## **Supporting information**

## Subnanometric Pt clusters dispersed over Cs-doped TiO<sub>2</sub> for CO<sub>2</sub> upgrading via low-temperature RWGS reaction: *operando* mechanistic insights to guide an optimal catalysts design

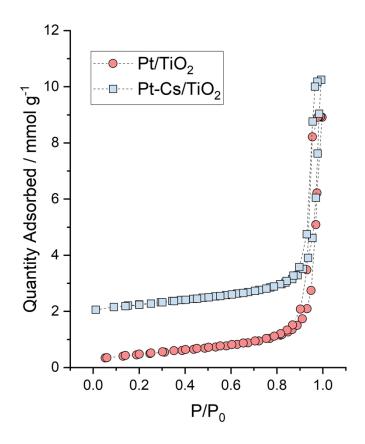
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**Figure S1.** N<sub>2</sub> adsorption-desorption isotherms at 77 K for both Pt/TiO2 and Pt-Cs/TiO<sub>2</sub> catalysts

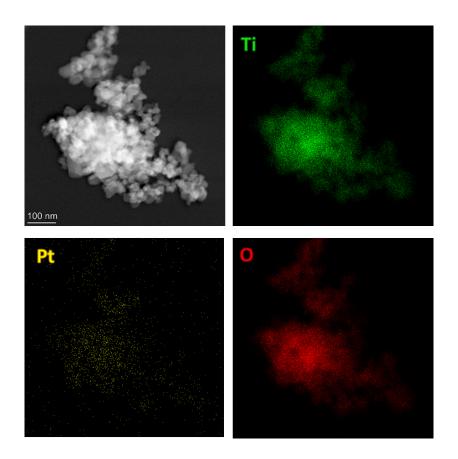


Figure S2. HAADF-STEM with elemental mapping images of Pt/TiO $_2$  catalyst after pre-treatment at 550 °C in 50 % H $_2$ /N $_2$  for 3 h

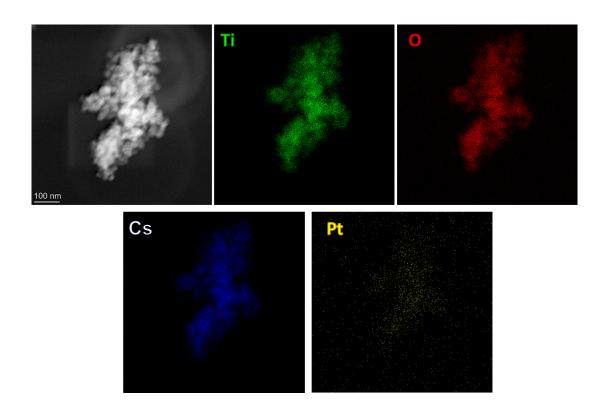
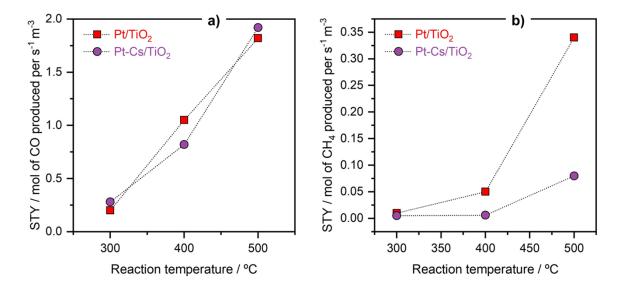
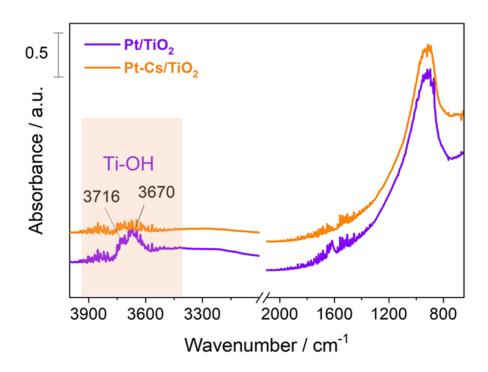


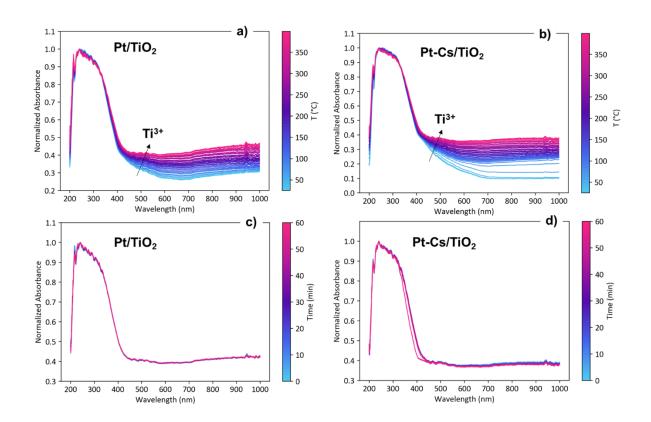
Figure S3. HAADF-STEM with elemental mapping images of Pt-Cs/TiO $_2$  catalyst after pre-treatment at 550 °C in 50 %  $H_2/N_2$  for 3 h



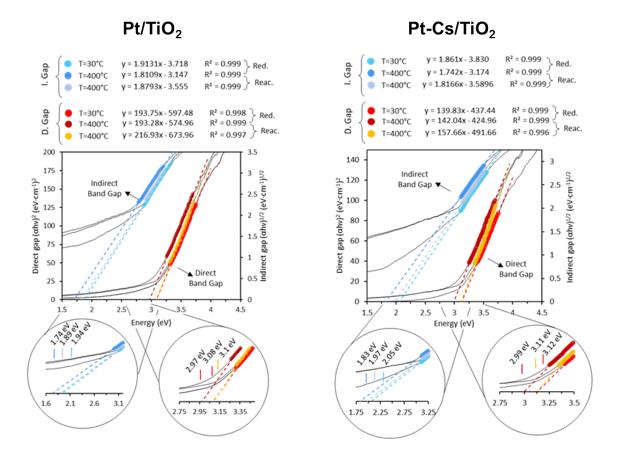
**Figure S4.** Space-time yield (STY) in terms of CO production (a) and CH<sub>4</sub> production (b) for Pt/TiO<sub>2</sub> and Pt-Cs/TiO<sub>2</sub> catalysts.



**Figure S5.** DRIFTS spectra of Pt/TiO<sub>2</sub> and Pt-Cs/TiO<sub>2</sub> after being activated at 400 °C for 1 h with a flow of 50 mL min<sup>-1</sup> of 10% H<sub>2</sub>/Ar



**Figure S6.** Evolution of UV-Vis spectra as a function of the temperature during the activation pretreatment in flow of 10%  $H_2/Ar$  (**a-b**) and as a function of the time during the RWGS reaction (5/20/25 mL min<sup>-1</sup> of  $CO_2/H_2/Ar$ , WHSV = 30 L g<sup>-1</sup> h<sup>-1</sup> and 1 bar) at 400 °C (**c-d**) for both catalysts.



**Figure S7.** Estimation of direct and indirect energy band gaps using the Tauc plot method for both fresh catalysts, after activation (50 mL min<sup>-1</sup> 10%  $H_2/Ar$ , 400 °C, 1h) and after 1h of RWGS reaction (5/20/25 mL min<sup>-1</sup> of  $CO_2/H_2/Ar$ , WHSV = 30 L g<sup>-1</sup> h<sup>-1</sup>, 400 °C and 1 bar)