

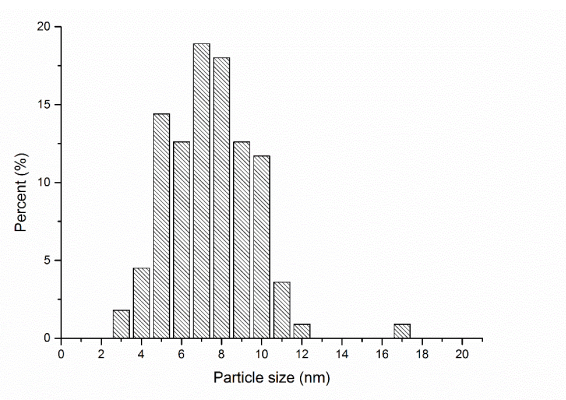
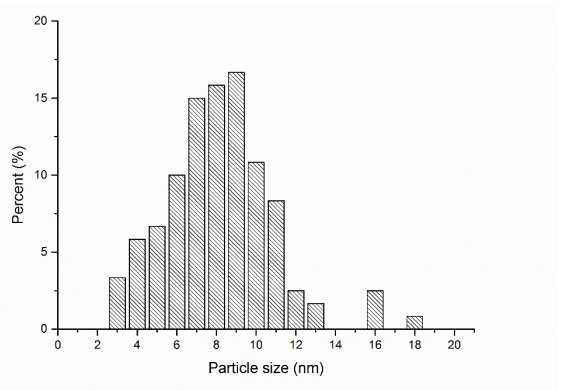
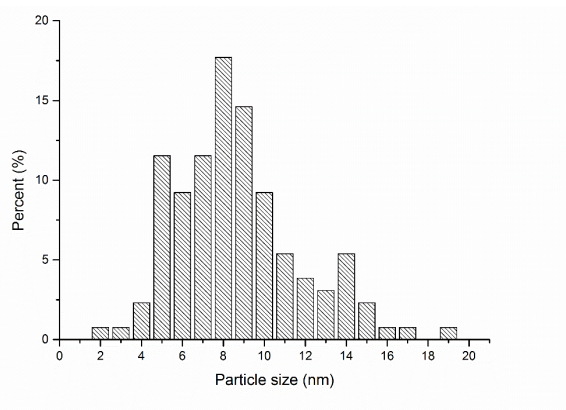
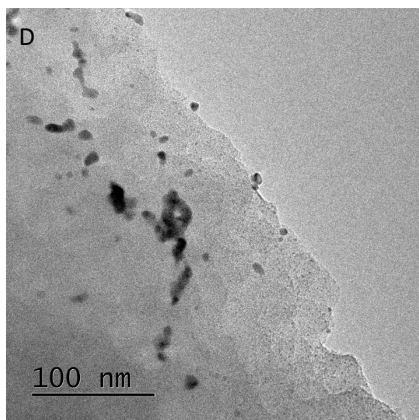
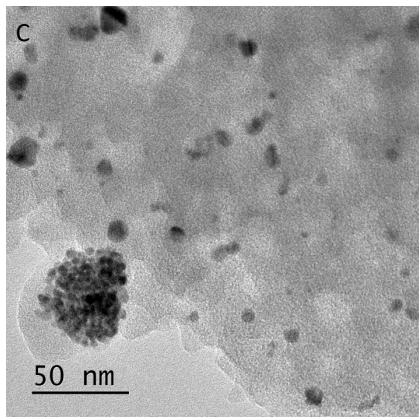
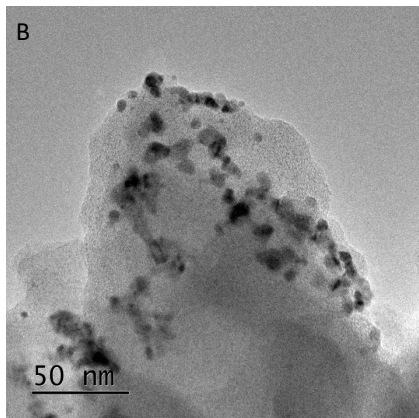
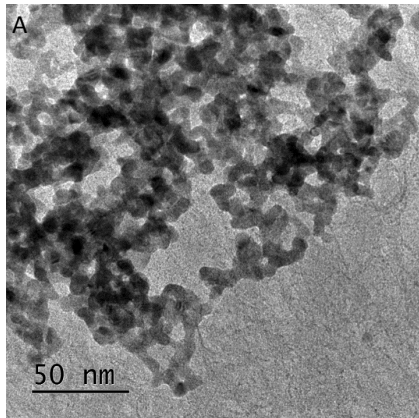
SUPPORTING INFORMATION

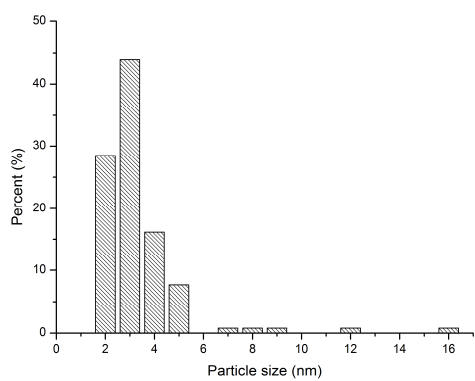
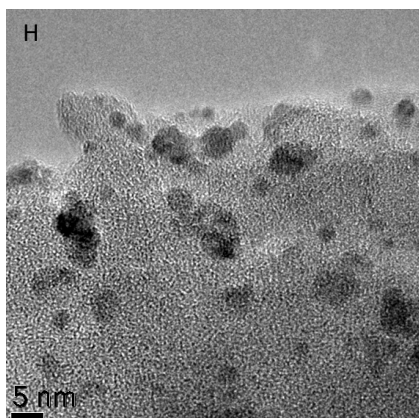
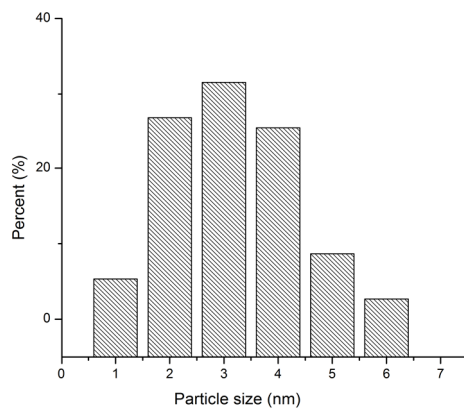
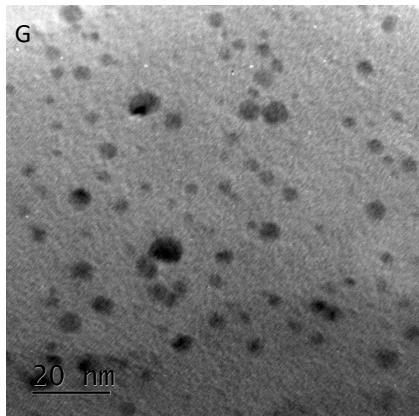
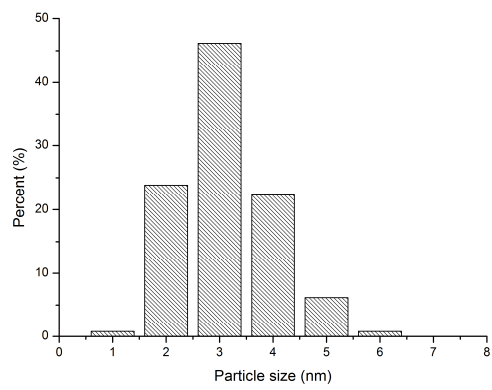
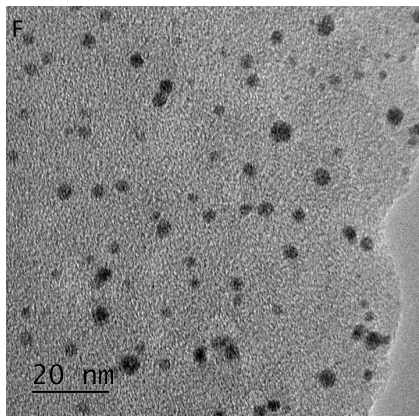
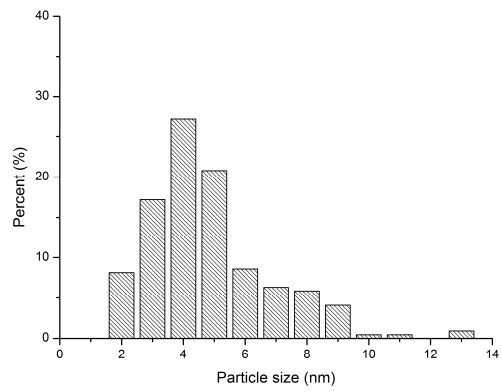
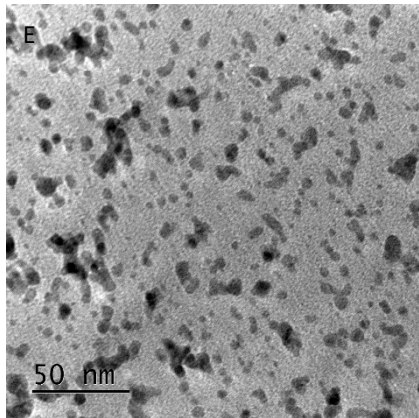
Table S1 Palladium atomic content and % Pd⁰ on the surface from XPS

Catalyst	Support	Pd wt%	Au wt%	%wt total metal	PVA/M weight ratio	NaBH ₄ /M molar ratio
Pd/AC-a	AC	1	0	1	0	5
Pd/AC-b	AC	1	0	1	0.05	5
Pd/AC-c	AC	1	0	1	0.1	5
Pd/AC-d	AC	1	0	1	0.2	5
Pd/AC-e	AC	1	0	1	0.3	5
Pd/AC-f	AC	1	0	1	0.65	5
Pd/AC-g	AC	1	0	1	1.2	5
Pd/AC-h	AC	1	0	1	0.65	10
0.2-Pd/AC-e	AC	0.2	0	0.2	0.3	5
0.5-Pd/AC-e	AC	0.5	0	0.5	0.3	5
0.7Pd/AC-e	AC	0.65	0	0.65	0.3	5
1.2-Pd/AC-e	AC	1.2	0	1.2	0.3	5
Pd/TiO ₂ -f	TiO ₂	1	0	1	0.65	5
Pd/TiO ₂ -h	TiO ₂	1	0	1	0.65	10
Pd/TiO ₂ -i	TiO ₂	1	0	1	0.3	10
Au/ TiO ₂	TiO ₂	0	1	1	0.3	10
Au ₁ Pd ₃ -TiO ₂	TiO ₂	0.75	0.25	1	0.3	10
Au ₁ Pd ₁ -TiO ₂	TiO ₂	0.5	0.5	1	0.3	10
Au ₃ Pd ₁ -TiO ₂	TiO ₂	0.25	0.75	1	0.3	10

Table S2 Pd elemental chemical composition and surface area analysis of the catalysts studied during optimisation of the sol-immobilisation method

Sample	PVA/Pd weight ratio	NaBH ₄ /Pd molar ratio	Pd (wt. %) by EDX	Surface area (m ² /g)
Pd/AC-a	0	5	1.03	62
Pd/AC-b	0.05	5	1.03	64
Pd/AC-c	0.1	5	1.17	62
Pd/AC-d	0.2	5	1.11	81
Pd/AC-e	0.3	5	1.07	56
Pd/AC-f	0.65	5	1.15	57
Pd/AC-g	1.2	5	1.25	54
Pd/AC-h	0.65	10	1.00	71
Pd/TiO ₂ -f	0.65	5	0.98	43
Pd/TiO ₂ -h	0.65	10	1.03	65





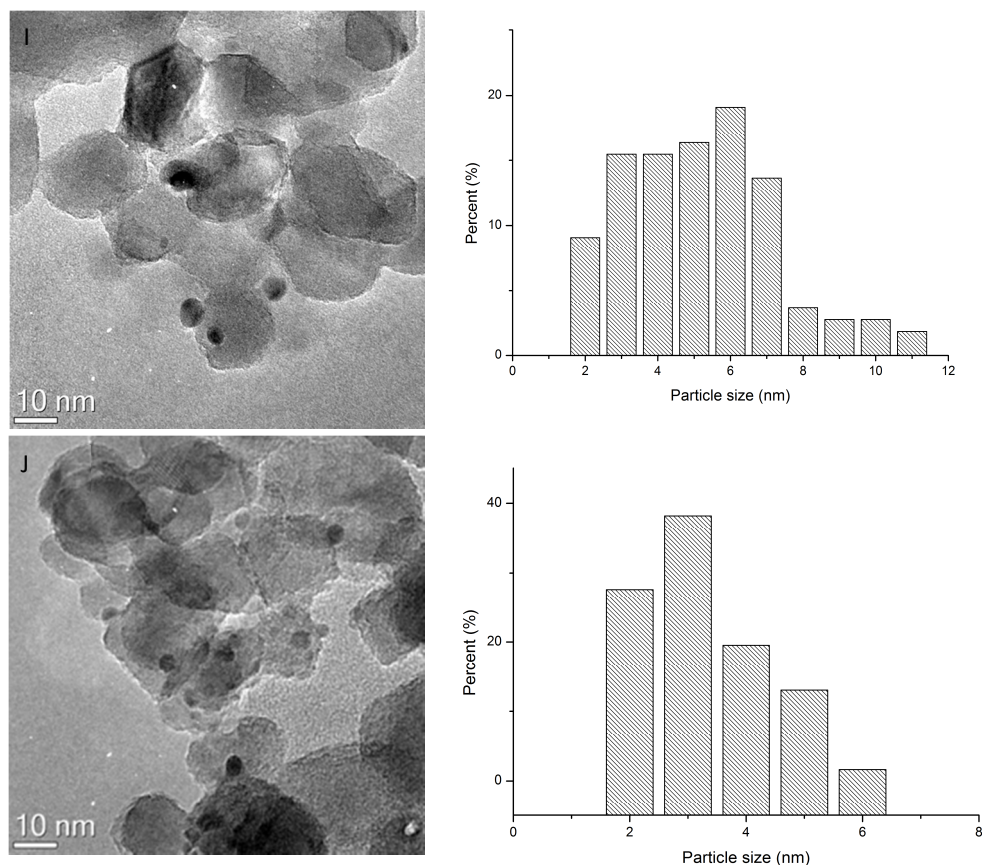


Figure S1. Bright field TEM micrographs and corresponding histograms of the particle size distributions of the catalysts. Unless stated, NaBH₄/Pd=5. A: Pd/AC-a (PVA/Pd=0), B: Pd/AC-b (PVA/Pd=0.05), C: Pd/AC-c (PVA/Pd=0.1), D: Pd/AC-d (PVA/Pd=0.2), E: Pd/AC-e (PVA/Pd=0.3), F: Pd/AC-f (PVA/Pd=0.65), G: Pd/AC-g (PVA/Pd=1.2), H: Pd/AC-h (PVA/Pd=0.65, NaBH₄/Pd=10), I: Pd/TiO₂-f (PVA/Pd=0.65) and J: Pd/TiO₂-h (PVA/Pd=0.65, NaBH₄/Pd=10).

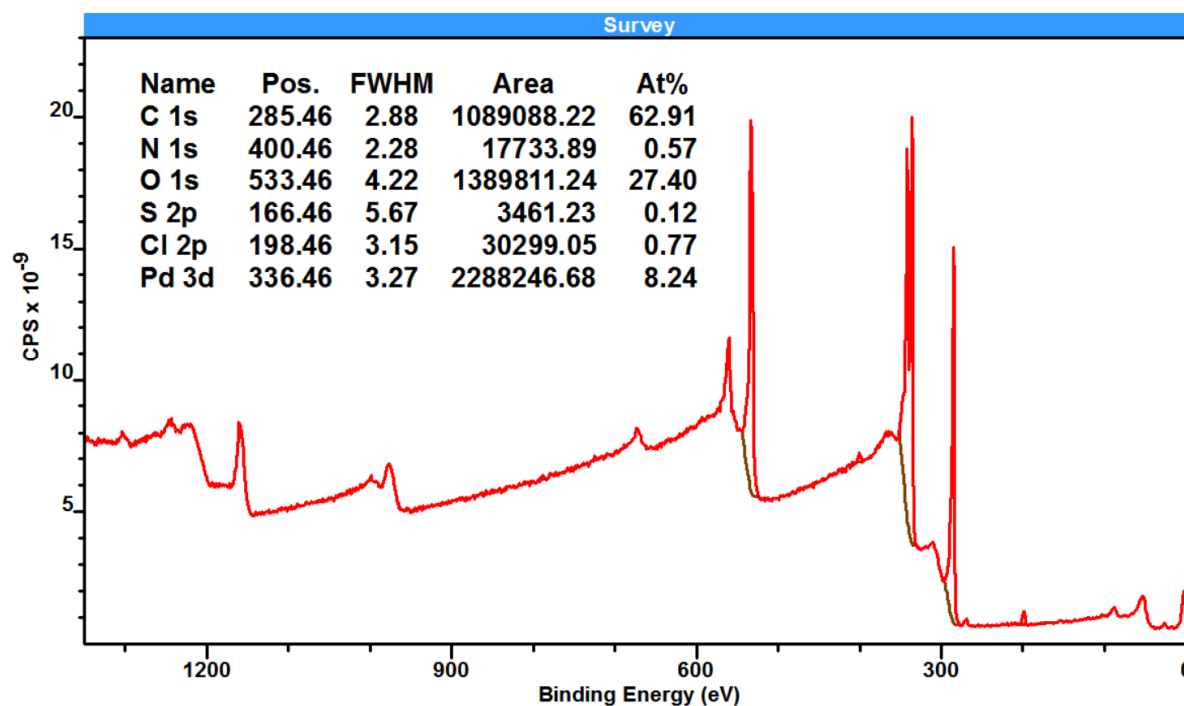


Figure S2. Representative XPS survey of Pd/AC-e (PVA/Pd=0.3) and **quantification of the elements present on the surface.**

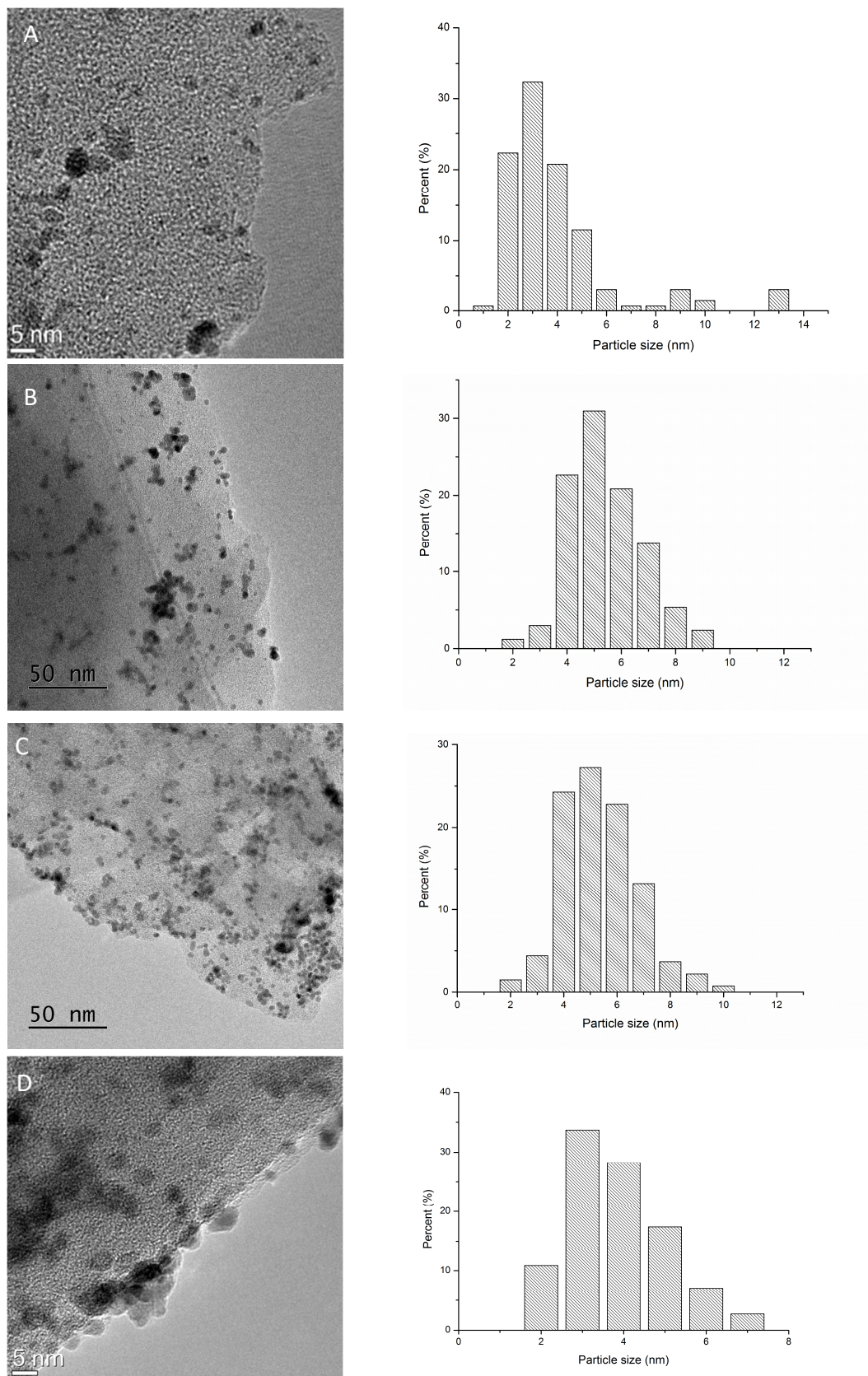


Figure S3. Bright field TEM micrographs and corresponding histograms of the particle size distributions of the Pd/AC catalysts as a function of Pd loading. A: 0.2 wt. % Pd/AC-e, B: 0.5 wt. % Pd/AC-e, C: 0.7 wt. % Pd/AC-e and D: 1.2 wt. % Pd/AC-e.

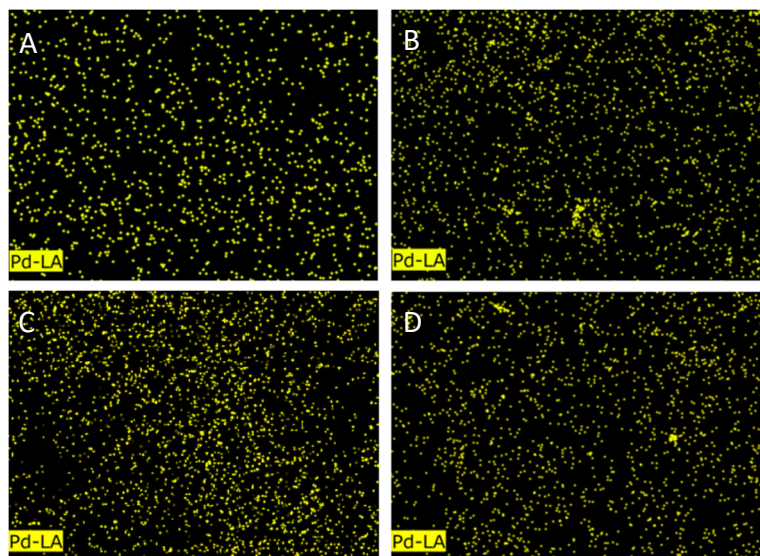


Figure S4. EDX mapping of Pd/AC catalysts as a function of Pd loading. A: loading 0.2 wt. %, B: loading 0.7 wt. %, C: loading 1 wt. %, D: loading 1.2 wt. %.

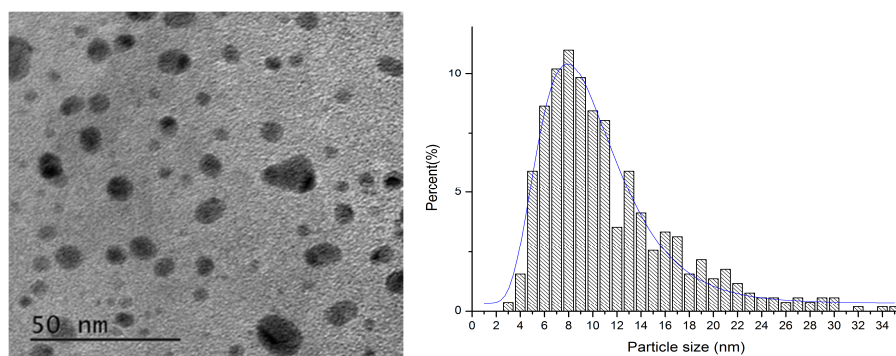


Figure S5. Bright field TEM micrograph and histogram of the particle size distribution of the Pd/AC-e after 5 cycles of use.

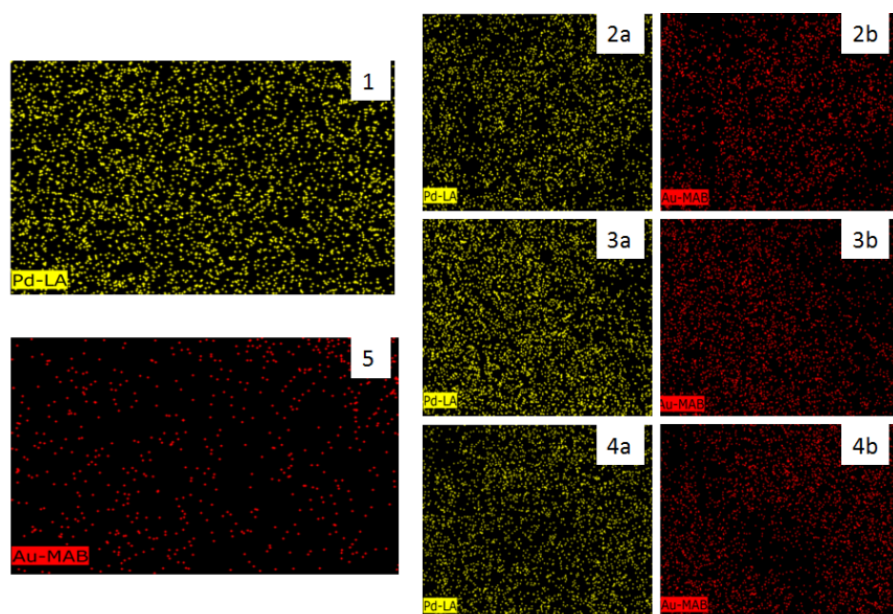


Figure S6. SEM-EDX mapping. 1) Pd-TiO₂, 2a) Pd in Au₁Pd₃-TiO₂, 2b) Au in Au₁Pd₃-TiO₂, 3a) Pd in Au₁Pd₁-TiO₂, 3b) Au in Au₁Pd₁-TiO₂, 4a) Pd in Au₃Pd₁-TiO₂, 4b) Au in Au₃Pd₁-TiO₂, 5) Au-TiO₂.

Table S3 Binding energy and binding energy shifts of the monometallic-bimetallic study

Sample	% mol [Pd ²⁺]	% mol [Au ³⁺]	B.E. (eV)		Δ B.E. (eV)	
			Pd3d _{3/2}	Au4f _{7/2}	Pd3d _{3/2}	Au4f _{7/2}
Pd-TiO ₂ -i	1	-	340.459			
Au ₁ Pd ₃ -TiO ₂	0.75	0.25	340.274	83.148	-0.185	-0.302
Au ₁ Pd ₁ -TiO ₂	0.50	0.50	340.295	83.317	-0.164	-0.133
Au ₃ Pd ₁ -TiO ₂	0.25	0.75	340.470	83.281	0.011	-0.169
Au-TiO ₂	-	1		83.450		