

## Supporting Information

### Evidence of highly active Co oxide catalyst for the Fisher-Tropsch Synthesis and CO<sub>2</sub> hydrogenation

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#### Experimental

**Synthesis of Macroporous TiO<sub>2</sub>:** Macroporous TiO<sub>2</sub> was prepared via a polymer templating strategy.<sup>1</sup> The polystyrene beads, utilized as the polymer template, were synthesized through an emulsifier-free emulsion polymerization technique.<sup>2</sup> Briefly, 14 g of styrene monomer and 0.7 g of divinylbenzene (a crosslinker) were washed 4 times with 0.1 M NaOH solution and with DI water to remove inhibitors. The mixture of styrene and divinylbenzene was then stirred in 140 mL of DI water at 70 °C, followed by purging under Ar flow for 1 h. Finally, potassium persulfate (0.03 g, 1.0M) was added as an initiator for the polymerization. After reacting at 70 °C for 12 h, the polystyrene beads with an average diameter of 500 nm were collected by centrifugation at 4300 rpm.

The next step is to add 20 mmol of titanium isopropoxide (Sigma-Aldrich, 97%) to P123 dissolved in ethanol and HCl. The combined solution was stirred for 5 h after which the dried polystyrene beads (4 g) was added. The solvent was evaporated at 60 °C for 48 h, and the resulting flakes were calcined at 700 °C in air for 6 h. After calcination, highly crystalline macroporous TiO<sub>2</sub> with an average pore size of 300 nm was obtained.

**Synthesis of 10 nm Co Nanoparticles :** 10 nm cobalt nanoparticle synthesis was carried out using standard Schlenk techniques under an argon atmosphere as described in detail elsewhere.<sup>3</sup> Briefly, after evacuation of oleic acid (130 mg, 99% pure, Aldrich) in a 250 ml round bottom flask for 20 min, anhydrous o-dichlorobenzene (15 mL, 99%, DCB, Aldrich) was added under Ar. Once the temperature was stabilized at 172°C, Co<sub>2</sub>(CO)<sub>8</sub> (stabilized with 1-5% hexane, Strem) in DCB (3 ml, 0.5 M) was injected quickly into the solution (25 ml SGE gas tight syringe equipped with a G13 needle [ID = 1.8 mm]) forming colloidal particles. This colloidal suspension was then aged for 20 min at constant temperature before cooling the flask in a flow of air. DCB (10 mL) and 2-propanol (ACS Grade, 20 mL) were added to this suspension, precipitating

nanoparticles, which could then be extracted by centrifugation (4300 rpm). The solid was re-dispersed and stored in chloroform until further use.

**Fabrication of Co/TiO<sub>2</sub> catalyst:** For the preparation of a 10 weight % Co/TiO<sub>2</sub> catalyst, as-synthesized Co nanoparticles dispersed in chloroform (~10 mg mL<sup>-1</sup>) were added to macroporous TiO<sub>2</sub> and sonicated for 1 h at room temperature. The precipitate was separated by centrifugation and washed with acetone and ethanol seven times, then dried at 100 °C.

**Catalytic testing:**

CO<sub>2</sub> hydrogenation was carried out the reactor consists of a U-shaped plug flow reactor bed, in which the reactor temperature is monitored with a K-type thermocouple. A reactant gas feed consisting of CO<sub>2</sub> and H<sub>2</sub> balanced with He is fed to the catalyst. The pressure, continuously monitored by a capacitance gauge, was regulated via a needle valve to 5-6 bar. The gases at the outlet of the reactor were analyzed using a Hewlett Packard HP 5890 Series II chromatograph equipped with both FID and TCD detectors. Hayesep-D packed columns were employed for both the chromatographic separation of CO<sub>2</sub>, CO, and CH<sub>4</sub> (TCD) and for detecting the presence of C1–C3 hydrocarbons (FID).

Fischer-Tropsch synthesis was carried out in a lab scale gravitational fixed bed reactor made of stainless steel (i.d. = 4.5mm). A Supelco tubular furnace in combination with temperature programmer was used to control the reaction temperature. The catalyst sample (~ 100mg) was retained between a plug of quartz wool and ground glass. All the gases used were of ultra high purity (99.999%). The CO flow was fed through a high temperature trap prior to introduction into the reactor to avoid the formation of carbonyls. The volumetric flow rate of each individual gas was controlled by calibrated mass flow controllers (Parker).

The effluent gaseous product was analyzed using an Agilent GC-MS (7890A) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The separation of reactants and products was achieved using two capillary columns (Hp-Plot/Q and HP-Molesieve). At the outlet of the columns, the gases were split in two: a small volume was directed to the mass spectrometer (Agilent 5975C) for qualitative analysis whereas the rest was directed to the TCD and the FID. A methanizer allowed for detection of CO and CO<sub>2</sub> at the FID. Argon (2 sccm) was also fed to the reactant stream for use as an internal standard for GC analysis.

Tunrover frequency or TOF was calculated using the cobalt surface area for each sample as estimated by TEM measurements and ICP-AES measurements.

**Methods:**

**Ex Situ:** STEM/EDS analyses were carried out using a Jeol2100F microscope equipped with an INCA energy dispersive spectrometer. The EDS analysis was carried out in the scanning mode using a 1.5 nm probe at 200 kV.

**In situ:** All synchrotron studies were conducted at the Advanced Light Source of the Lawrence Berkeley National Laboratory. Co catalyst powder was pressed into a thin (~200 $\mu$ m) pellet and used as-synthesized. The pellet was heated to 150°C under He (NEXAFS spectroscopy and XRD) or in vacuum (APXPS) before the experiments. The APXPS chamber in beamline 9.3.2 has been described elsewhere.<sup>4</sup> XPS data and error analysis was carried out using CasaXPS software. NEXAFS spectroscopy was carried out in beamline 8.0.1 (total electron yield detection at the Co and Ti L<sub>2,3</sub>, and the C K absorption edges) and 10.3.2<sup>5</sup> (fluorescence yield detection at the Co and Ti K absorption edge). The reaction cells used in beamline 8.0.1, 10.3.2 and 12.2.2 have been described elsewhere.<sup>6</sup>

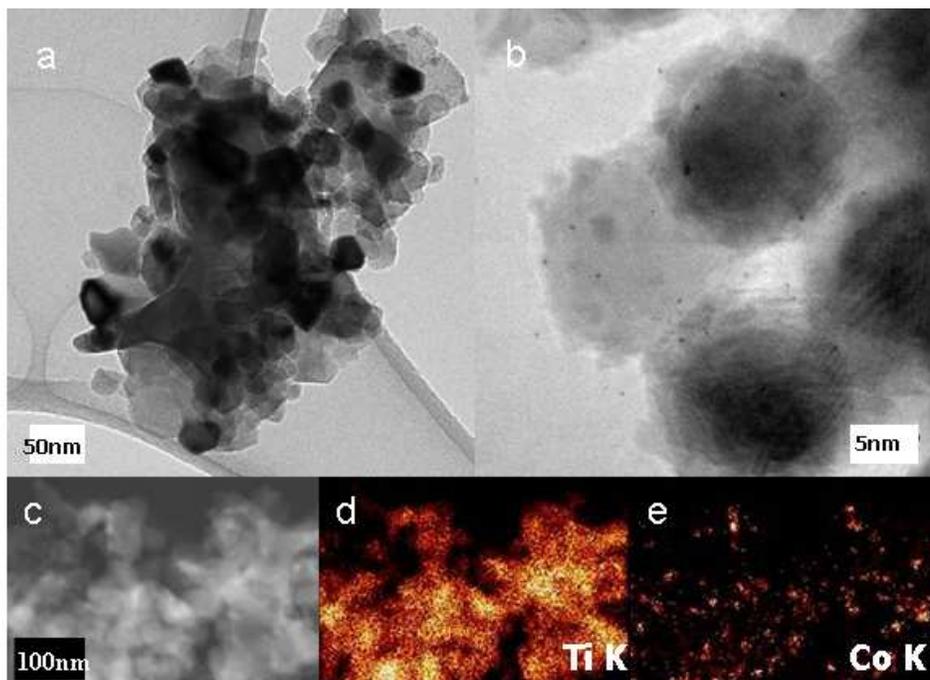
We used QuickXAS mode for the data acquisition in beamline 10.3.2. Deadtime correction, pre-edge removal and post-edge normalization<sup>5</sup> of the near edge spectra (up to 250 eV past the absorption threshold at the Co K edge) were carried out by employing the software at the beamline. The EXAFS signal  $k^2\chi(k)$  was extracted then Fourier-transformed using a Kaiser-Bessel window with a  $\Delta k$  range of 5  $\text{\AA}^{-1}$ .

The diffraction experiment was carried out in beamline 12.2.2<sup>7</sup> in a transmission geometry using 25 keV photons. Diffraction rings were collected over a Mar345 image plate detector. The x-ray beam was 99% horizontally polarized and all geometric and polarization correction were made during the angular integration using the program FIT2D. Sample-to-detector distance was calibrated by using a LaB<sub>6</sub> standard powder sandwiched between Kapton films and placed in the specimen holder.

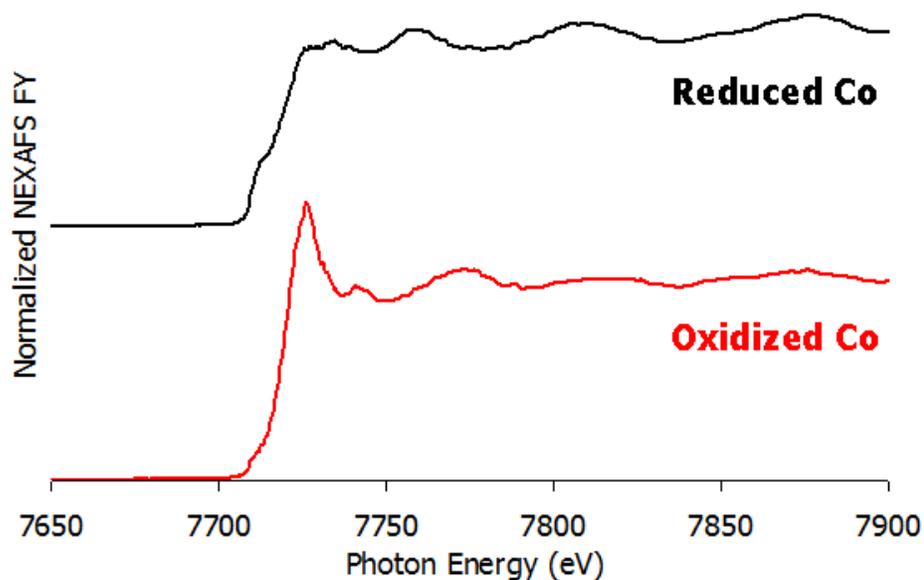
No data subtraction was applied to the powder diffraction data. Simulated XRD patterns were derived from known space groups and fractional atomic coordinates using Mercury program:<sup>8</sup> cubic CoO (space group Fm-3m), cubic Co (space group Fm-3m), spinel Co<sub>3</sub>O<sub>4</sub> (space group Fd3m), rutile TiO<sub>2</sub> (space group P<sub>42</sub>/mnm) and anatase TiO<sub>2</sub> (space group I<sub>41</sub>/amd).

For a given pressure and temperature condition, X-ray spectra or diffraction patterns were measured, usually for an hour or more, until no further change in the spectra or diffraction pattern was observed. The acquisition time of each X-ray technique is however varied: 2 minutes for XRD (a bulk measurement); 20 min for NEXAFS TEY (a surface measurement); 160 min for EXAFS (another bulk measurement). Likewise, typical exposure times for the APXPS experiments were in the order of hours during which multiple measurements, at various core (Co and Ti 2p; C and O 1s) and valence levels using different photon energies (940 eV for Co, 630 eV

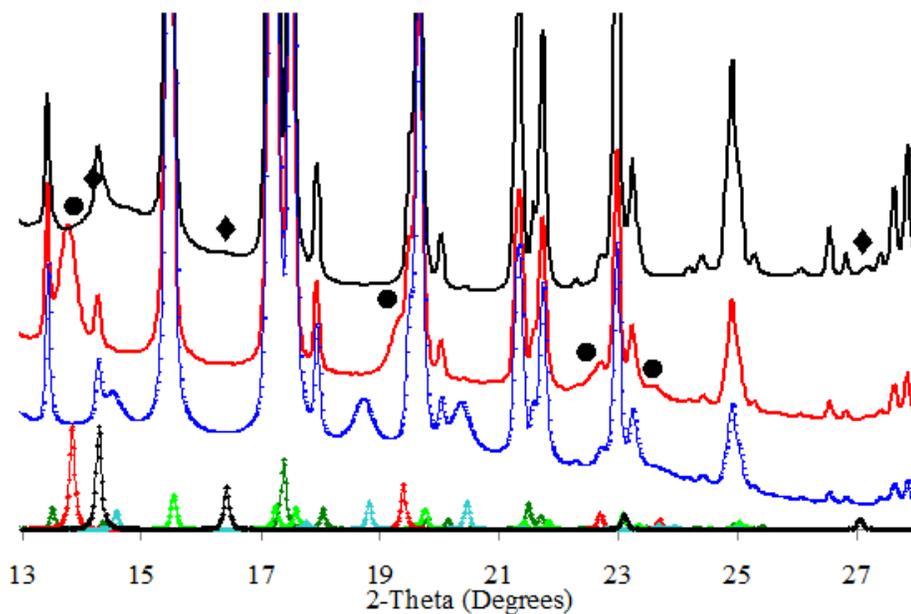
for Ti, C and O), were made until no further change in the spectral features could be detected. Note, that all the techniques showed the evidence of reduction (or oxidation) of Co (and TiO<sub>2</sub>) for the Co/TiO<sub>2</sub> catalyst, starting with the first measurement, and no significant change in the course of any experiment at any given condition. This suggests that the steady-state was reached rather quickly in the timescale of any X-ray technique used.



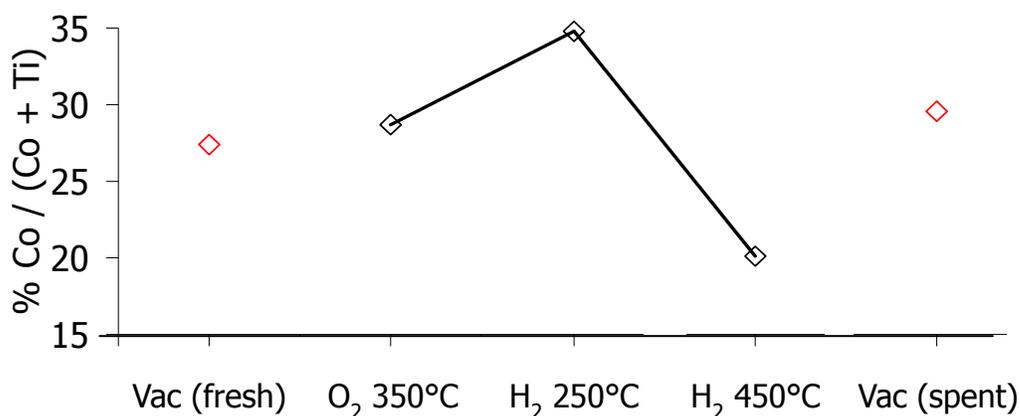
**Figure S1.** (a) TEM and (b) HR-TEM images of the Co/TiO<sub>2</sub> catalyst, obtained after cycles of redox treatments and the CO<sub>2</sub>/H<sub>2</sub> reaction. (c) STEM image and EDS elemental maps at (d) Ti K and (e) Co K lines of the same spent catalyst.



**Figure S2.** *In situ* NEXAFS FY spectra at Co K absorption edge, acquired under 1 atm of CO<sub>2</sub>/H<sub>2</sub>/Ar (1:3:0.5) at 250°C. Reduced and oxidized states of Co were obtained upon reductive H<sub>2</sub> (20 vol. % in Ar) treatments at 450°C and 250°C, respectively, following O<sub>2</sub> (20 vol. % in Ar) treatments at 350°C.



**Figure S3.** *In situ* XRD patterns, acquired under 20 vol. % O<sub>2</sub> in Ar (blue) or 1 atm of CO<sub>2</sub>/H<sub>2</sub>/Ar (1:3:0.5) at 250°C (black and red), of the Co/TiO<sub>2</sub> catalyst. The black XRD pattern belongs to the catalyst with reduced Co and the red XRD pattern belongs to that with oxidized Co. Simulated XRD patterns are shown on the x-axis: cubic CoO (space group Fm-3m, red), cubic Co (space group Fm-3m, black), spinel Co<sub>3</sub>O<sub>4</sub> (space group Fd3m, blue), rutile TiO<sub>2</sub> (space group P<sub>4</sub><sub>2</sub>/mnm, green) and anatase TiO<sub>2</sub> (space group I<sub>4</sub><sub>1</sub>/amd, light green). Diamonds denote reflections of cubic Co, and spheres denote those of cubic CoO.



**Figure S4.** % Co on surface, defined as % Co / (Co+Ti) from XPS, as a function of condition. AP-XPS data were obtained using 940 eV and 630 eV photons at Co 2p and Ti 2p levels, respectively, under given conditions in 100 mTorr. Lab XPS (Al K  $E_{\text{photon}}=1460$  eV) data (red) were obtained in  $\sim 10^{-8}$  Torr base pressure for the freshly prepared as well as spent catalysts.

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