Materials and Interfaces

Article

Supplementary Materials: Constructing Co Cluster Sites for Selective CO_2 Hydrogenation via Phase Segregation from Co-Doped TiO_2 Nanocrystals

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1. Experimental Section

1.1. Chemicals

Oleylamine (OAm, 70%), oleic acid (OAc, 90%), cobalt carbonyl ($Co_2(CO)_8$, moistened with 1–10% hexane) and titanium (IV) oxide (P25 nanopowder) were purchased from Sigma-Aldrich. 1-Octadecene (ODE, 90%), cobalt (II) acetylacetonate ($Co(acac)_2$, 99%) and titanium chloride ($TiCl_4$, 99.9%) were obtained from Acros Organics. 1,2,3,4-Tetrahydronaphthalene (99%), isopropanol (99.5%), ethanol (99.5%) and hexanes (98.5%) were purchased from Fisher Scientific.

1.2. Preparation of $TiCl_4$ Solution and Co Oleate Precursor Solution

Prior to synthesizing Co-TiO_2 and TiO_2 nanorods, a 0.2 M $TiCl_4$ solution and a 0.2 M Co oleate solution were prepared by dissolving the respective metal precursors in a mixture of oleic acid (OAc) and 1-octadecene (ODE), with a concentration of 1 M OAc in ODE. All manipulations involving Ti and Co precursors were conducted in a glove box, and the solvents were pre-dried at 90 °C under vacuum using standard Schlenk line techniques. Specifically, for the $TiCl_4$ solution, 2.19 mL of $TiCl_4$ was combined with 31.59 mL of OAc and 66.25 mL of ODE, stirred overnight at 100 °C to yield a 0.2 M $TiCl_4$ solution. Similarly, a 0.2 M Co oleate solution was synthesized by dissolving 5.14 g of $Co(acac)_2$ in 31.59 mL of OAc and 66.25 mL of ODE. Both solutions were stored in a nitrogen-filled glovebox. The Co oleate precursor solution was then mixed with the Ti precursor solution at the desired Ti/Co ratio to form the Co oleate-$TiCl_4$ mixed solution.

1.3. Synthesis of Co-TiO_2 and TiO_2 Nanorods

Co-TiO_2 and TiO_2 nanorods were synthesized via a colloidal method, as outlined in our previous publication [32]. For the Co-TiO_2 nanorods, 10 mL of ODE was mixed with 10 mL of oleylamine (OAm) and 0.48 mL of OAc. This mixture was heated under vacuum at 90 °C for 1 h to remove moisture and then cooled to 60 °C under a nitrogen atmosphere. Next, 1.5 mL of the Co oleate-$TiCl_4$ mixed solution was quickly injected into the above mixture and heated rapidly to 290 °C, maintaining this temperature for 10 min. An additional 8 mL of the Co oleate-$TiCl_4$ mixed solution was then injected at a rate of 0.3 mL min^{-1} using a syringe pump. Upon completing the injection, the reaction was allowed to cool to room temperature, and the nanorods were precipitated using 60 mL isopropanol and collected by centrifugation at 8,000 rpm for 8 min. The products were washed again with hexane and isopropanol. The Co doping levels in the Co-TiO_2 nanorods were adjusted by varying the Ti/Co ratio in the mixed precursor solution. According to our previous research [33], the Co doping levels were 4.2%, 7.5%, and 12% for Ti/Co ratios of 8:1, 8:2, and 8:3, respectively. TiO_2 nanorods without Co doping were synthesized similarly, using only the Ti precursor solution.

1.4. Synthesis of Co Nanoparticles

Co nanoparticles were synthesized via a thermal decomposition method, as previously reported [34]. Briefly, 18 mL of 1,2,3,4-tetrahydronaphthalene was mixed with 0.35 mL OAc, heated to 110 °C under nitrogen flow, and held at this temperature for 1 h to remove moisture and oxygen. The mixture was then cooled to room temperature. Subsequently, 0.54 g of $Co_2(CO)_8$ was added, and the solution was rapidly heated to 210 °C at a rate of 15 °C min^{-1}. The reaction proceeded for 30 min under nitrogen with vigorous stirring. Upon completion, the reaction mixture was cooled to room temperature, and the nanoparticles were purified through precipitation with ethanol, followed by centrifugation at 8,000 rpm for 8 min. The resulting nanoparticles were washed with ethanol 2–3 times and stored in hexane.

1.5. Catalyst Pretreatment

Co-TiO_2 nanorods were directly calcined in a muffle furnace at different temperatures (400–600 °C) for 2 h. The Co nanoparticles were loaded onto commercial P25 TiO_2 support with a final metal loading of 10 wt% verified by inductively coupled plasma-optical emission spectroscopy (ICP-OES). In a typical loading process, the desired amount of Co nanoparticles dispersed in hexane was mixed with a suspension of the P25 in hexane. After stirring for 2 h, the product was collected by centrifugation and dried overnight under vacuum. The catalyst was then calcined at 500 °C in air for 2 h.

1.6. Catalytic Performance Testing

Catalytic testing was conducted in a quartz tube fixed-bed reactor (inner diameter of 6 mm) under atmospheric pressure. Catalysts containing 6 mg of cobalt were loaded into the reactor with quartz wool. For each activity test, 50 mg of 12% Co-TiO_2, 80 mg of 7.5% Co-TiO_2, and 143 mg of 4.2% Co-TiO_2 were used, ensuring an equal mass of cobalt for all measurements. Before testing, the catalysts were reduced in a gas mixture of 1 vol.% CO_2 + 4 vol.% H_2 + 95 vol.% N_2 at 400 °C for 2 h with a ramp rate of 5 °C min^{-1} and a total flow of 25 mL min^{-1}, corresponding to a gaseous hourly space velocity (GHSV) of 30,000 mL h^{-1} g^{-1}. The reaction temperature was varied between 450 °C and 300 °C in 50 °C increments, with each step held for 2 h. Gas products were analyzed online using a gas chromatograph (Buck Scientific 910) equipped with HP-PLOT and MolSieve columns, and flame ionization and thermal conductivity detectors. Conversion (X), yield (Y), and selectivity (S) were calculated using the following equations:

$$X_{CO_2} = \frac{F_{CO_2,inlet} - F_{CO_2,outlet}}{F_{CO_2,inlet}} \tag{1}$$

$$Y_{CO} = \frac{F_{CO,outlet}}{F_{CO_2,inlet}} \tag{2}$$

$$Y_{CH_4} = \frac{F_{CH_4,outlet}}{F_{CO_2,inlet}} \tag{3}$$

$$S_{CO} = \frac{Y_{CO}}{X_{CO_2}} \tag{4}$$

$$S_{CH_4} = \frac{Y_{CH_4}}{X_{CO_2}} \tag{5}$$

where F denotes the flow rate of reactants/products (mol min^{-1}) and W is the weight of the catalyst used (g).

1.7. Catalyst Characterization

Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai Spirit (120 kV). Inductively coupled plasma-optical emission spectrometry (ICP-OES) analyses were conducted on a PerkinElmer Avio-200 ICP optical emission spectrometer. Synchrotron X-ray diffraction (SXRD) measurements were carried out at the Lawrence Berkeley National Laboratory, with an X-ray wavelength of λ = 0.6199 Å. Powder XRD was performed using an Empyrean X-ray diffractometer equipped with a Cu anode (λ = 1.54 Å). X-ray absorption spectroscopy (XAS) was performed in fluorescence mode with Passivated Implanted Planar Silicon detector at beamline 7-BM of the National Synchrotron Light Source II at the Argonne National Laboratory. All data processing was performed using the IFEFFIT package [50] Data alignment, edge calibration, deglitching, normalization, and background subtraction were done with Athena.

H_2-temperature-programmed reduction (TPR) was carried out using a Micromeritics AutoChem II 2920 instrument equipped with a thermal conductivity detector. All catalysts were heated to 200 °C under Ar before switching to a reducing gas mixture. The reduction was conducted in a 5% H_2/Ar atmosphere at a heating rate of 10 °C min^{-1}. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were conducted using a Thermo Scientific Nicolet iS50 FTIR spectrometer equipped with a mercury cadmium telluride detector and a Pike Technologies DiffusIR™ diffuse reflectance high-temperature cell. All spectra were obtained at a resolution of 2 cm^{-1} from 1000 to 4000 cm^{-1} under atmospheric pressure. The catalyst was firstly reduced at 450 °C in a mixed gas of 1 vol.% CO_2, 4 vol.% H_2, and 95 vol.% N_2 for 30 min (total flow rate of 25 mL min^{-1}). Subsequently, the catalyst was purged with N_2 at 450 °C for 30 min to remove potential adsorbates. After cooling to room temperature, spectra of the samples were recorded to serve as the background. Then the reaction gas of a 2 vol.% CO_2 +8 vol.% H_2 + 90 vol.% N_2 mixture with a total flow rate of 10 mL min^{-1} was introduced at 300 °C for 1 h to reach an equilibrium state.

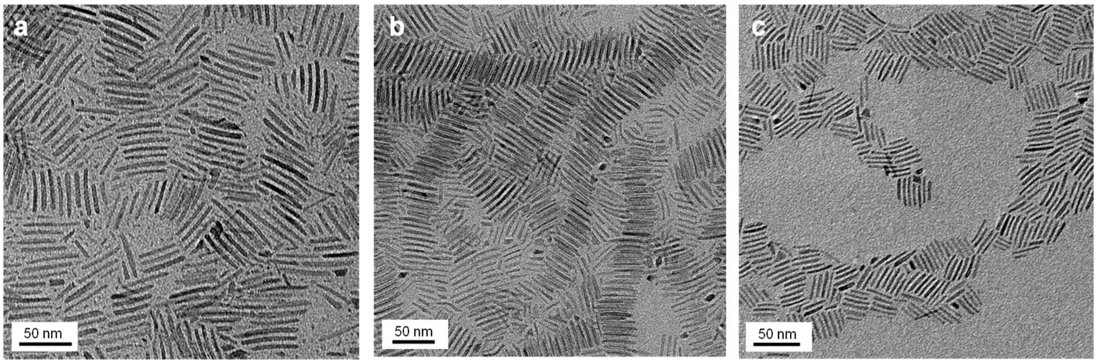

Figure S1. TEM images of Co-TiO_2 and TiO_2 nanorods with different doping level. (**a**–**c**) 4.2% Co-TiO_2, 7.5% Co-TiO_2 and TiO_2 nanorods, respectively.

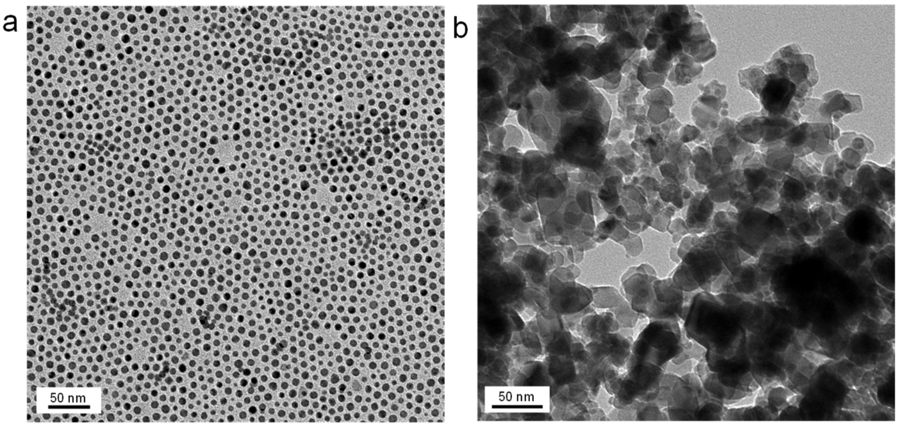

Figure S2. TEM images of (**a**) as-synthesized Co NPs and (**b**) Co NPs/TiO_2.

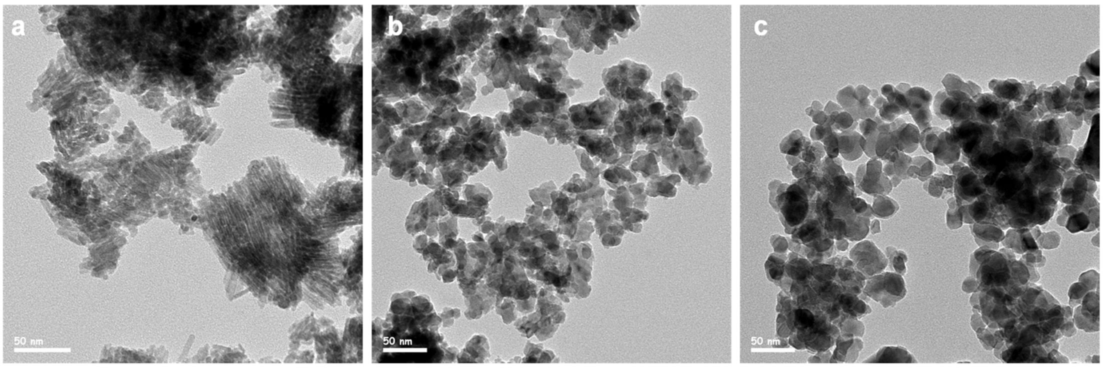

Figure S3. TEM images of Co-TiO_2 after calcination at different temperature. (**a**–**c**) 400 °C, 500 °C and 600 °C, respectively.

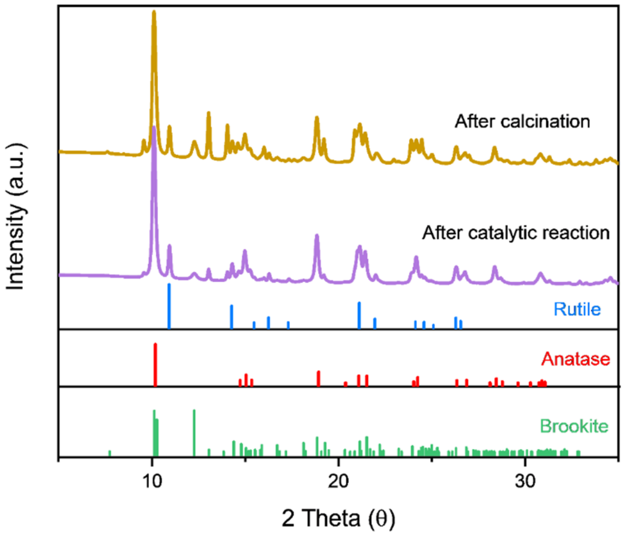

Figure S4. SXRD patterns of Co-TiO_2 after calcination at 500 °C and after catalytic reaction at 450 °C and the Bragg positions for anatase, brookite, and rutile TiO_2, respectively.

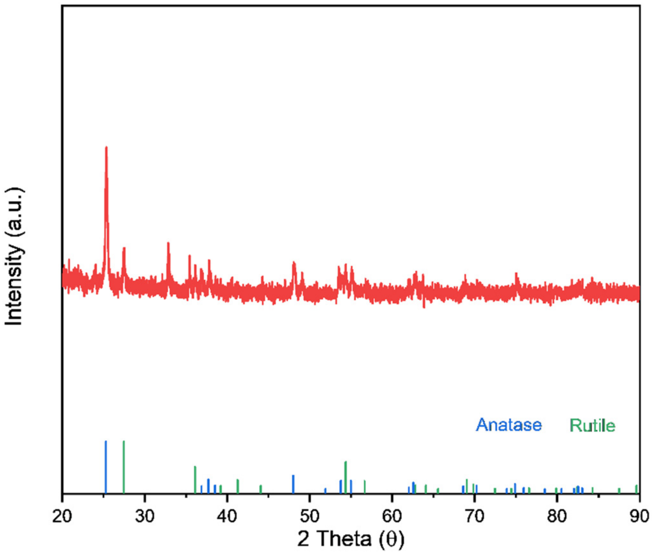

Figure S5. XRD pattern of Co-TiO_2 after calcination at 600 °C and the Bragg positions for anatase and rutile TiO_2, respectively.

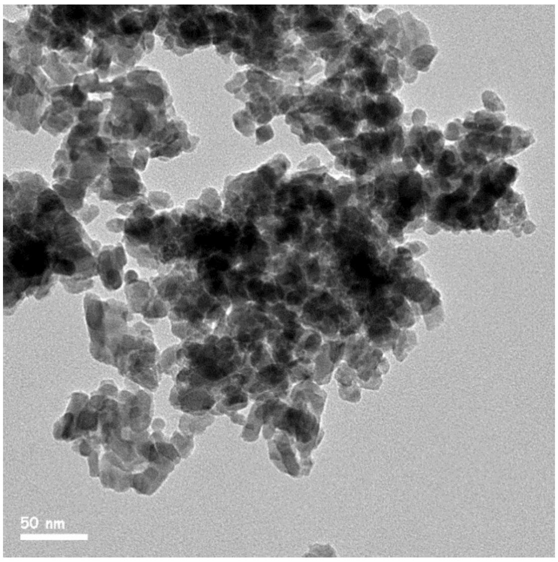

Figure S6. TEM image of Co-TiO_2-500 after the stability test.

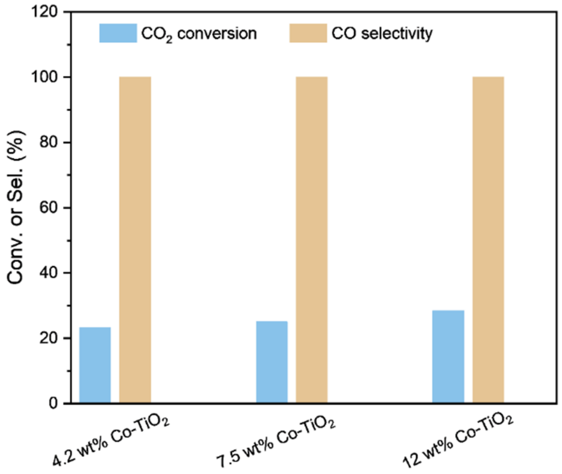

Figure S7. Catalytic data of Co-TiO_2-500 with different doping level. 4.2% Co-TiO_2, 7.5% Co-TiO_2 and 12% Co-TiO_2 were used in these activity and selectivity tests. Reaction conditions: 1 vol % CO_2 + 4 vol % H_2 + 95 vol % N_2 at ambient pressure, 400 °C.

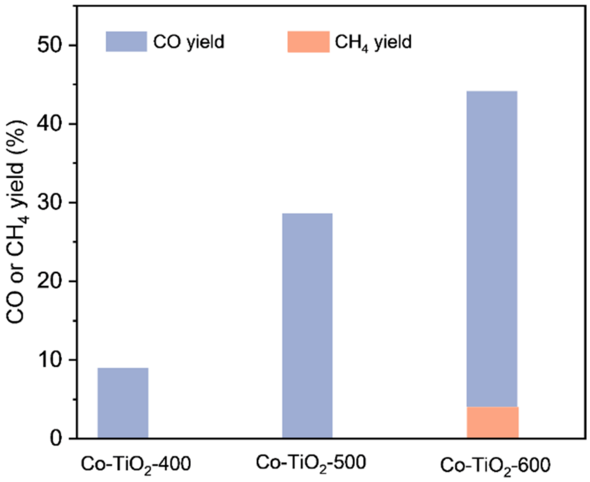

Figure S8. Catalytic data of Co-TiO_2 treated with different calcination conditions. Co-TiO_2-400, Co-TiO_2-500 and Co-TiO_2-600 were used in these activity and selectivity tests. Reaction conditions: 1 vol % CO_2 + 4 vol % H_2 + 95 vol % N_2 at ambient pressure, 400 °C.

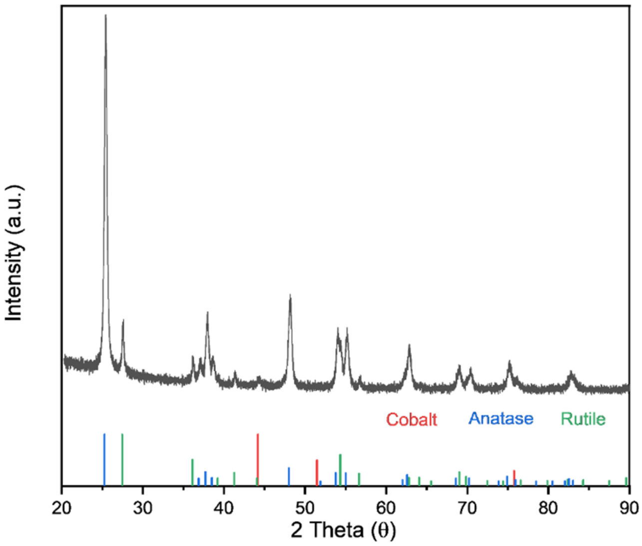

Figure S9. XRD patterns of Co NPs/TiO_2 after catalytic reaction at 400 °C and the Bragg positions for cobalt, anatase TiO_2, and rutile TiO_2, respectively.