

The effect of Co incorporation on the CO oxidation activity of LaFe_{1-x}Co_xO₃ perovskites

Supplementary Materials

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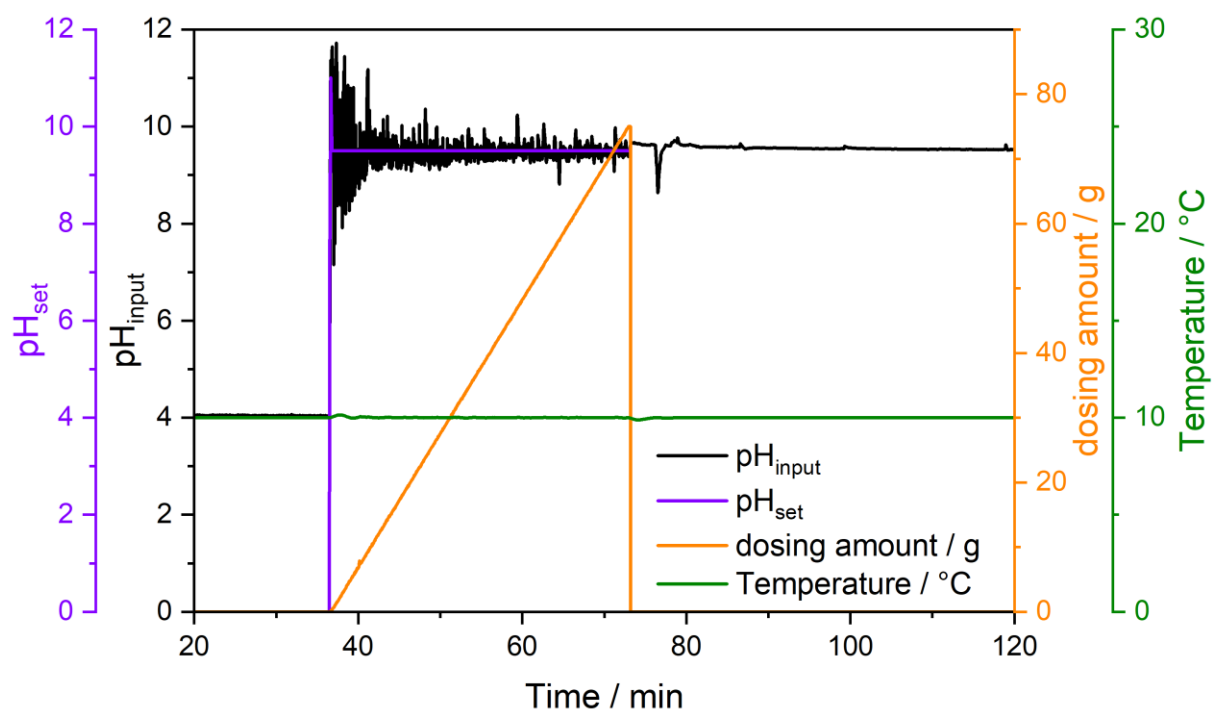


Figure S1: Synthesis protocol of sample $x = 0.00$.

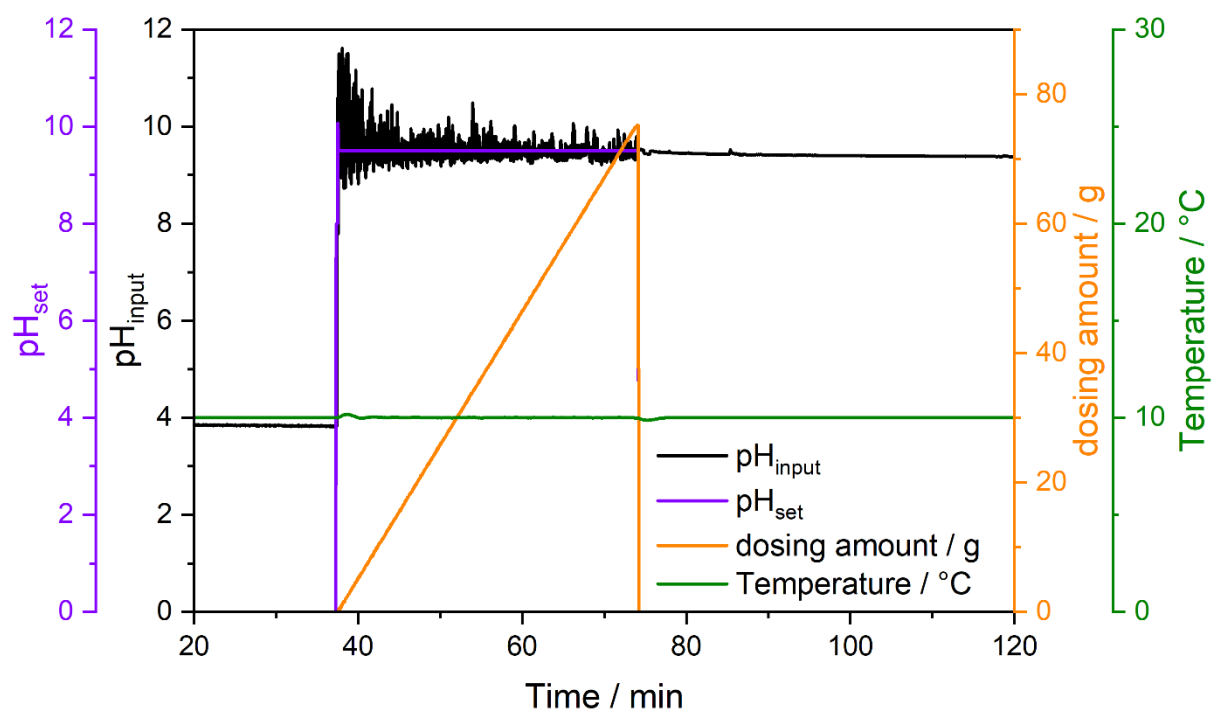


Figure S2: Synthesis protocol of sample $x = 0.05$.

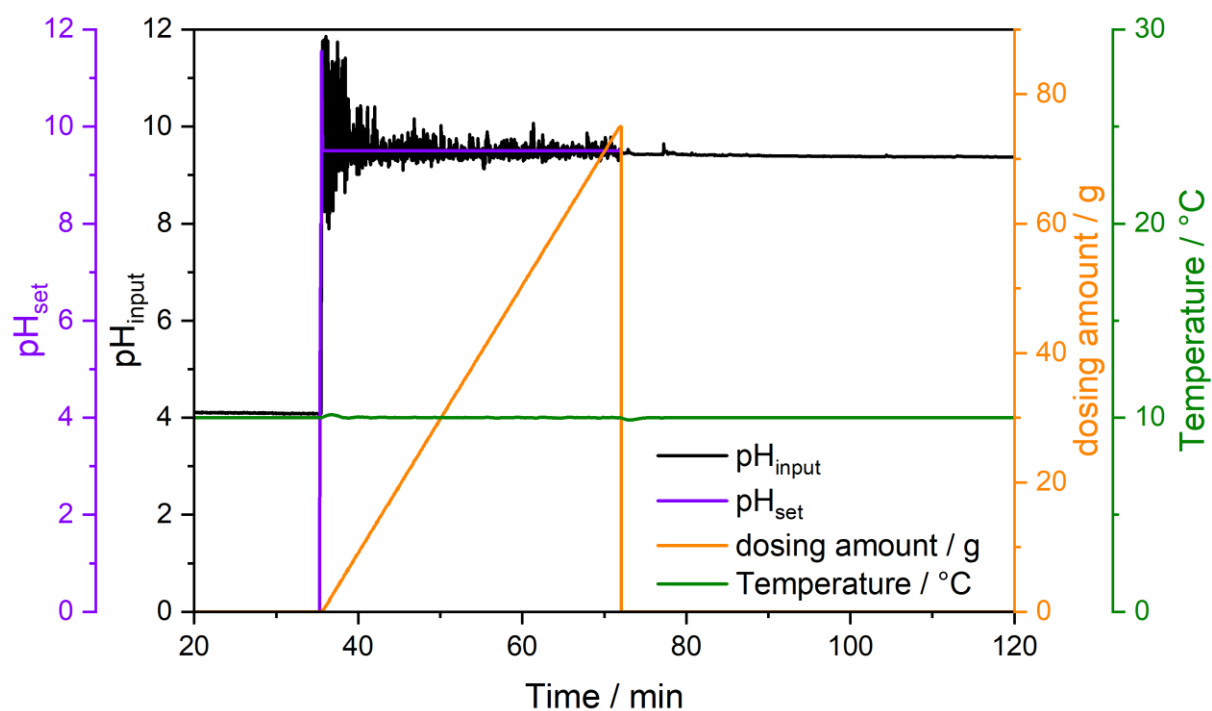


Figure S3. Synthesis protocol of sample $x = 0.10$.

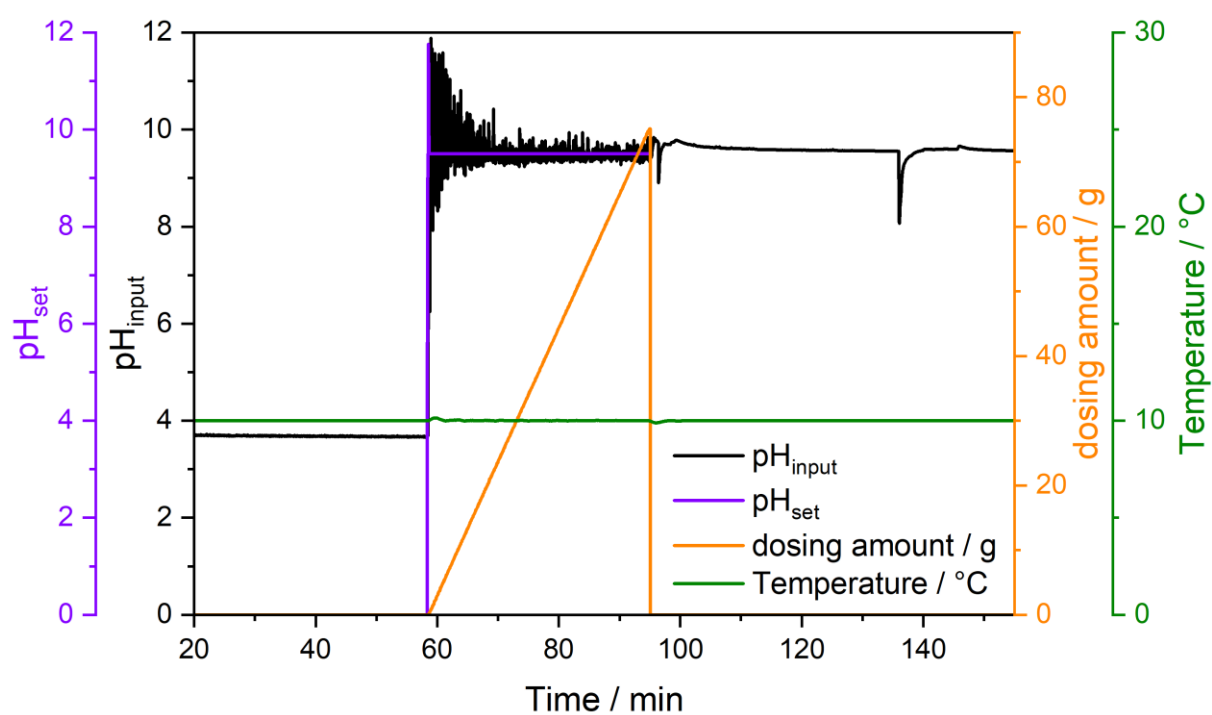


Figure S4. Synthesis protocol of sample $x = 0.15$.

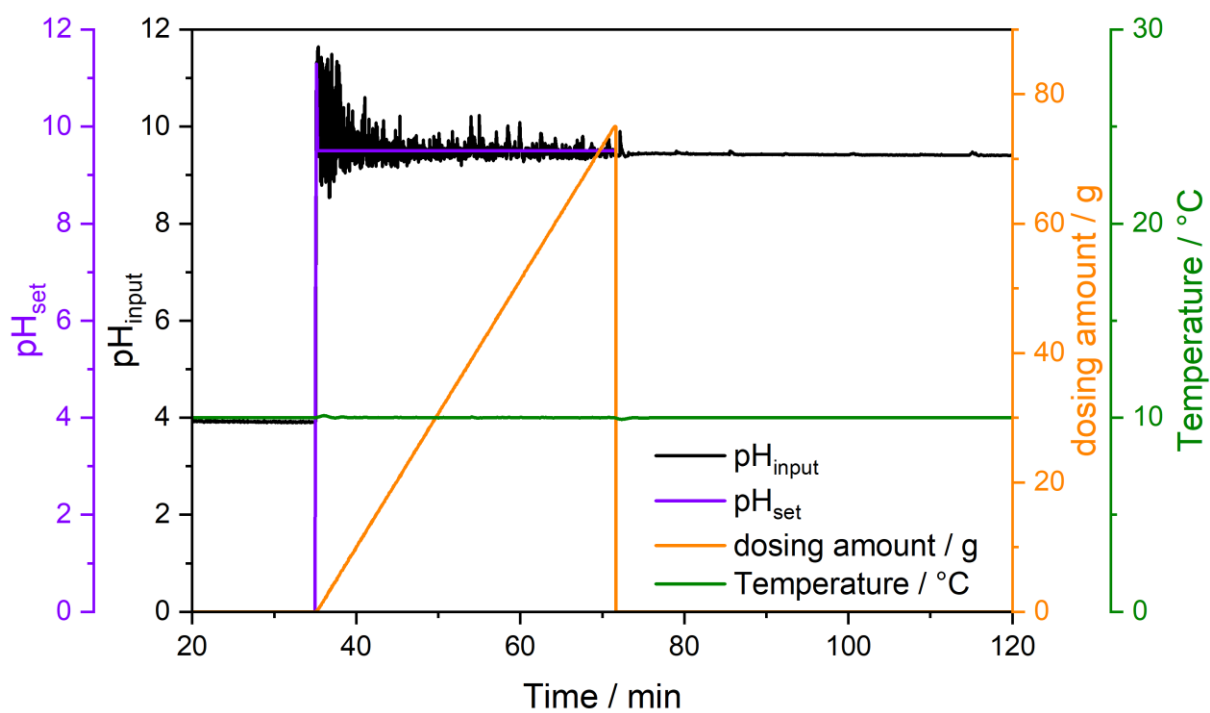


Figure S5. Synthesis protocol of sample $x = 0.20$.

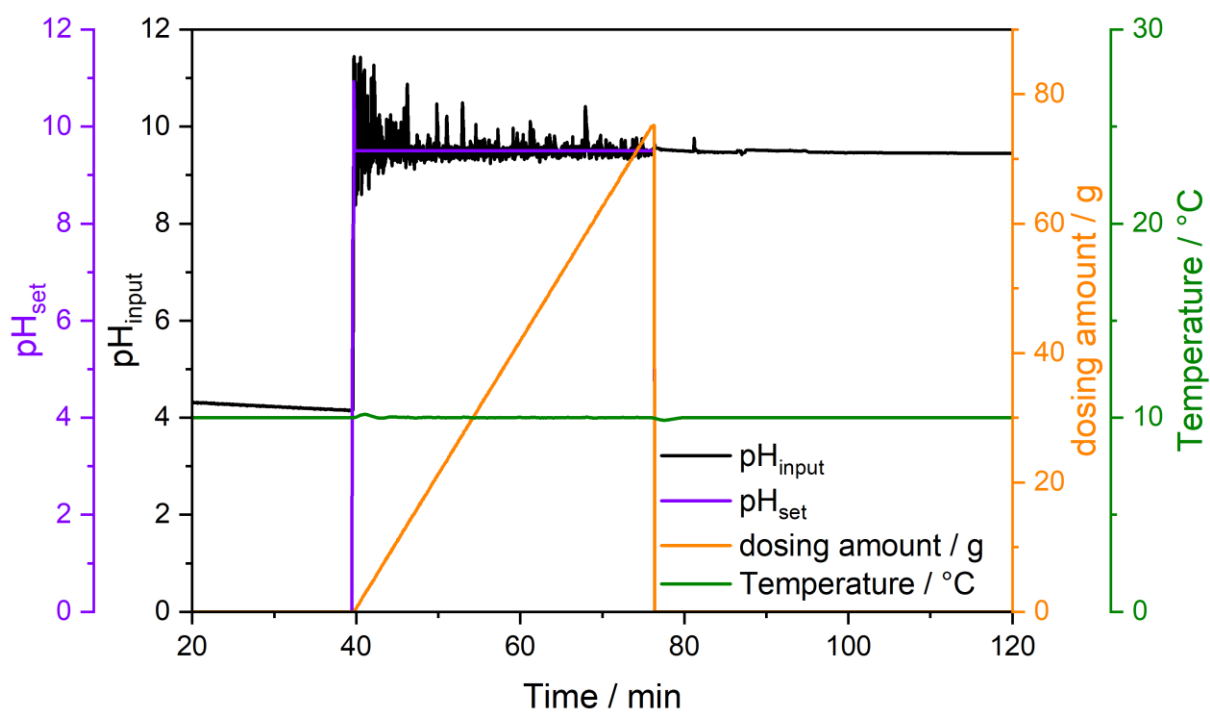


Figure S6. Synthesis protocol of sample $x = 0.25$.

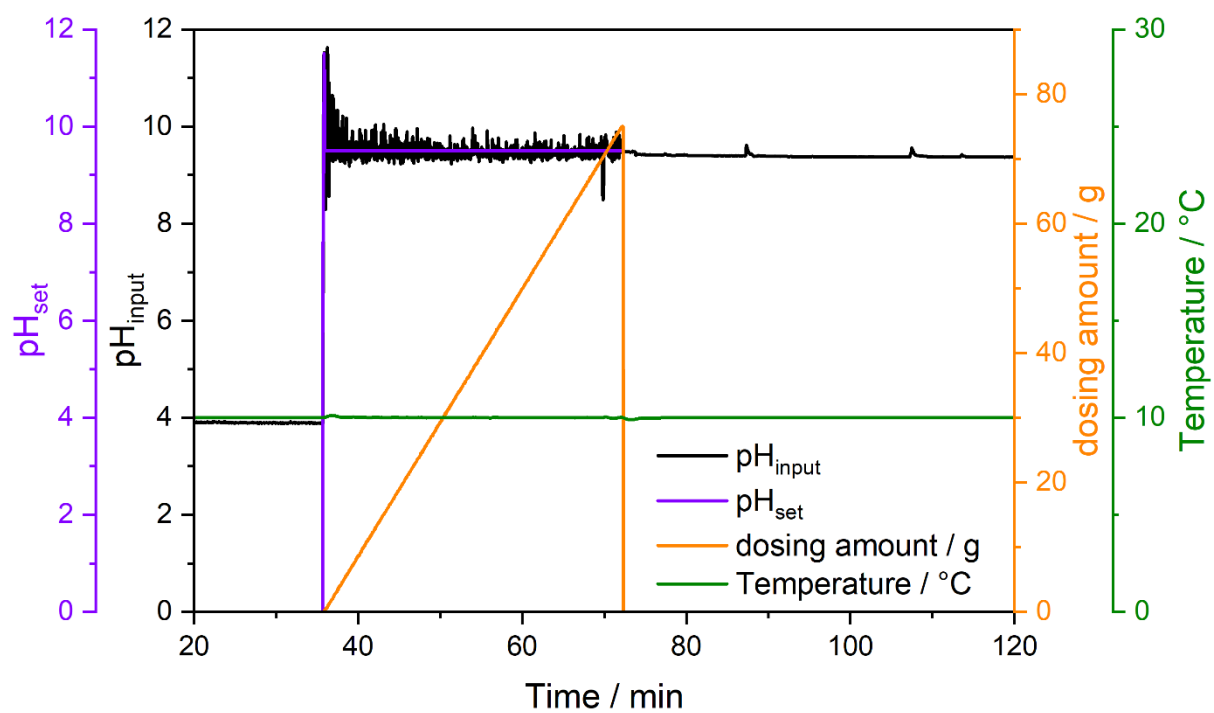


Figure S7. Synthesis protocol of sample $x = 0.30$.

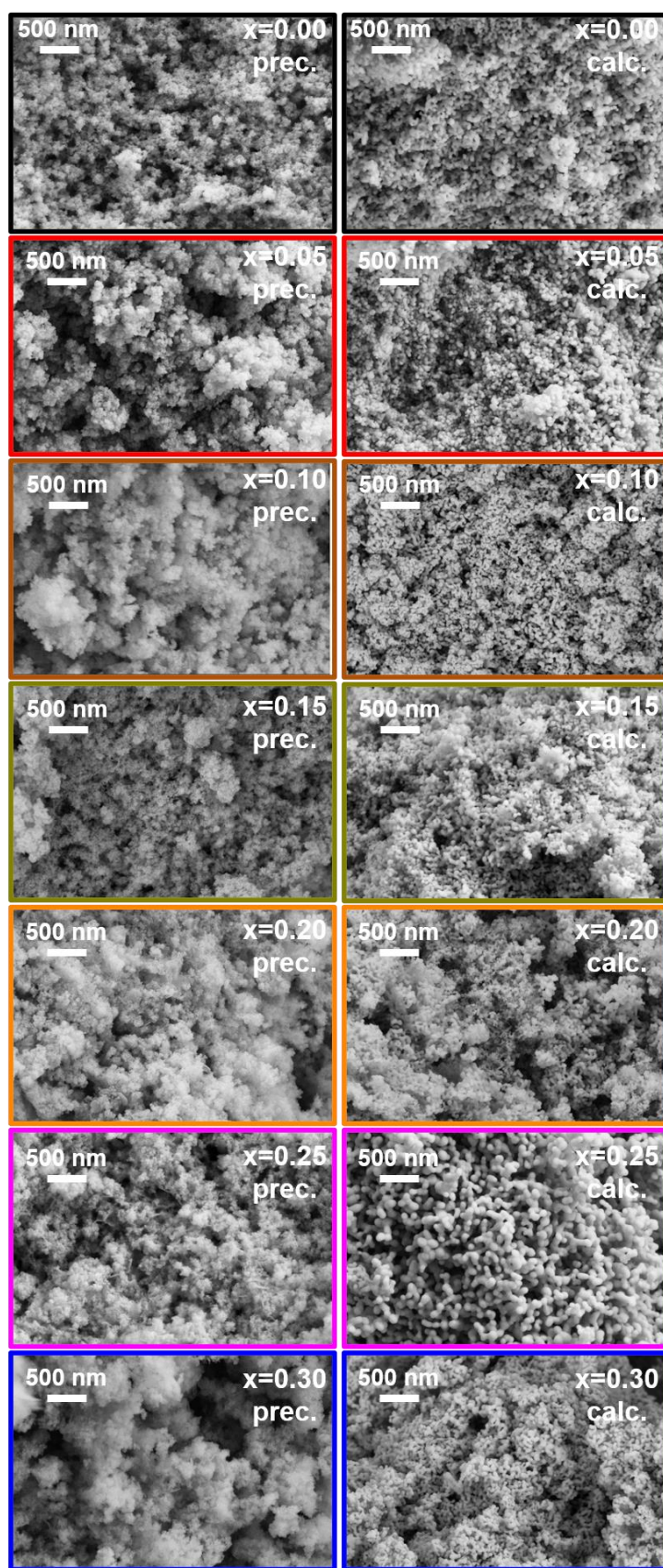


Figure S8. SEM images of the precursors (left column) and the calcined materials (right column).

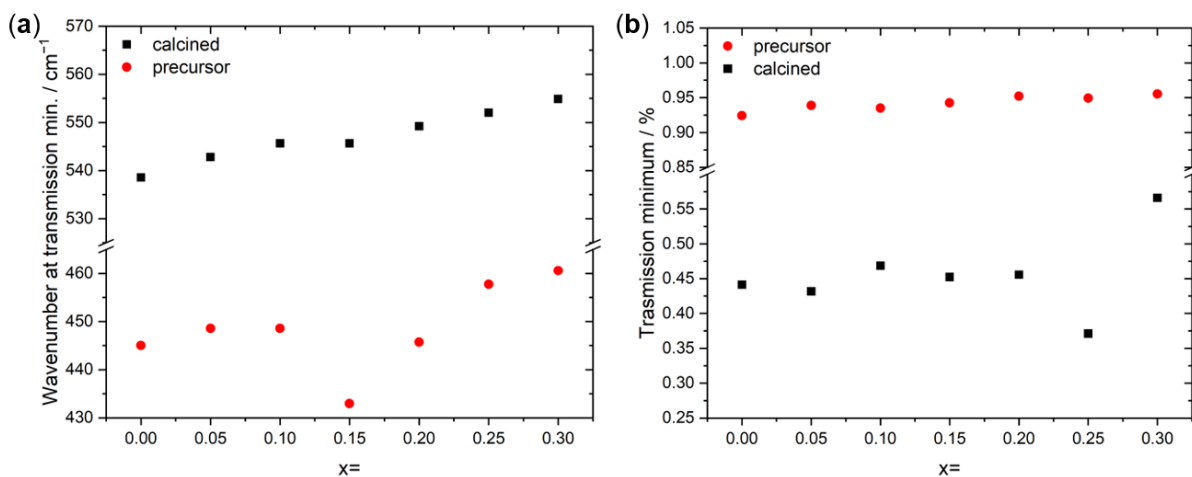


Figure S9. (a) Positions of the transmission minimum in the M-O and M-OH region ($< 580 \text{ cm}^{-1}$) in the IR spectra. (b) Transmission minimum in IR spectra in the M-O and M-OH region ($< 580 \text{ cm}^{-1}$) corresponding to the minimum positions shown in (a).

Table 1. Criteria of fit for the Rietveld Refinements of the X-ray diffraction patterns of the calcined samples.

Sample	R_{exp}	R_{wp}	R_{exp}'	R_{wp}'	R_p'	GOF	R_{Bragg}
$x=0.00$	7.88	10.10	4.68	6.00	4.73	1.28	2.572
$x=0.05$	9.20	11.29	4.79	5.87	4.68	1.23	2.933
$x=0.10$	7.79	11.49	4.54	6.69	5.24	1.47	3.904
$x=0.15$	10.02	12.52	5.70	7.12	5.41	1.25	3.582
$x=0.20$	8.24	12.48	4.71	7.14	5.38	1.52	4.586
$x=0.25$	7.84	13.08	4.41	7.36	5.81	1.67	5.205
$x=0.30$	7.59	13.50	4.47	7.95	5.98	1.78	5.230

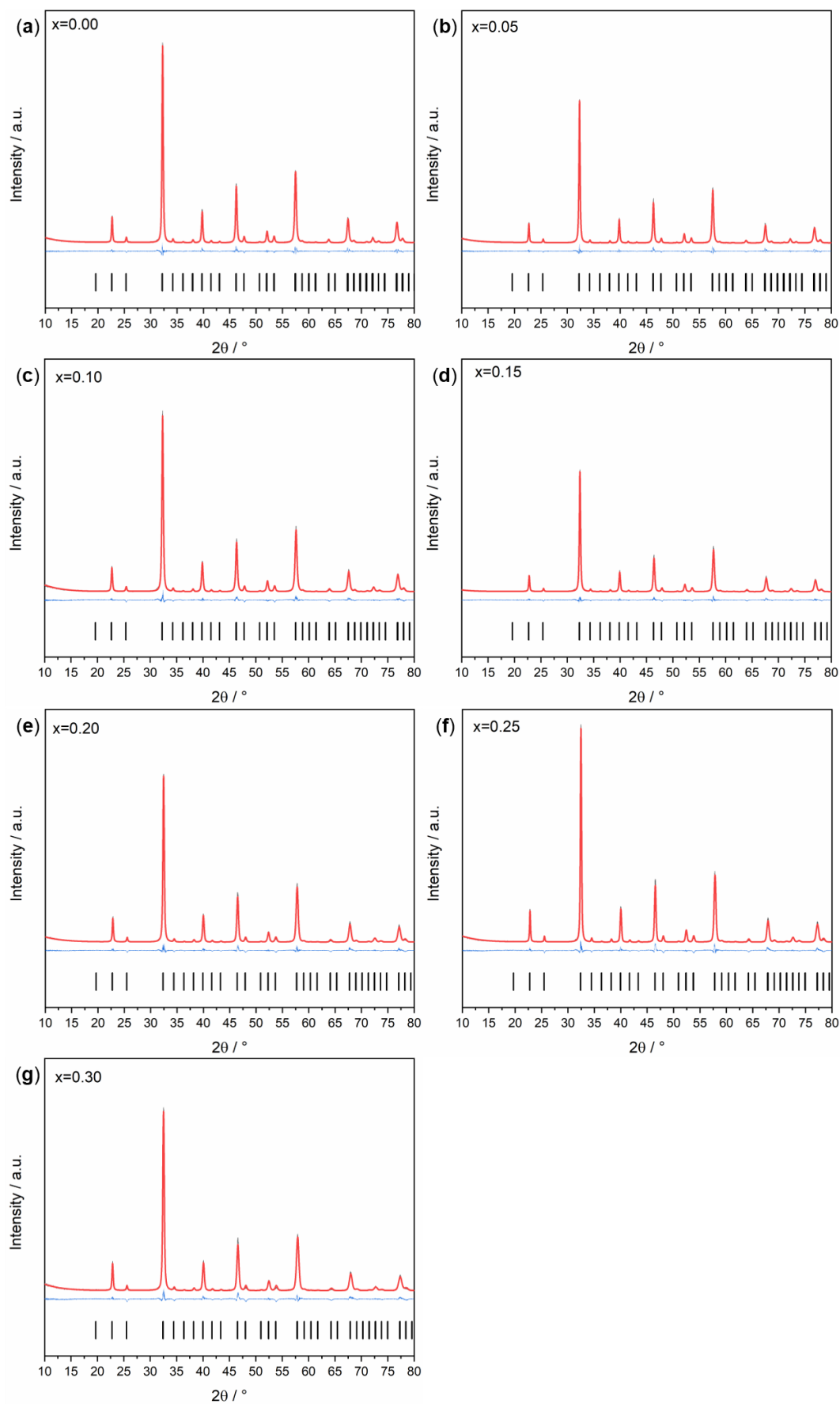


Figure S10. (a) Rietveld plots of $x=0.00$. (b) Rietveld plots of $x=0.05$. (c) Rietveld plots of $x=0.10$. (d) Rietveld plots of $x=0.15$. (e) Rietveld plots of $x=0.20$. (f) Rietveld plots of $x=0.25$. (g) Rietveld plots of $x=0.30$. Grey: experimental pattern; red: calculated pattern; blue: difference plot; black: Bragg peak position

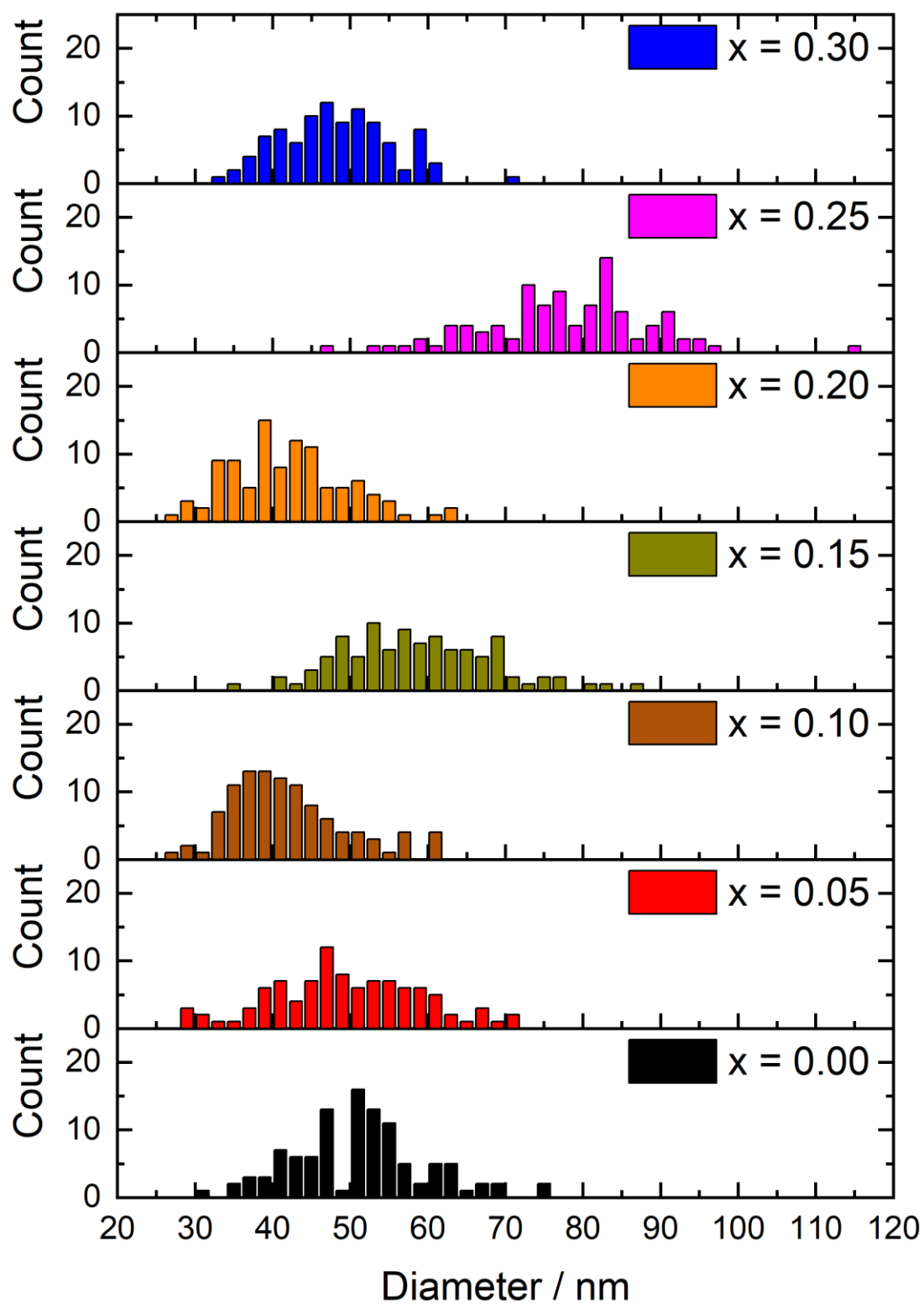


Figure S11. SEM particle size counts of all samples after calcination from 100 particles per sample.

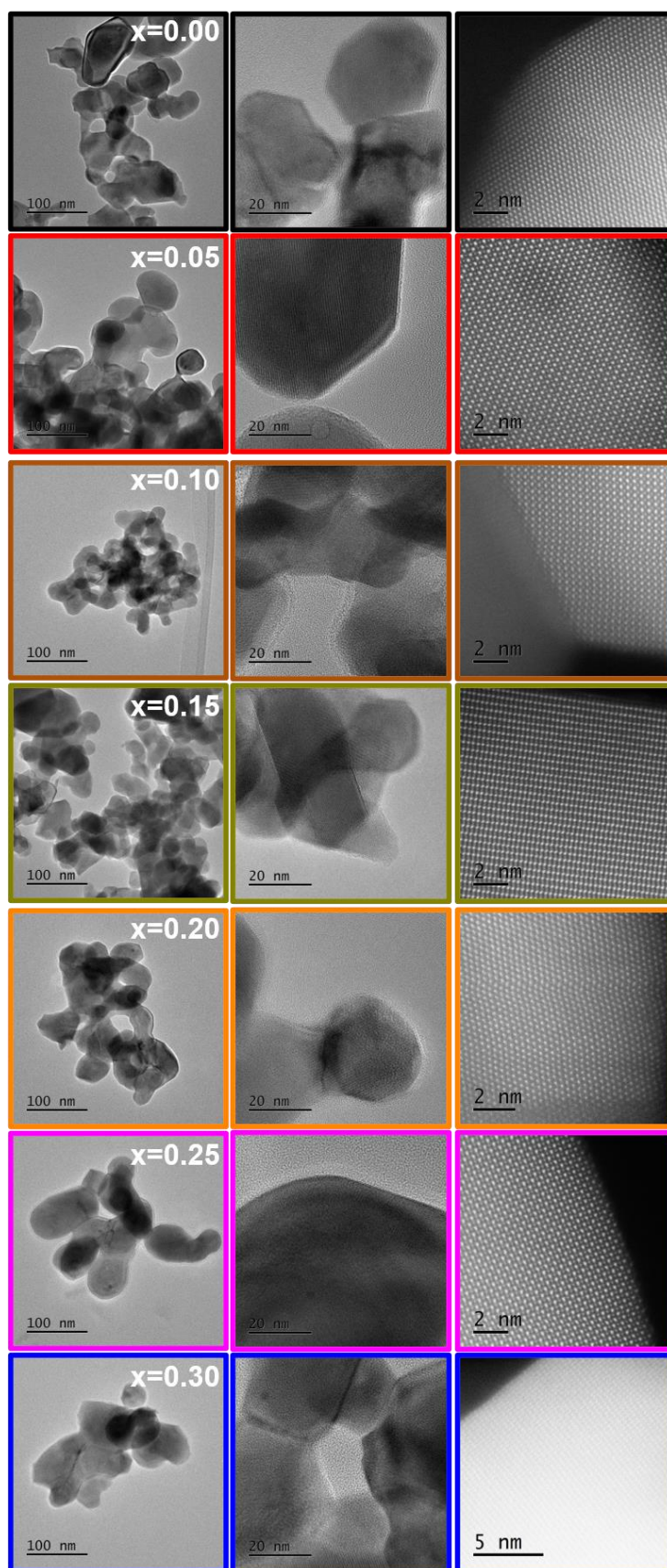


Figure S12. TEM images in the magnifications 60 k (left column), 300 k (middle column), and 10 M (right column).

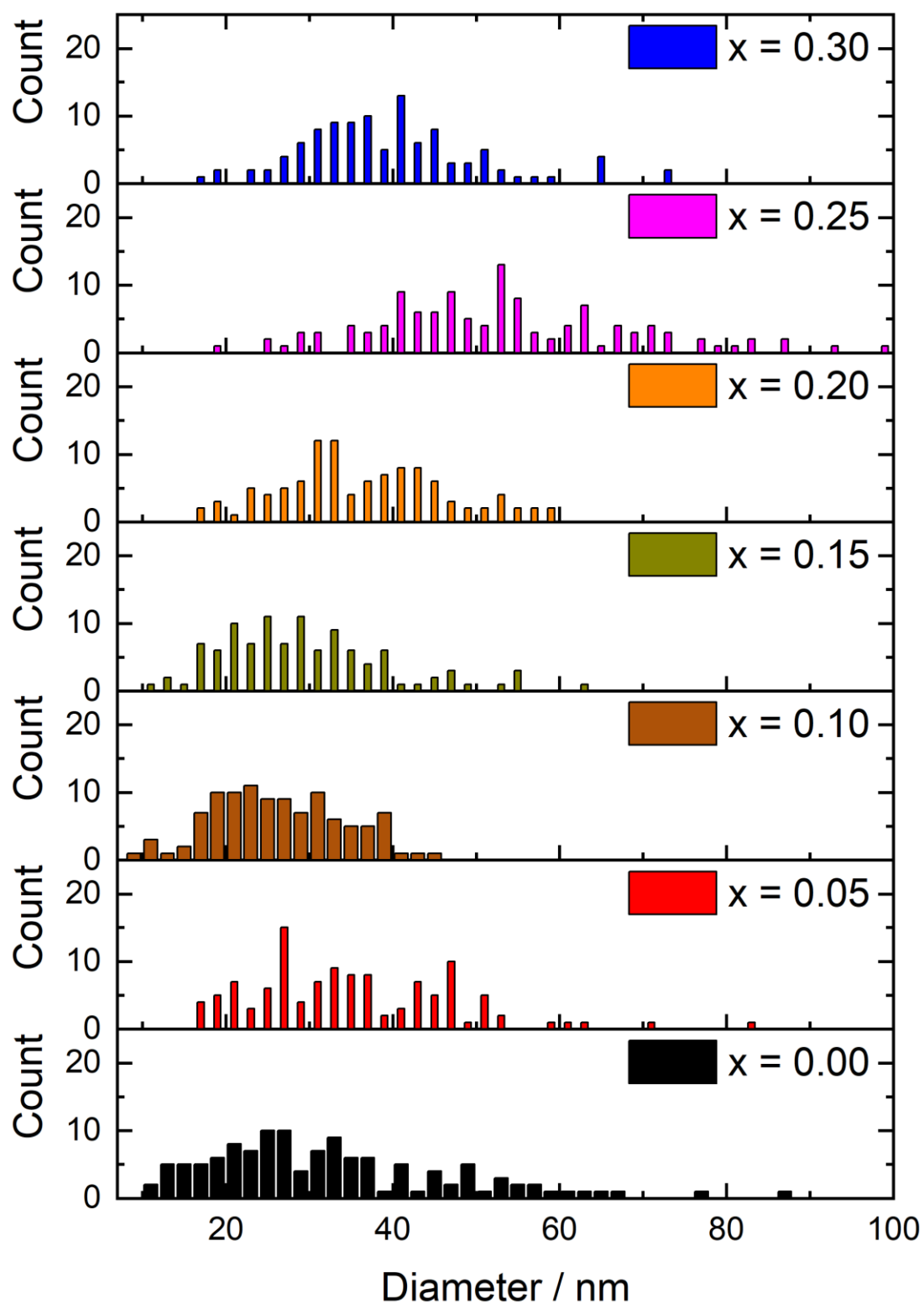


Figure S13. TEM particle size counts of all samples after calcination from 100 particles per sample.

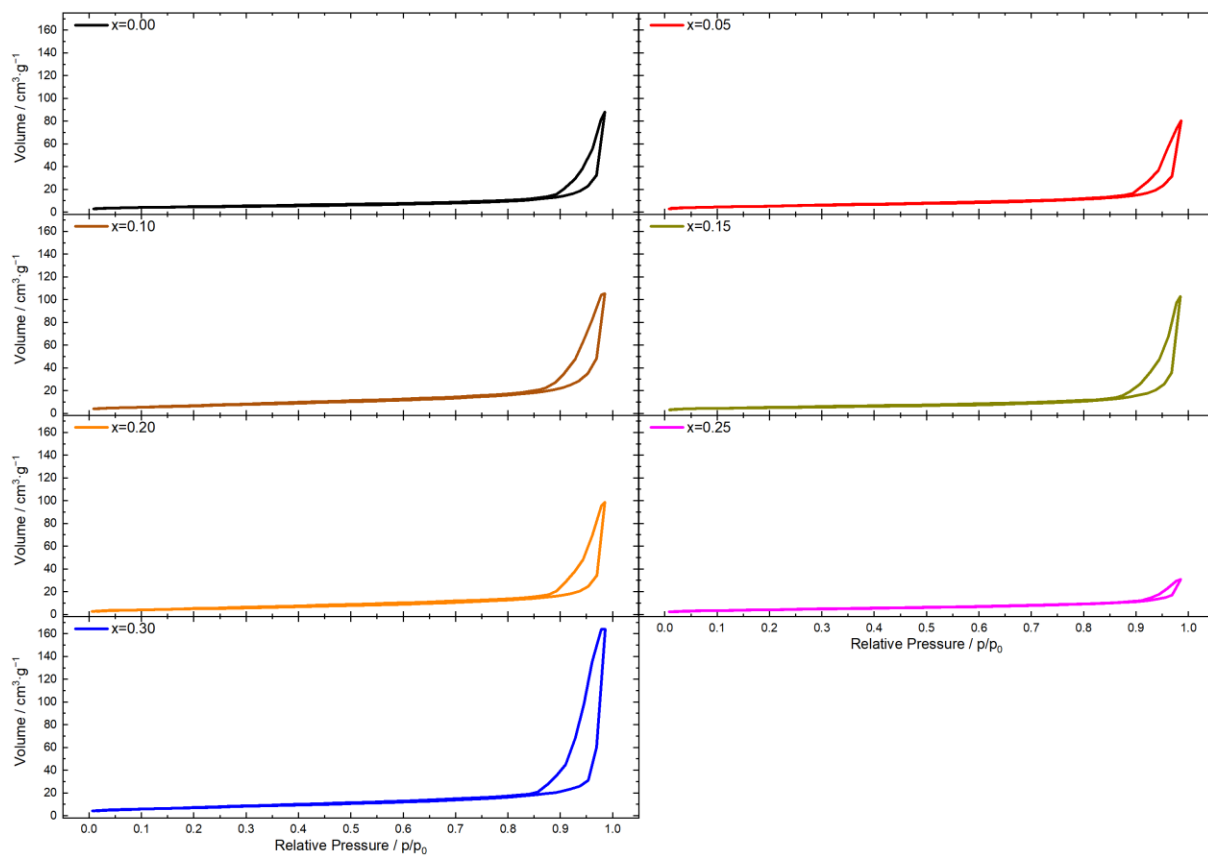


Figure S14. BET isotherms of all samples.

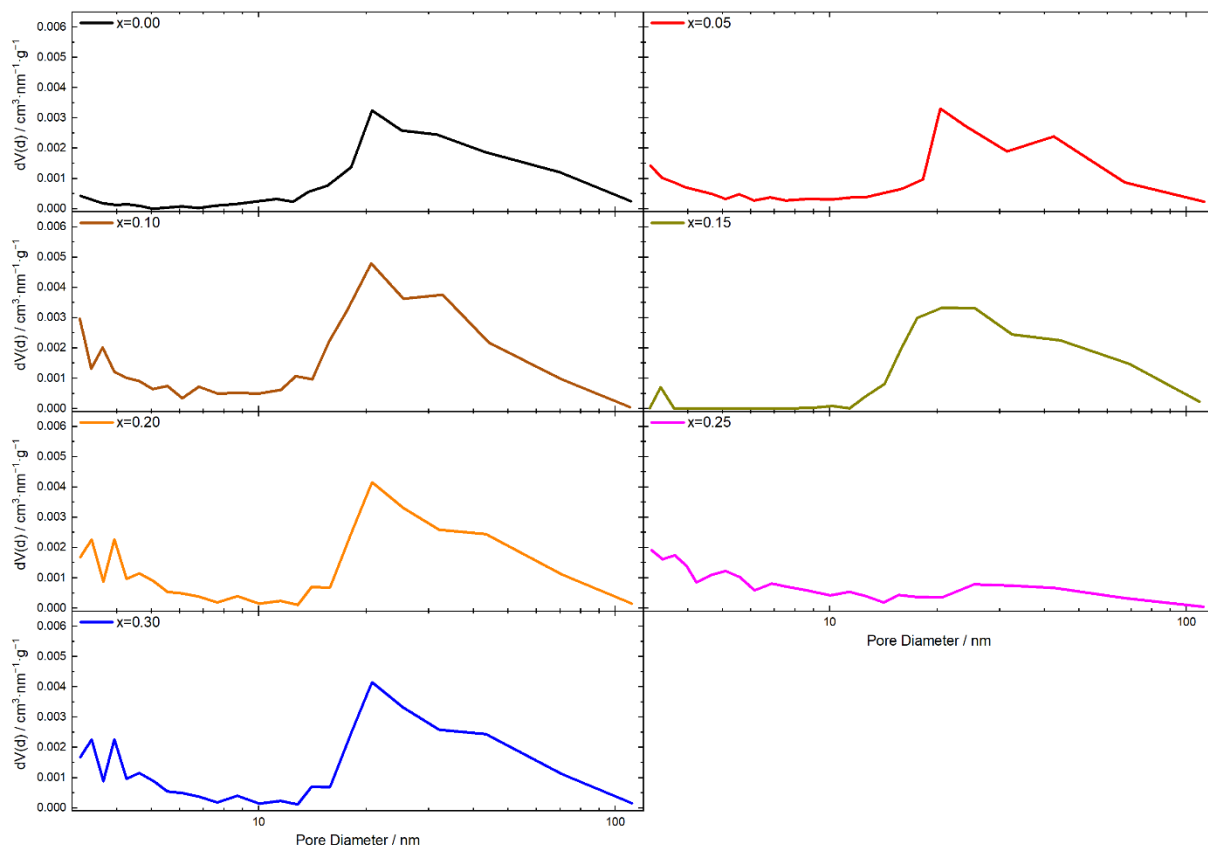


Figure S15. Pore size distribution of all samples.

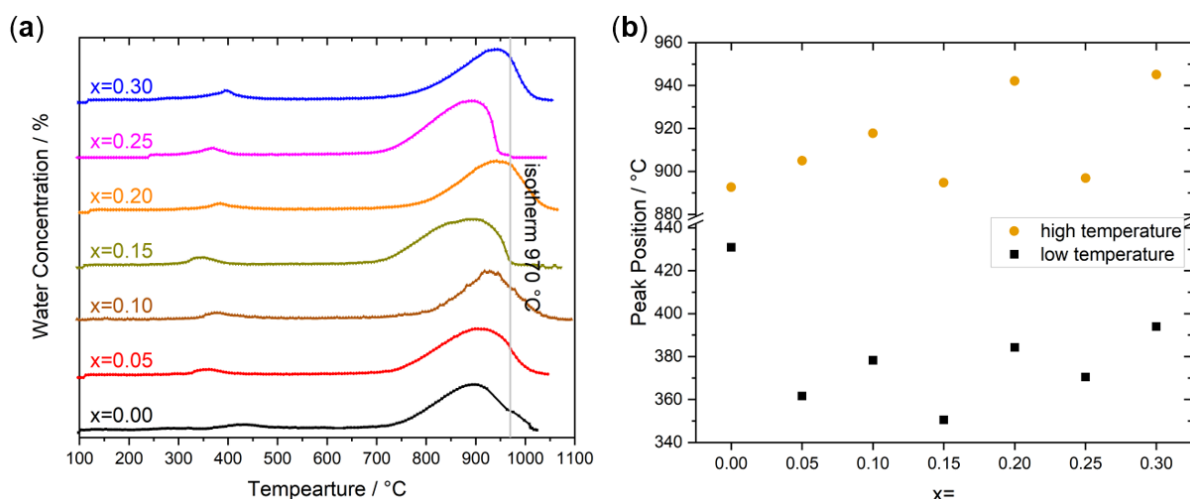


Figure S16. (a) H₂-TPR profiles of the sample series. (b) Positions of the maxima below 500 °C (labelled low temperature) and above 500 °C (labelled high temperature) derived from the TPR curves in (a).

In Figure S16a, temperature-programmed reduction in hydrogen curves (H₂-TPR) are shown.

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 was placed in a quartz reactor (inner diameter = 8 mm).

For H₂-TPR, 20 mg (sieve fraction 250–355 μm) of each calcined catalyst was placed inside a U-shaped quartz tube reactor. Each sample was pre-treated by heating at 3 °C min⁻¹ in N₂ from room temperature to 100 °C, kept constant for 1 hr. After that, the sample was cooled down in N₂ to 50 °C. Afterwards, a mixture of 7 % H₂ in Ar with a flow rate of 80 mL min⁻¹ was used for H₂-TPR with a linear heating rate of 6 K min⁻¹ up to 1000 °C. The latter was held for 15 min. The reduction profile were obtained from the H₂O concentrations derived from GC measurements.

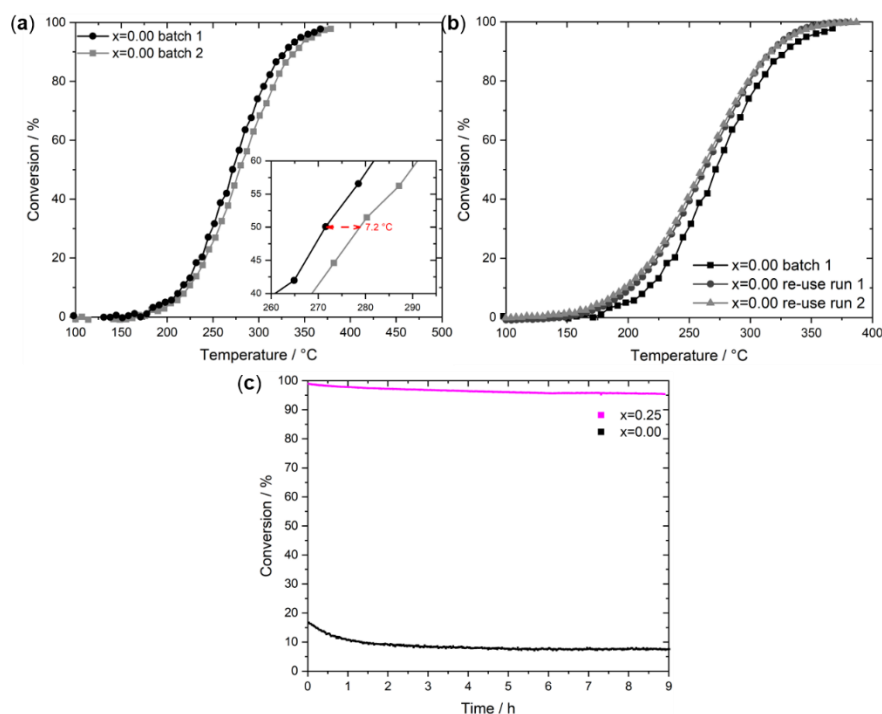


Figure S17. (a) Transient CO oxidation conversion curves of $x=0.00$ derived from two different synthesis batches in the reaction mixture of 2% CO+20% O₂ balanced in He. (b) Transient CO oxidation conversion curves of sample $x=0.00$ batch 1 in the reaction mixture of 2% CO+20% O₂ balanced in He and reusability test and reproducibility test after storage in air in the reaction mixture of 2% CO+20% O₂ balanced in N₂. (c) Stability test of the re-used $x=0.00$ after temperature-programmed oxidation and a fresh batch $x=0.25$ after temperature-programmed oxidation at 200 °C in the reaction mixture of 2% CO+20% O₂ balanced in N₂.

In Figure S17a and S17b, transient CO oxidation curves are shown that derived from another instrument compared to transient oxidation curves in Figure S17a. 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 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 was placed in a quartz reactor (inner diameter = 8 mm).

The protocol of the re-use of $x=0.00$ from batch 1 (mixture was unloaded from the reactor after the initial measurement and stored in air) consisted of three different exposures to a reaction mixture of 2% CO and 20% O₂ (balanced in N₂). Prior to each run, a temperature-programmed oxidation (TPO) was performed in 20% O₂ in N₂ with a heating rate of 3 °C min⁻¹ up to 300 °C and a dwell time of 1 h. After cooling down to 50 °C, the catalyst was purged with N₂, afterwards equilibrated in the reaction mixture for 15 min. For the transient CO oxidation, the temperature was increased linearly with a heating rate of 3 °C min⁻¹ up to 500 °C and dwelled for 15 min. Afterwards, the reactor was cooled to 50 °C and purged with N₂ for 90 min. After TPO, a second exactly same transient reaction was performed to investigate restorability of the activity. The third step contained a similar TPO was performed with the deviation of cooling only being performed to 200 °C, again purged with the reaction mixture for 15 min and afterwards, 9 h of reaction have been investigated on the catalyst at 200 °C to judge on the stability. The results are shown in Figure S17c.

For the stability test of $x=0.25$, 100 mg of a fresh batch were diluted with 500 mg of SiC. Afterwards, the stability test was performed at 200 °C for 10 h in 2% CO and 20% O₂ balanced in N₂ as specified above.

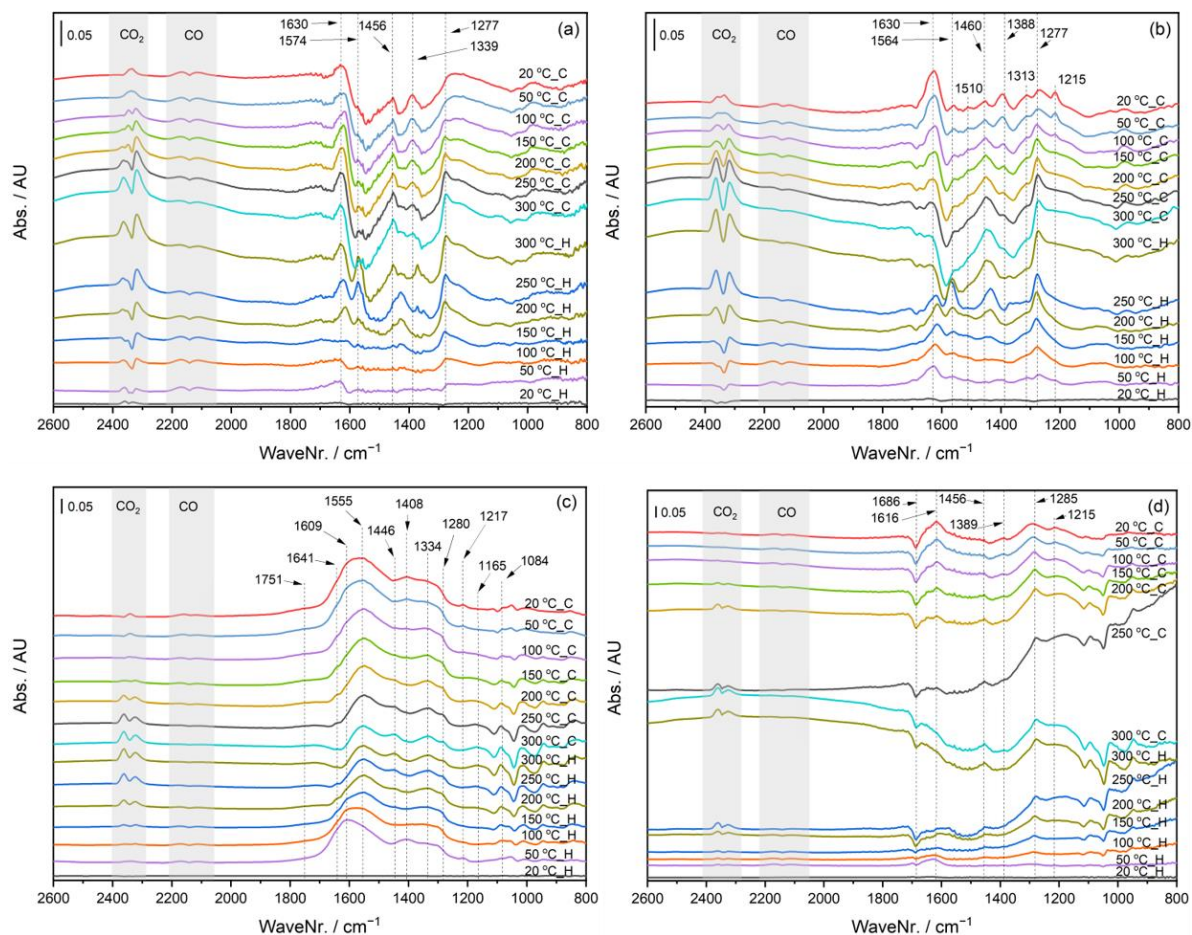


Figure S18. DRIFTS spectra of the selected catalysts exposed to the reaction mixture of 0.2% CO+2% O₂ balanced in He, after a He-treatment at 150 °C during a transient experiment; (a) $x=0.00$, (b) $x=0.05$, (c) $x=0.20$ and (d) $x=0.30$ Co incorporation. In the legends, H and C designate the heating and cooling segments, respectively.

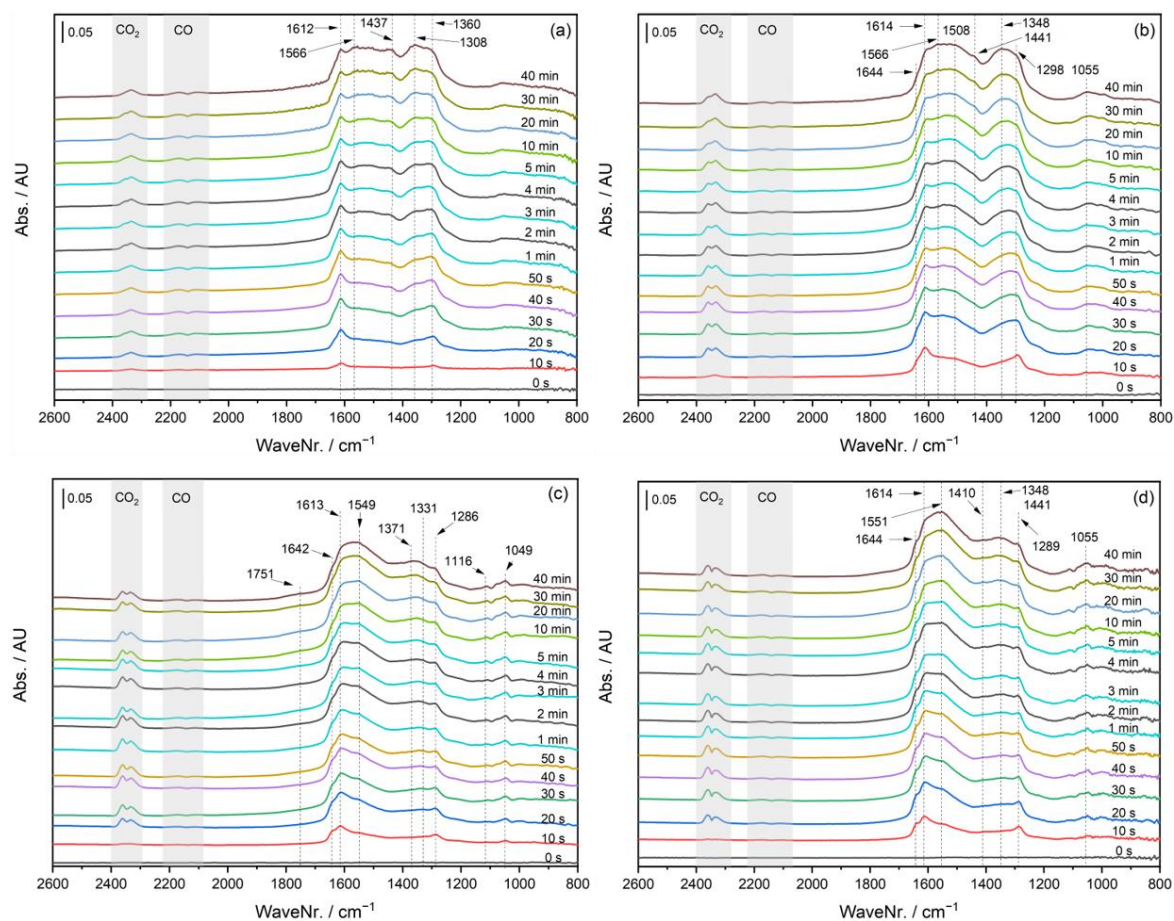


Figure S19. DRIFTS spectra of the selected catalysts exposed to the reaction mixture of 0.2% CO+2% O₂ balanced in He, after an oxidative treatment during 40 min of steady-state condition at 200 °C; (a) $x=0.00$, (b) $x=0.05$, (c) $x=0.20$ and (d) $x=0.30$ Co incorporation.

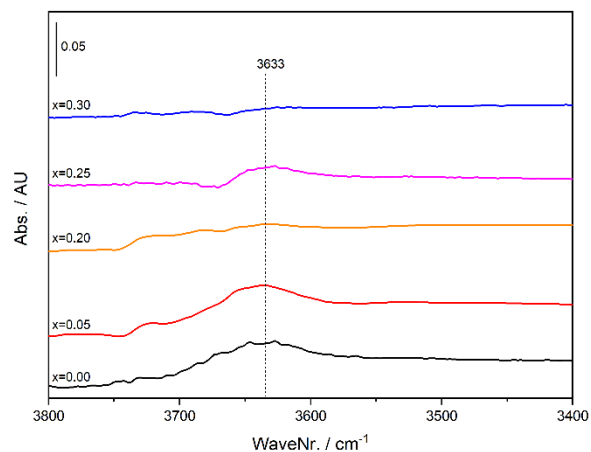


Figure S20. OH-region DRIFTS spectra of the selected catalysts exposed to the reaction mixture of 0.2% CO+2% O₂ balanced in He, after an oxidative treatment during 40 min of steady-state condition at 200 °C.

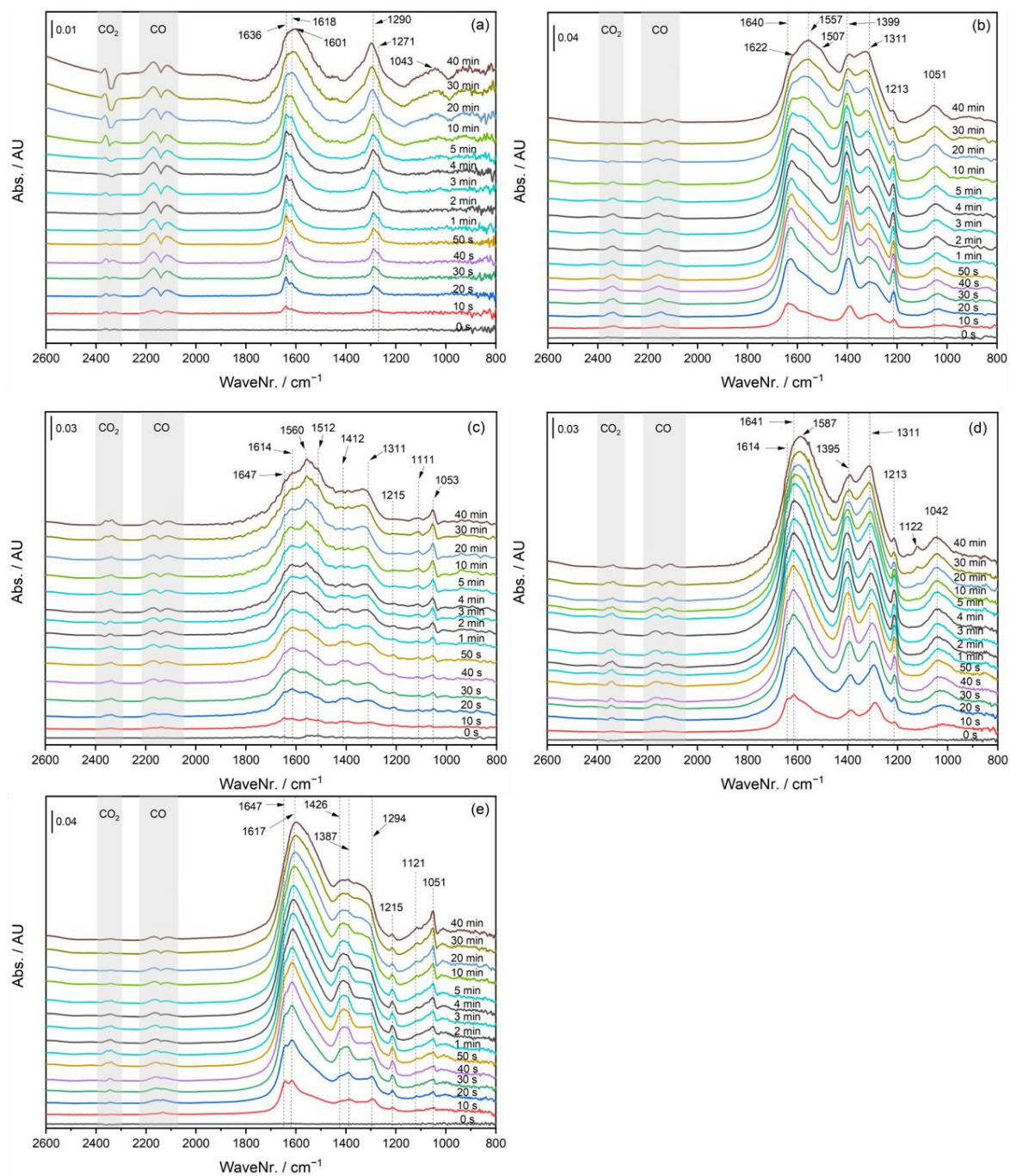


Figure S21. DRIFTS spectra of the selected catalysts exposed to the probe gas of 0.2% CO in He, after an oxidative treatment during 40 min of steady-state condition at 10 °C; (a) $x=0.00$, (b) $x=0.05$, (c) $x=0.20$, (d) $x=0.25$ and (e) $x=0.30$ Co incorporation.