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

Effects of Pd and Co Intimacy in Pd-modified Co/TiO_2 Catalysts for Direct CO_2 Hydrogenation to Fuels: the Closer not the Better

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Supporting Information

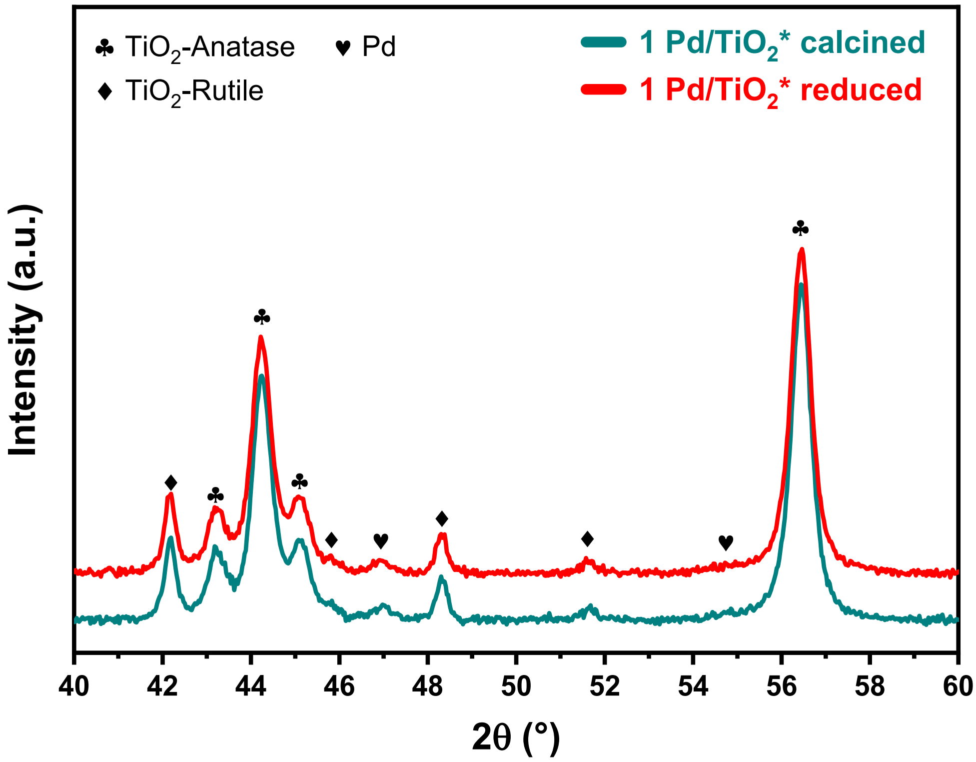


Figure S1. XRD diffractograms (40°-60°) of the 1Pd/TiO_2* catalyst after calcination and subsequent reduction (4 h, 350 °C, 40% H_2/Ar).

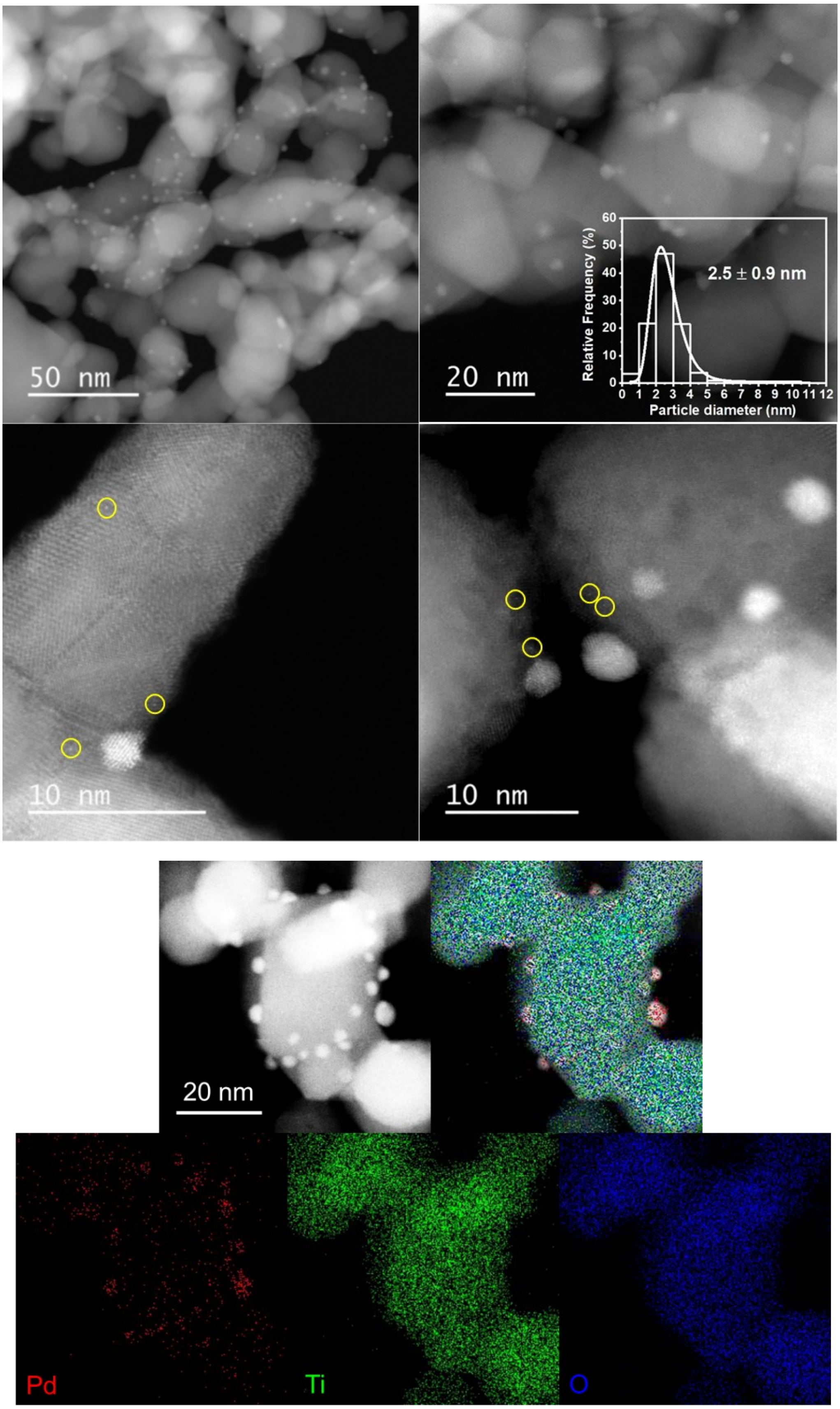


Figure S2. HAADF-STEM micrographs with Pd particle size distribution and EDX analysis of the reduced 1Pd/TiO_2* catalyst. Pd single atoms are surrounded by a yellow circle for better visualization.

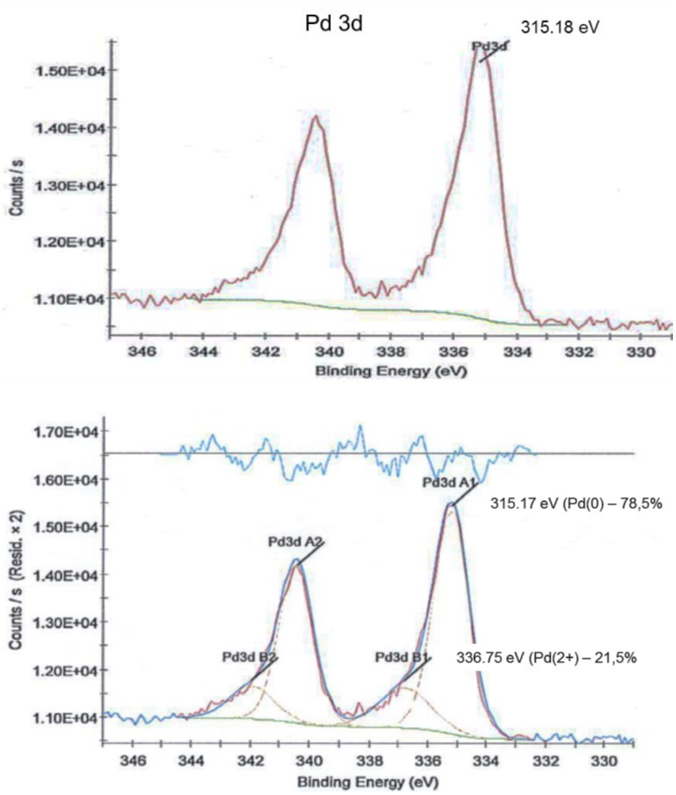


Figure S3. High-resolution XPS spectrum of Pd 3d of the sample 1Pd/TiO_2*.

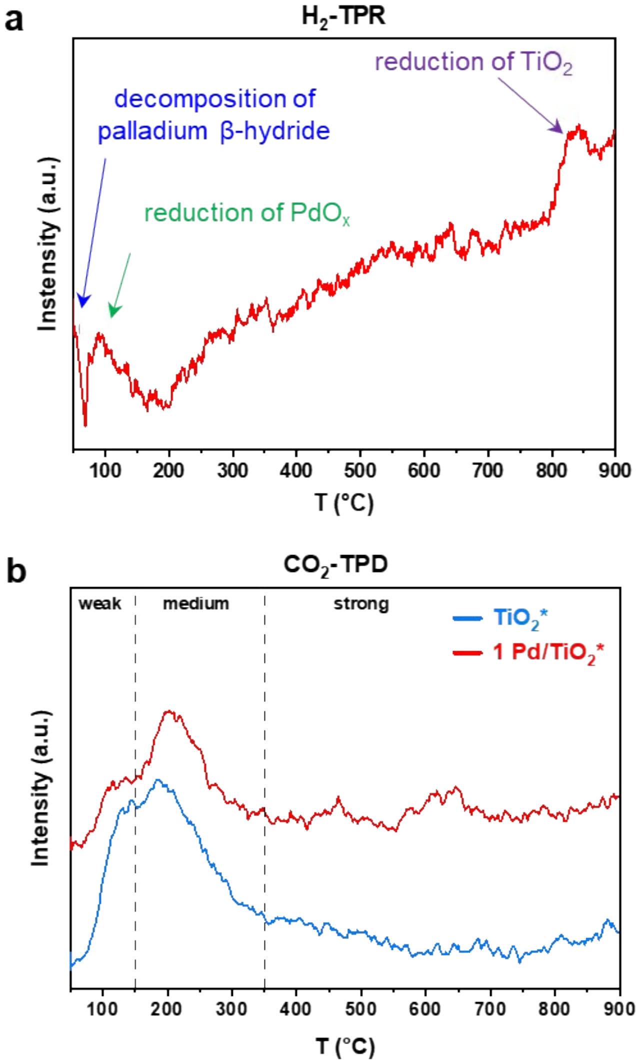


Figure S4. a H_2-TPR profile of the 1Pd/TiO_2* catalyst; and **b** CO_2-TPD profiles of the 1Pd/TiO_2* catalyst and of the TiO_2* support.

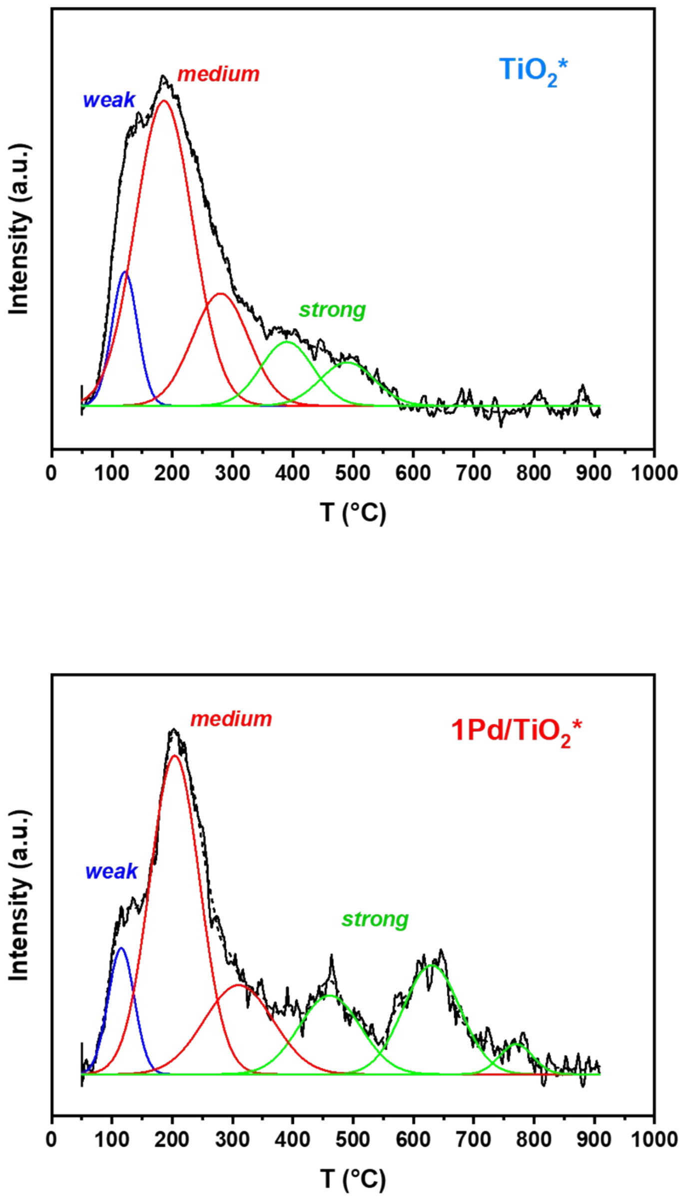


Figure S5. CO_2-TPD profiles and deconvolutions of the support and the $1Pd/TiO_2$* catalyst.

Tables S1. CO_2 adsorption (as $cm^3.g^{-1}$ and as %) resulting from CO_2-TPD for all the materials used in this study.

As cm^3/g:

Catalyst	CO_2 Total ($cm^3\ g^{-1}$)	CO_2 Weak ($cm^3\ g^{-1}$)	CO_2 Medium ($cm^3\ g^{-1}$)	CO_2 Strong ($cm^3\ g^{-1}$)	CO_2 [w/(m+s)]
TiO_2*	69.8	7.2	50.6	12	0.12
1Pd/TiO_2*	45.0	4.0	26.6	14.5	0.10
10Co/TiO_2*	38.7	20.7	17.2	0.8	1.15
0.1Pd-10Co-o/TiO_2*	46.3	8.4	34.0	3.9	0.22
0.1Pd-10Co-r/TiO_2*	35.4	5.2	18.4	11.8	0.17
1Pd-10Co-o/TiO_2*	28.3	3.4	19.8	5.1	0.14

As percentage:

Catalyst	CO_2 Total (%)	CO_2 Weak (%)	CO_2 Medium (%)	CO_2 Strong (%)	CO_2 [w/(m+s)]
TiO_2*	100	10.4	72.4	17.2	0.12
1Pd/TiO_2*	100	8.8	59.0	32.2	0.10
10Co/TiO_2*	100	53.5	44.4	2.1	1.15
0.1Pd-10Co-o/TiO_2*	100	18.2	73.5	8.3	0.22
0.1Pd-10Co-r/TiO_2*	100	14.6	52.1	33.4	0.17
1Pd-10Co-o/TiO_2*	100	12.1	70.0	17.9	0.14

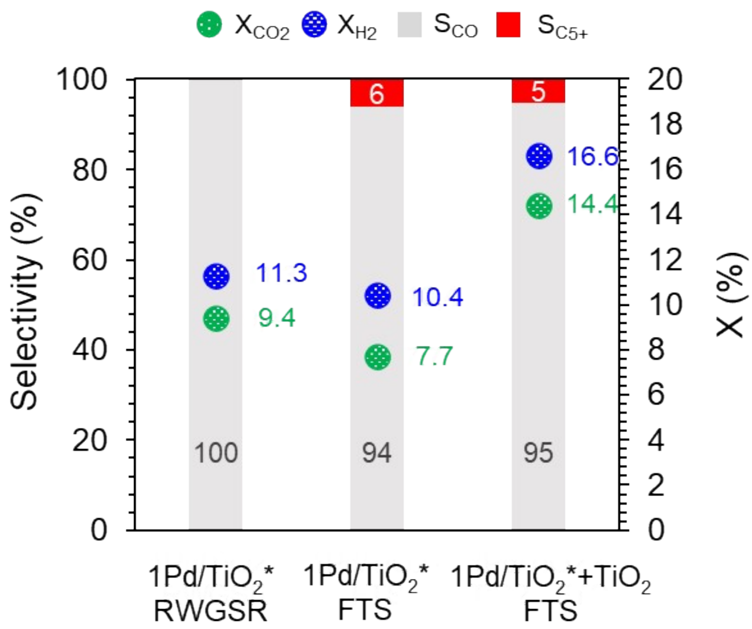


Figure S6. Conversions X (CO_2: green; H_2: blue) and selectivity (CO: grey; C_{5+}: red) for the 1%Pd/TiO_2* catalyst at 60 hours on stream under various conditions, T = 220 °C, P = 20 bar, WHSV = 1620 mL g_{cat}^{-1} h^{-1}. RWGSR and FTS correspond to the feeding ratio of H_2/CO_2 = 1/1 and 2/1, respectively.

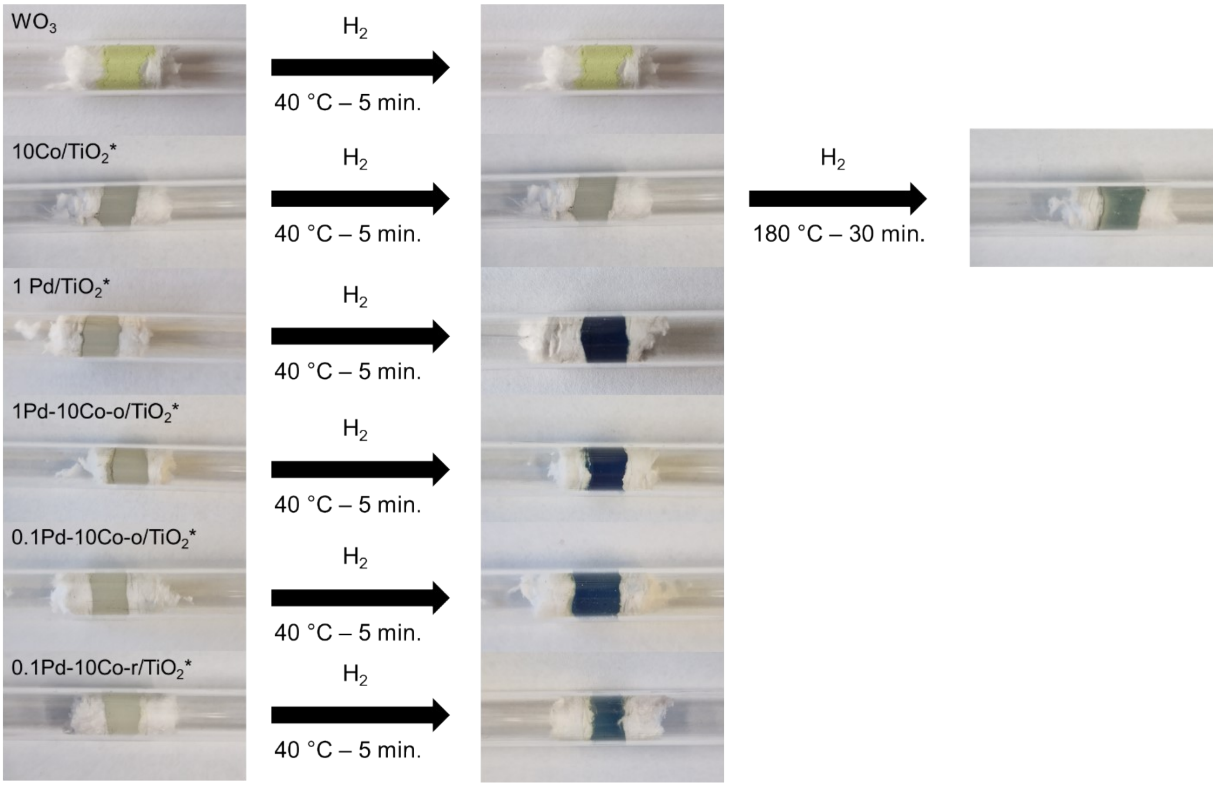


Figure S7. Photographs of samples made with 1 g of WO_3 mixed or not with 5 mg of the catalysts investigated in this study before (left) and after (right) treatment with H_2 (10 mL min^{-1}) at 40 °C for 5 min.

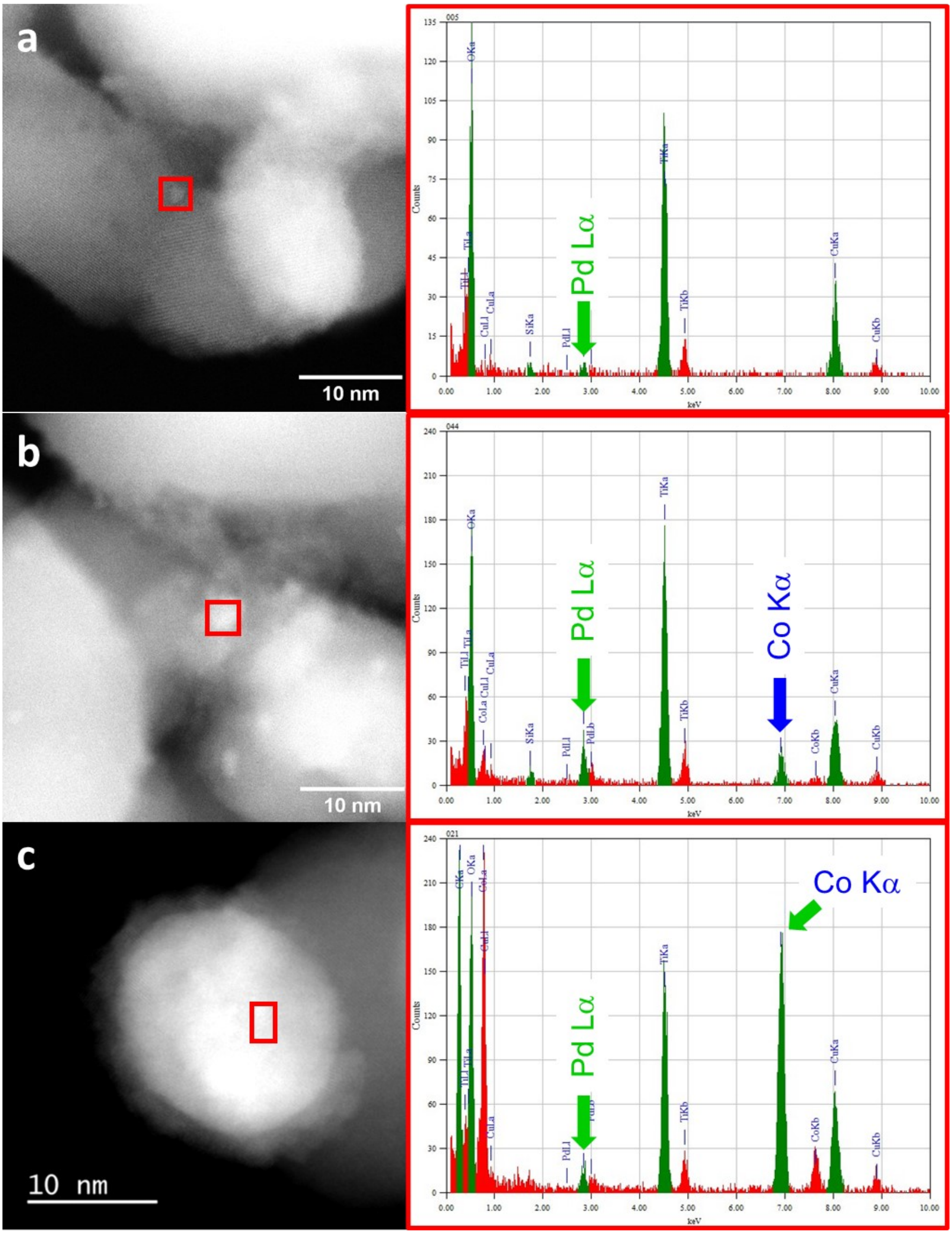


Figure S8. HAADF-STEM micrographs and EDX analysis of the reduced: **a** and **b** 0.1Pd-10Co-o/TiO_2*; and **c** 0.1Pd-10Co-r/TiO_2* catalysts.

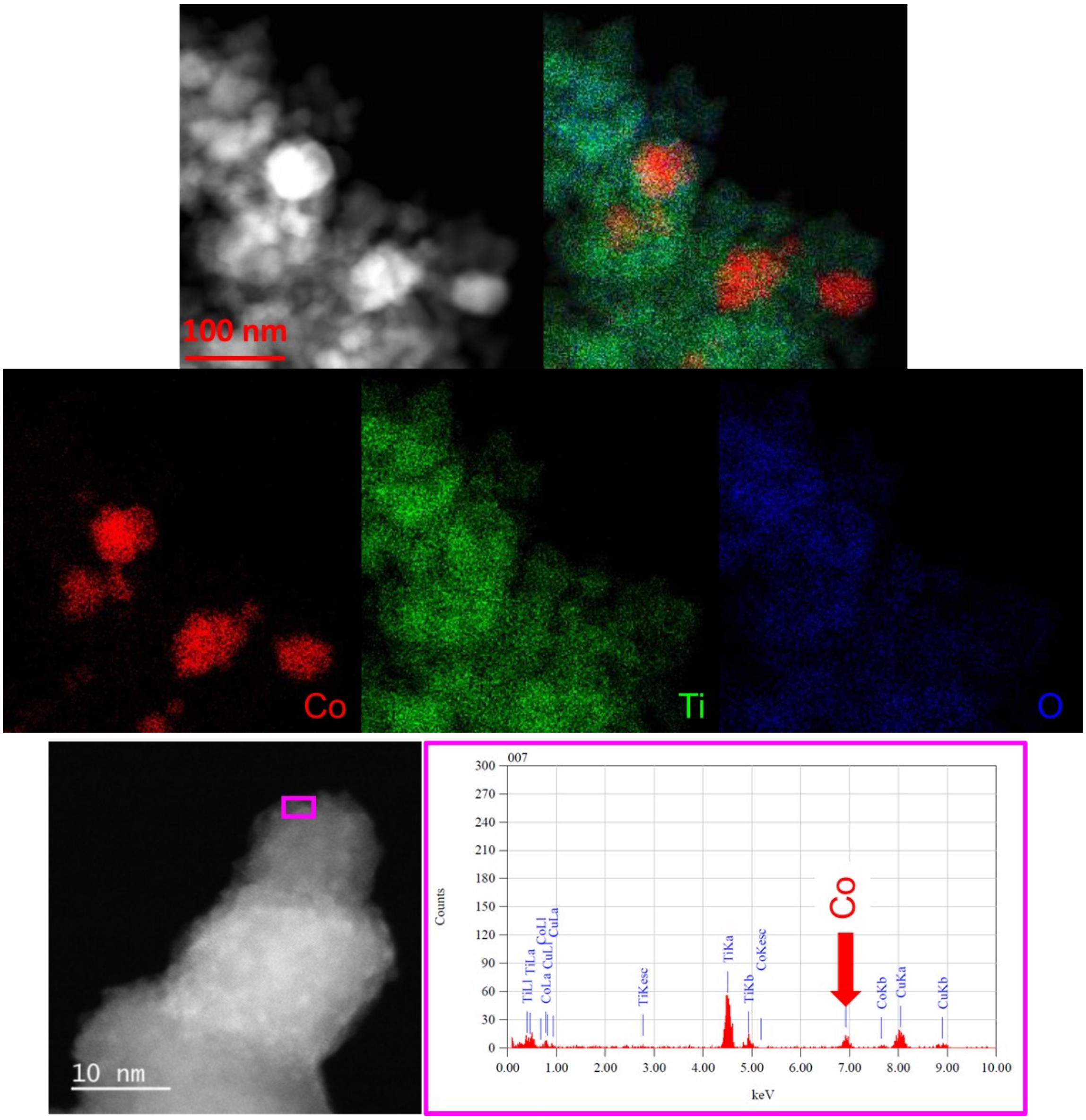


Figure S9. HAADF-STEM micrographs and EDX analysis of the reduced 10Co/TiO_2* catalyst.

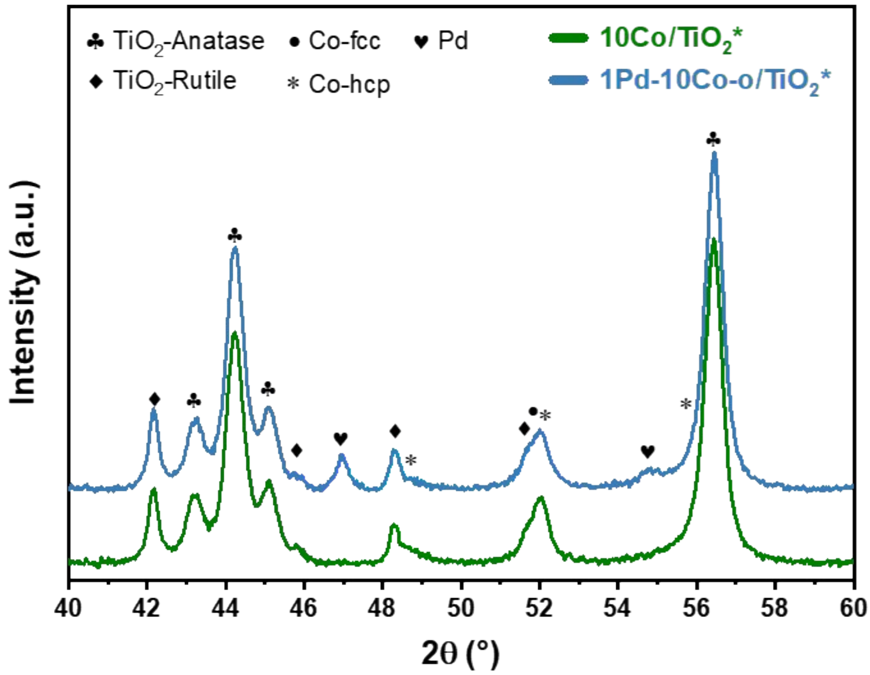


Figure S10. XRD diffractograms (40°-60°) of the 10Co/TiO_2* and 1Pd-10Co-o/TiO_2* catalysts.

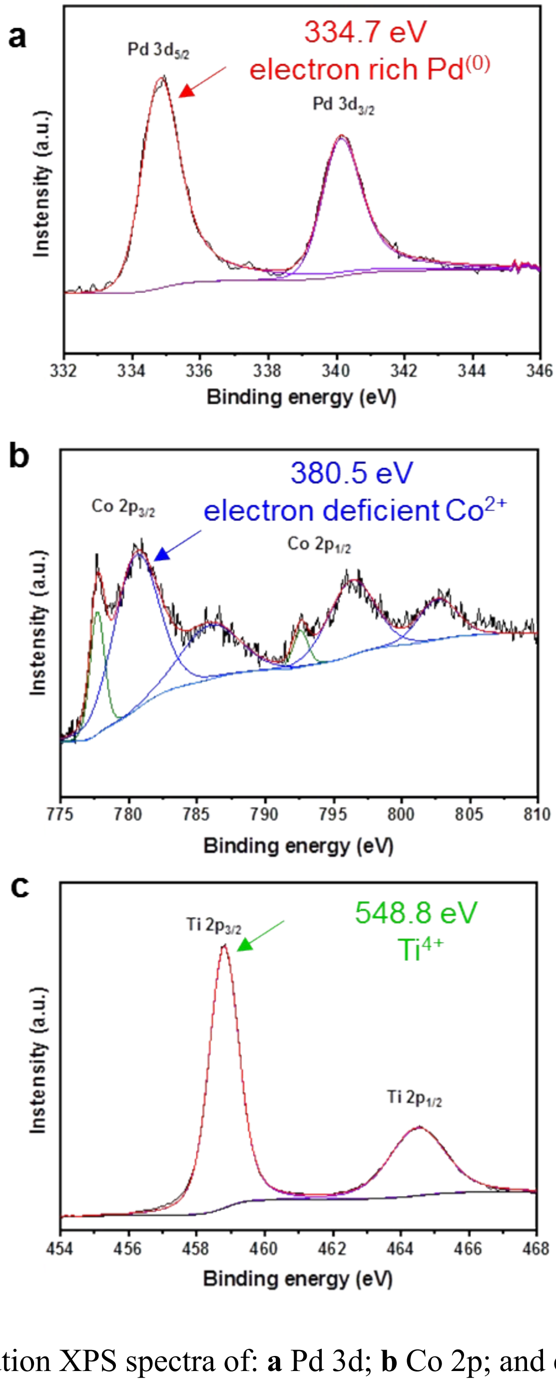
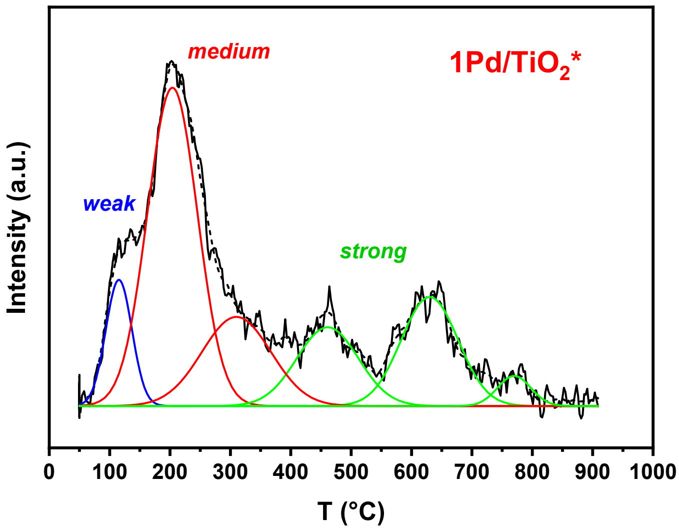


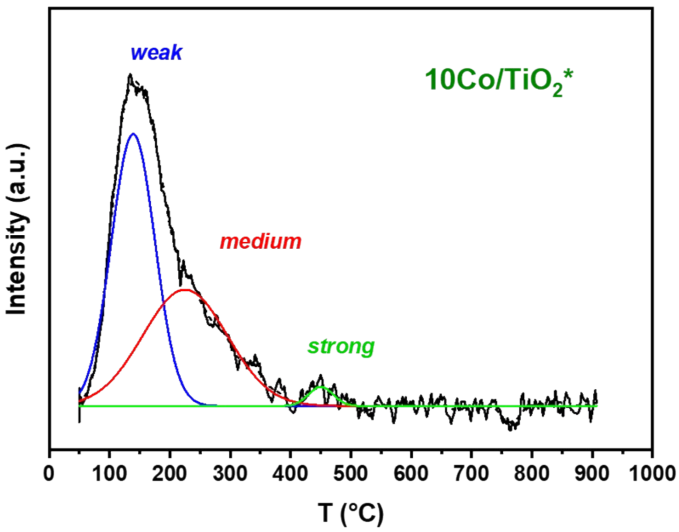
Figure S11. High-resolution XPS spectra of: **a** Pd 3d; **b** Co 2p; and **c** Ti 2p regions of the 1Pd-10Co-o/TiO_2* catalyst.

Table S2. H_2 consumption (cm^3/g) from H_2-TPR for the catalyst monometallic 10Co/TiO_2* and bimetallic catalysts.

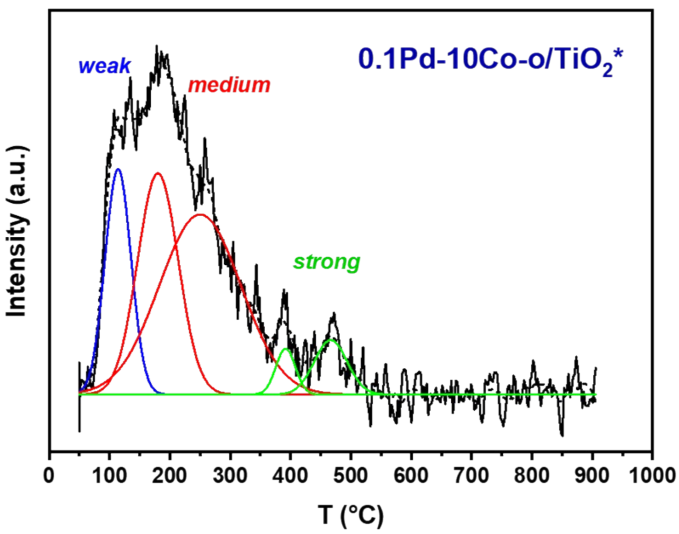
Catalyst	**H_2-TPR** ($cm^3\ g^{-1}$)
10Co/TiO_2*	47.3
0.1Pd-10Co-o/TiO_2*	43.7
0.1Pd-10Co-r/TiO_2*	37.0
1Pd-10Co-o/TiO_2*	48.2



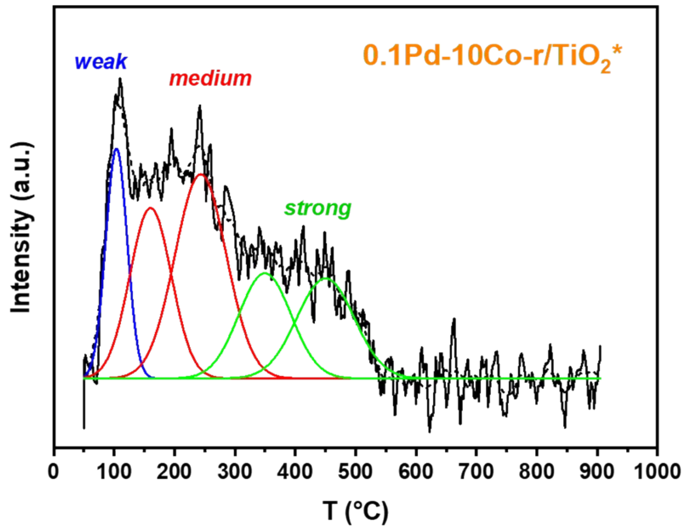
1Pd/TiO2*
weak
medium
strong
Intensity (a.u.)
T (°C)
0 100 200 300 400 500 600 700 800 900 1000



10Co/TiO2*
weak
medium
strong
Intensity (a.u.)
T (°C)
0 100 200 300 400 500 600 700 800 900 1000



0.1Pd-10Co-o/TiO2*
weak
medium
strong
Intensity (a.u.)
T (°C)
0 100 200 300 400 500 600 700 800 900 1000



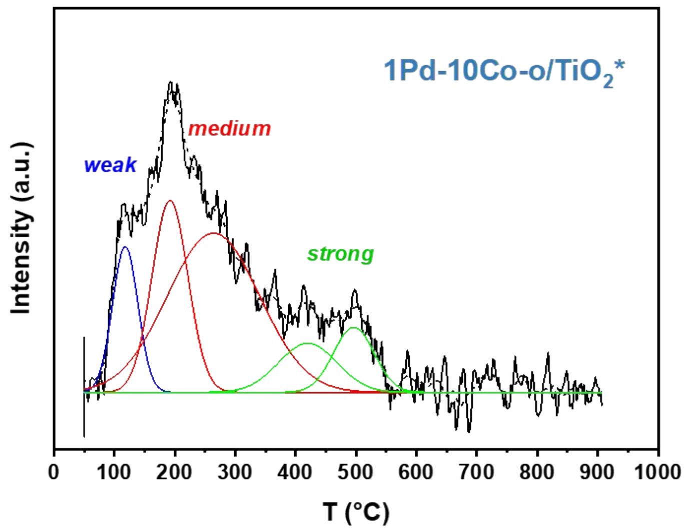


Figure S12. CO_2-TPD profiles and deconvolutions of mono and bimetallic catalysts.

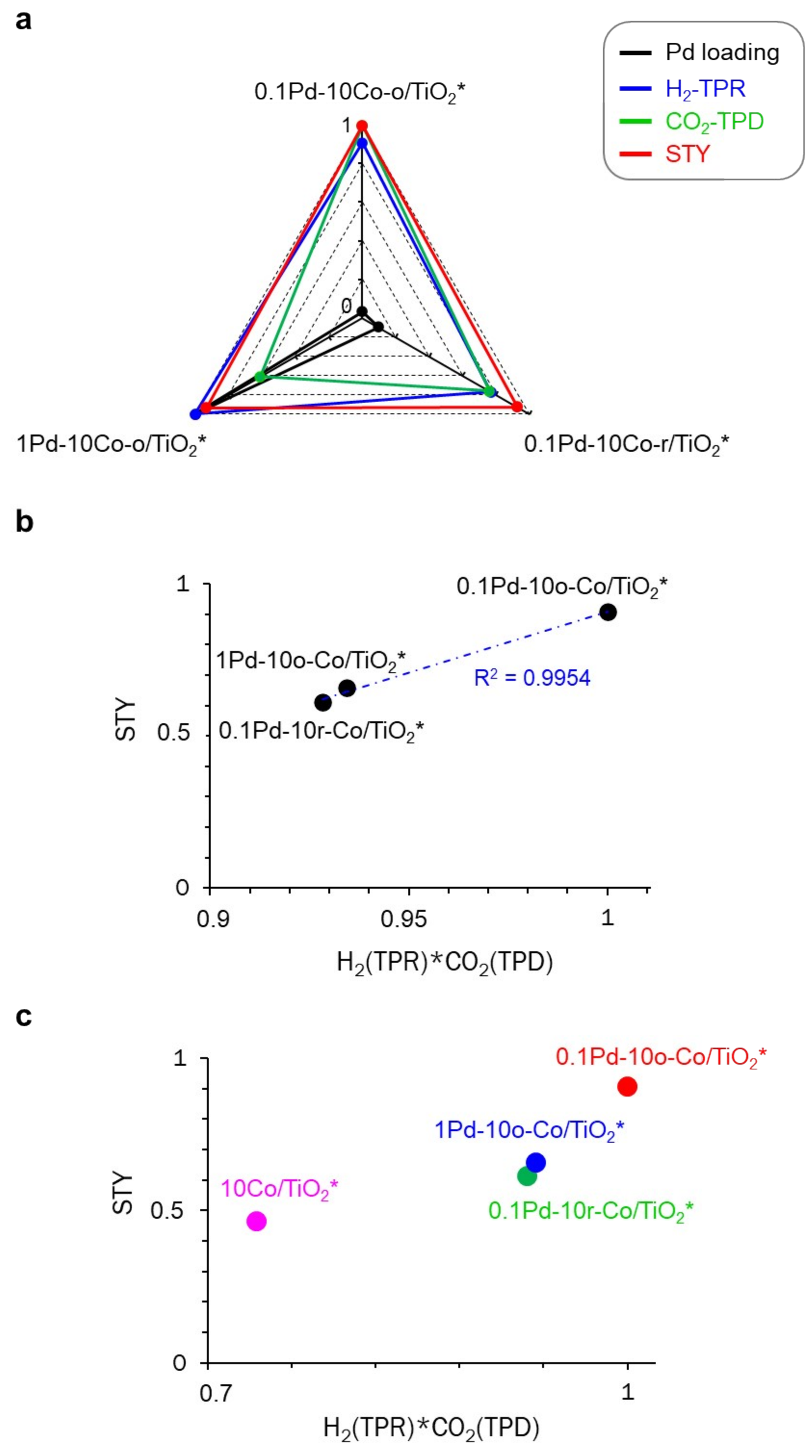


Figure S13. a Radar chart including the main measured parameters and the measured STY on a 0-1 scale. **b** Correlation between the two most relevant parameters and STY taken the values calculated on a 0-1 scale. **c** Correlation between the two most relevant parameters and STY taken the values calculated on a 0-1 scale for the $10Co/TiO_2$* catalyst and the bimetallic catalysts.

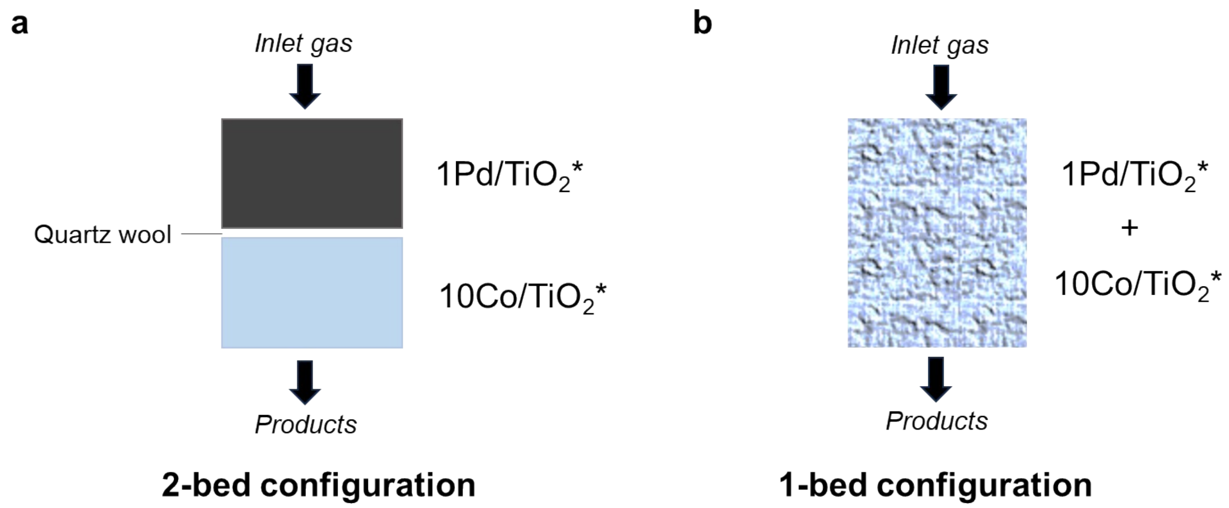


Figure S14. Different configurations used for the monometallic catalysts: **a** 2-beds configuration; and **b** 1-bed configuration.

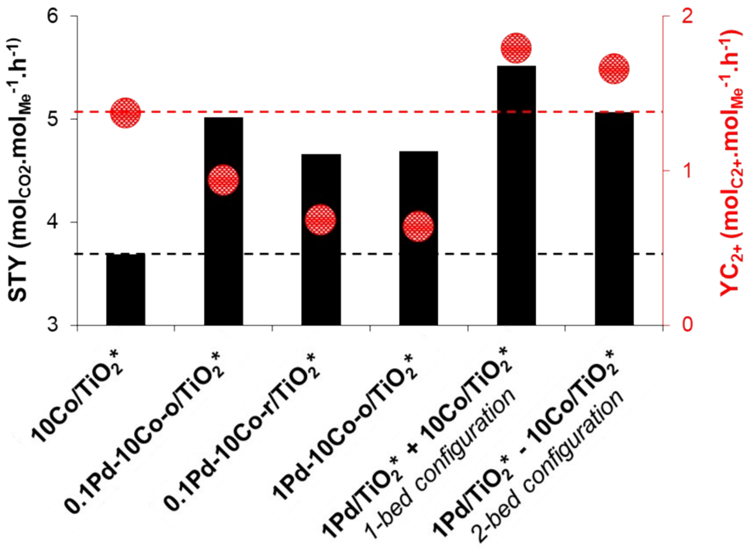


Figure S15. STY (mol$_{CO2}$ mol$_{Me}^{-1}$ h^{-1}) and yields Y (mol$_Z$ mol$_{Me}^{-1}$ h^{-1}, Z = C_{2+}) of the mono- and bimetallic catalysts at 25 hours on stream, T = 220 °C, P = 20 bar, WHSV = 1620 mL g$_{cat}^{-1}$ h^{-1}.