

## **Electronic Supplementary Information:**

“X-ray Nanoscopy of Cobalt Fischer-Tropsch Catalysts at Work” by

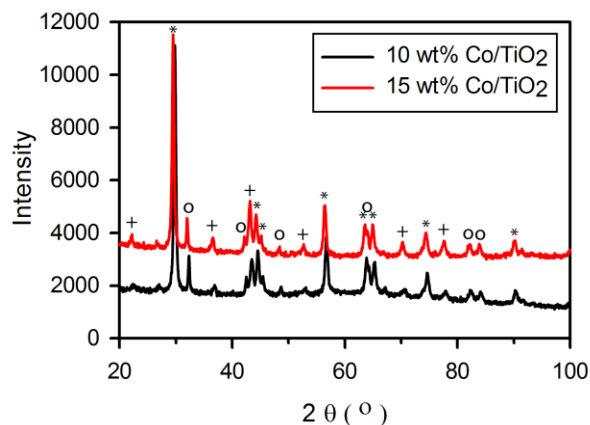
**Korneel H. Cats, Ines D. Gonzalez-Jimenez, Yijin Liu, Johanna L. Nelson, Douglas van Campen, Florian Meirer, Ad M.J. van der Eerden, Frank M.F. de Groot, Joy C. Andrews, and Bert M. Weckhuysen**

### **1. Catalyst Preparation**

Two catalysts were prepared by the Incipient Wetness Impregnation (IWI) method. About 2 g of TiO<sub>2</sub> (P25 support) was evacuated in a round-bottom flask. About 1 mL of a saturated solution of Co(NO<sub>3</sub>)<sub>2</sub> · 9 H<sub>2</sub>O loaded into a syringe and carefully injected into the flask through a septum until the pores of the TiO<sub>2</sub> were completely filled. The vacuum in the flask was broken after about 10 min and the catalyst was placed overnight in a drying oven kept at a temperature of 60°C. The following day the catalyst was calcined at a temperature of 350°C (ramp: 5°C/min) under a flow of air. The catalyst was kept at 350°C for 3 h. Performing this procedure once results in a catalyst with a loading of 10 wt% Co/TiO<sub>2</sub>. A second catalyst sample with a loading of 15 wt% Co/TiO<sub>2</sub> was prepared by following the procedure twice.

### **2. X-Ray Diffraction**

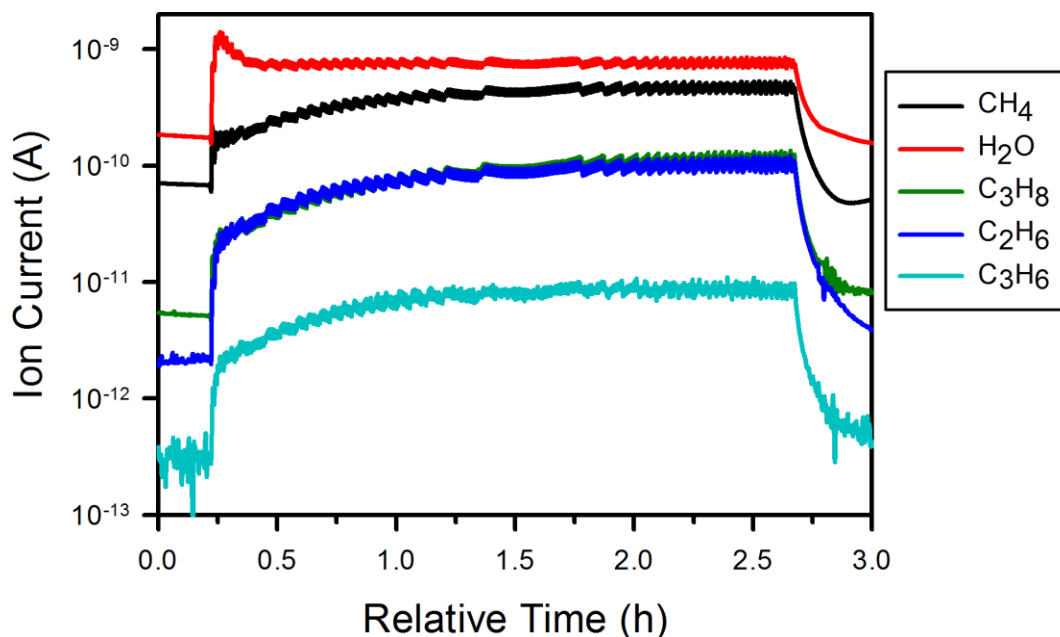
X-ray Diffraction (XRD) patterns of the calcined catalysts were measured using a Bruker-AXS D2 X-ray diffractometer using Co-K<sub>α</sub> radiation ( $\lambda = 1.789 \text{ \AA}$ ). The diffractograms, shown in Figure S1, indicate that cobalt is present as Co<sub>3</sub>O<sub>4</sub> after calcination. Scherrer analysis of the diffraction peaks, belonging to Co<sub>3</sub>O<sub>4</sub> and marked with ‘+’ in Figure S1, reveals an average particle size of about 18 nm.



**Figure S1:** X-ray diffractograms of calcined 10 wt% (black) and 15 wt% Co/TiO<sub>2</sub> (red) catalysts. The diffraction peaks due to TiO<sub>2</sub> are marked with ‘\*’ (anatase) and ‘o’ (rutile), while the diffraction peaks of Co<sub>3</sub>O<sub>4</sub> are marked with ‘+’.

### 3. Mass Spectrometry

The validity of our in-situ TXM set-up was confirmed during a separate catalysis experiment by loading the 15 wt% Co/TiO<sub>2</sub> catalyst into a capillary and subjecting the material to the same treatment as for the in-situ experiment, described in the main text. The outlet of the reactor was coupled to a Pfeiffer ThermoStar mass spectrometer. Mass traces for  $m/z = 16$  (CH<sub>4</sub>), 18 (H<sub>2</sub>O), 30 (C<sub>3</sub>H<sub>6</sub>), 42 (C<sub>3</sub>H<sub>6</sub>), 44 (C<sub>3</sub>H<sub>8</sub>) and 58 (C<sub>4</sub>H<sub>10</sub>) were measured over a period of about 3 h, as illustrated in Figure S2. After the system was pressurized to 10 bar (after about 0.25 h), a sharp increase in the ion current of a selection of Fischer-Tropsch reaction products, i.e., CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>, is seen. This qualitatively proves the activity of the catalyst under the in-situ conditions.

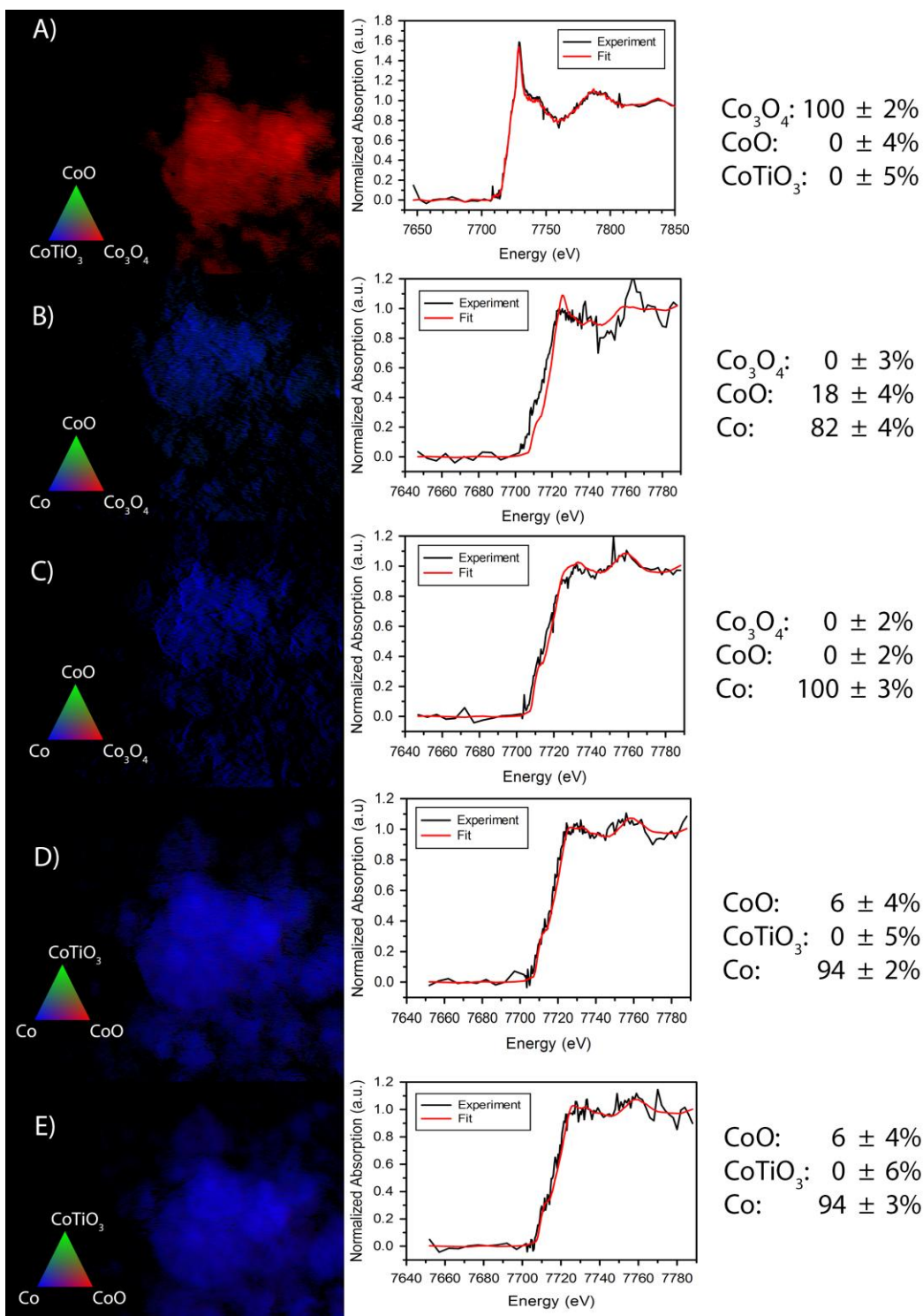


**Figure S2:** Mass spectrometry data obtained for a 15 wt% Co/TiO<sub>2</sub> at 10 bar and 250°C during an experiment similar to, but separate from the in-situ TXM experiment described in the main article, to validate the catalytic performance of the reactor system as Fischer-Tropsch products, such as water, methane, ethane, propene and propane are formed.

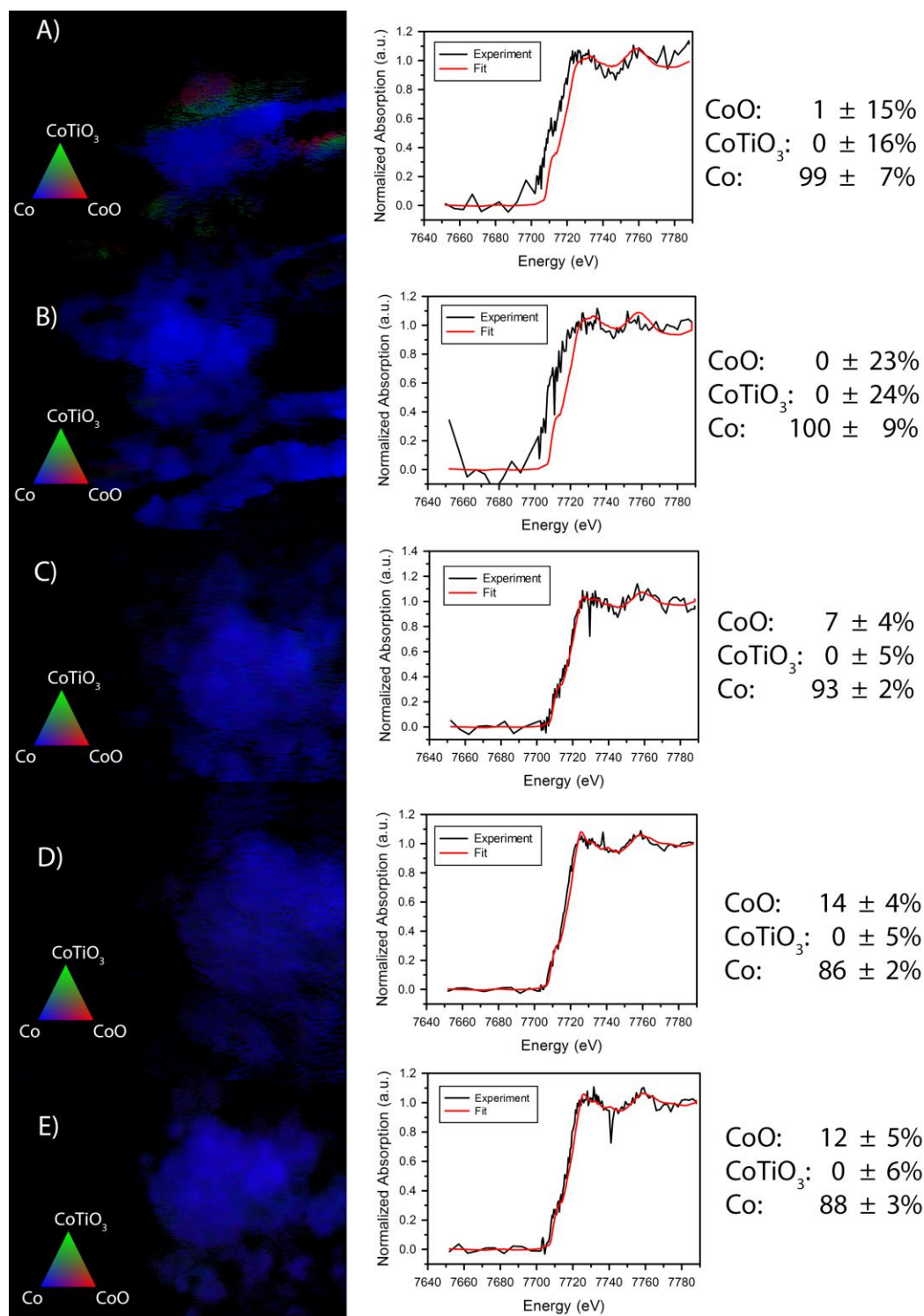
### 4. Transmission X-ray Microscopy

The complete set of 2D chemical maps that has been collected during the in-situ TXM experiment, as outlined in the main text, is shown in Figures S3–S5.

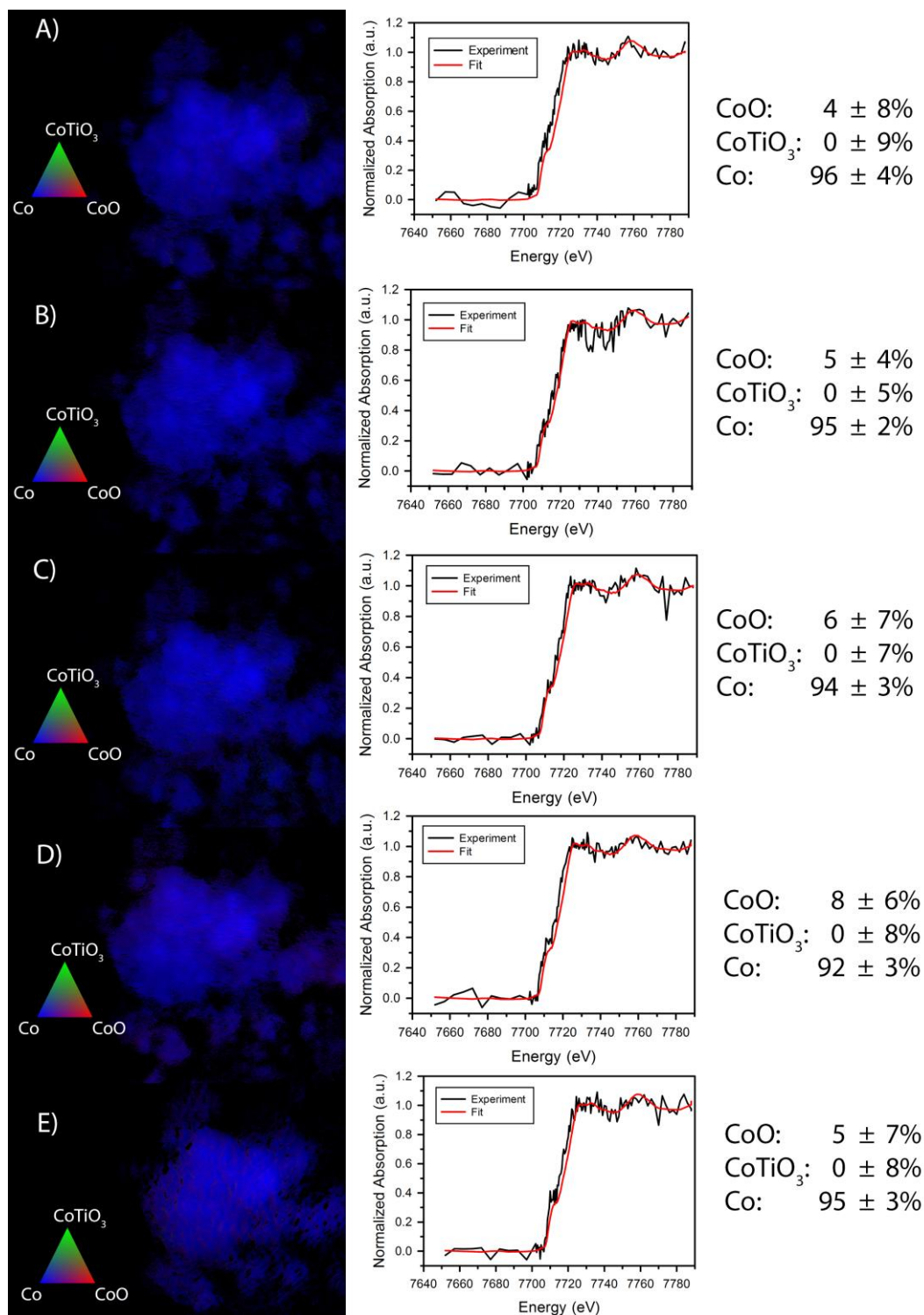
Each XANES scan took about 30 – 45 min. This relatively long scan time (compared to the rate of reduction at 350 °C) means that the Co oxidation state changes during the scan. This has negatively affected the quality of the XANES data, especially during the early phases of reduction (i.e. figure S3 (B)), when changes in oxidation state are greatest.



**Figure S3:** 2-D Transmission X-ray Microscopy images of a 10 wt% Co/TiO<sub>2</sub> catalyst particle. Left panel, Chemical maps, middle panel, Average X-ray Absorption Near Edge Spectra (XANES) and right panel, least squares fitting results of the spectra in the middle plane. The data were measured: (A) at room temperature, (B–D) during reduction under H<sub>2</sub> at 350°C after 0 min (B), 45 min (C) and 90 min (D), (E) during Fischer-Tropsch synthesis at 250°C and 10 bar pressure in CO/H<sub>2</sub> in a ratio 1:2 for 0 h on stream.



**Figure S4:** 2-D Transmission X-ray Microscopy images of a 10 wt% Co/TiO<sub>2</sub> catalyst particle. Left plane, chemical maps, middle plane, Average X-ray Absorption Near Edge Spectra (XANES) and right plane, least squares fitting results of the spectra in the middle plane. The data were measured during Fischer-Tropsch synthesis at 250°C and 10 bar pressure in CO/H<sub>2</sub> in a ratio 1:2 for 2.25 h (A), 3 h (B), 3.5 h (C), 6.5 h (D), 7.75 h (E) on stream.

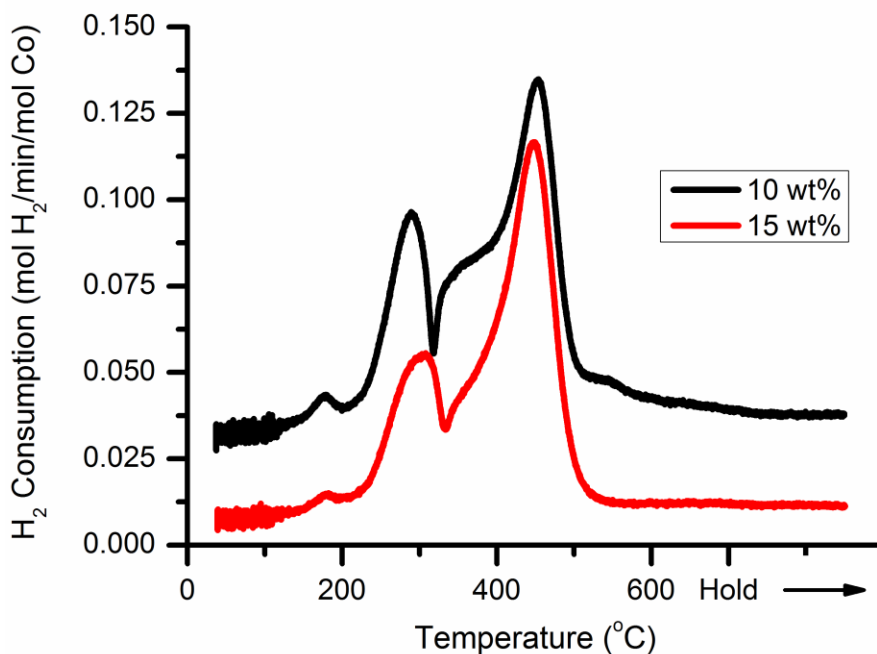


**Figure S5:** 2-D Transmission X-ray Microscopy images of a 10 wt% Co/TiO<sub>2</sub> catalyst particle. Left plane, chemical maps, middle plane, Average X-ray Absorption Near Edge Spectra (XANES) and right plane, least squares fitting results of the spectra in the middle plane. The data were measured during Fischer-Tropsch synthesis at 250°C and 10 bar pressure in CO/H<sub>2</sub> in a ratio 1:2 for 8.5 h (A), 9 h (B), 9.75 h (C), 10.5 h (D), 11.25 h (E) on stream.

## 5. Temperature Programmed Reduction

The reduction behaviors of both the 10 wt% and 15 wt% catalysts were investigated with Temperature Programmed Reduction (TPR) on a Micromeritics AutoChem II 2920 instrument. The samples were first dried by heating to 120°C (ramp rate: 10.0°C/min) under an argon flow. The samples were kept at 120°C for 2 h. After cooling to 40°C, the samples were heated to 700°C with a ramp rate of 10.0°C/min under a flow of 5% H<sub>2</sub> in Ar. The temperature was kept at 700°C for 10 min. The hydrogen concentration of the outflowing gas mixture was measured with a previously calibrated Thermal Conductivity Detector (TCD). Water that was formed during the reduction was trapped with an *i*-propanol/dry ice trap.

The results of the TPR experiments are shown in Figure S6. Both catalysts are reduced in a two-step process. The first step is the reduction from Co<sub>3</sub>O<sub>4</sub> to CoO. The peak of the hydrogen consumption for this step appears at about 300°C. The second step is the reduction of CoO to metallic Co. The maximum hydrogen consumption happens at about 450°C.

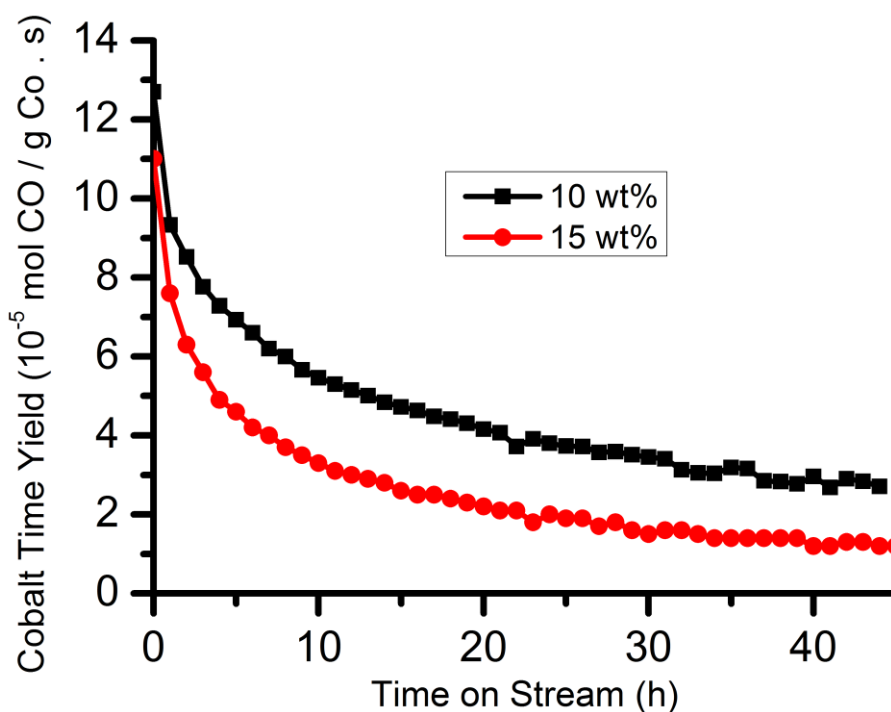


**Figure S6:** Temperature Programmed reduction profiles of 10 wt% and 15 wt% Co/TiO<sub>2</sub> catalyst samples in the presence of H<sub>2</sub>.

## 6. Catalytic Testing

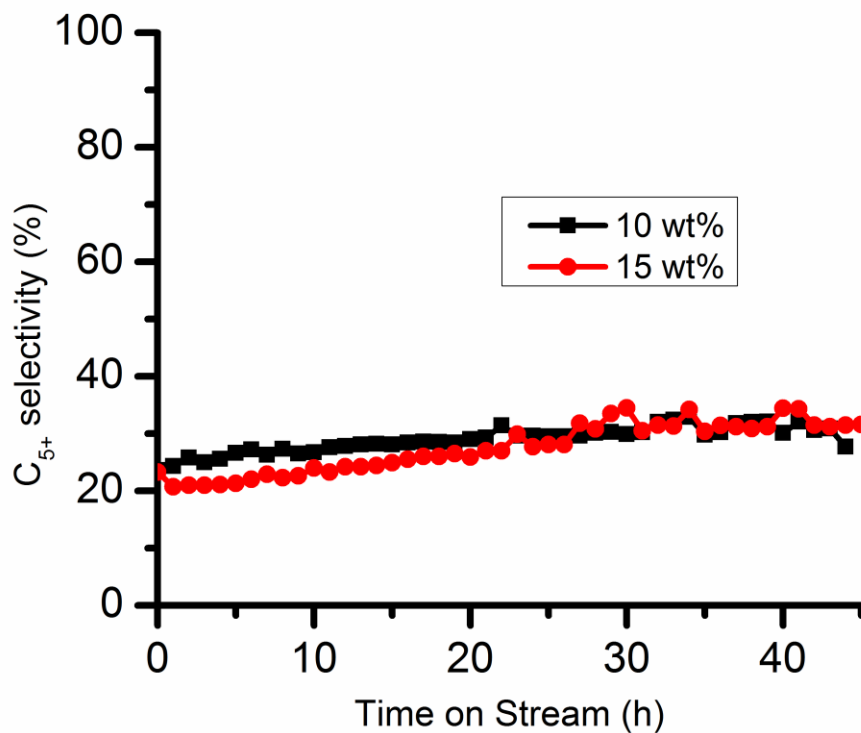
The 10 wt% and 15 wt% Co/TiO<sub>2</sub> catalysts were tested for their activity in the Fischer-Tropsch process in a separate experiment from the in-situ TXM experiment described in the main text. About 20 mg of catalyst material was diluted with about 80 mg of SiC. The diluted catalyst was supported on a glass frit in a U-shaped reactor. The catalyst was first reduced by heating to 350°C with a ramp rate of 5°C/min under a flow of 20 mL/min of H<sub>2</sub>. This temperature was kept for 2 h. Then the catalyst was cooled down to the reaction temperature of 250°C. Once the catalyst reached this temperature, the gas flows were changed to 2 mL/min of CO and 4 mL/min of H<sub>2</sub>. The experiments were performed at atmospheric pressure. A gas phase sample was analyzed every hour by an on-line Gas Chromatograph (GC).

The catalytic activity (expressed as cobalt time yield: mol CO converted per second per gram of cobalt) over the first 45 h of time on stream for both catalysts is shown in Figure S7. It is observed that the activity of both catalysts decreases remarkably during the first 45 h of reaction. The activity of the 10 wt% catalyst decreases from about  $13 \times 10^{-5}$  mol CO/g Co.s to about  $3 \times 10^{-5}$  mol CO/g Co.s. Likewise, the activity of the 15 wt% catalyst decreases from about  $11 \times 10^{-5}$  mol CO/g Co.s to about  $2 \times 10^{-5}$  mol CO/g Co.s.



**Figure S7:** Catalytic activity of 10 wt% and 15 wt% Co/TiO<sub>2</sub> catalysts as a function of time on stream.

The selectivity towards the desired liquid products ( $C_{5+}$ ) is shown in Figure S8. The selectivity stayed more or less constant during the first 45 h of time on stream at about 30% for both catalysts.



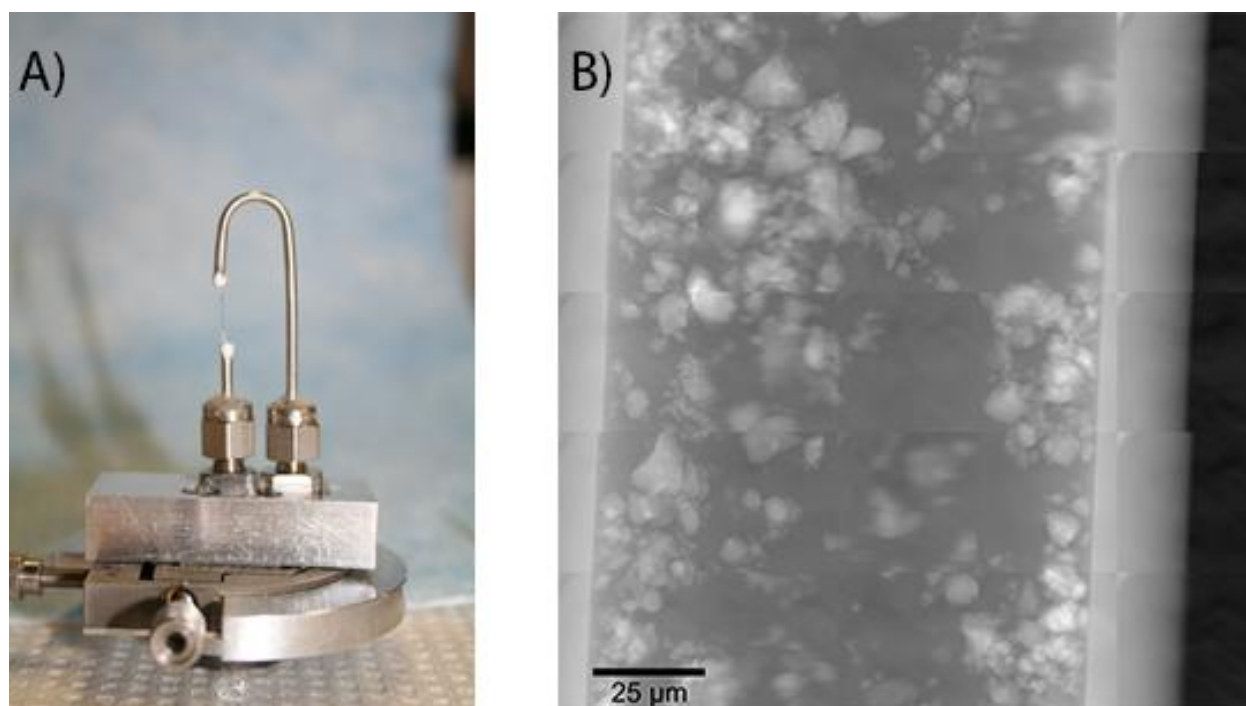
**Figure S8:** Selectivity towards liquid product ( $C_{5+}$ ) of 10 wt% and 15 wt% Co/TiO<sub>2</sub> catalysts as a function of time on stream.



## 7. In-Situ Set-Up

A photograph of the in-situ holder that was used in the experiment is shown in Figure S9. A quartz capillary is attached to the holder using high-temperature epoxy. The capillary is mounted vertically and in the center of the rotation stage on the beam line to allow in-situ tomography experiments.

A transmission image of the capillary is also shown in Figure S9. The image was recorded as a 5 by 5 mosaic. The edges of the capillary are easily recognized, as are some particles that are stuck to the wall.



**Figure S9:** (A) Photograph of the in-situ holder that was used during the experiment described in the main text. (B) Transmission X-ray Microscopy image of the capillary filled with some particles as a 5 by 5 mosaic.