

Dynamics of Reactive Oxygen Species on Cobalt-Containing Spinel Oxides in Cyclic CO  
Oxidation

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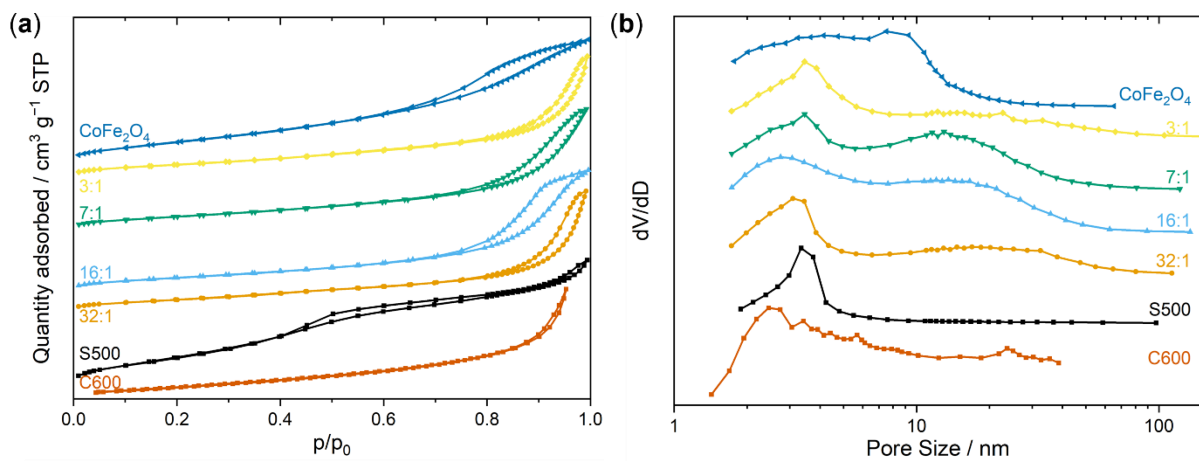


Figure S1: Normalized  $N_2$  adsorption-desorption isotherms (a) and normalized BJH pore size distribution (b).

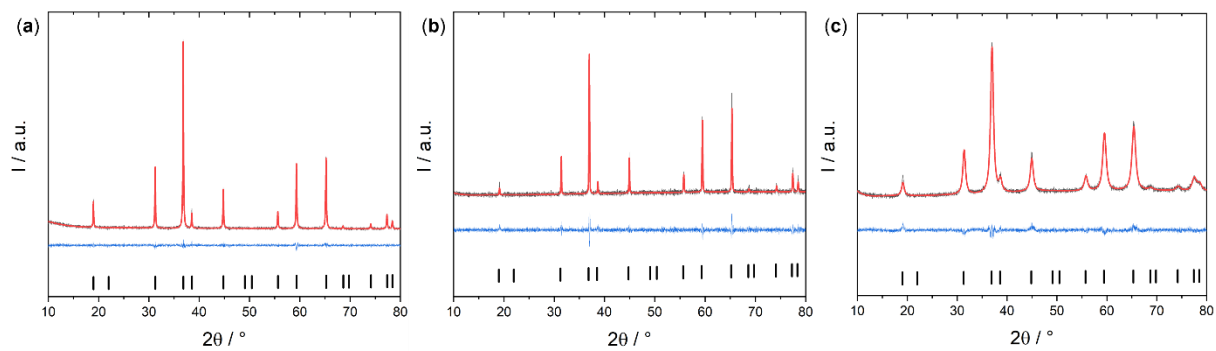


Figure S2: Rietveld refinement plots of C600 (a), P800 (b) and S500 (c).

Table S1. Criteria of fit for the Rietveld Refinements of the X-ray diffraction patterns of the calcined samples.

Sample	$R_{exp}$	$R_{wp}$	$R_p$	$R_{exp}'$	$R_{wp}'$	$R_p'$	GOF	$R_{Bragg}$
C600	5.67	8.20	6.35	9.10	13.17	11.22	1.45	1.527
P800	9.59	13.85	10.83	15.18	21.94	21.05	1.45	2.175
C500	3.57	4.09	3.23	6.34	7.27	6.60	1.15	1.262

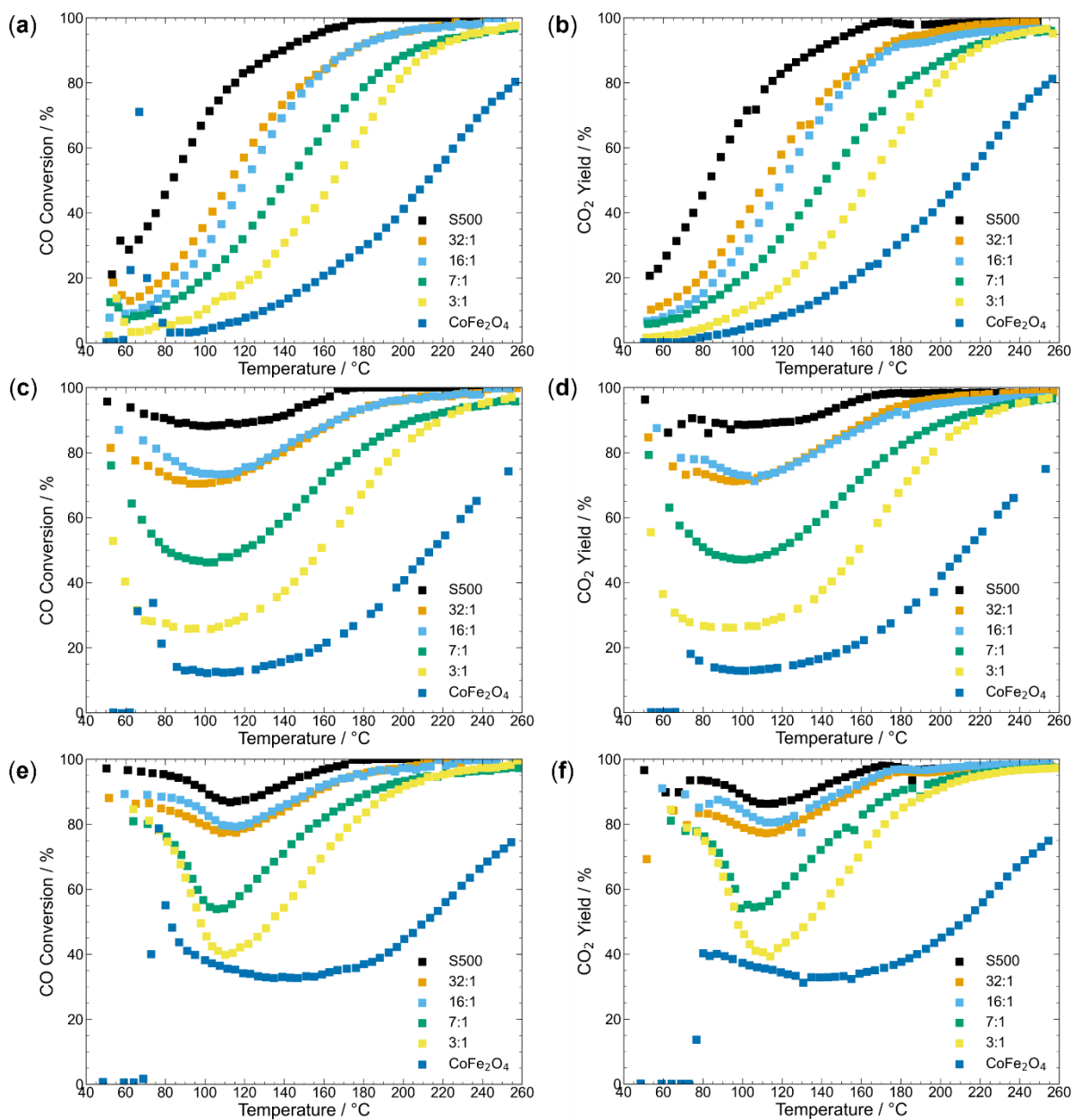


Figure S3: Comparison of CO conversion and  $\text{CO}_2$  yield for the SBA-15 templated catalyst series. CO conversion in the 1<sup>st</sup> run (a).  $\text{CO}_2$  yield in the 1<sup>st</sup> run (b). CO conversion in the 2<sup>nd</sup> run (c).  $\text{CO}_2$  yield in the 2<sup>nd</sup> run (d). CO conversion in the 3<sup>rd</sup> run (e).  $\text{CO}_2$  yield in the 3<sup>rd</sup> run (f).

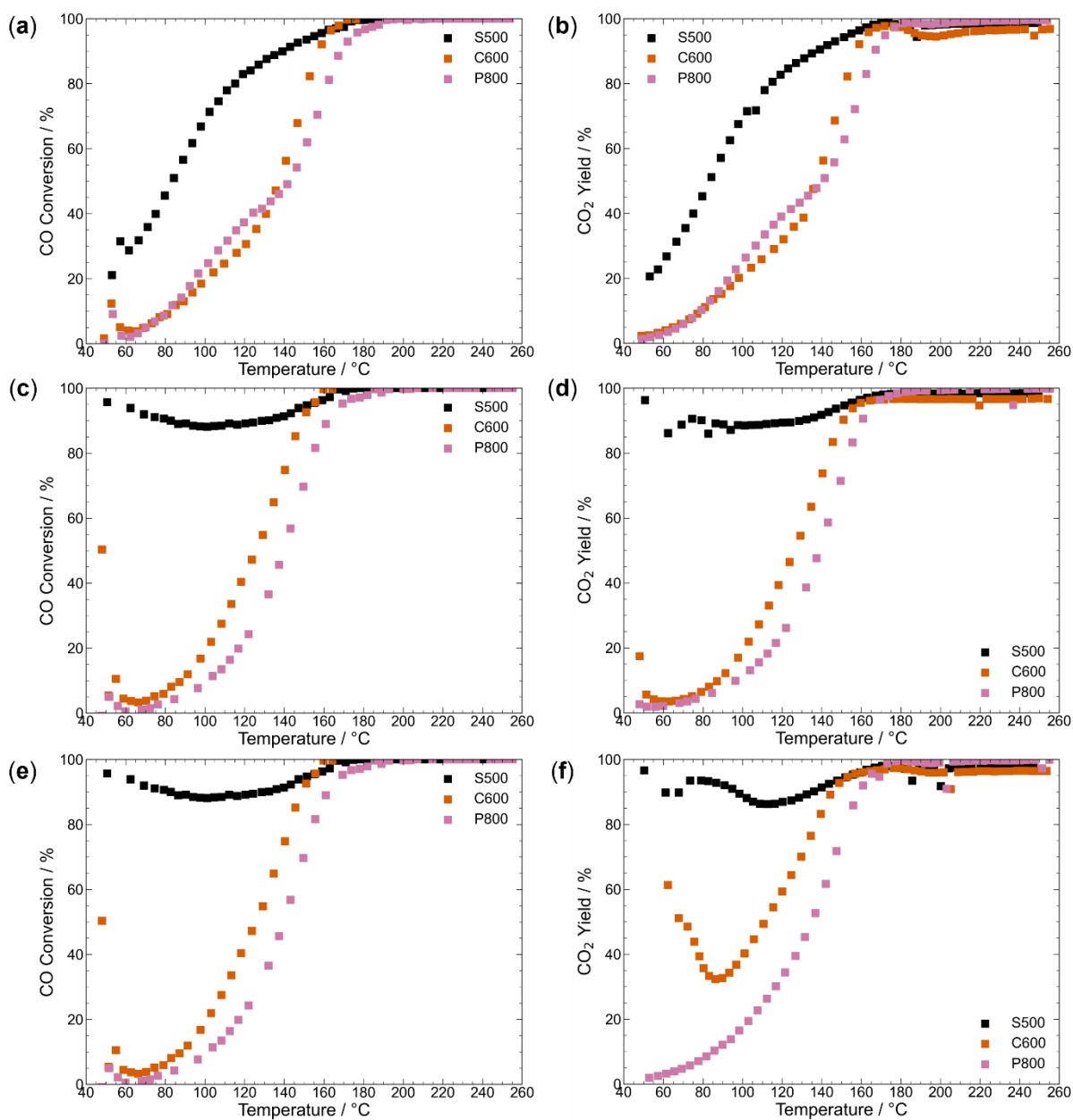


Figure S4: Comparison of CO conversion and CO<sub>2</sub> yield for the different Co<sub>3</sub>O<sub>4</sub> catalysts. CO conversion in the 1st run (a). CO<sub>2</sub> yield in the 1st run (b). CO conversion in the 2nd run (c). CO<sub>2</sub> yield in the 2nd run (d). CO conversion in the 3rd run (e). CO<sub>2</sub> yield in the 3rd run (f).

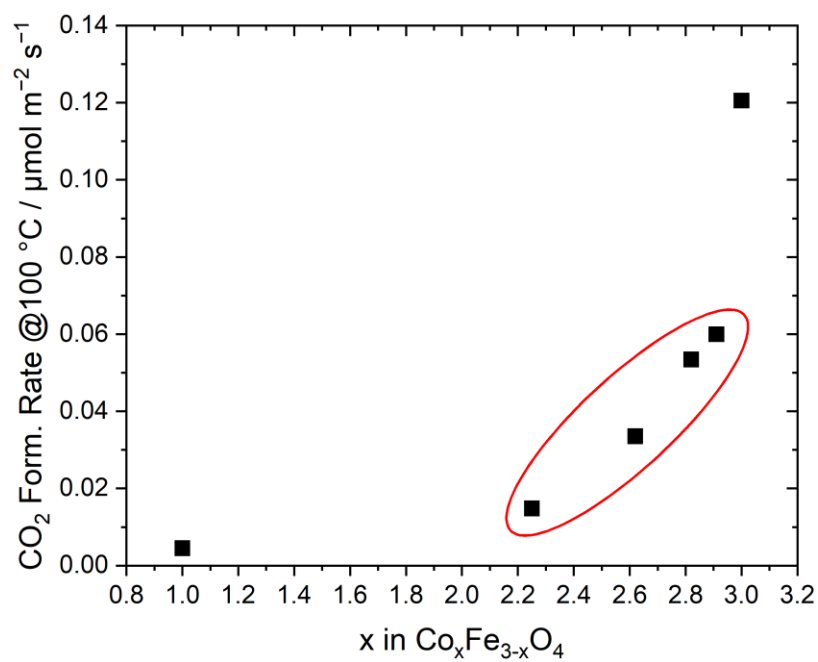


Figure S5: Correlation between  $\text{CO}_2$  formation rate at 100 °C and the cobalt content in the spinel materials. The red circle shows for clarity where a linear correlation between reaction rate and Co content can be observed.

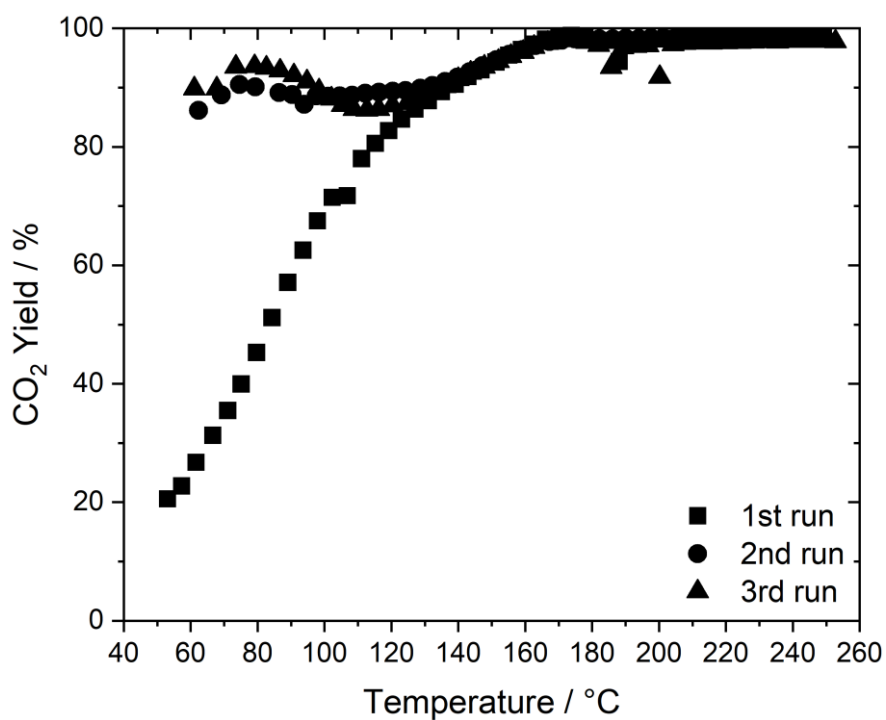


Figure S6: CO oxidation activity in the different runs for S500.

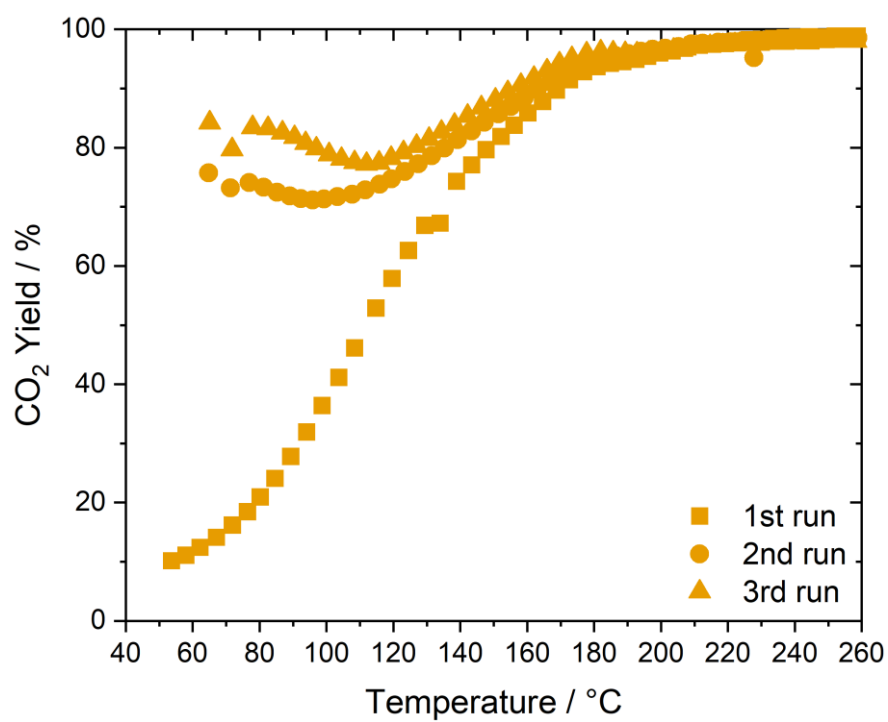


Figure S7: CO oxidation activity in the different runs for SBA-15 templated Co:Fe 32:1.

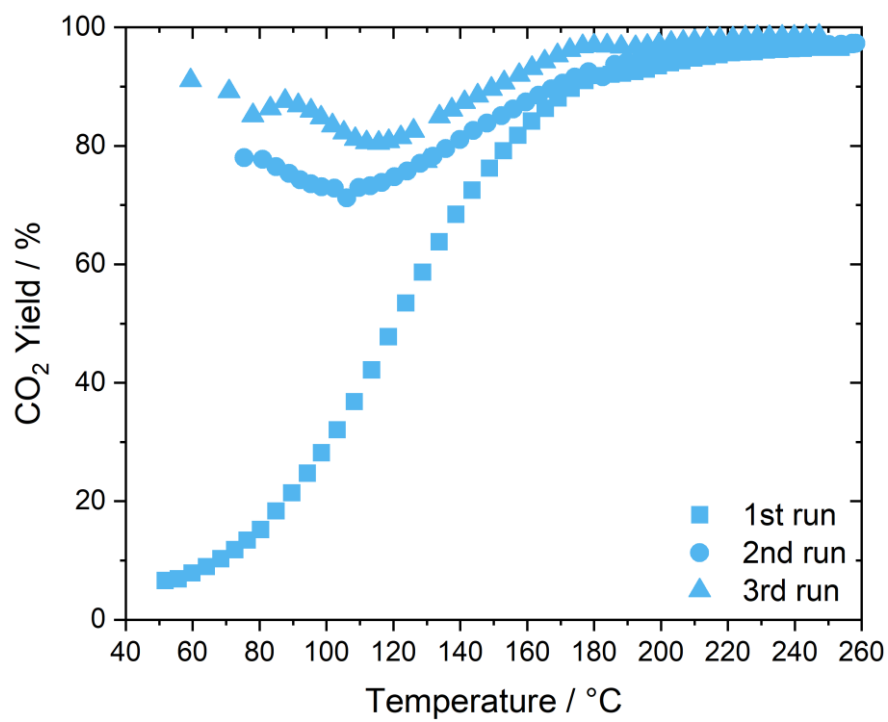


Figure S8: CO oxidation activity in the different runs for SBA-15 templated Co:Fe 16:1.

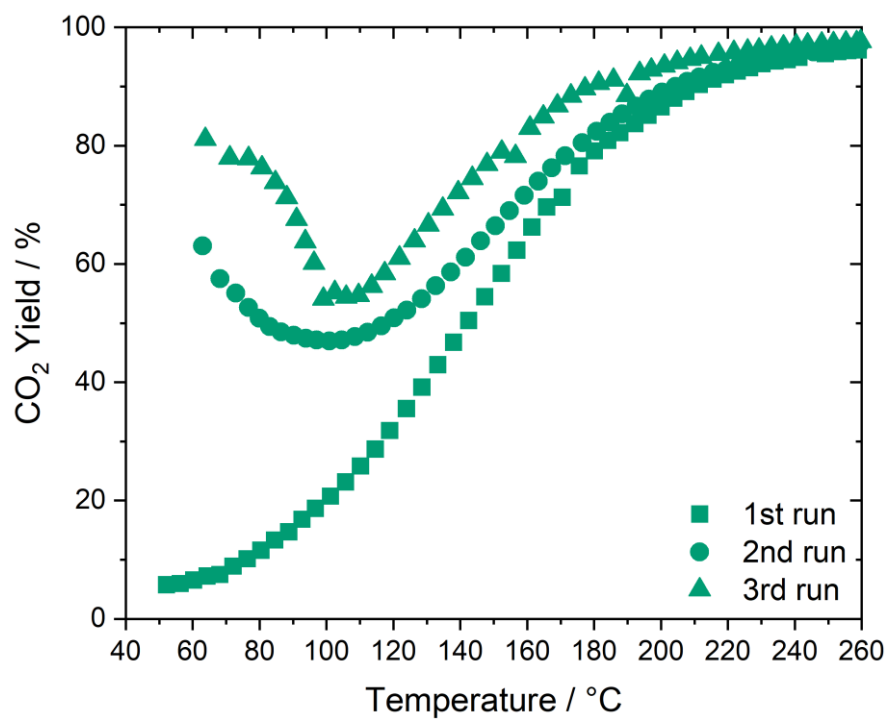


Figure S9: CO oxidation activity in the different runs for SBA-15 templated Co:Fe 7:1.

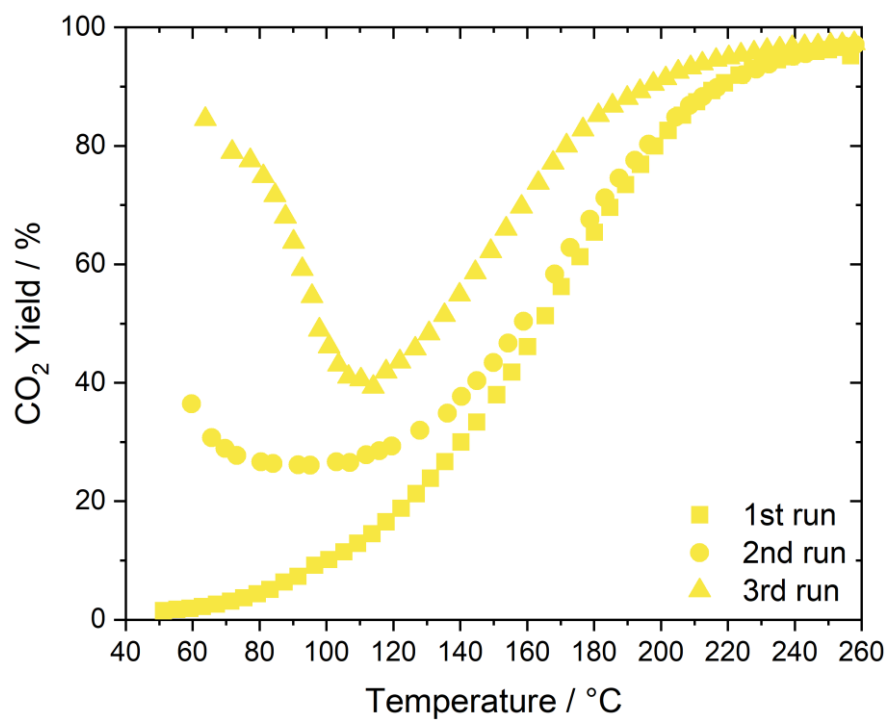


Figure S10: CO oxidation activity in the different runs for SBA-15 templated Co:Fe 3:1.

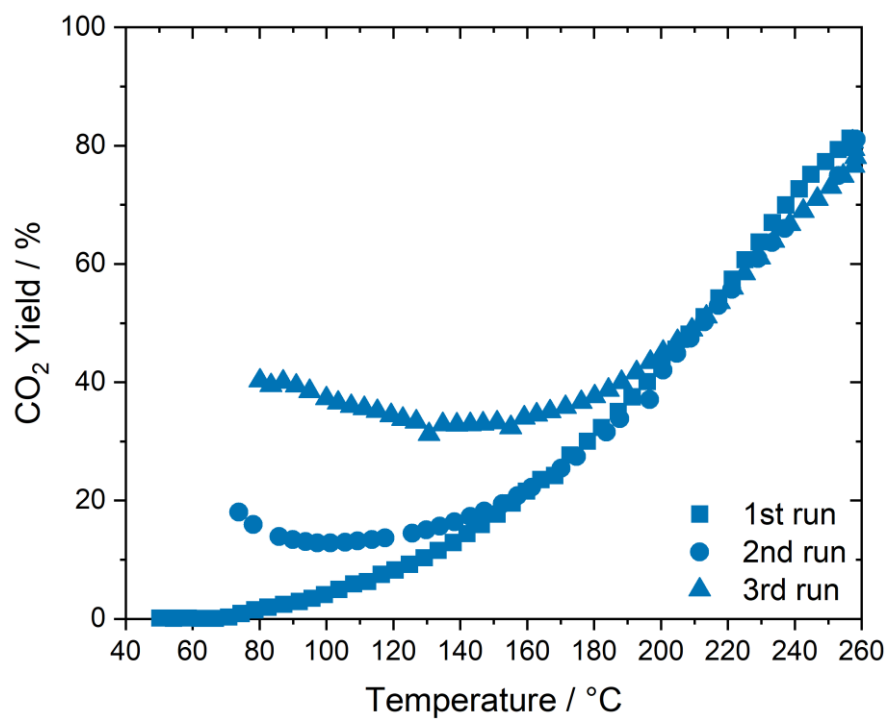


Figure S11: CO oxidation activity in the different runs for SBA-15 templated  $\text{CoFe}_2\text{O}_4$ .

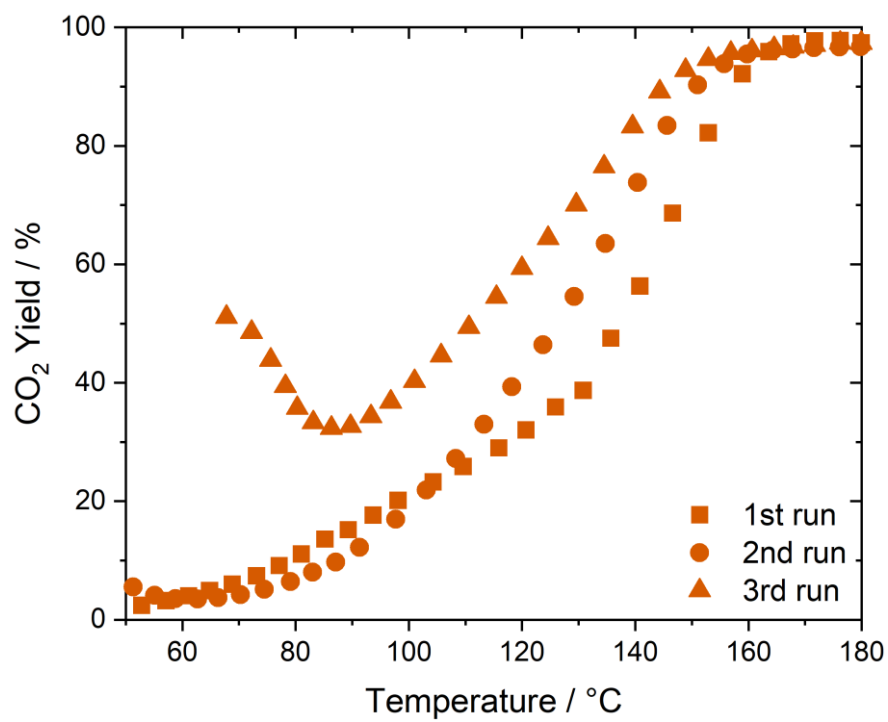


Figure S12: CO oxidation activity in the different runs for  $\text{Co}_3\text{O}_4$  C600.



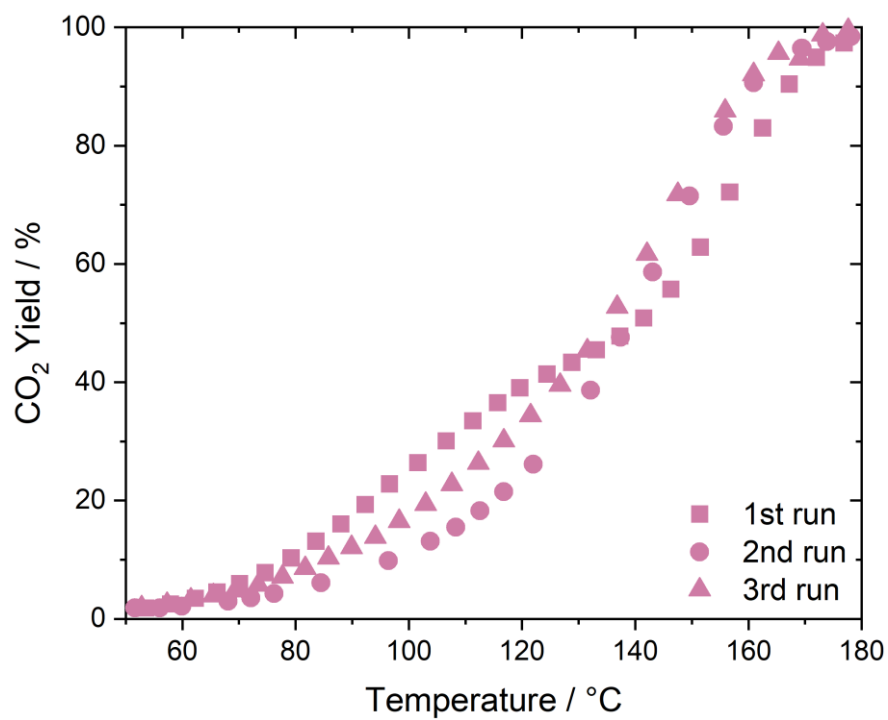


Figure S13: CO oxidation activity in the different runs for Co<sub>3</sub>O<sub>4</sub> P800.

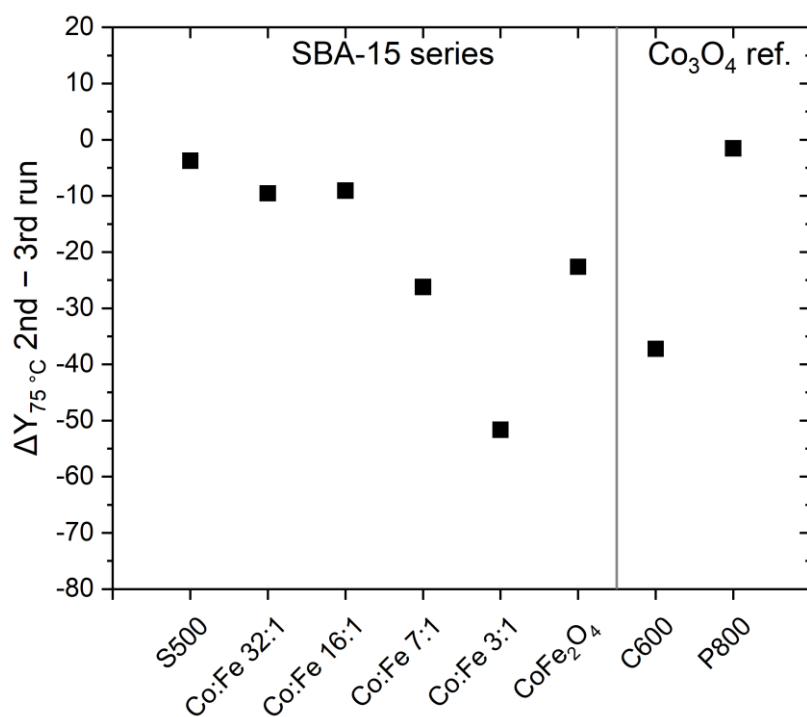


Figure S14: Differences in conversion at 75 °C between the 2nd and the 3rd run of CO oxidation.

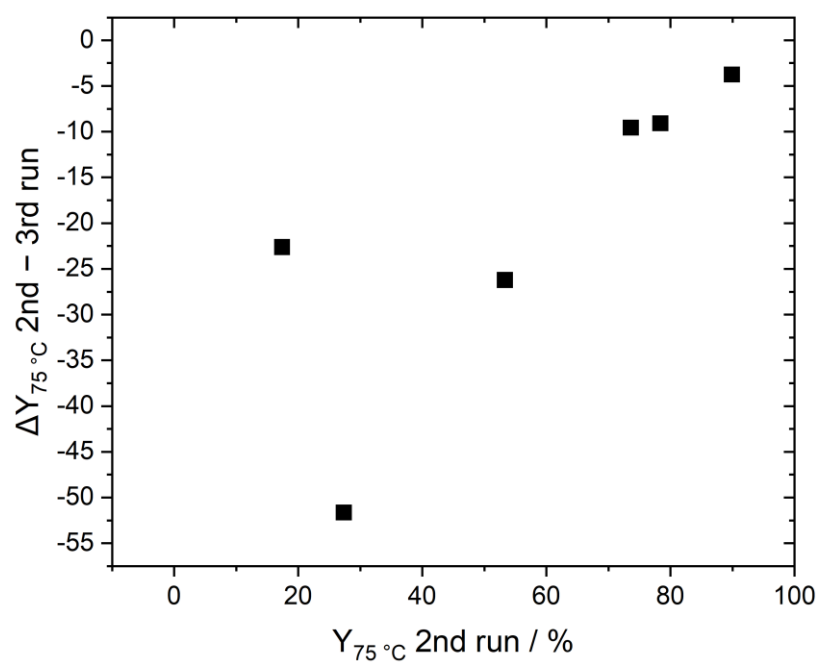


Figure S15: Conversion at 75 °C in the 2nd run compared to the activation between 2nd and 3rd run for the SBA-15 templated materials.

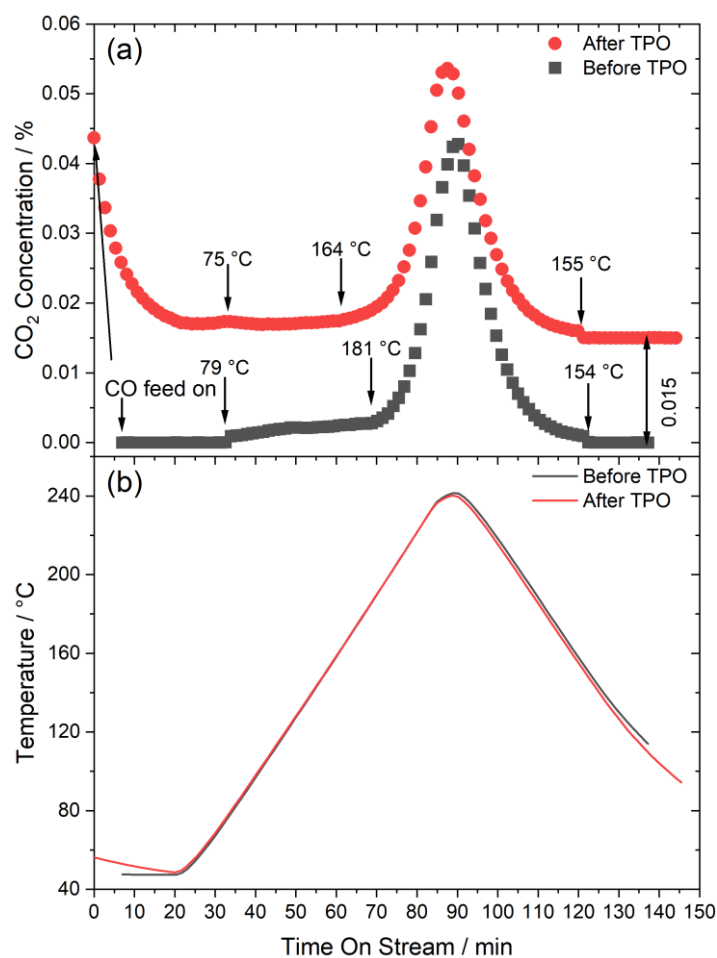


Figure S16: CO temperature programmed reduction of C600 without TPO and after TPO showing the evolved  $\text{CO}_2$  concentration (a) and the temperature in the reactor (b). The time on stream was calibrated based on the time when the maximum temperature was reached.

The CO-TPR experiments shown in Figure S16 were performed in a self-constructed apparatus consisting of a gas dosing unit (HovaGAS N G6 VOC-S, IAS GmbH, Germany) and a Tube Furnace MTF 10/25/130 (Carbolite Gero, Neuhausen, Germany) which is placed in a heating cabinet Thermocenter TC100 (SalvisLab, Rotkreuz, Switzerland). The reaction mixture, either going through or by-passing the reactor, was analyzed on a downstream dual-carrier gas Fusion Micro GC (Inficon GmbH, Bad Ragaz, Switzerland) equipped with four separation modules (2x Rt-Molsieve 5A, 1x Stabilwax DB, 1x Rt-Q-Bond). The catalyst mixture consisted of 60 mg (sieve fraction 250–355  $\mu\text{m}$ ) calcined catalyst C600 sample diluted with 300 mg of silicon carbide (>355  $\mu\text{m}$ ) and was placed in a quartz reactor (inner diameter = 8 mm) on a quartz wool support. The total gas flow in all segments of the catalytic experiment was 80 mL  $\text{min}^{-1}$ .

The protocol consisted of two different exposures to a reaction mixture of 2% CO balanced in  $\text{N}_2$ . Prior to the 1st TPR, the catalyst/SiC mixture was pre-treated by heating at 3  $^{\circ}\text{C min}^{-1}$  in  $\text{N}_2$  from room temperature to 100  $^{\circ}\text{C}$ , which was kept constant for 1 h. Thereafter, the sample was cooled down in  $\text{N}_2$  to 50  $^{\circ}\text{C}$ . The temperature was stabilized in a  $\text{N}_2$  flow and afterward the

reaction mixture was purged for 15 min to equilibrate the gas composition. Thereafter, the temperature was increased to 250 °C at a heating rate of 3 °C min<sup>-1</sup> for the 1st run. Then, the sample was cooled in the reaction mixture to 50 °C with at a heating rate of 3 °C min<sup>-1</sup> the temperature was equilibrated in N<sub>2</sub>.

For the preparation of the 2nd run, the sample was cooled down at a heating rate of 3 °C min<sup>-1</sup> in the reactive atmosphere to 100 °C, purged with N<sub>2</sub> for 5 min and then temperature-programmed oxidation was performed in 20% O<sub>2</sub> in N<sub>2</sub> to a maximum temperature of 500 °C with a heating rate of 10 °C min<sup>-1</sup>. The temperature of 500 °C was chosen to mimic the calcination protocol of the SBA-15 templated materials. The maximum temperature was kept constant for 30 min after which the sample was cooled down with a heating rate of 10 °C min<sup>-1</sup> to 50 °C in 20% O<sub>2</sub> balanced with N<sub>2</sub> and temperature was equilibrated in N<sub>2</sub>. Afterward, the sample was purged with the reaction mixture for 15 min at 50 °C. The 3rd run was performed by increasing the temperature to 250 °C at a heating rate of 3 °C min<sup>-1</sup> and a 5 min dwell at the maximum temperature. Afterward, the sample was again cooled down at a heating rate of 3 °C min<sup>-1</sup> in the reactive atmosphere to 50 °C.

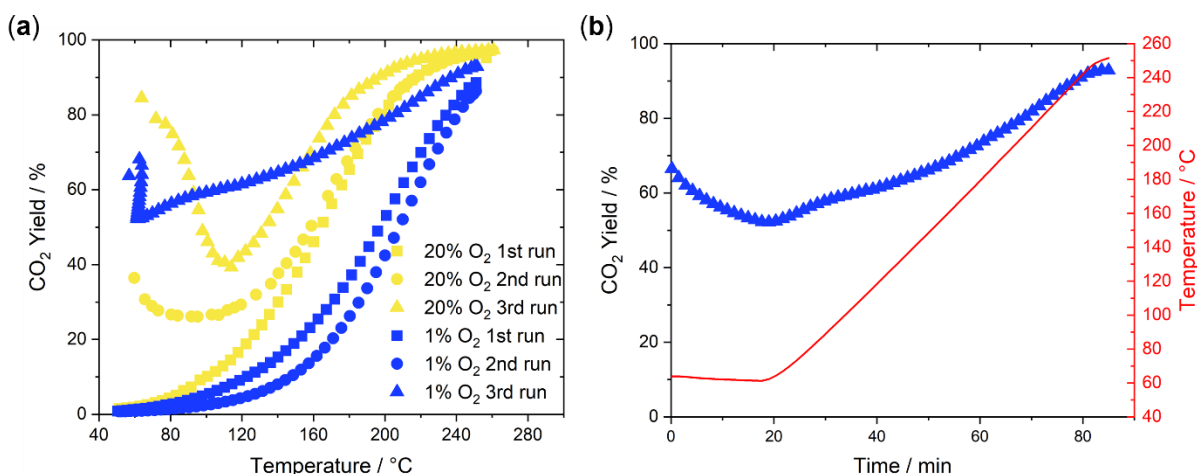


Figure S17: (a) Initial measurement of 3:1 in the cyclic CO oxidation in 2% CO and 20% O<sub>2</sub> in comparison to a new measurement in 2% CO and 1% O<sub>2</sub> performed on another setup. (b) Representation of Run 3 in 1% O<sub>2</sub> versus time.

The data shown in Figure S17 for 1% O<sub>2</sub> are derived from another instrument compared to transient oxidation curves in Figures 2-6 and S6 to S13 and 20% O<sub>2</sub> in the same Figure as the originally used instrument was not available. Due to its unfavorable gas switching properties, the U-shaped curve is clearly seen only if the conversion is plotted versus time as the conversion changes already during the isothermal period at the beginning of the experiment. The measurements were performed in a home-built apparatus consisting of a gas dosing unit (HovaGAS N G6 VOC-S, IAS GmbH, Germany) and a Tube Furnace MTF 10/25/130 (Carbolite Gero, Neuhausen, Germany) which is placed in a heating cabinet Thermocenter TC100 (SalvisLab, Rotkreuz, Switzerland). The reaction mixture, either going through or bypassing the reactor, was analyzed on a downstream dual-carrier gas Fusion Micro GC (Inficon GmbH, Bad Ragaz, Switzerland) equipped with four separation modules (2x Rt-Molsieve 5A, 1x Stabilwax DB, 1x Rt-Q-Bond). The catalyst mixture consisted of 60 mg (sieve fraction 250–355  $\mu\text{m}$ ) calcined catalyst C600 sample diluted with 300 mg of silicon carbide (>355  $\mu\text{m}$ ) and was placed in a quartz reactor (inner diameter = 8 mm) on a quartz wool support. The total gas flow in all segments of the catalytic experiment was 80 mLn min<sup>-1</sup>.

The protocol consisted of three different exposures to a reaction mixture of (2% CO and 1% O<sub>2</sub> balanced in N<sub>2</sub>). Prior to the 1st run, the catalyst/SiC mixture was pre-treated by heating at 3 °C min<sup>-1</sup> in N<sub>2</sub> from room temperature to 100 °C, which was kept constant for 1 h. Thereafter, the sample was cooled down in N<sub>2</sub> to 50 °C. The temperature was stabilized in a N<sub>2</sub> flow and afterward the reaction mixture was purged for 15 min to equilibrate the gas composition. Thereafter, the temperature was increased to 250 °C at a heating rate of 3 °C min<sup>-1</sup> for the 1st run. Then, the sample was cooled in the reaction mixture to 50 °C with at a heating rate of 3 °C min<sup>-1</sup> the temperature was equilibrated in N<sub>2</sub>.

Afterward, the sample was purged with the reaction mixture for 15 min at 45 °C and a 2nd consecutive run was performed by increasing the temperature to 250 °C at a heating rate of 3 °C min<sup>-1</sup> and 5 min dwell time at the maximum temperature.

For the preparation of the 3rd run, the sample was again cooled down at a heating rate of 3 °C min<sup>-1</sup> in the reactive atmosphere to 100 °C, purged with N<sub>2</sub> for 5 min and then temperature-programmed oxidation was performed in 20% O<sub>2</sub> in N<sub>2</sub> to a maximum temperature of 500 °C with a heating rate of 10 °C min<sup>-1</sup>. The temperature of 500 °C was chosen to mimic the calcination protocol of the SBA-15 templated materials. The maximum temperature was kept constant for 30 min after which the sample was cooled down with a heating rate of 10 °C min<sup>-1</sup> to 50 °C in 20% O<sub>2</sub> balanced with N<sub>2</sub> and temperature was equilibrated in N<sub>2</sub>. Afterward, the sample was purged with the reaction mixture for 15 min at 50 °C. The 3rd run was performed by increasing the temperature to 250 °C at a heating rate of 3 °C min<sup>-1</sup> and a 5 min dwell at the maximum temperature. Afterward, the sample was again cooled down at a heating rate of 3 °C min<sup>-1</sup> in the reactive atmosphere to 50 °C.

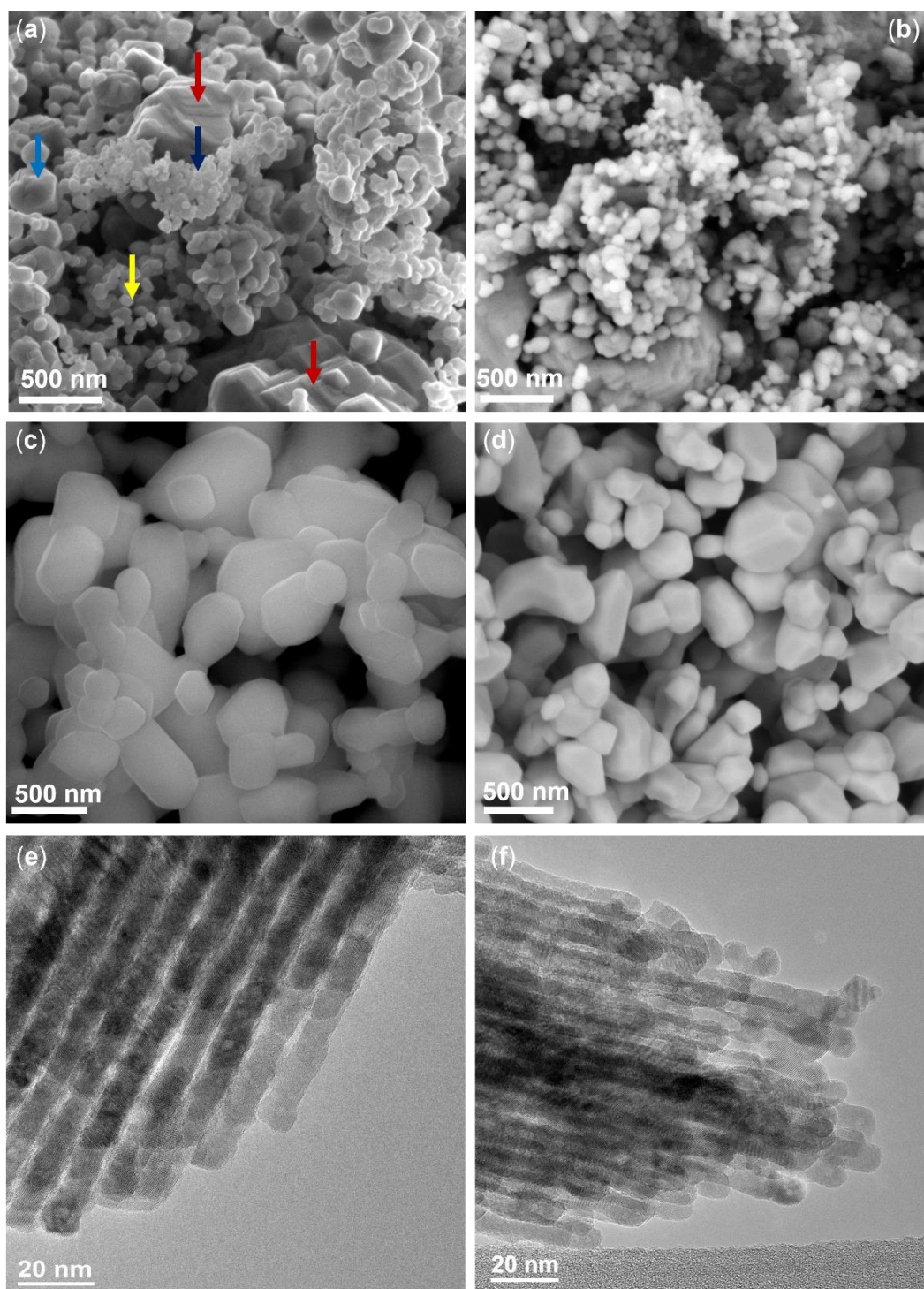


Figure S18: (a) SEM image of C600 before catalysis. (b) SEM image of C600 after catalysis. (c) SEM image of C800 before catalysis. (d) TEM image of C800 after catalysis. (e) SEM image of S500 before catalysis. (f) TEM image of S500 after catalysis. Figures (a), (c) and (e) are shown in the main text as Figures 1b, 1c and 1d.

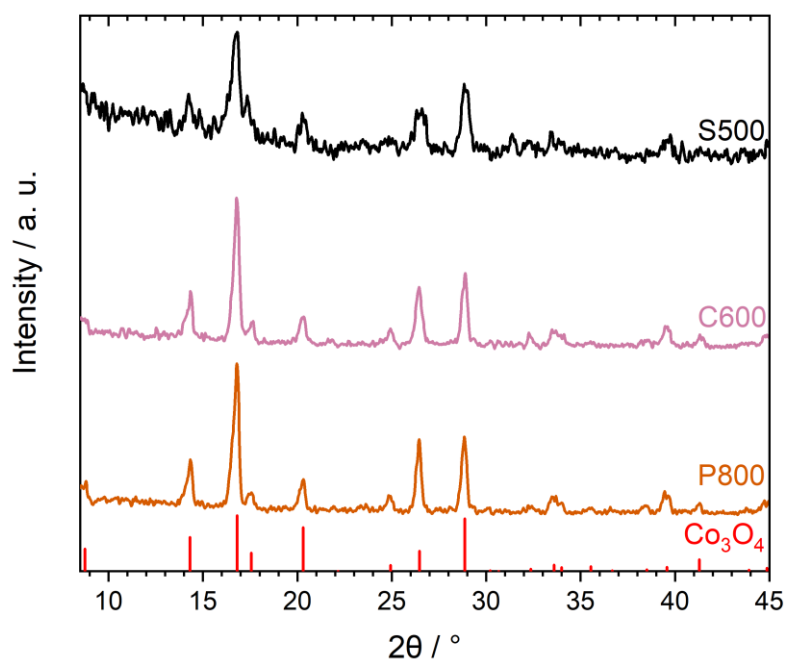


Figure S19: XRD patterns of the spent catalysts.

XRD patterns of the spent catalysts shown in Figure S19 were recorded on a STOE transmission diffractometer STADI P in Debye-Scherrer geometry at room temperature using a curved image-plate position sensitive detector ( $R = 150$  mm, Ge crystal monochromator filtered  $\text{MoK}\alpha_1$  radiation). A  $2\theta$  range of  $2 \times 70^\circ$  (only positive values were shown in the range between  $8.5$  and  $45^\circ$ ) and a step width of  $0.0015^\circ$  were applied with an overall counting time of  $1800$  s.