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Supporting Information

Cinnamaldehyde hydrogenation using Au-Pd catalysts prepared by sol immobilisation

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Table S1. MP-AES and XPS quantification analysis of the Au_xPd_y catalysts.

Catalyst	Metal loading (wt %) MP-AES	Au/Pd ratio (mol/mol)			Binding energy (eV)	
		Theoretical	MP-AES	XPS	Au4f _{7/2}	Pd3d _{5/2}
Au ₁₀₀ Pd ₀ /TiO ₂	0.94	100 : 0	100 : 0	100 : 0	83.5	-
Au ₉₅ Pd ₅ /TiO ₂	1.00	95 : 5	96 : 4	92 : 8	83.7	335.0
Au ₆₅ Pd ₃₅ /TiO ₂	0.92	65 : 35	68 : 32	64 : 36	83.4	334.9
Au ₅₀ Pd ₅₀ /TiO ₂	1.00	50 : 50	47 : 53	54 : 46	83.4	335.0
Au ₃₅ Pd ₆₅ /TiO ₂	0.96	35 : 65	39 : 61	36 : 64	83.2	335.0
Au ₀ Pd ₁₀₀ /TiO ₂	0.98	0 : 100	0 : 100	0 : 100	-	335.0

Figure S1. Particle size distribution of (a) Au/TiO₂ (b) Au₉₅Pd₅/TiO₂ (c) Au₆₅Pd₃₅/TiO₂ (d) Au₅₀Pd₅₀/TiO₂ (e) Au₃₅Pd₆₅/TiO₂ (f) Pd/TiO₂.

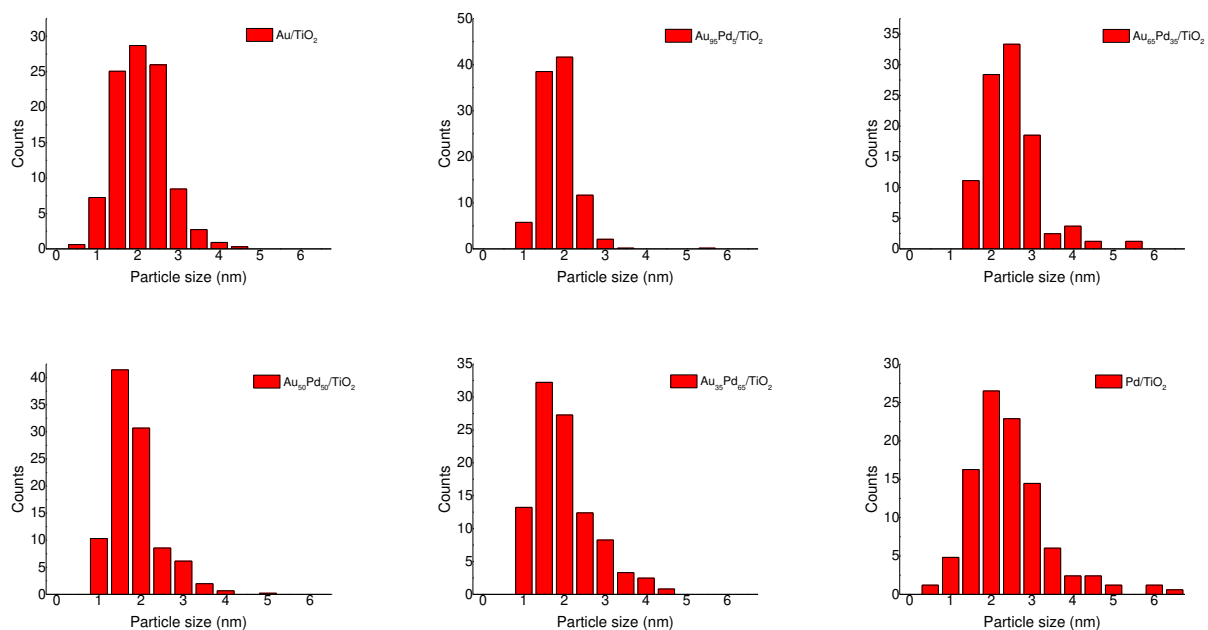


Table S2. Mean and median values (nm) obtained by TEM of the supported monometallic and bimetallic catalysts.

	Au/TiO ₂	Au ₉₅ Pd ₅ /TiO ₂	Au ₆₅ Pd ₃₅ /TiO ₂	Au ₅₀ Pd ₅₀ /TiO ₂	Au ₃₅ Pd ₆₅ /TiO ₂	Pd/TiO ₂
Mean	2.4	Mean 2.1	Mean 2.7	Mean 2.1	Mean 2.3	Mean 2.7
Std-dev	0.7	Std-dev 0.4	Std-dev 0.7	Std-dev 0.6	Std-dev 0.8	Std-dev 1.0
Median	2.3	Median 2.0	Median 2.6	Median 2.0	Median 2.1	Median 2.5

Figure S2. (i) Typical XRD pattern of a AuPd/TiO₂ catalyst in the 10-80 2 Theta (°) range, and (ii) of (a) Au₁₀₀Pd₀/TiO₂ (b) Au₉₅Pd₅/TiO₂ (c) Au₆₅Pd₃₅/TiO₂ (d) Au₅₀Pd₅₀/TiO₂ (e) Au₃₅Pd₆₅/TiO₂ (f) Au₀Pd₁₀₀/TiO₂ in the 40-48 2 (°) Theta range. It is possible to notice a single peak typical of alloy formation that shifts in the range 44-45 2-Theta (°) with variation of the Au/Pd molar ratio.

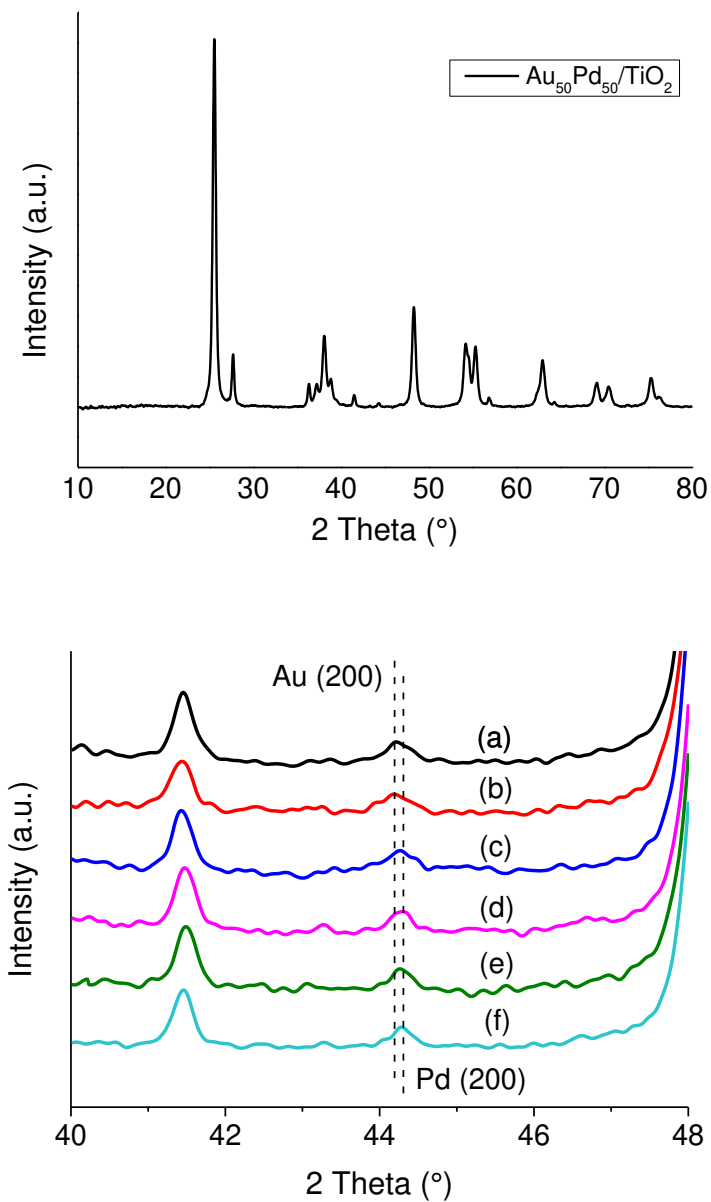


Table S3. Surface area and pore volume for the bare support (TiO₂) and the Au₅₀Pd₅₀/TiO₂ catalyst.

Catalyst	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
TiO ₂	56	0.35
Au ₅₀ Pd ₅₀ /TiO ₂	54	0.32

Figure S3. Au (4f) XPS spectra of $\text{Au}_x\text{Pd}_y/\text{TiO}_2$ catalysts. From the top Pd/TiO_2 , $\text{Au}_{35}\text{Pd}_{65}/\text{TiO}_2$, $\text{Au}_{50}\text{Pd}_{50}/\text{TiO}_2$, $\text{Au}_{65}\text{Pd}_{35}/\text{TiO}_2$, $\text{Au}_{95}\text{Pd}_5/\text{TiO}_2$ and Au/TiO_2 . Au binding energy shifts due to the addition of Pd.

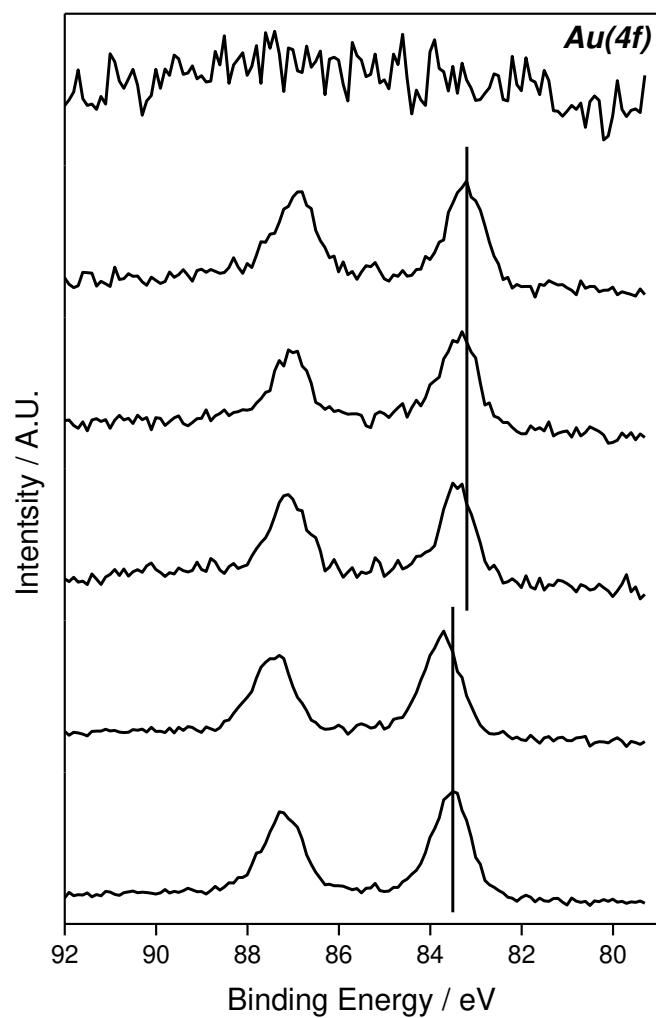


Figure S4. DRIFTS spectra of 1 wt% Au/TiO₂ after an exposure time of 1 and 10 minutes in CO/N₂.

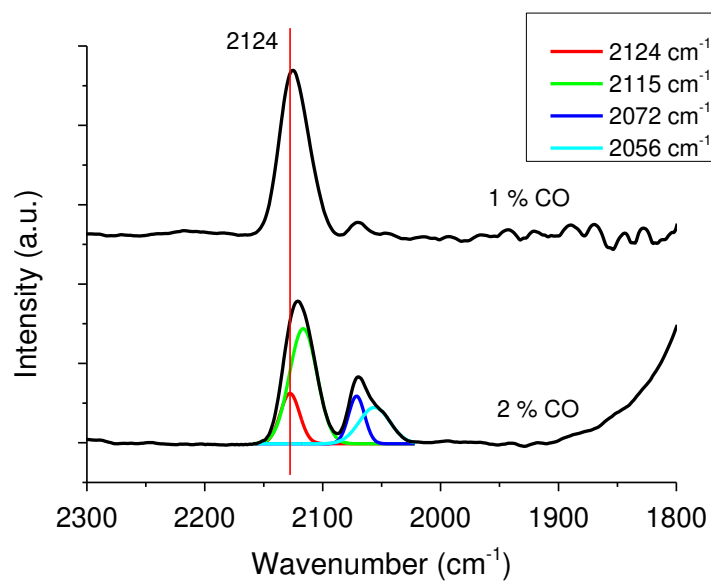


Figure S5. DRIFTS spectra of 1 wt% Pd/TiO₂ after reaching equilibrium (10 minutes) in CO/N₂.

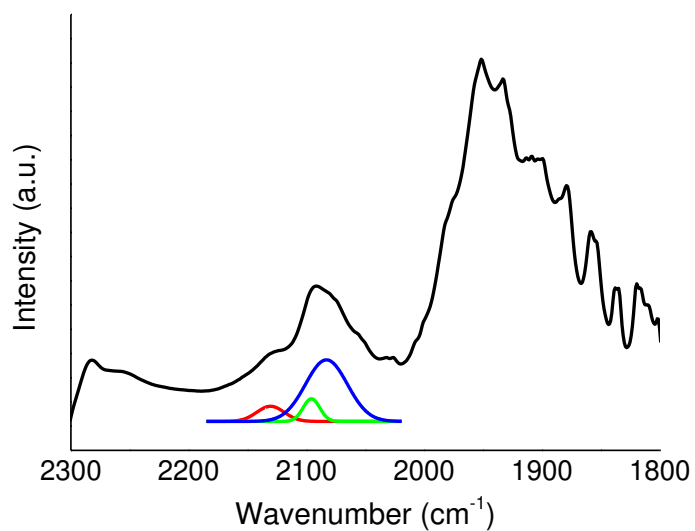


Figure S6. DRIFTS spectra of $\text{Au}_{35}\text{Pd}_{65}/\text{TiO}_2$, $\text{Au}_{50}\text{Pd}_{50}/\text{TiO}_2$ and $\text{Au}_{65}\text{Pd}_{35}/\text{TiO}_2$ after reaching equilibrium (10 minutes) in CO/N_2 .

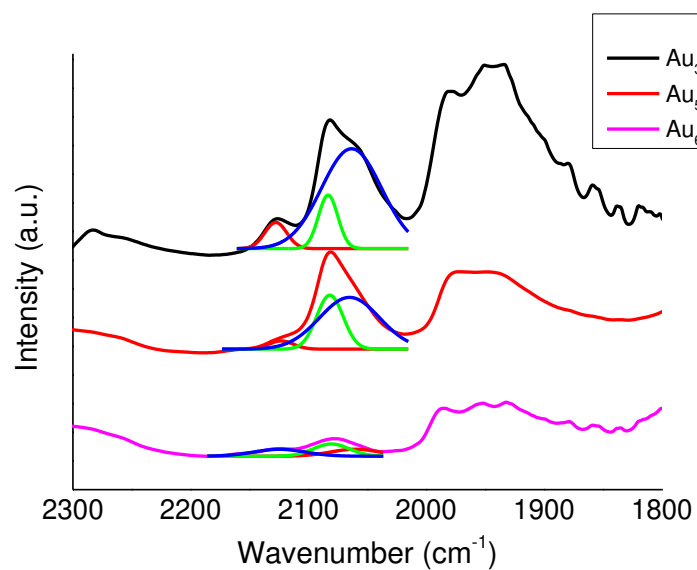


Figure S7. DRIFTS spectra of $\text{Au}_{95}\text{Pd}_5/\text{TiO}_2$ after reaching equilibrium (10 minutes) in CO/N_2 .

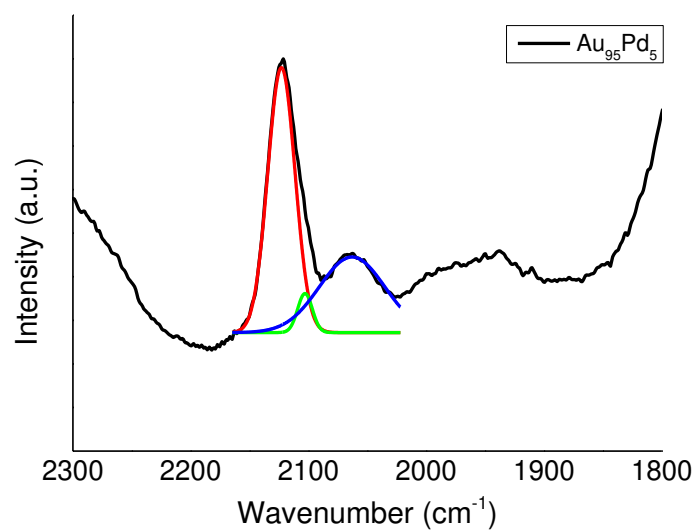


Figure S8. Effect of (a) stirring speed and (b) catalyst amount on the TOF of the reaction.

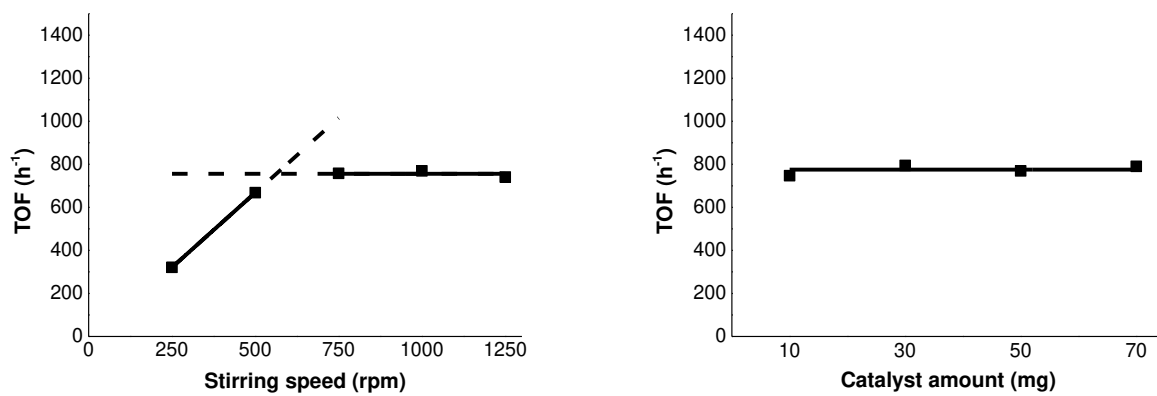


Figure S9. (a) Stirring effect (b) catalyst amount effect (c) temperature effect and (d) H₂ pressure effect on the selectivity at iso-conversion (30 % conversion).

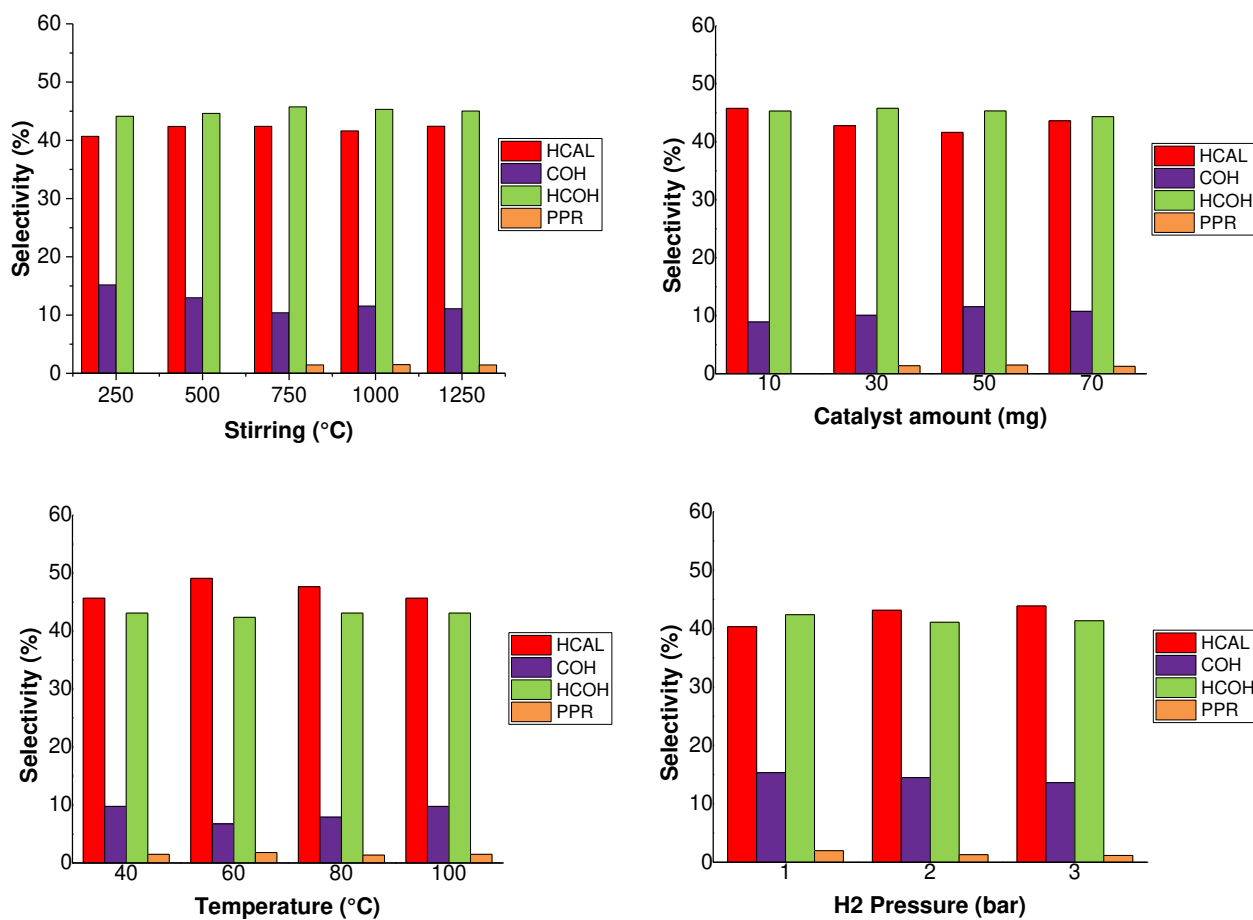


Figure S10. Arrhenius plot for the Au₅₀Pd₅₀/TiO₂ catalyst.

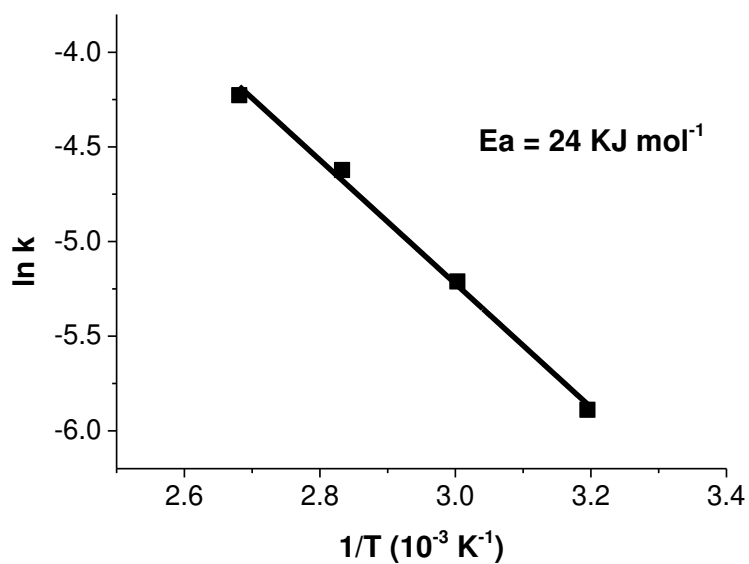


Table S4. Cinnamaldehyde hydrogenation activation energy for different catalysts.

Catalyst	Activation Energy (kJ mol ⁻¹)	Ref.
5 % Pd/SiO ₂	30.1	1
Co-B	18	2
Raney Co	35	
CoPt	17.3	3
5 % Ir/C	37	4
2 % Pt/SBA-15	21	5

Figure S11. FTIR analysis of the fresh and used catalyst.

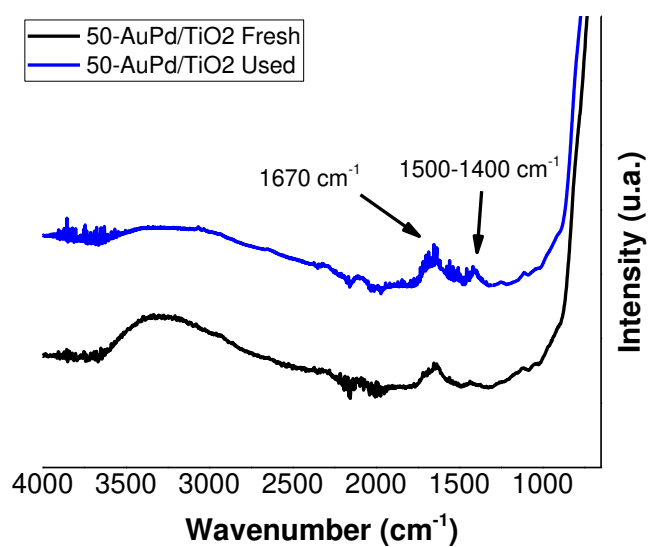


Figure S12. FTIR spectra of pure PVA.

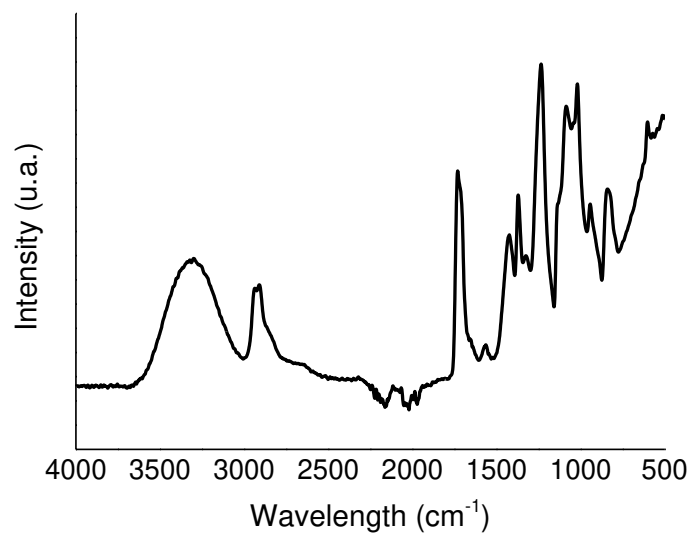


Figure S13. FTIR spectra of pure (a) CAL, (b) HCAL, (c) COH and (d) HCOH.

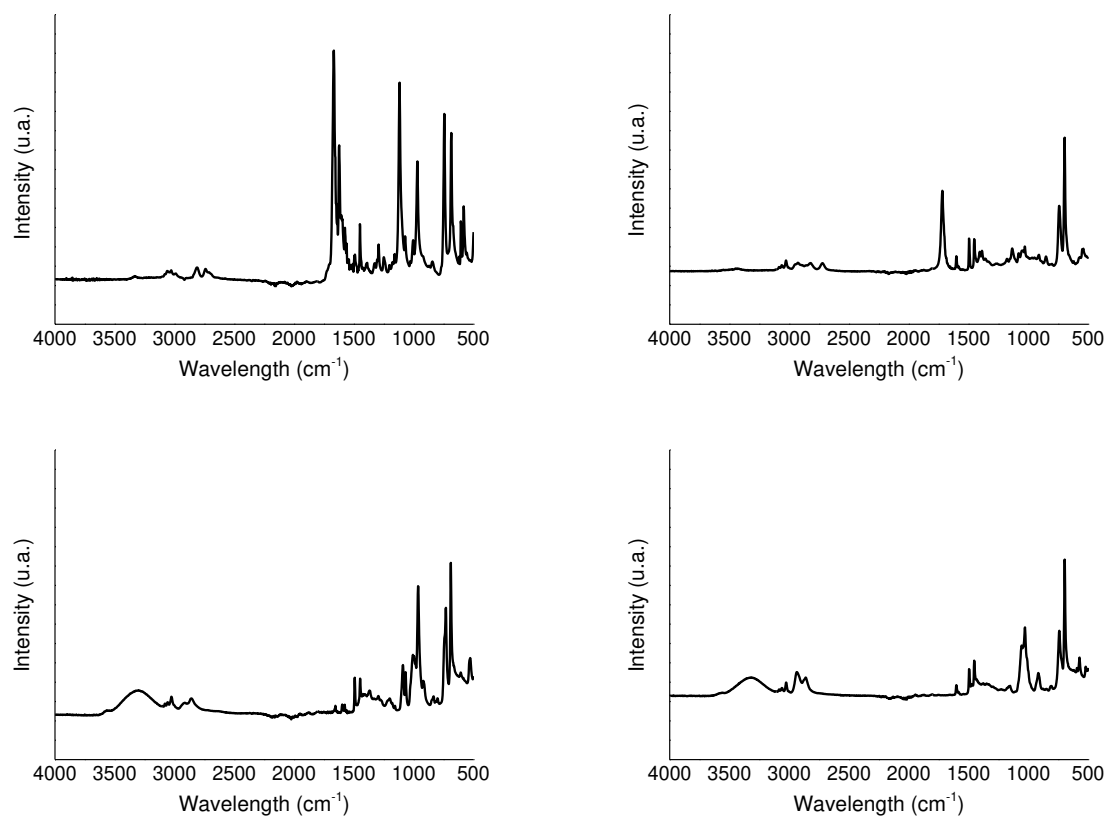


Figure S14. Particle size distribution of fresh and used catalysts (a) Au₅₀Pd₅₀/TiO₂ calcined at 200 °C fresh (b) Au₅₀Pd₅₀/TiO₂ calcined at 200 °C used (c) Au₅₀Pd₅₀/TiO₂ calcined at 300 °C fresh (d) Au₅₀Pd₅₀/TiO₂ calcined at 300 °C used (e) Au₅₀Pd₅₀/TiO₂ calcined at 400 °C fresh (f) Au₅₀Pd₅₀/TiO₂ calcined at 400 °C used.

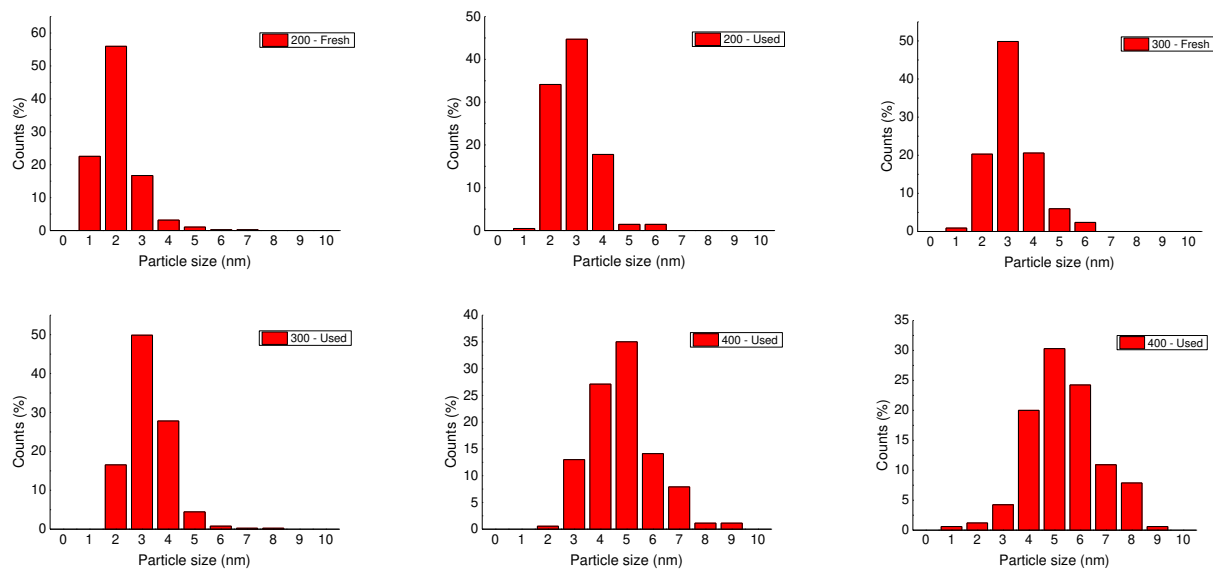


Table S5. XPS quantification analysis on heat treated Au₅₀Pd₅₀/TiO₂ after reaction.

Catalyst	Au/Pd ratio (mol/mol)
Au ₅₀ Pd ₅₀ /TiO ₂	47 : 53
Au ₅₀ Pd ₅₀ /TiO ₂ – 200 °C Used	44 : 56
Au ₅₀ Pd ₅₀ /TiO ₂ – 300 °C Used	39 : 61
Au ₅₀ Pd ₅₀ /TiO ₂ – 400 °C Used	42 : 58

Table S6. Mean and median values obtained by TEM of Au₅₀Pd₅₀/TiO₂ catalysts in nm heat treated at different temperature.

Au ₅₀ Pd ₅₀ /TiO ₂ – 200°C fresh		Au ₅₀ Pd ₅₀ /TiO ₂ – 200 °C used		Au ₅₀ Pd ₅₀ /TiO ₂ – 300°C fresh		Au ₅₀ Pd ₅₀ /TiO ₂ – 300 °C used		Au ₅₀ Pd ₅₀ /TiO ₂ – 400 °C fresh		Au ₅₀ Pd ₅₀ /TiO ₂ – 400 °C used	
Mean	2.5	Mean	3.2	Mean	3.7	Mean	3.8	Mean	5.3	Mean	5.9
Std-dev	0.8	Std-dev	0.8	Std-dev	1.0	Std-dev	0.8	Std-dev	1.2	Std-dev	1.3
Median	2.4	Median	3.2	Median	3.5	Median	3.7	Median	5.2	Median	5.9

Table S7. Activity comparison with other AuPd based catalysts reported in literature.

Catalyst	Solvent	P _{H2} (bar)	T (° C)	TOF (h ⁻¹)	Sel _{H₂CO} (%)	Ref.
Au ₅₀ Pd ₅₀	BMIM	1	40	150	38	6
5 wt% Au ₅₆ Pd ₄₄ /AC	Toluene	1	22	22	38	7
1 wt% Au ₅₀ Pd ₅₀ /SiO ₂	i-Propanol	20	80	6600 ^a	55	8
3.5 wt% Au ₃₀ Pd ₇₀ /SiO ₂	Hexane	5	50	1200	84	9
1 wt% Au ₅₀ Pd ₅₀ /TiO ₂ -300	Toluene	1	100	642	81	This study

^a TOF calculated using exposed metallic surface as active site.

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