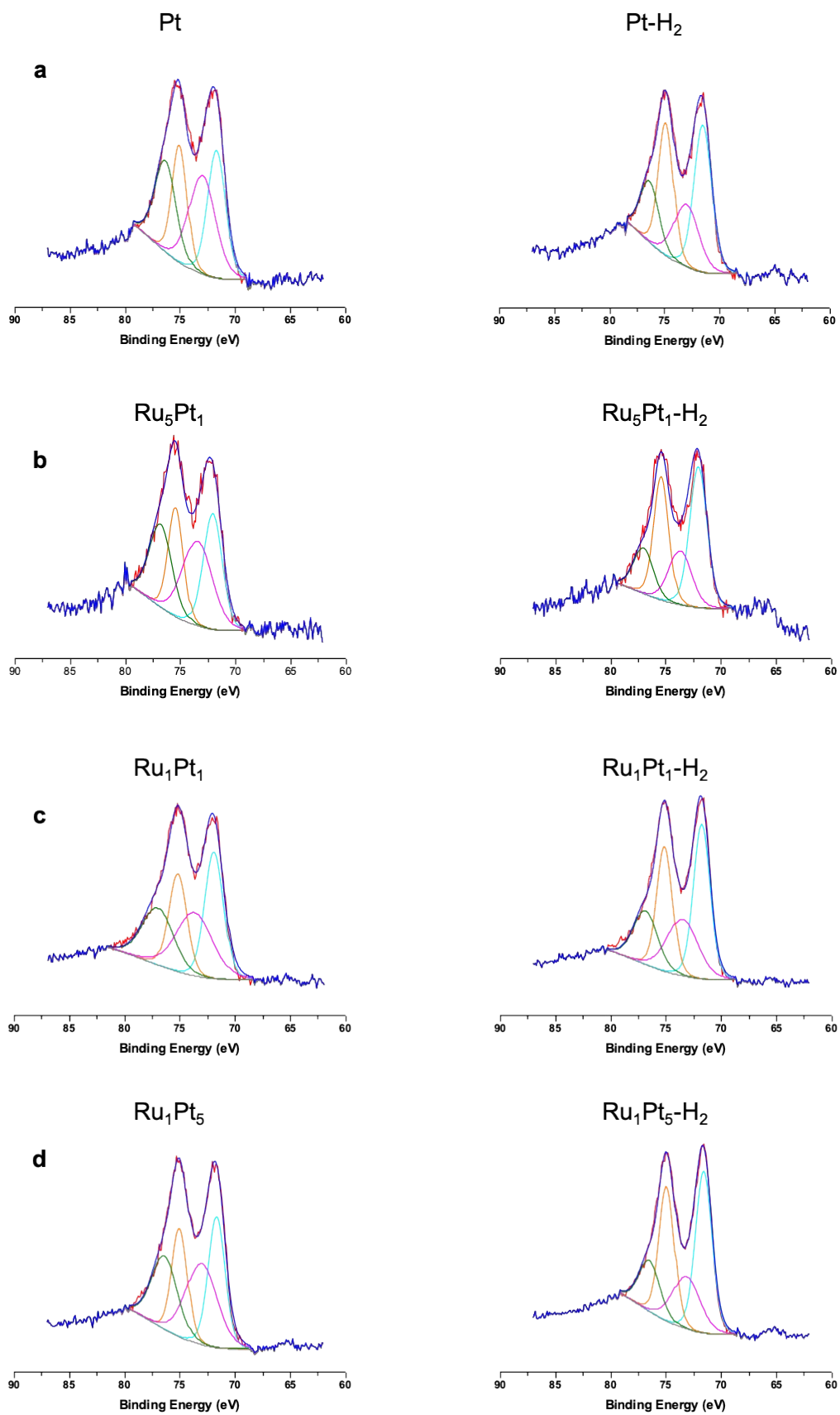


Figure S6. XPS of Pt 4f area of Pt/NH₂-rGO (a), Pt₁Ru₅/NH₂-rGO (b), Pt₁Ru₁/NH₂-rGO (c) and Pt₅Ru₁/NH₂-rGO (d) before (left) and after reduction conditions (right).

6. Metal compositions of bimetallic catalysts

Table S3. Comparison of the metal compositions (atomic % and molar ratios) of bimetallic catalysts determined by ICP-AES, XRF, EDX and XPS.

Catalyst	ICP-AES and XRF		EDX		XPS	
	Pt _x Ru _y (% _{at.})	Pt:Ru (molar ratio)	Pt _x Ru _y (% _{at.})	Pt:Ru (molar ratio)	Pt _x Ru _y (% _{at.})	Pt:Ru (molar ratio)
Pt ₁ Ru ₅ /NH ₂ -rGO	Pt ₂₂ Ru ₇₈	1:4.7	Pt ₂₁ Ru ₇₉	1:4.7	Pt ₂₈ Ru ₇₂	1:4.3
Pt ₁ Ru ₁ /NH ₂ -rGO	Pt ₄₅ Ru ₅₅	1:1.1	Pt ₄₈ Ru ₅₂	1:1	Pt ₅₆ Ru ₄₄	1.1:1
Pt ₅ Ru ₁ /NH ₂ -rGO	Pt ₇₅ Ru ₂₅	4.5:1	Pt ₇₆ Ru ₂₄	4.6:1	Pt ₇₈ Ru ₂₂	4.7:1

7. Hydrogenation reactions

Table S4: Amount of catalyst added depending on the metal.

Catalyst	Mass (mg)
Ru/NH ₂ -rGO	10
Pt ₁ Ru ₅ /NH ₂ -rGO	12
Pt ₁ Ru ₁ /NH ₂ -rGO	15
Pt ₅ Ru ₁ /NH ₂ -rGO	18
Pt/NH ₂ -rGO	20

8. TEM

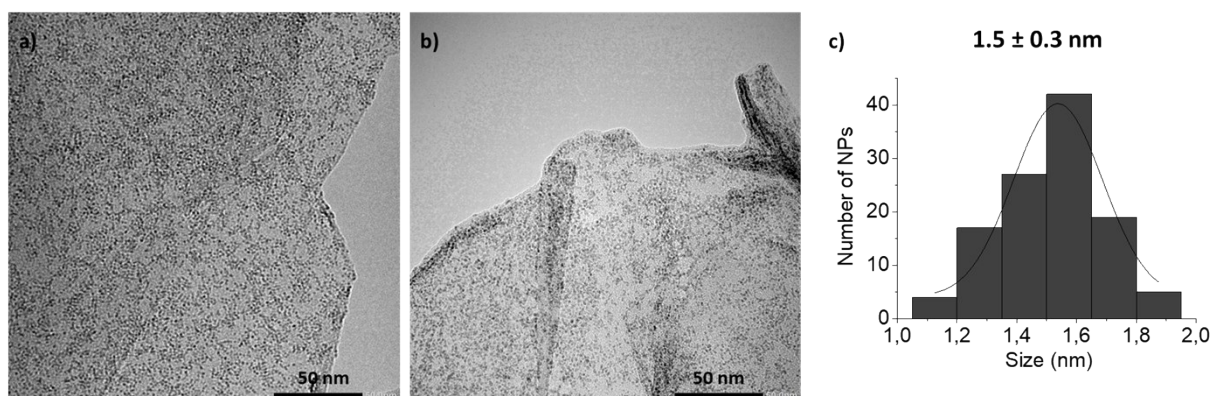


Figure S7. TEM micrographs (a, b) and the corresponding size histogram (c) of Ru-Bu₃Sn/NH₂-rGO.

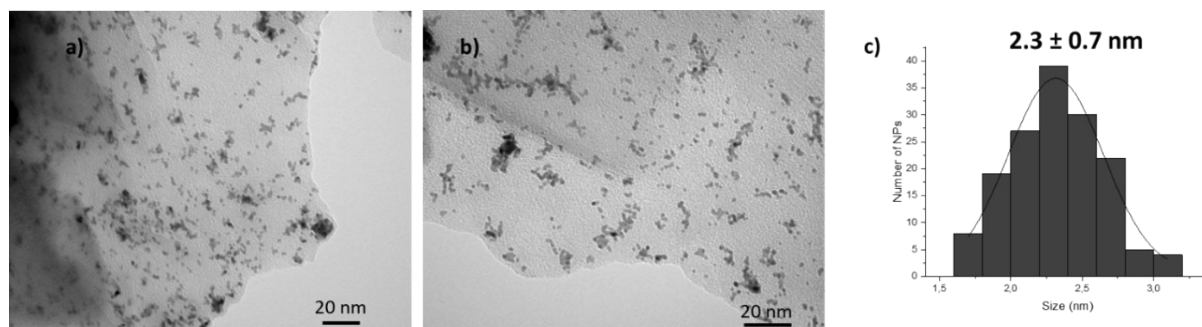


Figure S8. TEM micrographs (a, b) and the corresponding size histogram (c) of $\text{Pt}_5\text{Ru}_1/\text{NH}_2\text{-rGO}$ after catalytic conditions (i.e. acetophenone hydrogenation, 130 °C, 50 bar H_2 , 20h, THF).

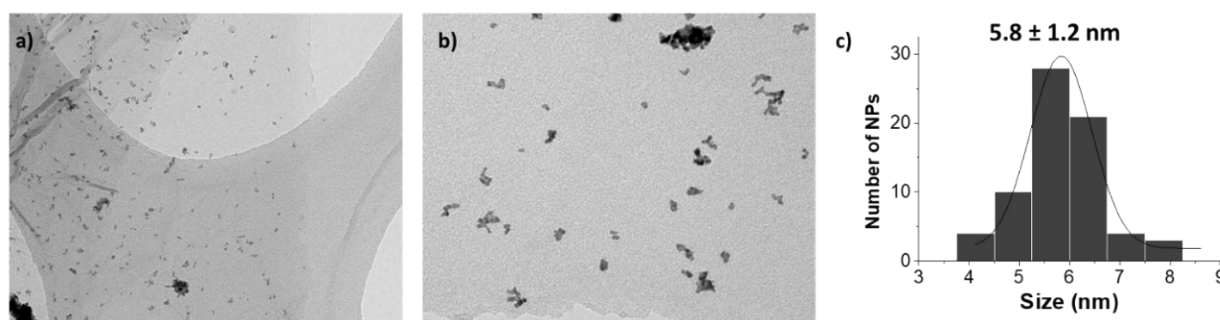


Figure S9. TEM micrographs (a, b) and the corresponding size histogram (c) of $\text{Pt}_5\text{Ru}_1/\text{rGO}$ after catalytic conditions (i.e. acetophenone hydrogenation, 130 °C, 50 bar H_2 , 20h, THF).

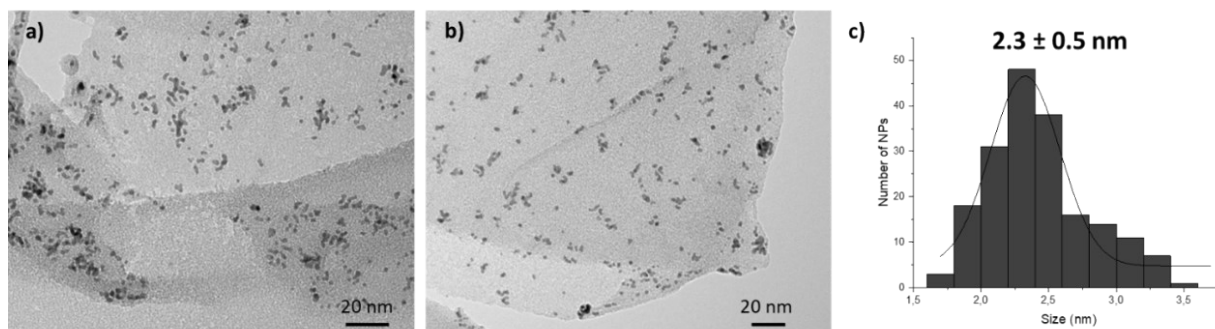


Figure S10. TEM micrographs (a, b) and the corresponding size histogram (c) of $\text{Pt}_5\text{Ru}_1/\text{NH}_2\text{-rGO}$ after multiple addition experiment (i.e. nitrobenzene hydrogenation, 100 °C, 30 bar H_2 , THF)

9. “Hot filtration”

Table S5: Conversions of $\text{Pt}_5\text{Ru}_1/\text{NH}_2\text{-rGO}$ in the hydrogenation of HMF after thermal filtration^a and in the presence of catalyst.^b

Catalyst	50 min	4 h
$\text{Pt}_1\text{Ru}_5/\text{NH}_2\text{-rGO}^a$	63 %	63 %
$\text{Pt}_1\text{Ru}_5/\text{NH}_2\text{-rGO}^b$	62 %	94%