

## Supporting Information

### Cinnamaldehyde hydrogenation using Au-Pd catalysts prepared by sol immobilisation

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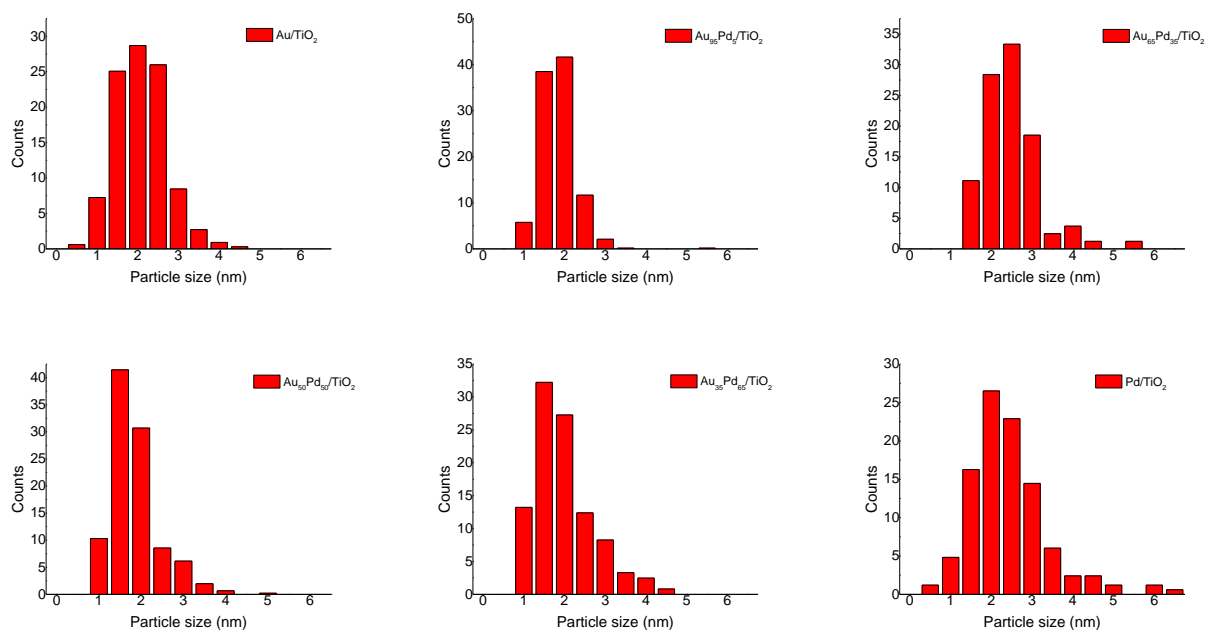
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**Table S1.** MP-AES and XPS quantification analysis of the Au<sub>x</sub>Pd<sub>y</sub> catalysts.

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

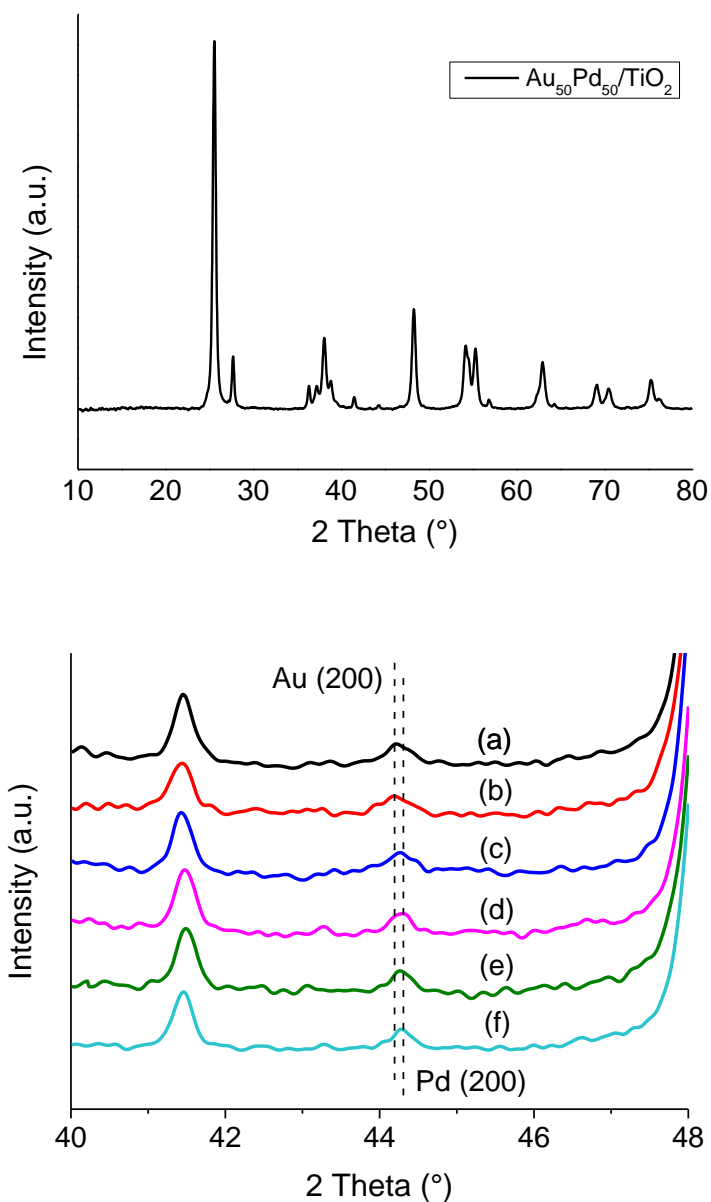
**Figure S1.** Particle size distribution of (a) Au/TiO<sub>2</sub> (b) Au<sub>95</sub>Pd<sub>5</sub>/TiO<sub>2</sub> (c) Au<sub>65</sub>Pd<sub>35</sub>/TiO<sub>2</sub> (d) Au<sub>50</sub>Pd<sub>50</sub>/TiO<sub>2</sub> (e) Au<sub>35</sub>Pd<sub>65</sub>/TiO<sub>2</sub> (f) Pd/TiO<sub>2</sub>.



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

	Au/TiO <sub>2</sub>	Au <sub>95</sub> Pd <sub>5</sub> /TiO <sub>2</sub>	Au <sub>65</sub> Pd <sub>35</sub> /TiO <sub>2</sub>	Au <sub>50</sub> Pd <sub>50</sub> /TiO <sub>2</sub>	Au <sub>35</sub> Pd <sub>65</sub> /TiO <sub>2</sub>	Pd/TiO <sub>2</sub>
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

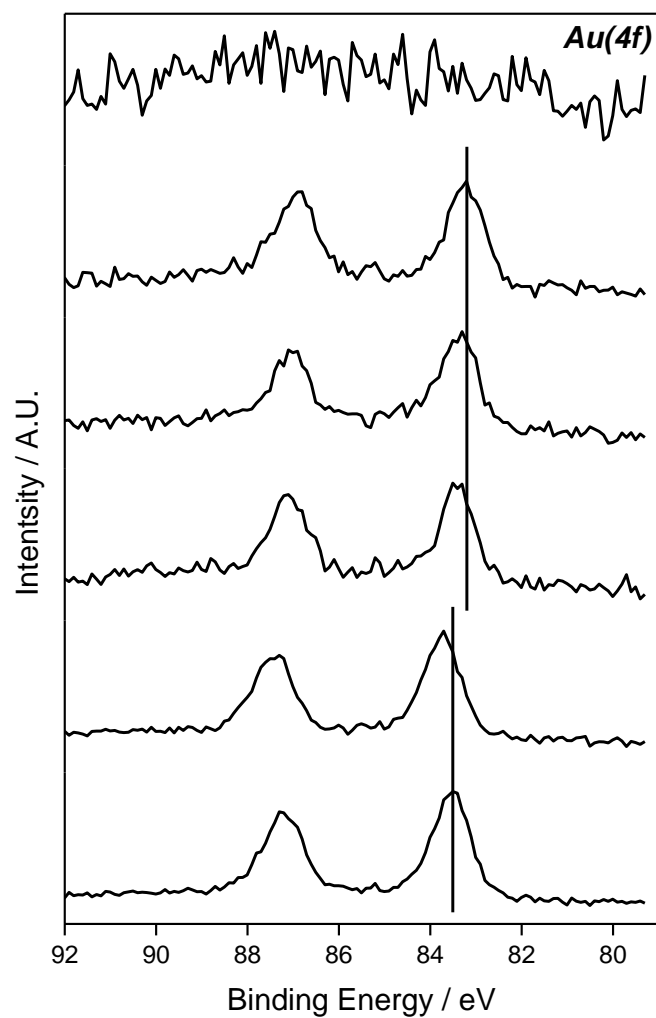
**Figure S2.** (i) Typical XRD pattern of a AuPd/TiO<sub>2</sub> catalyst in the 10-80 2 Theta (°) range, and (ii) of (a) Au<sub>100</sub>Pd<sub>0</sub>/TiO<sub>2</sub> (b) Au<sub>95</sub>Pd<sub>5</sub>/TiO<sub>2</sub> (c) Au<sub>65</sub>Pd<sub>35</sub>/TiO<sub>2</sub> (d) Au<sub>50</sub>Pd<sub>50</sub>/TiO<sub>2</sub> (e) Au<sub>35</sub>Pd<sub>65</sub>/TiO<sub>2</sub> (f) Au<sub>0</sub>Pd<sub>100</sub>/TiO<sub>2</sub> 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.



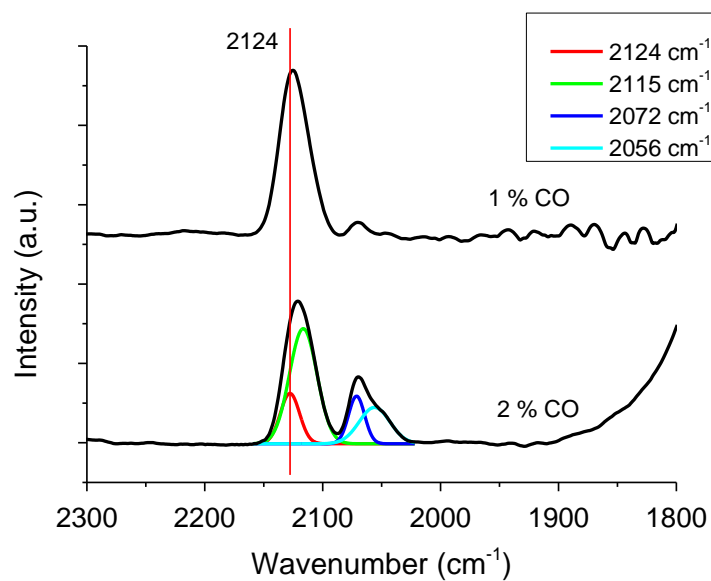
**Table S3.** Surface area and pore volume for the bare support (TiO<sub>2</sub>) and the Au<sub>50</sub>Pd<sub>50</sub>/TiO<sub>2</sub> catalyst.

Catalyst	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )
TiO <sub>2</sub>	56	0.35
Au <sub>50</sub> Pd <sub>50</sub> /TiO <sub>2</sub>	54	0.32

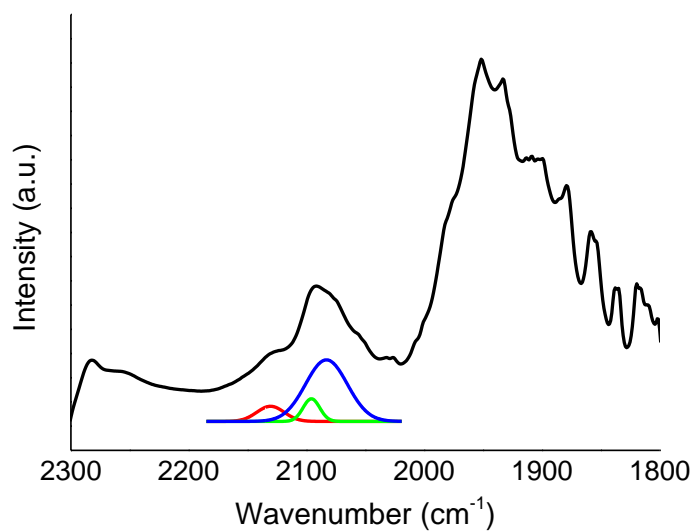
**Figure S3.** Au (4f) XPS spectra of  $\text{Au}_x\text{Pd}_y/\text{TiO}_2$  catalysts. From the top  $\text{Pd}/\text{TiO}_2$ ,  $\text{Au}_{35}\text{Pd}_{65}/\text{TiO}_2$ ,  $\text{Au}_{50}\text{Pd}_{50}/\text{TiO}_2$ ,  $\text{Au}_{65}\text{Pd}_{35}/\text{TiO}_2$ ,  $\text{Au}_{95}\text{Pd}_5/\text{TiO}_2$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



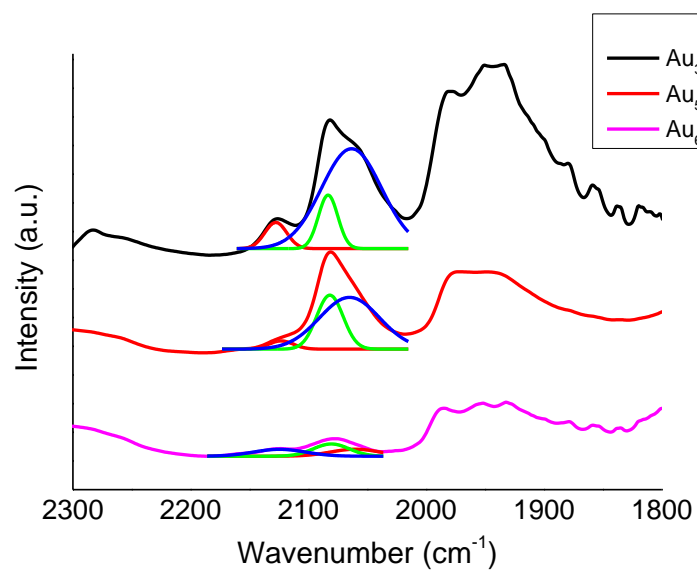
**Figure S4.** DRIFTS spectra of 1 wt% Au/TiO<sub>2</sub> after an exposure time of 1 and 10 minutes in CO/N<sub>2</sub>.



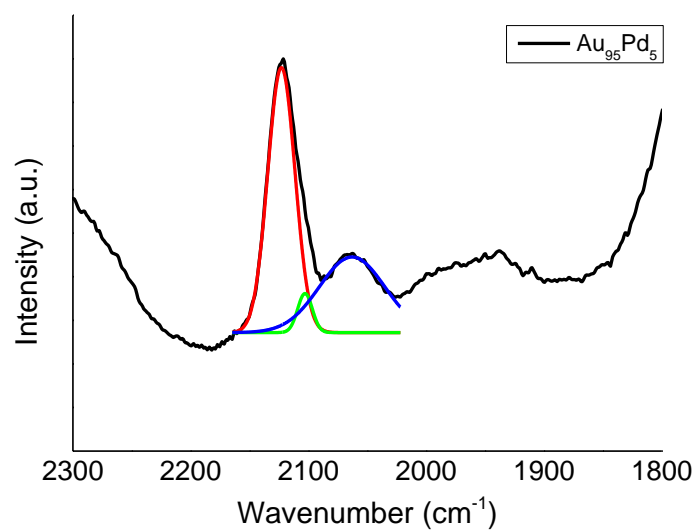
**Figure S5.** DRIFTS spectra of 1 wt% Pd/TiO<sub>2</sub> after reaching equilibrium (10 minutes) in CO/N<sub>2</sub>.



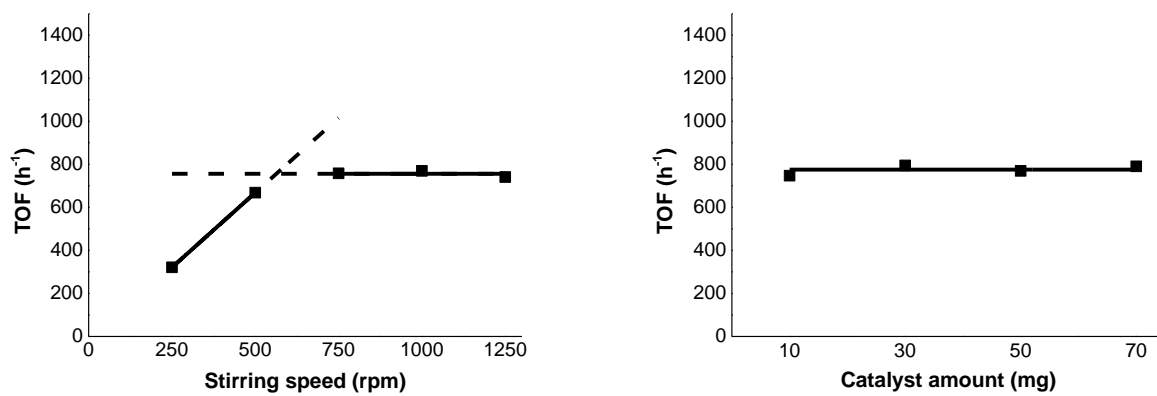
**Figure S6.** DRIFTS spectra of  $\text{Au}_{35}\text{Pd}_{65}/\text{TiO}_2$ ,  $\text{Au}_{50}\text{Pd}_{50}/\text{TiO}_2$  and  $\text{Au}_{65}\text{Pd}_{35}/\text{TiO}_2$  after reaching equilibrium (10 minutes) in  $\text{CO}/\text{N}_2$ .



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

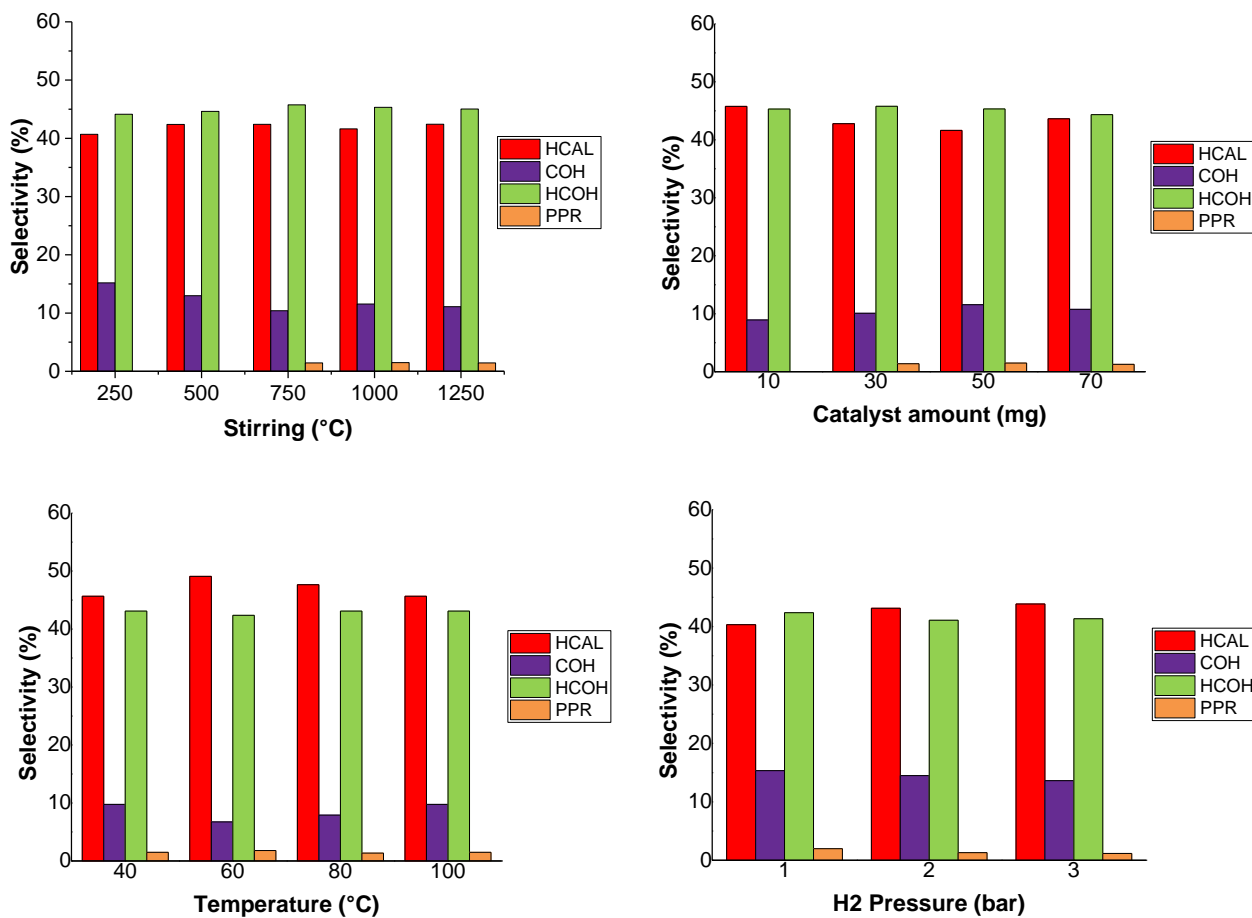


**Figure S8.** Effect of (a) stirring speed and (b) catalyst amount on the TOF of the reaction.

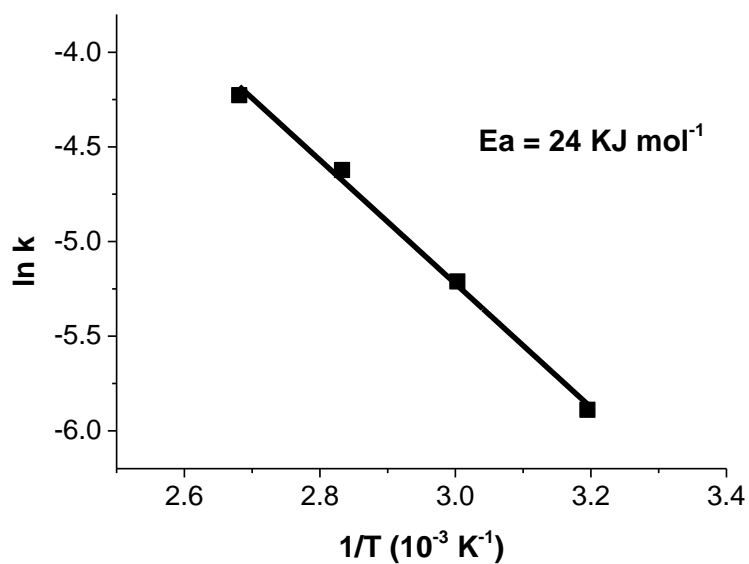




**Figure S9.** (a) Stirring effect (b) catalyst amount effect (c) temperature effect and (d) H<sub>2</sub> pressure effect on the selectivity at iso-conversion (30 % conversion).



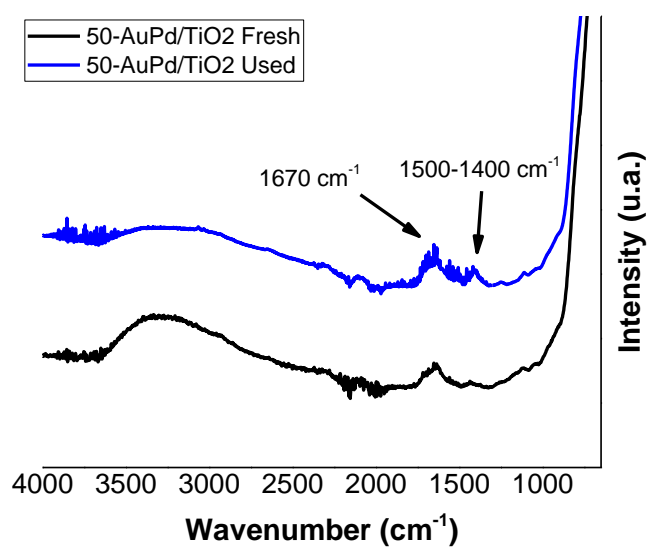
**Figure S10.** Arrhenius plot for the Au<sub>50</sub>Pd<sub>50</sub>/TiO<sub>2</sub> catalyst.



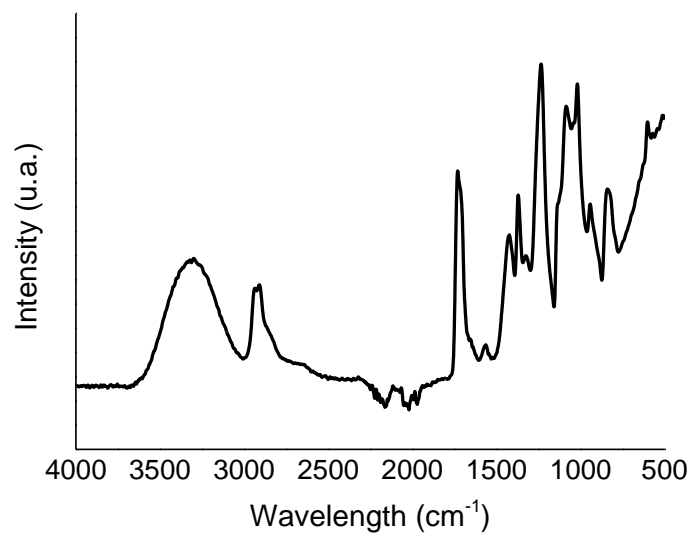
**Table S4.** Cinnamaldehyde hydrogenation activation energy for different catalysts.

Catalyst	Activation Energy (kJ mol <sup>-1</sup> )	Ref.
5 % Pd/SiO <sub>2</sub>	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

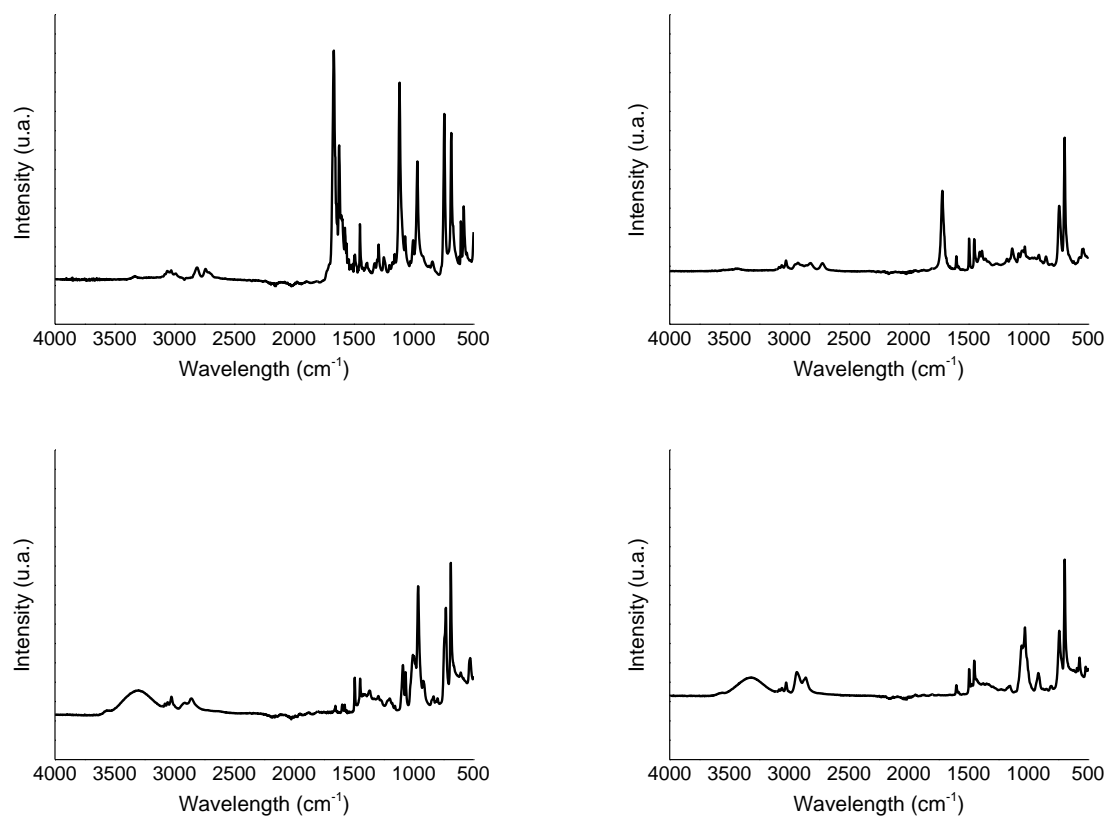
**Figure S11.** FTIR analysis of the fresh and used catalyst.



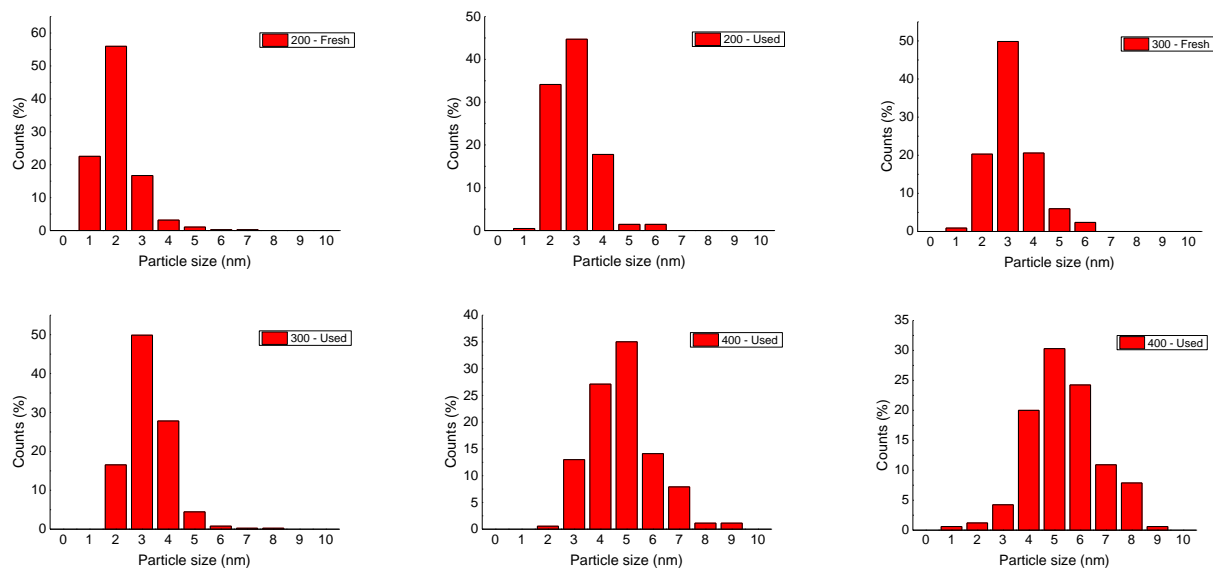
**Figure S12.** FTIR spectra of pure PVA.



**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<sub>50</sub>Pd<sub>50</sub>/TiO<sub>2</sub> calcined at 200 °C fresh (b) Au<sub>50</sub>Pd<sub>50</sub>/TiO<sub>2</sub> calcined at 200 °C used (c) Au<sub>50</sub>Pd<sub>50</sub>/TiO<sub>2</sub> calcined at 300 °C fresh (d) Au<sub>50</sub>Pd<sub>50</sub>/TiO<sub>2</sub> calcined at 300 °C used (e) Au<sub>50</sub>Pd<sub>50</sub>/TiO<sub>2</sub> calcined at 400 °C fresh (f) Au<sub>50</sub>Pd<sub>50</sub>/TiO<sub>2</sub> calcined at 400 °C used.



**Table S5.** XPS quantification analysis on heat treated Au<sub>50</sub>Pd<sub>50</sub>/TiO<sub>2</sub> after reaction.

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

**Table S6.** Mean and median values obtained by TEM of Au<sub>50</sub>Pd<sub>50</sub>/TiO<sub>2</sub> catalysts in nm heat treated at different temperature.

Au <sub>50</sub> Pd <sub>50</sub> /TiO <sub>2</sub> – 200°C fresh		Au <sub>50</sub> Pd <sub>50</sub> /TiO <sub>2</sub> – 200 °C used		Au <sub>50</sub> Pd <sub>50</sub> /TiO <sub>2</sub> – 300°C fresh		Au <sub>50</sub> Pd <sub>50</sub> /TiO <sub>2</sub> – 300 °C used		Au <sub>50</sub> Pd <sub>50</sub> /TiO <sub>2</sub> – 400 °C fresh		Au <sub>50</sub> Pd <sub>50</sub> /TiO <sub>2</sub> – 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 <sub>H2</sub> (bar)	T (° C)	TOF (h <sup>-1</sup> )	Sel <sub>H<sub>2</sub>AL</sub> (%)	Ref.
Au <sub>50</sub> Pd <sub>50</sub>	BMIM	1	40	150	38	6
5 wt% Au <sub>56</sub> Pd <sub>44</sub> /AC	Toluene	1	22	22	38	7
1 wt% Au <sub>50</sub> Pd <sub>50</sub> /SiO <sub>2</sub>	i-Propanol	20	80	6600 <sup>a</sup>	55	8
3.5 wt% Au <sub>30</sub> Pd <sub>70</sub> /SiO <sub>2</sub>	Hexane	5	50	1200	84	9
1 wt% Au <sub>50</sub> Pd <sub>50</sub> /TiO <sub>2</sub> -300	Toluene	1	100	642	81	This study

<sup>a</sup> TOF calculated using exposed metallic surface as active site.

## Reference

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