Supporting Information

Steam Reforming of Methanol over Oxide decorated Nanoporous Gold Catalysts: A Combined In-situ FTIR and Flow Reactor Study

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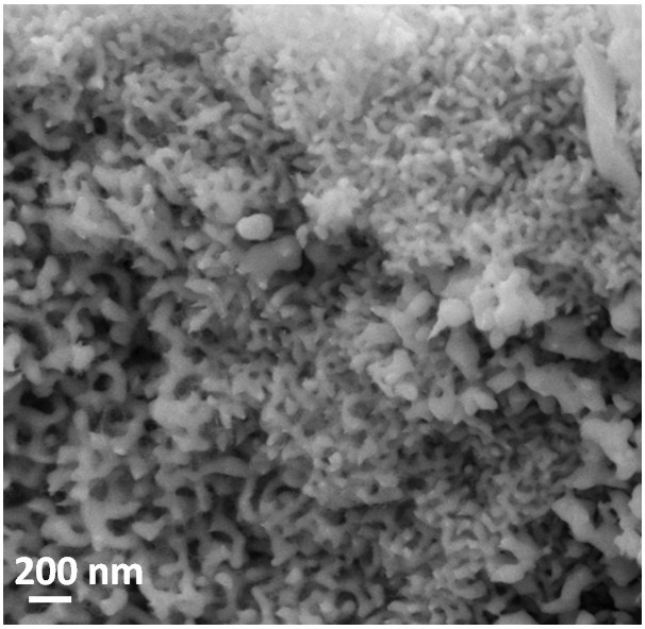

Figure S1. SEM of the cross section of a CeO_x/npAu disk (~150 µm thick) before SRM testing

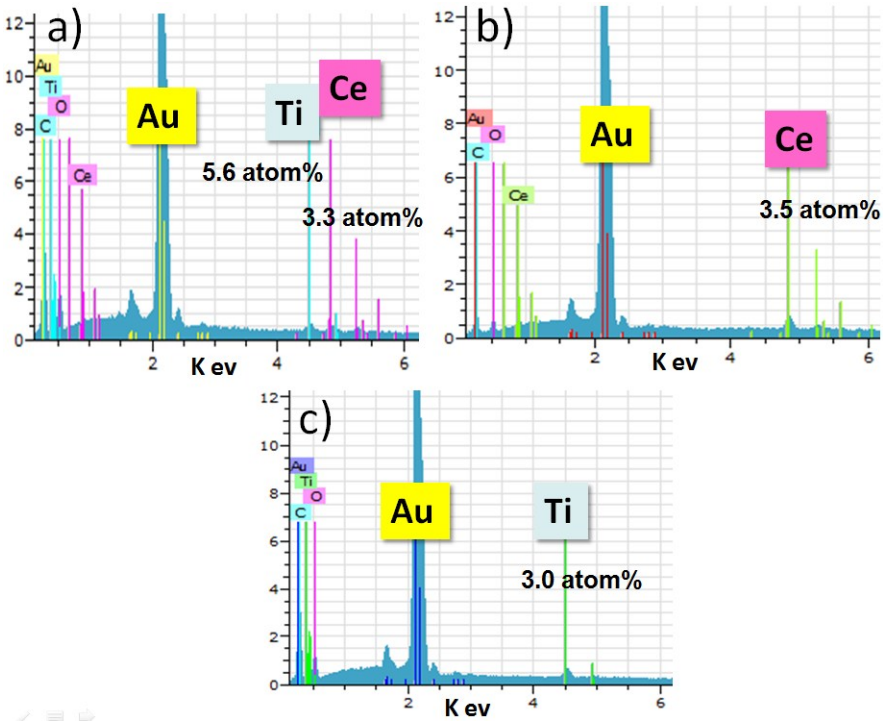

Figure S2. EDX measurement from three samples a) $Ce_1Ti_2O_x$/npAu b) CeO_x/npAu c) TiO_x/npAu.

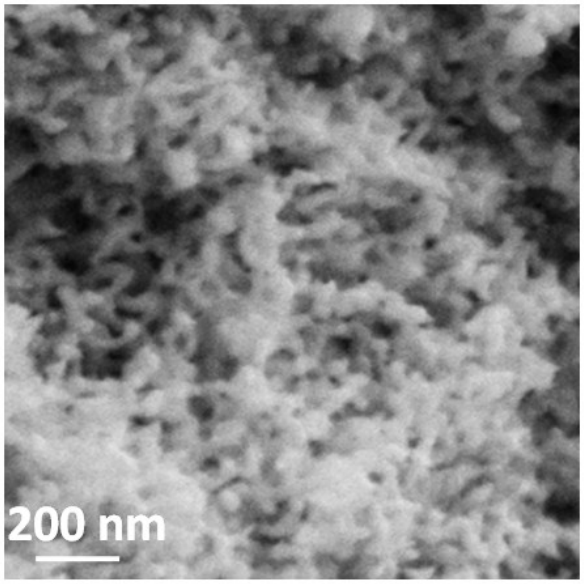

Figure S3. SEM of the cross section of a TiO_x/npAu disk (~150 µm thick, from the middle part) after 5h annealing treatment at 450°C in air.

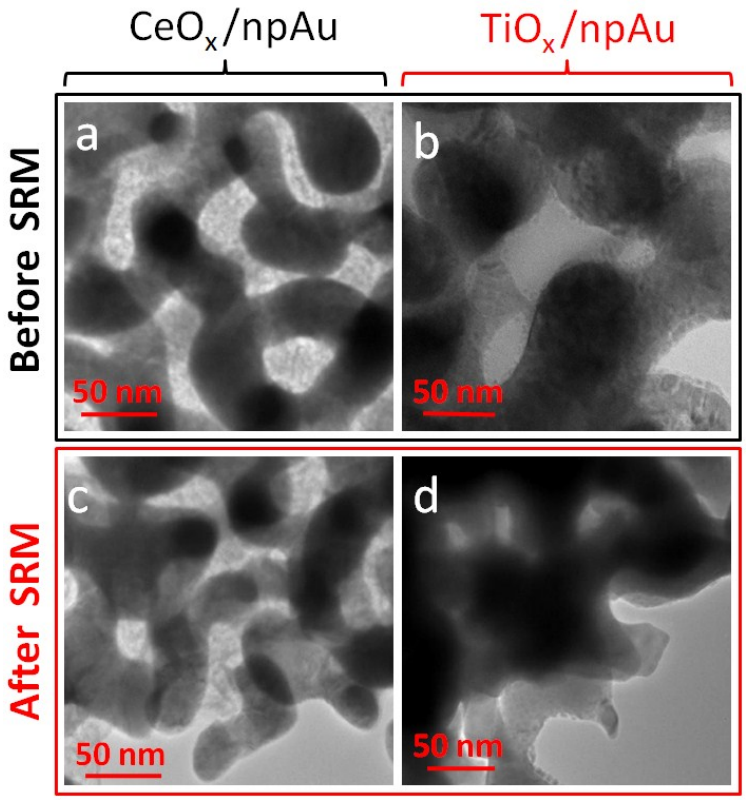

Fig. S4. a/b) TEM images of nanoporous gold modified by ceria oxides (CeO_x/npAu) and titania (TiO_x/npAu) after calcination at 450°C in helium for 2h; c/d) TEM after SRM testing.

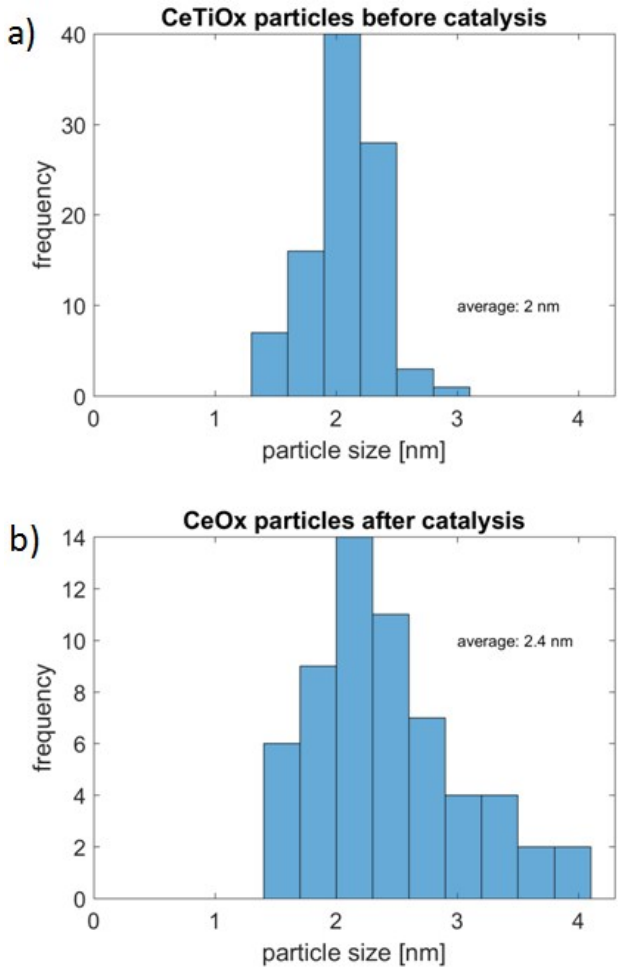

Fig. S5. Histogram for the oxide nanoparticles on npAu a) $CeTiO_x$ particles before catalysis b) CeO_x particles after catalysis

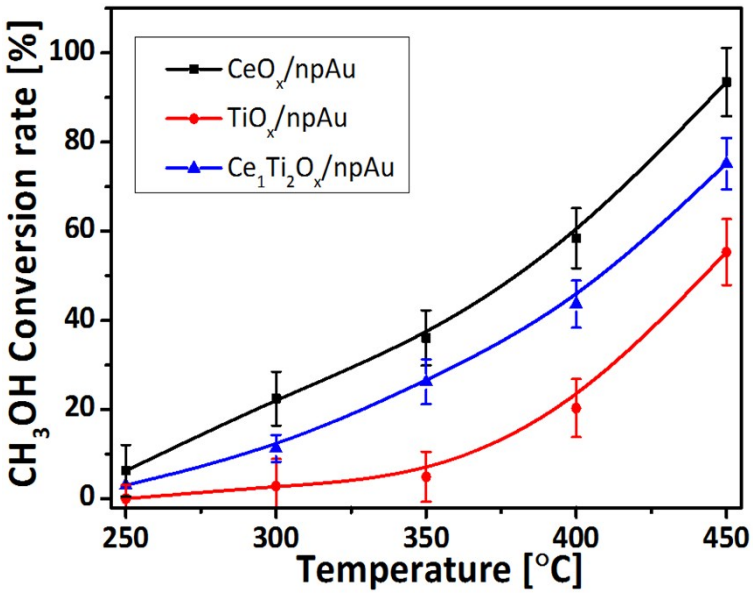

Fig. S6. CH_3OH conversion rate (%) in steady-state tests of steam reforming of

methanol over $Ce_1Ti_2O_x$/npAu, CeO_x/npAu and TiO_x/npAu.

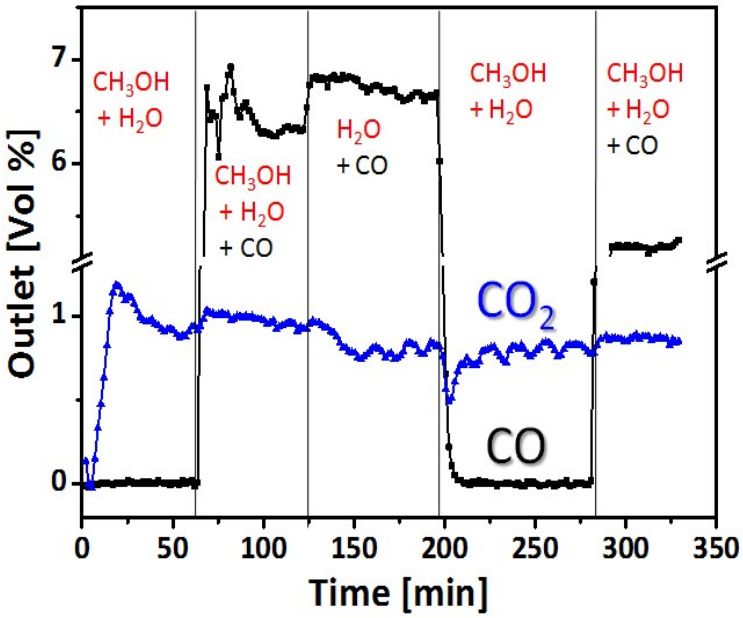

Fig. S7. Effect of the addition/removal of carbon monoxide in the reaction gas mixture over CeO_x/npAu operating at steady-state SRM at 300°C, 2.0 vol% CH_3OH, 20.0 vol% H_2O, total flow rate 35 mL/min; GHSV =350,000 mL $h^{-1}g^{-1}_{cat}$.

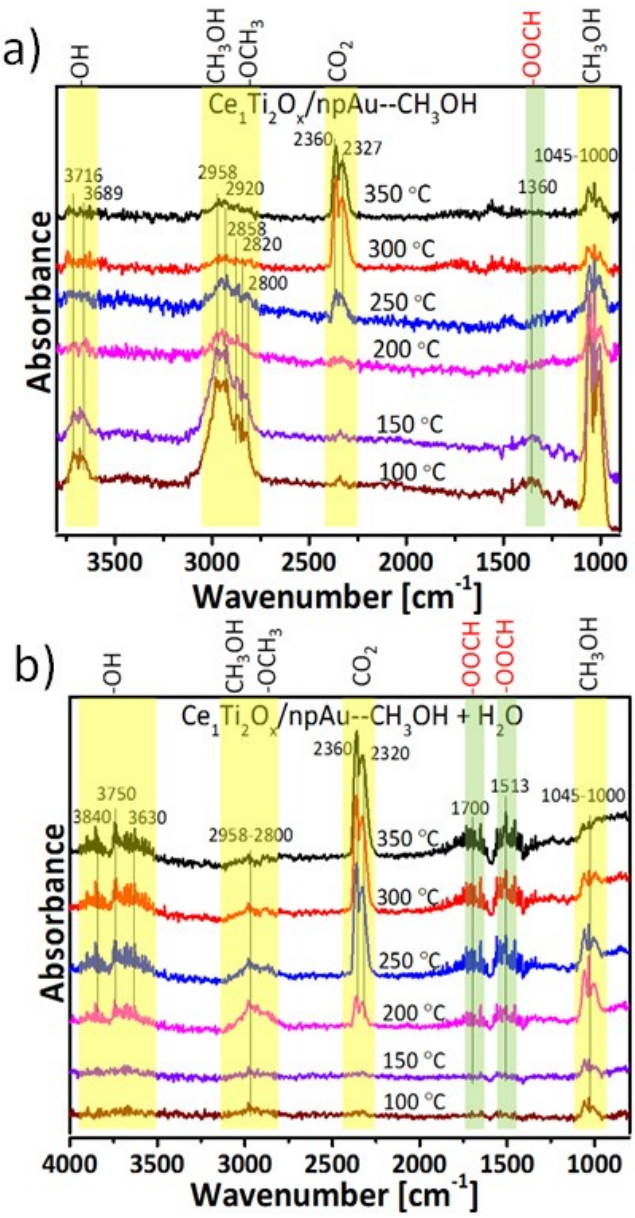

Fig. S8. In-situ DRIFT spectra recorded for $Ce_1Ti_2O_x$/npAu catalysts between 100°C and 350°C (flow rate of 30 mL/min). (a) exposure to CH_3OH (13 vol%), (d) exposure to CH_3OH (1.3 vol%) and H_2O (2.0 vol%).

The formate pathway

$$CH_3OH \rightarrow CH_3O^* + H^* \rightarrow H_2CO^* + 2H^*$$

$$O^*/OH^* + H_2CO^* \rightarrow HCOO^* + H^*/H_2$$

$$HCOO^* \rightarrow CO_2 + H^*$$

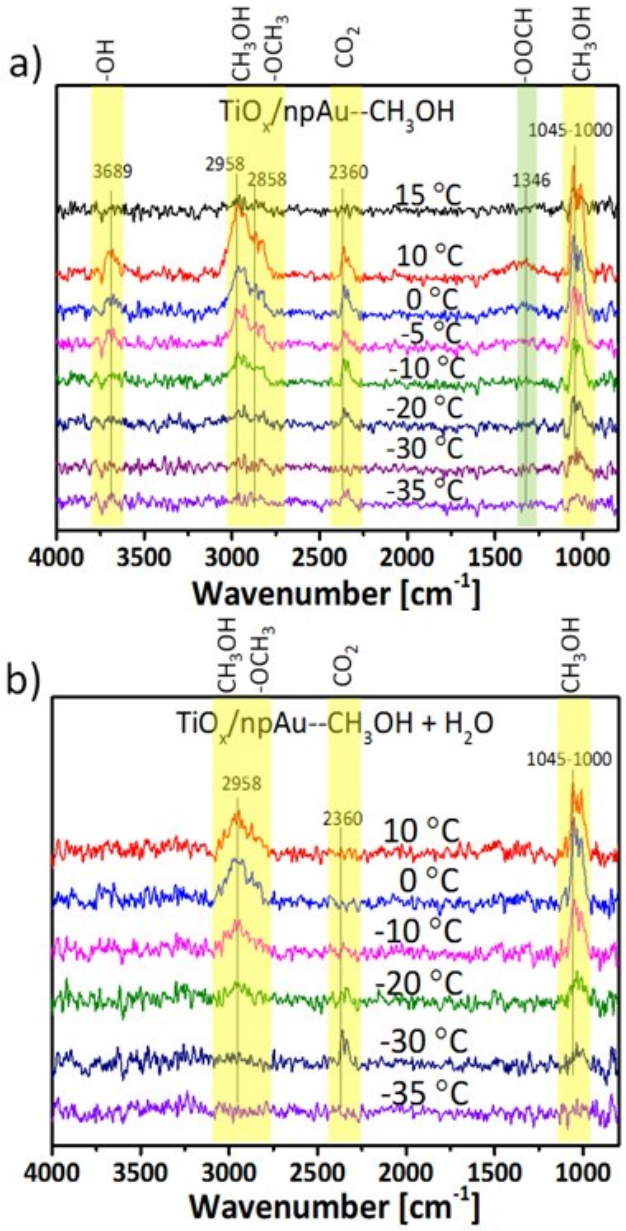

Fig. S9: Low temperature in-situ DRIFT spectra under He atmosphere (30 mL/min) for the TiO_x/npAu catalyst (a) after exposure to only CH_3OH and (b) after exposure to CH_3OH and H_2O at - 35°C.

Methyl formate pathway

$$CH_3OH \rightarrow CH_3O^* + H^* \rightarrow H_2CO^* + 2H^*$$

$$CH_3O^* + H_2CO^* \rightarrow HCOOCH_3 + H^*$$

$$HCOOCH_3 + H_2O \rightarrow HCOOH + CH_3OH$$

$$HCOO^* \rightarrow CO_2 + H^*$$