

Supporting Information

Tandem catalysis for CO₂ hydrogenation to C₂- C₄ hydrocarbons

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Chemicals and Methods:

Chemicals

Cerium nitrate hexahydrate (99 % trace metals basis), poly(vinylpyrrolidone) (PVP, $M_w = 360,000$), PVP ($M_w = 29000$), Tetradecyltrimethylammonium bromide (TTAB), cetyltrimonium bromide (CTAB) (99 %), tetraethyl orthosilicate (TEOS) (99.999% trace metal basis), cobalt carbonyl (moistened with hexanes, (hexanes 1-10%), >90% Co), oleic acid (99%), o-dichlorobenzene (DCB) (anhydrous ,99%, DCB) were purchased from Sigma-Aldrich. Ammonium hexachloroplatinate (IV) $((NH_4)_2PtCl_6$, Pt 43.4 % min) was purchased from Alfa Aesar. Ethanol, ethylene glycol, hexanes, 2-propanol were purchased from Fisher Chemical. Ammonia solution (28-30 %) was purchased from EMD Millipore. All chemicals were used as received without further purification.

Synthesis of CeO₂-Pt@mSiO₂ nanoparticles (NPs)

The CeO₂-Pt@mSiO₂ NPs were synthesized following our previous report *via* a three-step procedure.¹

Synthesis of CeO₂ NPs:

Cerium nitrate hexahydrate (0.85 g) was dissolved in the mixture solution of deionized water (5 mL) and ethanol (5 mL). 30 ml of PVP ($M_w = 360,000$)-ethanol solution (60 mg/ml) was added to the solution. This reaction mixture was then transferred to a stainless-steel autoclave and heated to 140 °C for 24 hours. The as-synthesized CeO₂ nanoparticles were collected by centrifugation (12000 rpm, 60 minutes) and then washed twice with water and ethanol and stored in ethanol for further use.

Overgrowth of Pt NPs on as-synthesized CeO₂ NPs:

The pre-synthesized CeO₂ NPs (40 mg) were dispersed in 20 mL ethanol. To this solution, TTAB (36.8 mg) and PVP (M_w=29000, 21.8 mg) dissolved in ethylene glycol (16 mL) were added. (NH₄)₂Pt(IV)Cl₆ (9.75 mg) was dissolved into ethylene glycol (4 mL) at 80 °C in a 25 mL three-neck round flask under Ar atmosphere. This Pt precursor solution was then mixed with the CeO₂ NPs/ethanol solution and heated to 140 °C for 6 hours in a stainless-steel autoclave. The as-synthesized CeO₂-Pt NPs were separated by centrifugation (12000 rpm, 45 minutes) and re-dispersed in 40 mL deionized water.

Synthesis of CeO₂-Pt@mSiO₂:

The CeO₂-Pt@mSiO₂ core-shell NPs were prepared by a sol-gel method. 225mg CTAB in ethanol (30 mL) was added to the solution of pre-synthesized CeO₂-Pt (40 mg in 45 mL deionized water). An ammonia solution (0.2 mL) was added to the above solution. Then a controlled amount of 1 vol % TEOS diluted with ethanol was slowly added under continuous magnetic stirring at room temperature. After 6 hours, the as-synthesized CeO₂-Pt@SiO₂ nanoparticles were obtained by centrifugation (6000 rpm, 5 minutes). The product was calcined at 350 °C for 1 hour in static air to remove CTAB template to generate CeO₂-Pt@mSiO₂ particles.

Synthesis of CeO₂-Pt@mSiO₂-Co NPs

The CeO₂-Pt@mSiO₂ nanoparticle powders (100 mg) were first dispersed in hexanes (20 mL) and sonicated for 15 minutes. The as-synthesized oleic acid-capped Co NPs were dissolved in hexanes to form a solution with a concentration of ~ 0.5 mg/mL. Then the Co NPs/hexanes solution was added to the CeO₂-Pt@mSiO₂ solution and stirred for 3 hours before the solids were centrifuged. The amount of Co NPs/hexanes solution added

was calculated from the desired loading of Co. The product was then dried at 100°C and calcined in static air at 350 °C for 1 hour to remove the organic ligands.

Synthesis of oleic acid-capped Cobalt NPs

The monodisperse cobalt NPs were synthesized by a reported method with some modification.² In a typical synthesis, oleic acid (130 mg) in a 250 mL round bottom flask was evacuated for 30 minutes, and anhydrous o-dichlorobenzene (15 ml) was added under Argon. The solution was heated at 172°C for 30 minutes under magnetic stirring. Then $\text{Co}_2(\text{CO})_8$ (512 mg) dissolved in o-dichlorobenzene (3 ml) was quickly injected into this solution. This colloidal solution was kept at 172°C for 20 min prior to cooling down to room temperature. The particles were precipitated with 2-propanol and by centrifugation (12000 rpm, 5 mins) and then re-dispersed in hexane for further use.

Characterization.

The morphology of $\text{CeO}_2\text{-Pt@mSiO}_2\text{-Co}$ NPs was analyzed using transmission electron microscopy (TEM) on a Hitachi H7650 and on a FEI Tecnai F20. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) mapping were carried out with an FEI TitanX 60-300, which provided the elemental distribution of the catalysts. Surface area and pore size distribution of the catalyst were obtained by nitrogen physisorption experiments, which were carried out on a Quantachrome Autosorb-1 analyser. Platinum and cobalt quantitative analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES) was carried out on a PerkinElmer optical emission spectrometer (Optima 7000 DV).

Before ICP-AES measurement, catalyst was digested in aqua regia for 24 hours and diluted in deionized water. The clear solution for ICP-AES measurement was obtained by centrifuging at 4000 rpm to remove the sediment.

Catalytic Reaction Testing

Catalytic reactions were performed using a commercial tubular plug flow reactor from Parr Company (i.d. 7 mm). The catalyst sample (50 mg) was retained between plugs of quartz wool, and the reactor temperature monitored with a J type thermocouple. The catalysts were conditioned at 350 °C in flowing 50 vol. % H₂ in balance with He for 1 hour for *in situ* reduction prior to reaction. The reaction was carried out at 90 psi of CO₂: H₂: He (CO₂ to H₂ ratio was tuned from 0.3 to 7) with a total flow of 42 sccm (standard cubic centimeters per minute), which was delivered carefully via calibrated Brooks mass flow controllers. The gas hourly space velocity was kept constant at 50,400 cm³/h·g_{cal}. Products were analyzed by an online gas chromatograph (Shimadzu 2010), which was equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Calibration of retention times and peak intensities was made directly with all observed reactants and products.

CO₂ conversion was calculated on a carbon atom basis:

$$Con_{CO_2} = \frac{CO_2(inlet) - CO_2(outlet)}{CO_2(inlet)} \times 100\%$$

Where CO₂ (inlet) and CO₂ (outlet) represent moles of CO₂ at the inlet and outlet, respectively.

CO selectivity (Sel_{CO}) was calculated according to:

$$Sel_{CO} = \frac{CO(outlet)}{CO_2(inlet) - CO_2(outlet)} \times 100\%$$

Where CO (*outlet*) denotes moles of CO at the outlet.

The selectivity of individual hydrocarbon C_nH_m ($Sel_{C_nH_m}$) was obtained according to:

$$Sel_{C_nH_m} = \frac{nC_nH_{m_{outlet}}}{\sum_1^n nC_nH_{m_{outlet}}} \times 100\%$$

The carbon balance was over 95%.

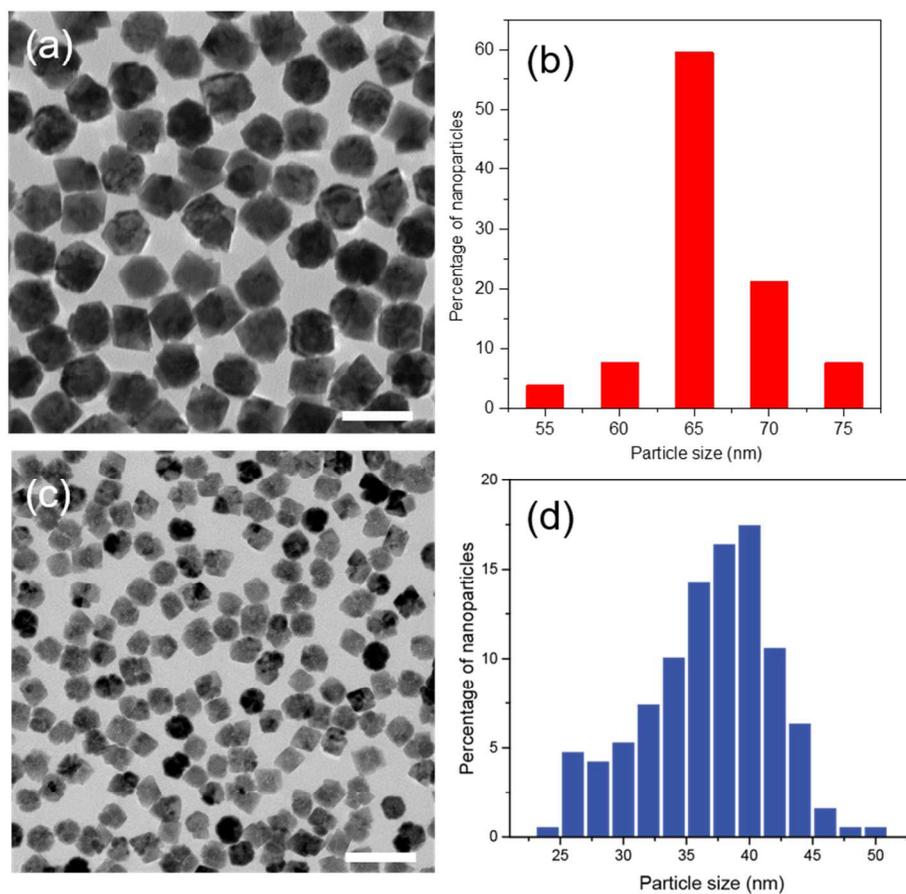


Figure S1. Tuning the size of CeO₂ NPs by changing the ethanol and water ratio. TEM images (scale bar: 100 nm) of CeO₂ NPs with different ethanol and water amount: (a) 10 mL H₂O and 30 mL ethanol and (b) corresponding diameter distribution statistics; (c) 5 mL H₂O and 35 mL ethanol and (d) corresponding diameter distribution statistics.

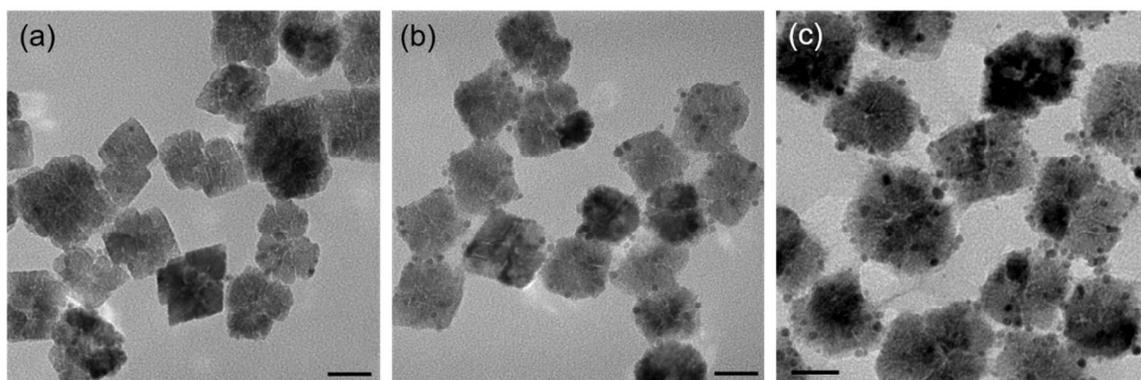


Figure S2. TEM images of CeO₂-Pt NPs with Pt loading amount around (a), 1%; (b), 5% and (c), 10%. The loading amount of Pt was calculated based on the mass of CeO₂-Pt NPs. Scale bar: 20 nm.

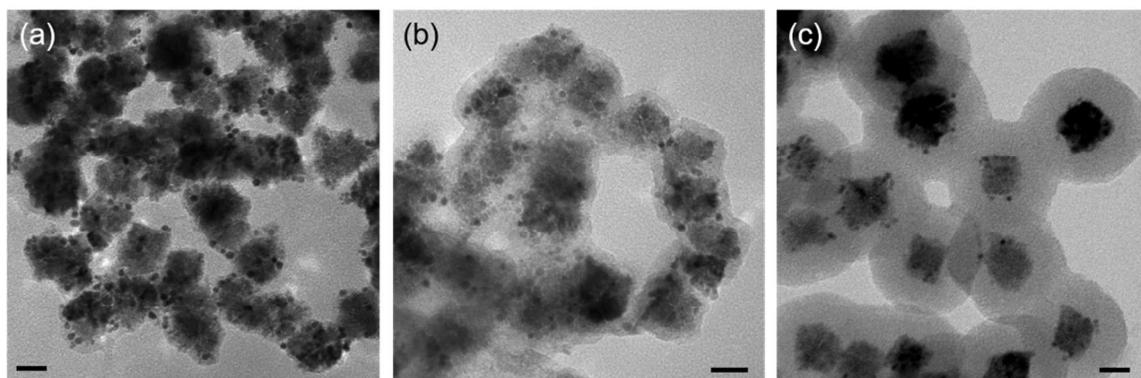


Figure S3. Silica shell thickness tuning of $\text{CeO}_2\text{-Pt@mSiO}_2$ NPs by changing the added volume of TEOS. TEM images of $\text{CeO}_2\text{-Pt@mSiO}_2$ when the added volume of TEOS is (a) 25 μL , scale bar: 20 nm; (b) 50 μL , scale bar: 20 nm and (c) 120 μL , scale bar: 50 nm.

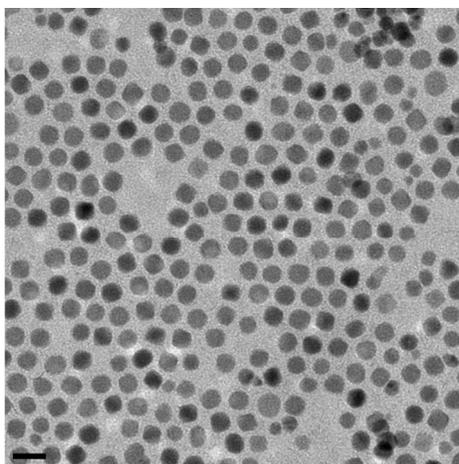


Figure S4. TEM image of monodisperse cobalt NPs. Scale bar: 20 nm.

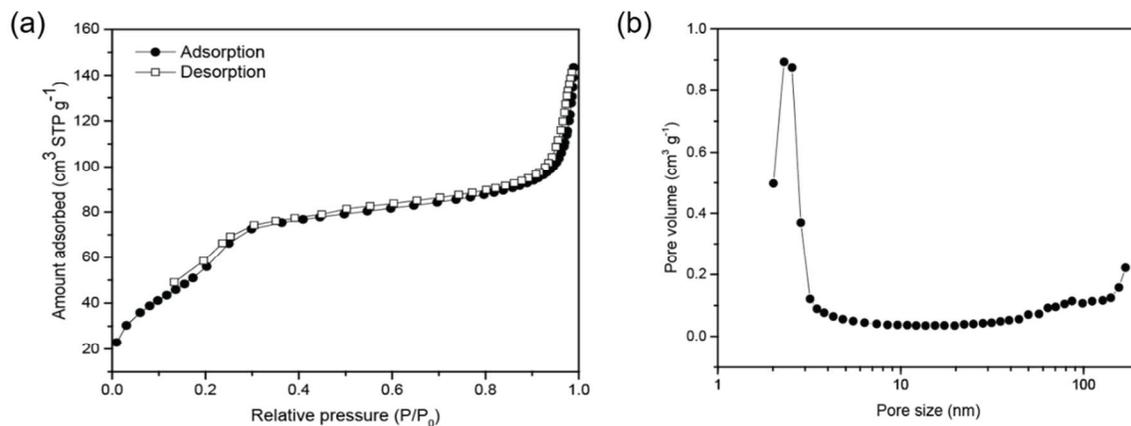


Figure S5. Porosity characterization of CeO₂-Pt@mSiO₂-Co nanoparticles. (a) Nitrogen adsorption-desorption isotherms. (b) Pore size distribution calculated from the adsorption branch of the isotherms.

Table S1. Pt and Co loading amount for the catalysts used for CO₂ hydrogenation according to ICP-AES.

Catalyst	Pt loading amount (%)	Co loading amount (%)
CeO ₂ -Pt@mSiO ₂ -Co	4.3	5.8
CeO ₂ -Pt@mSiO ₂	4.4	0
CeO ₂ @mSiO ₂ -Co	0	5.3
Physical mixture	4.4	5.3

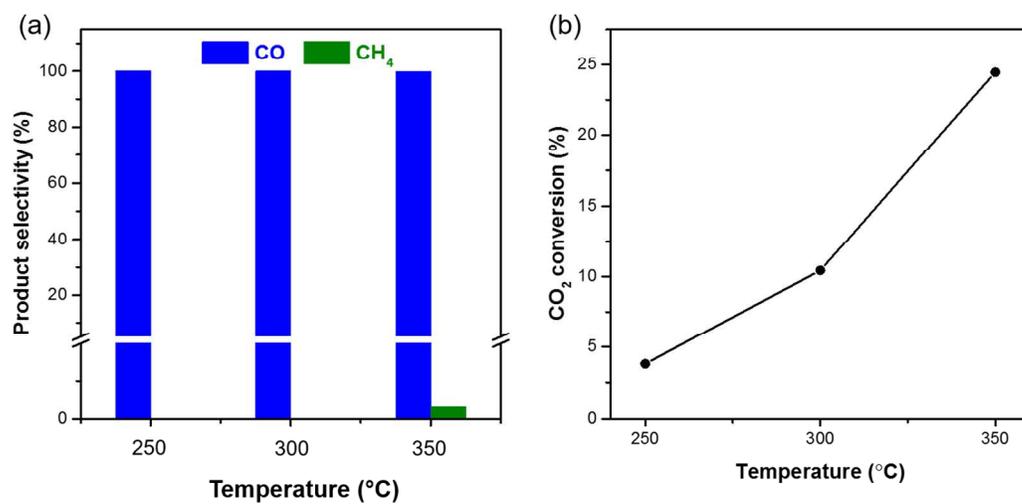


Figure S6. Catalytic performance of CeO₂-Pt@mSiO₂ under different temperatures. (a) products distribution, (b) CO₂ conversion at H₂/CO₂ ratio of 3.0 and total pressure of 90 psi.

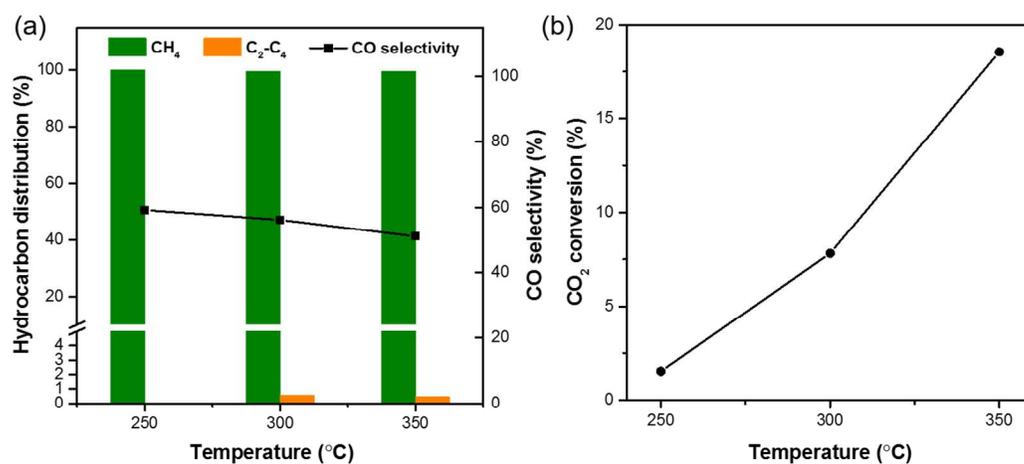


Figure S7. Catalytic performance of CeO₂@mSiO₂-Co under different temperatures. (a) hydrocarbons distribution (left axes) and CO selectivity (right axes). (b) CO₂ conversion at H₂/CO₂ ratio of 3.0 and total pressure of 90 psi.

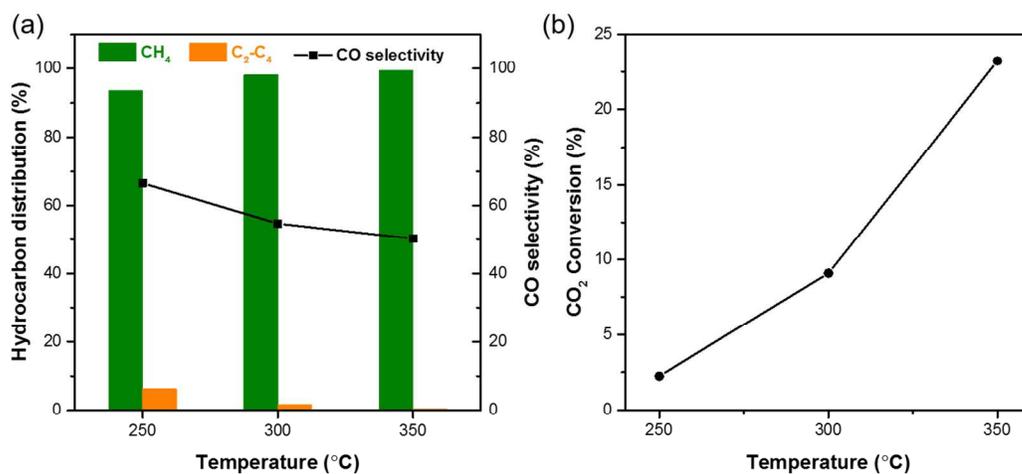


Figure S8. Catalytic performance of physical mixture of CeO₂-Pt@mSiO₂ and CeO₂@mSiO₂-Co under different temperatures. (a) hydrocarbons distribution (left axes) and CO selectivity (right axes). (b) CO₂ conversion at H₂/CO₂ ratio of 3.0 and total pressure of 90 psi.

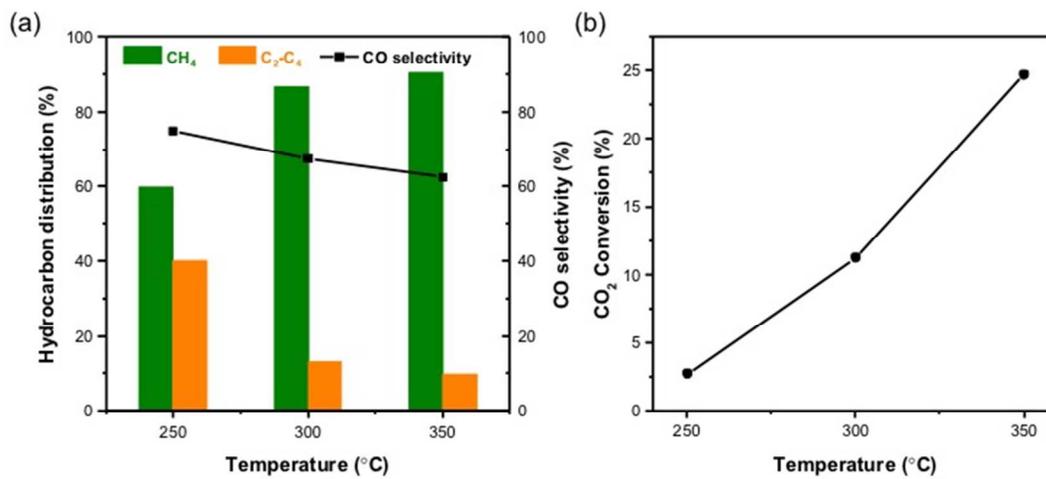


Figure S9. Catalytic performance of tandem catalyst CeO₂-Pt@mSiO₂-Co under different temperatures. (a) hydrocarbons distribution (left axes) and CO selectivity (right axes). (b) CO₂ conversion at H₂/CO₂ ratio of 3.0 and total pressure of 90 psi.

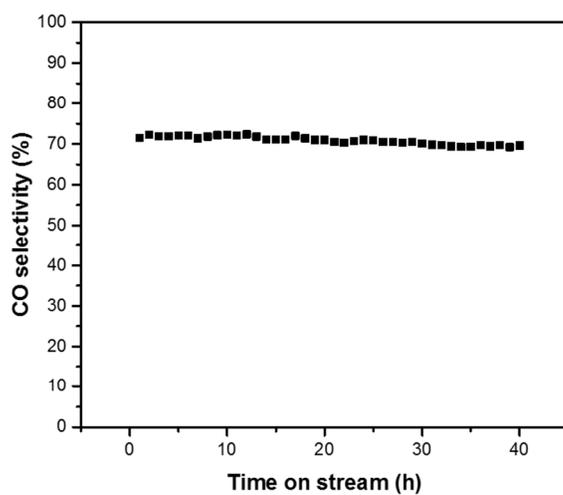


Figure S10. Stability test of CO selectivity over the tandem catalyst $\text{CeO}_2\text{-Pt@mSiO}_2\text{-Co}$ at temperature 250 °C and H_2/CO_2 ratio of 3.0 and total pressure of 90 psi.

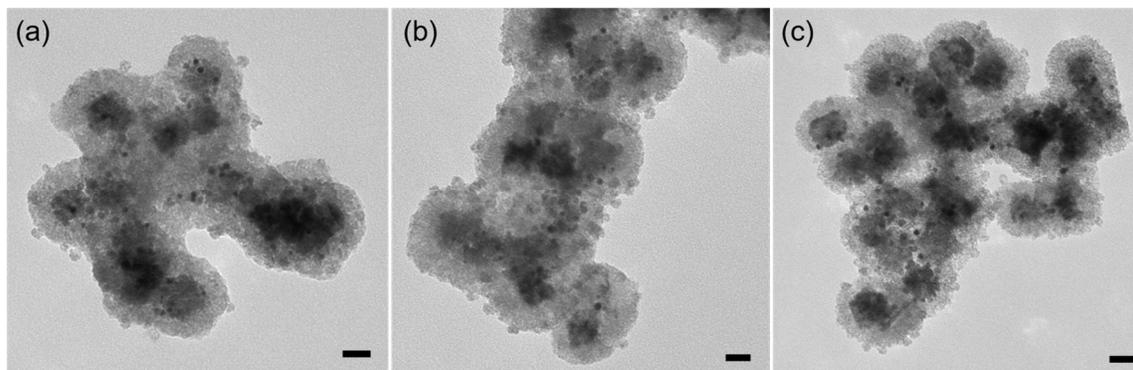


Figure S11. TEM images of tandem catalyst $\text{CeO}_2\text{-Pt@mSiO}_2\text{-Co}$ after reaction. Scale bar: 20 nm.

- (1) Su, J.; Xie, C.; Chen, C.; Yu, Y.; Kennedy, G.; Somorjai, G. A.; Yang, P. *J. Am. Chem. Soc.* **2016**, *138*, 11568-11574
- (2) Iablokov, V.; Beaumont, S. K.; Alayoglu, S.; Pushkarev, V. V.; Specht, C.; Gao, J.; Alivisatos, A. P.; Kruse, N.; Somorjai, G. A. *Nano Lett.* **2012**, *12*, 3091-3096