Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Cinnamaldehyde hydrogenation using Au-Pd catalysts prepared by sol immobilisation

Stefano Cattaneo, Simon J. Freakley, David J. Morgan, Meenakshisundaram Sankar, Nikolaos Dimitratos, and Graham J. Hutchings*

Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, CF10 3AT, United Kingdom.

* Hutch@cardiff.ac.uk

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

Catalyst	Metal loading (wt %)	Au/Pd ratio (mol/mol)			Binding energy (eV)	
	MP-AES	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_0Pd_{100}/TiO_2	0.98	0 : 100	0 : 100	0 : 100	-	335.0

Figure S1. Particle size distribution of (a) Au/TiO_2 (b) $Au_{95}Pd_5/TiO_2$ (c) $Au_{65}Pd_{35}/TiO_2$ (d) $Au_{50}Pd_{50}/TiO_2$ (e) $Au_{35}Pd_{65}/TiO_2$ (f) Pd/TiO_2.

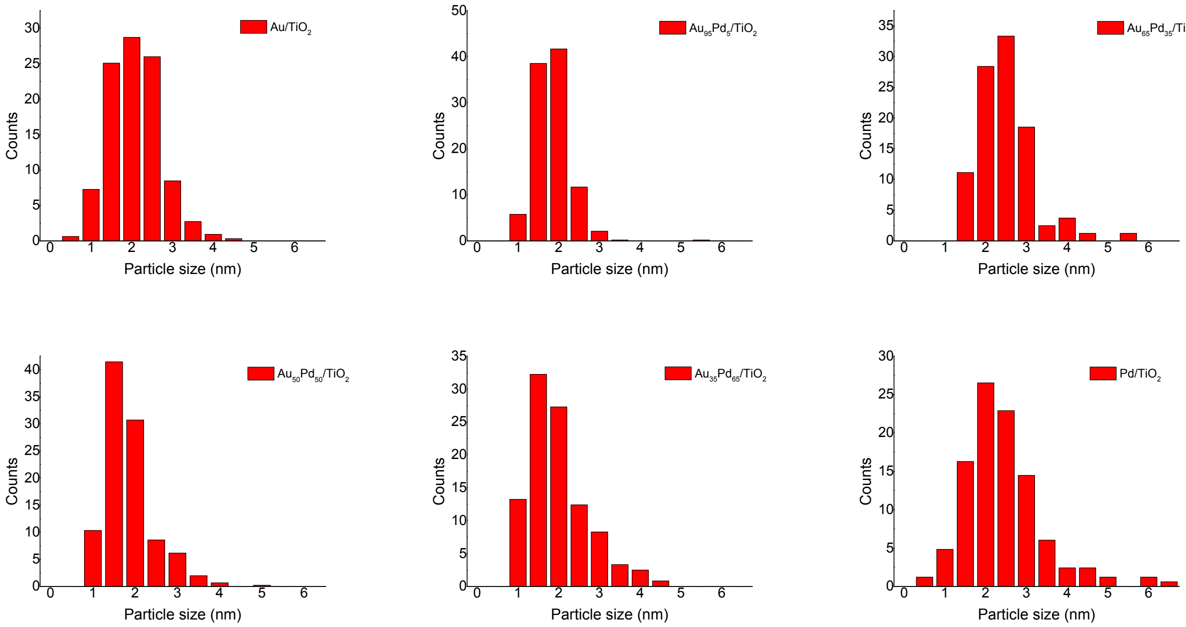

Table S2. Mean and median values (nm) obtained by TEM of the supported monometallic and bimetallic catalysts.

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/TiO_2 catalyst in the 10-80 2 Theta (°) range, and (ii) of (a) $Au_{100}Pd_0/TiO_2$ (b) $Au_{95}Pd_5/TiO_2$ (c) $Au_{65}Pd_{35}/TiO_2$ (d) $Au_{50}Pd_{50}/TiO_2$ (e) $Au_{35}Pd_{65}/TiO_2$ (f) Au_0Pd_{100}/TiO_2 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.

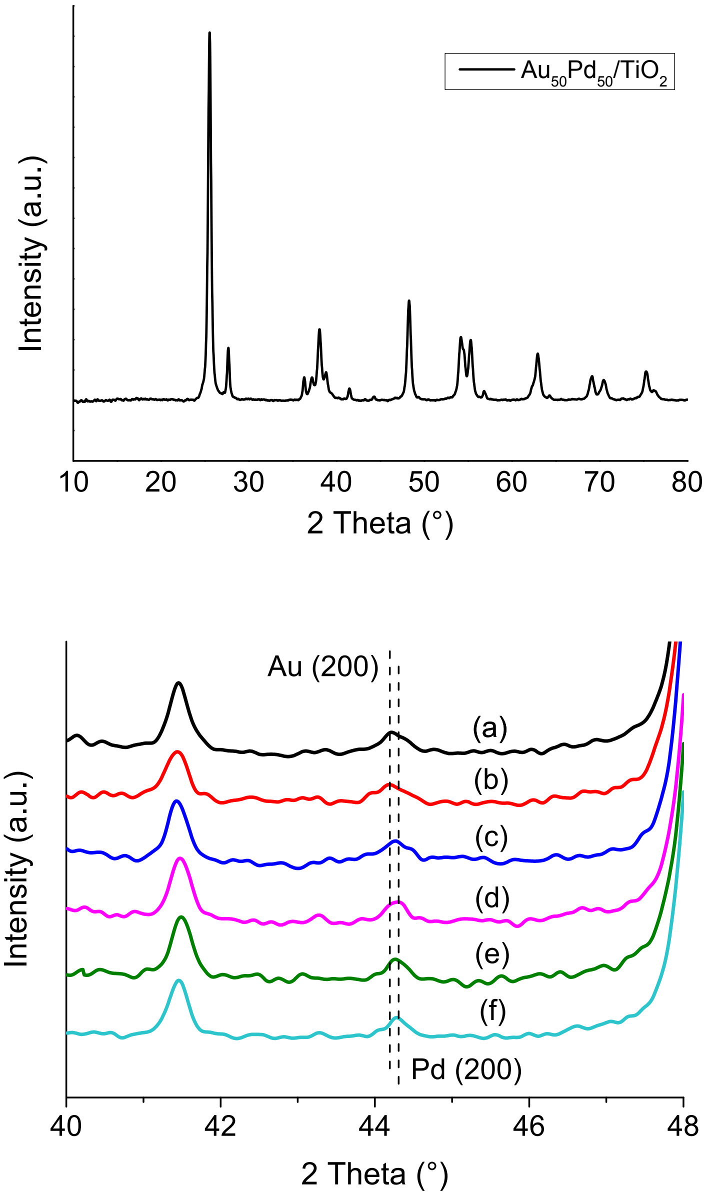

Table S3. Surface area and pore volume for the bare support (TiO_2) and the $Au_{50}Pd_{50}/TiO_2$ catalyst.

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 Au_xPd_y/TiO_2 catalysts. From the top Pd/TiO_2, $Au_{35}Pd_{65}/TiO_2$, $Au_{50}Pd_{50}/TiO_2$, $Au_{65}Pd_{35}/TiO_2$, $Au_{95}Pd_5/TiO_2$ and Au/TiO_2. Au binding energy shifts due to the addition of Pd.

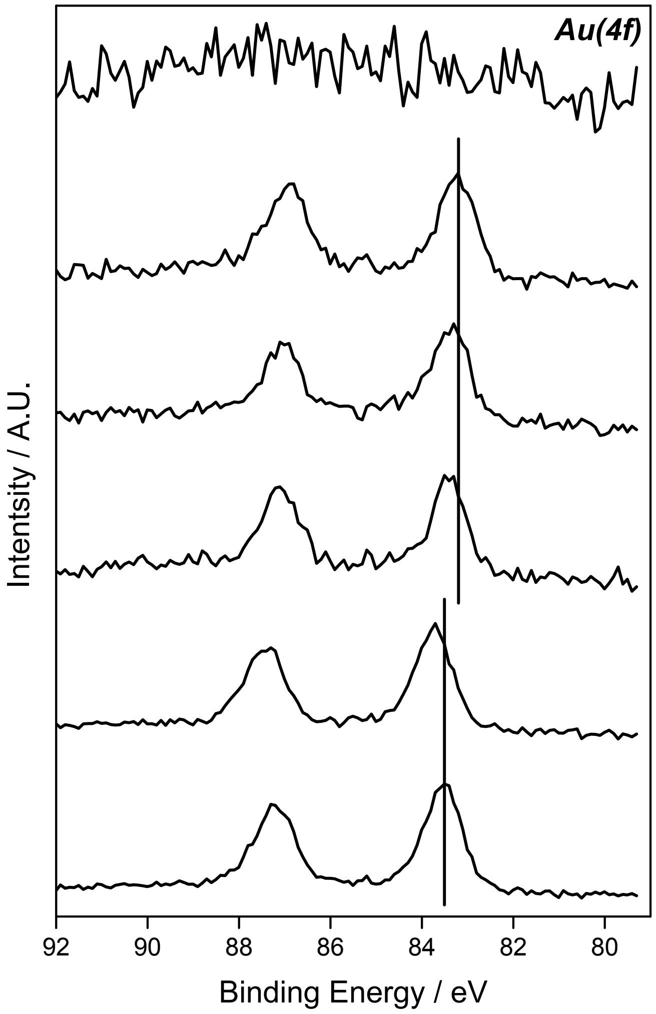

Figure S4. DRIFTS spectra of 1 wt% Au/TiO_2 after an exposure time of 1 and 10 minutes in CO/N_2.

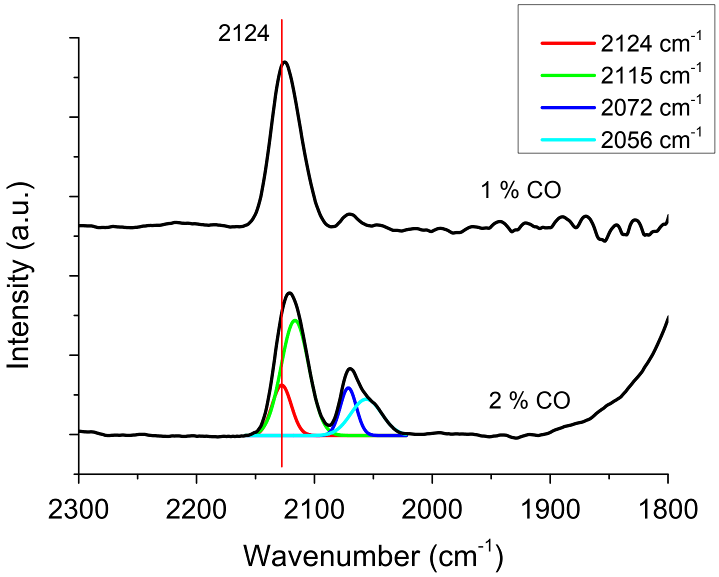

Figure S5. DRIFTS spectra of 1 wt% Pd/TiO_2 after reaching equilibrium (10 minutes) in CO/N_2.

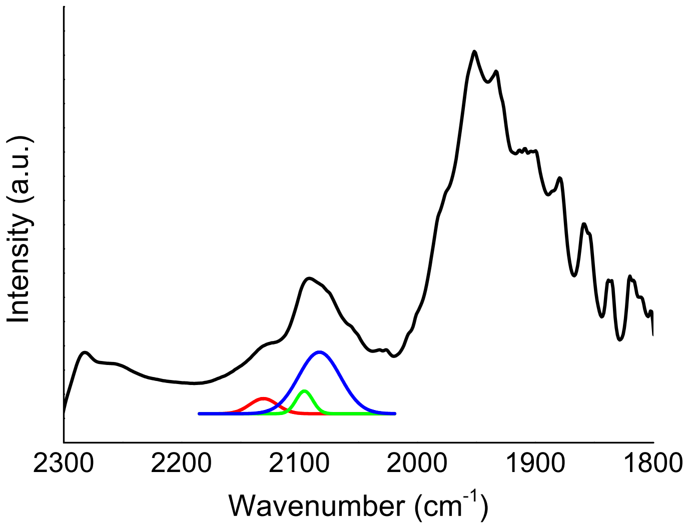

Figure S6. DRIFTS spectra of $Au_{35}Pd_{65}/TiO_2$, $Au_{50}Pd_{50}/TiO_2$ and $Au_{65}Pd_{35}/TiO_2$ after reaching equilibrium (10 minutes) in CO/N_2.

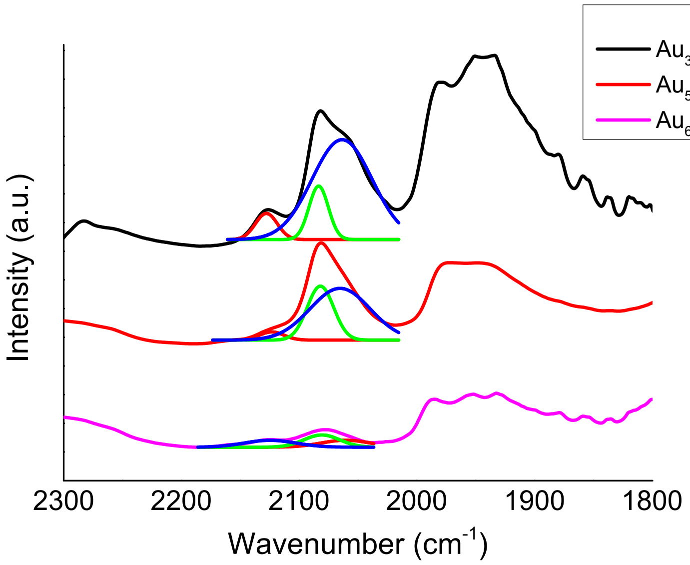

Figure S7. DRIFTS spectra of of $Au_{95}Pd_5/TiO_2$ after reaching equilibrium (10 minutes) in CO/N_2.

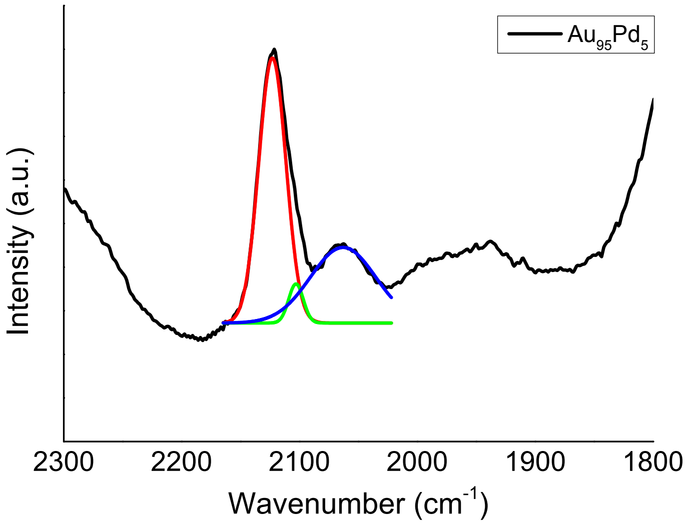

Figure S8. Effect of (a) stirring speed and (b) catalyst amount on the TOF of the reaction.

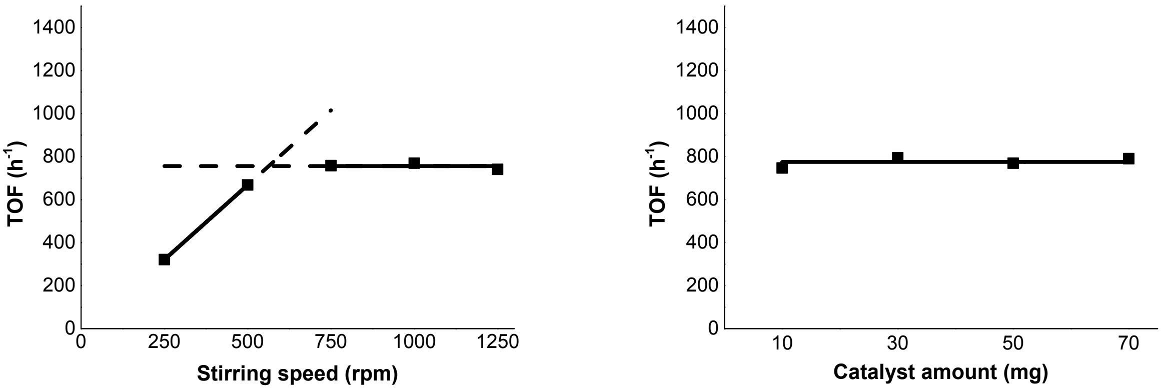

Figure S9. (a) Stirring effect (b) catalyst amount effect (c) temperature effect and (d) H_2 pressure effect on the selectivity at iso-conversion (30 % conversion).

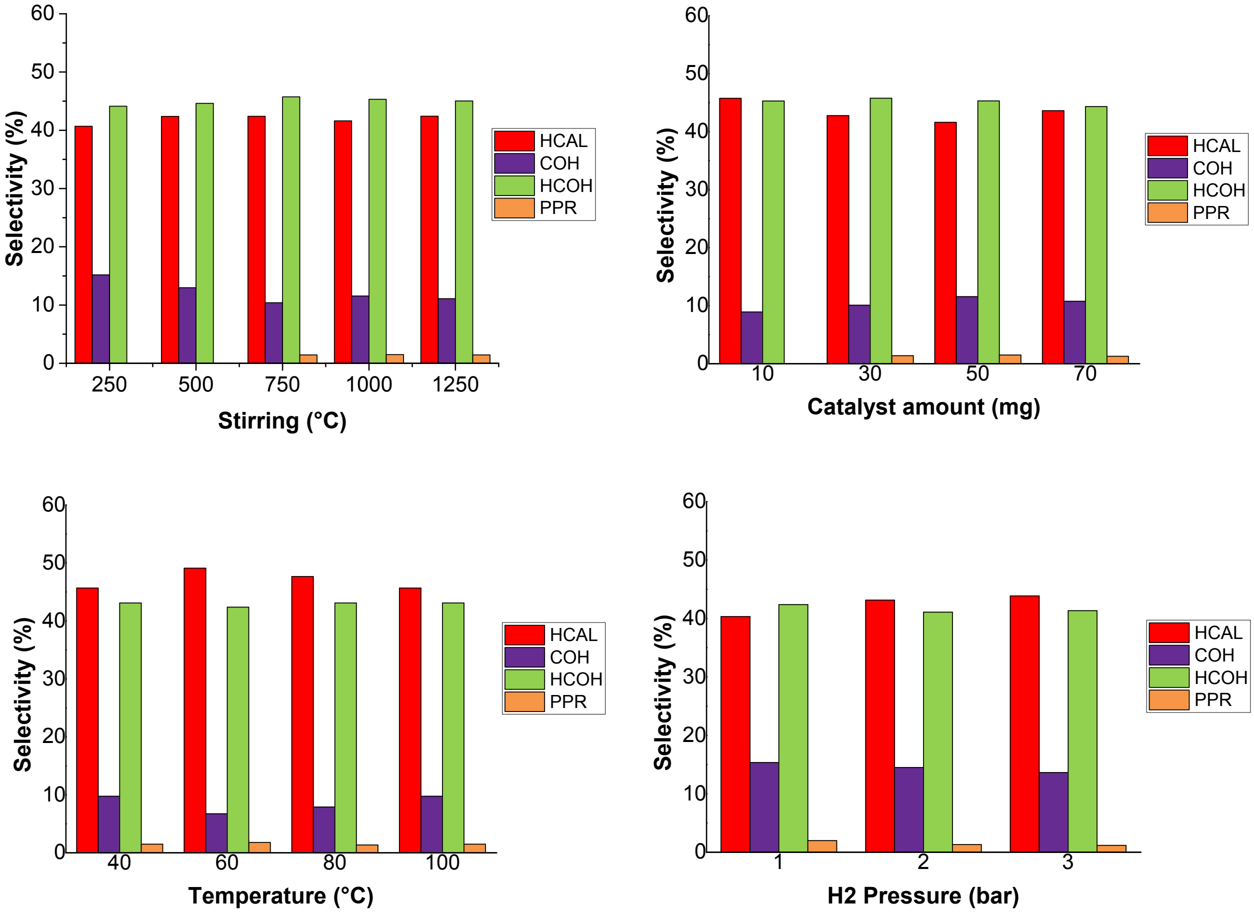

Figure S10. Arrhenius plot for the $Au_{50}Pd_{50}/TiO_2$ catalyst.

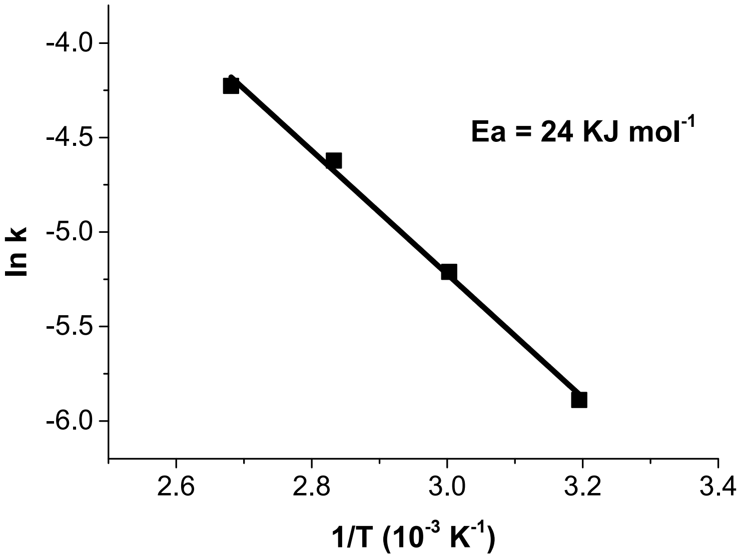

Table S4. Cinnamaldehyde hydrogenation activation energy for different catalysts.

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.

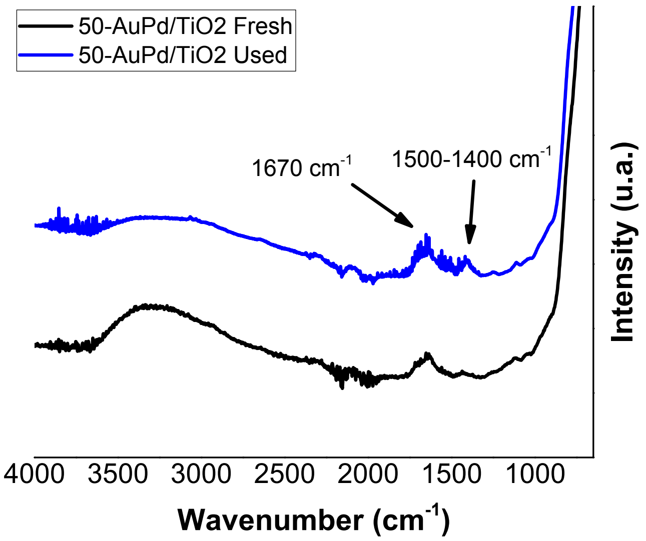

Figure S12. FTIR spectra of pure PVA.

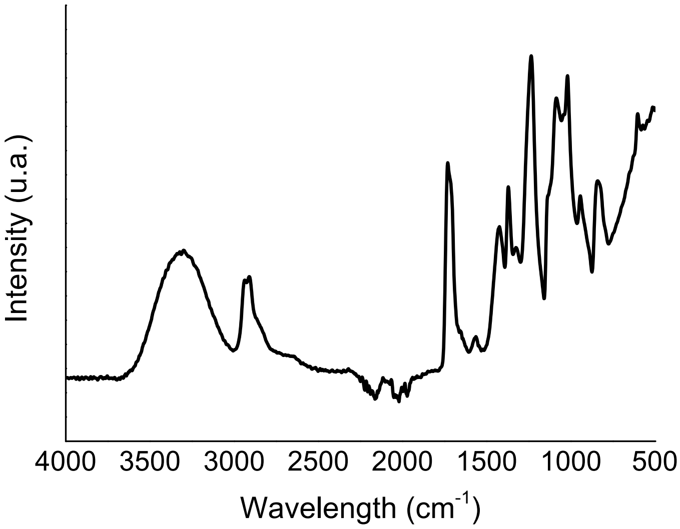

Figure S13. FTIR spectra of pure (a) CAL, (b) HCAL, (c) COH and (d) HCOH.

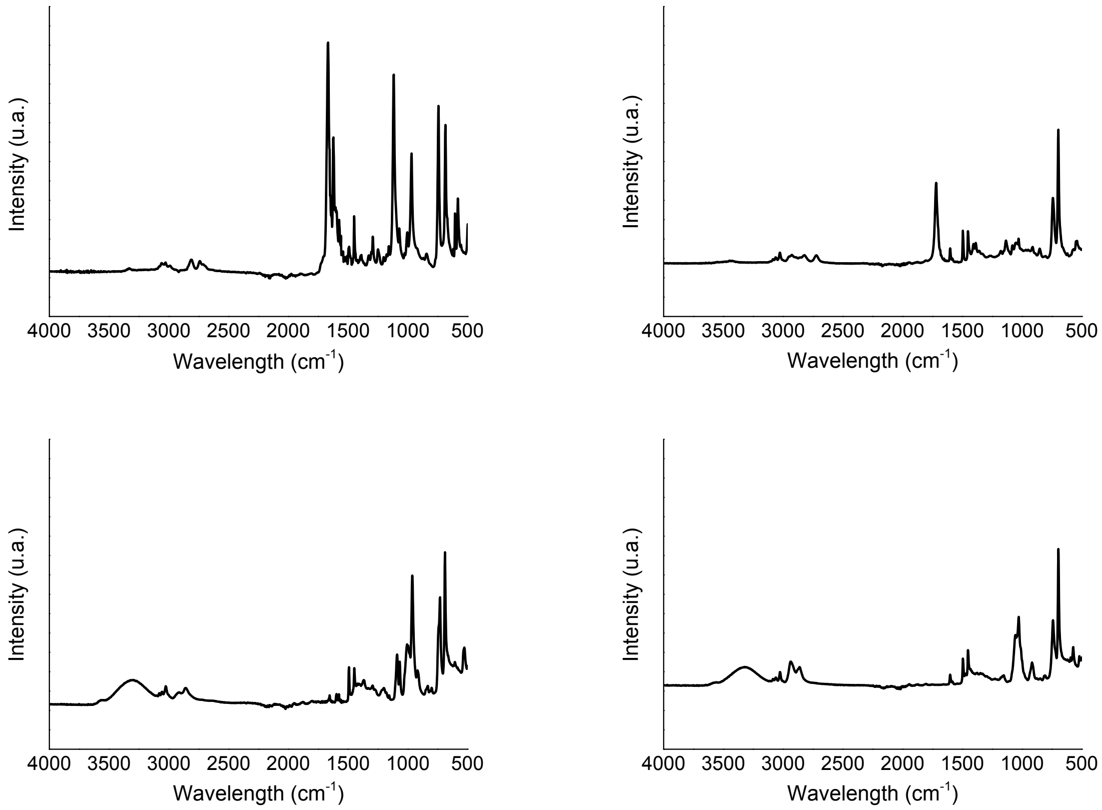

Figure S14. Particle size distribution of fresh and used catalysts (a) $Au_{50}Pd_{50}/TiO_2$ calcined at 200 °C fresh (b) $Au_{50}Pd_{50}/TiO_2$ calcined at 200 °C used (c) $Au_{50}Pd_{50}/TiO_2$ calcined at 300 °C fresh (d) $Au_{50}Pd_{50}/TiO_2$ calcined at 300 °C used (e) $Au_{50}Pd_{50}/TiO_2$ calcined at 400 °C fresh (f) $Au_{50}Pd_{50}/TiO_2$ calcined at 400 °C used.

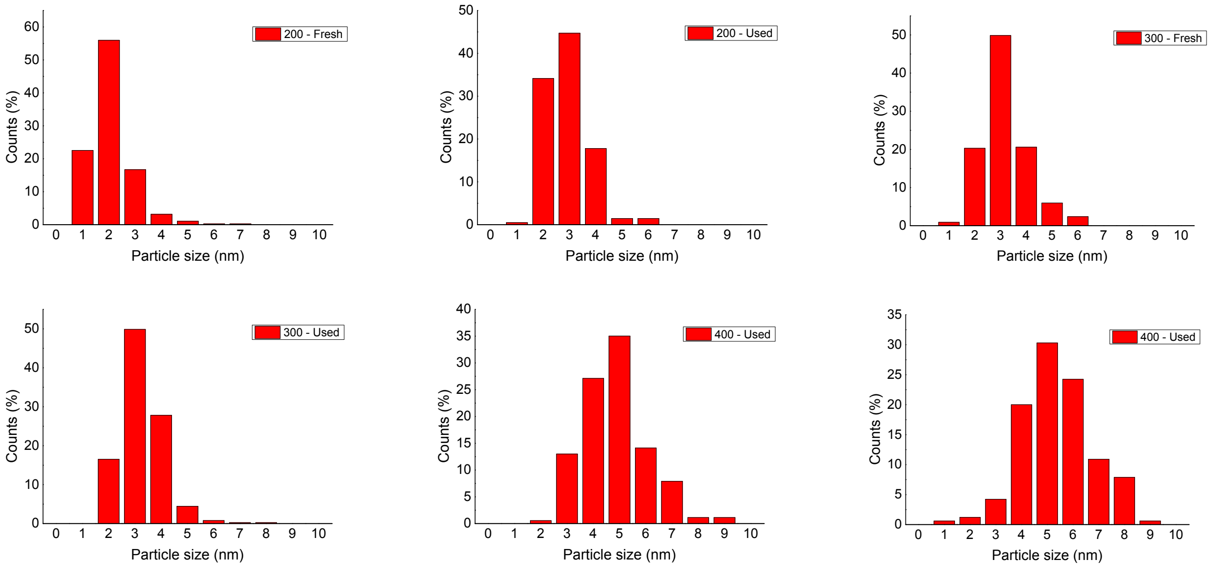

Table S5. XPS quantification analysis on heat treated $Au_{50}Pd_{50}/TiO_2$ after reaction.

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 $Au_{50}Pd_{50}/TiO_2$ 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_{HCAL} (%)	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.

Reference

1 S. Mahmoud, A. Hammoudeh, S. Gharaibeh and J. Melsheimer, *J. Mol. Catal. A Chem.*, 2002, **178**, 161–167.

2 H. Li, X. Chen, M. Wang and Y. Xu, *Appl. Catal. A Gen.*, 2002, **225**, 117–130.

3 W. O. Oduro, N. Cailuo, K. M. K. Yu, H. Yang and S. C. Tsang, *Phys. Chem. Chem. Phys.*, 2011, **13**, 2590–602.

4 J. P. Breen, R. Burch, J. Gomez-Lopez, K. Griffin and M. Hayes, *Appl. Catal. A Gen.*, 2004, **268**, 267–274.

5 L. J. Durndell, C. M. a. Parlett, N. S. Hondow, M. a. Isaacs, K. Wilson and A. F. Lee, *Sci. Rep.*, 2015, **5**, 9425.

6 P. Dash, N. A. Dehm and R. W. J. Scott, *J. Mol. Catal. A Chem.*, 2008, **286**, 114–119.

7 T. Szumełda, A. Drelinkiewicz, R. Kosydar and J. Gurgul, *Appl. Catal. A Gen.*, 2014, **487**, 1–15.

8 V. I. Pârvulescu, V. Pârvulescu, U. Endruschat, G. Filoti, F. E. Wagner, C. Kübel and R. Richards, *Chem. - A Eur. J.*, 2006, **12**, 2343–2357.

9 X. Yang, D. Chen, S. Liao, H. Song, Y. Li, Z. Fu and Y. Su, *J. Catal.*, 2012, **291**, 36–43.