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Electronic Supplementary Information (ESI)

Bridging the gap between industry and synchrotron: *Operando* study at 30 bar over 300 h on the Fischer-Tropsch synthesis

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1) *Operando* setup and high-pressure cell for combined XAS&XRD

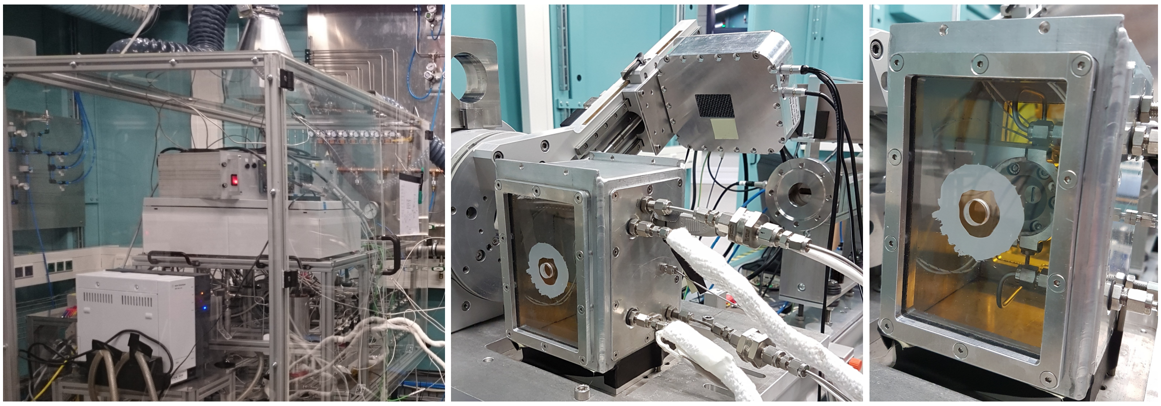

Figure S1: Pictures of the gas-dosing and -analysis unit (left), operando XAS&XRD setup (middle), high-pressure cell in safety box (c).

2) Product analysis

Table S1: Calibrated gases of the µ-GC for the long-term Fischer-Tropsch experiments.

Species	**Gas**		
C1	CH_4	CO_2	CO
C2	C_2H_2	C_2H_4	C_2H_6
C3	C_3H_6	C_3H_8	
C4	Cis-/trans-2-C_4H_8	i-/n-C_4H_8	i-/n-C_4H_{10}
Others	H_2	N_2	O_2

3) *Ex situ* "post-mortem" analysis after the 310 h long-term FTS experiment

X-ray diffraction (XRD) patterns were recorded using a PANalytical X'Pert PRO diffractometer with Ni-filtered Cu-Kα radiation (λ = 1.54060 Å) at 2θ = 8-80° with a step size of 0.0167° (1.25 s per scan step). The catalyst powders were measured *ex situ* on a rotating sample holder.

Ex situ Raman spectroscopy was performed on an inVia Reflex Raman Spectrometer system (Renishaw). The system was equipped with a HeNe laser (633 nm) and a Leica microscope. For all measurements, a 100x objective and a 1800 lines mm^{-1} grating were used. Data was acquired for five different carbon agglomerates at ten different spots each (three spectra averaged for each single spot). For each acquisition in the range from ~1000 to 2000 cm^{-1}, the laser intensity was set to 1 % (~0.043 mW at the sample) and the acquisition time was set to 30 s. Spectra were recorded at room temperature. For data treatment, including cosmic ray removal, noise filtering and background subtraction, the software WiRE 4.1 (Renishaw) was used. Since all obtained spectra were quite similar, they were averaged, resulting in one spectrum. For peak fitting of the averaged spectrum, the software Origin 2019 was used. Fitting for the D1, D4 and G band was performed with Lorentzian shaped curves, as reported by Sadezki *et al.*[1]

TG-MS analysis was performed with a STA 449 F3 "Jupiter" coupled with a QMS 403 D "Aëolos" (NETZSCH). The sample-chamber was flushed over night with 100 mL min^{-1} N_2. For the temperature-programmed reduction (H_2-TPR), the gases were adjusted to 90 mL min^{-1} N_2 and 10 mL min^{-1} H_2. After 1 h, the catalyst was heated to 800 °C (5 K min^{-1}) and the temperature was kept for 1 h. Subsequently, the catalyst was cooled down to room temperature. A temperature-programmed oxidation (TPO) was performed with the reduced catalyst using 90 mL min^{-1} N_2 and 10 mL min^{-1} O_2. After 1 h, the catalyst was heated to 1000 °C (5 K min^{-1}), the temperature was kept constant for 1 h after reaching the setpoint. Finally, the catalyst was cooled down to room temperature.

4) Long-term studies

4.1 Catalyst activation

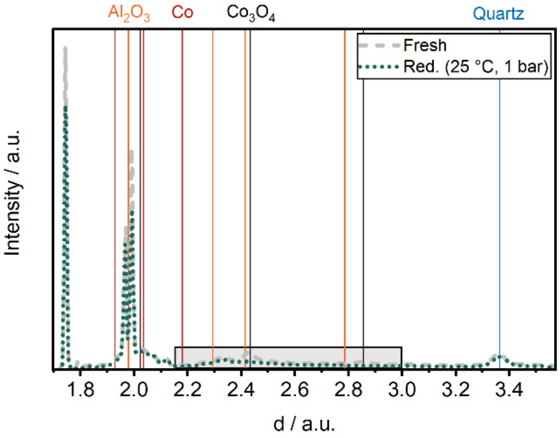

Figure S2: Full X-ray diffraction patterns of the Co-Ni-Re/γ-Al_2O_3 catalyst before (grey) and after activation procedure (green). Marked area represents the data presented in main manuscript.

4.2 Overview on EXAFS

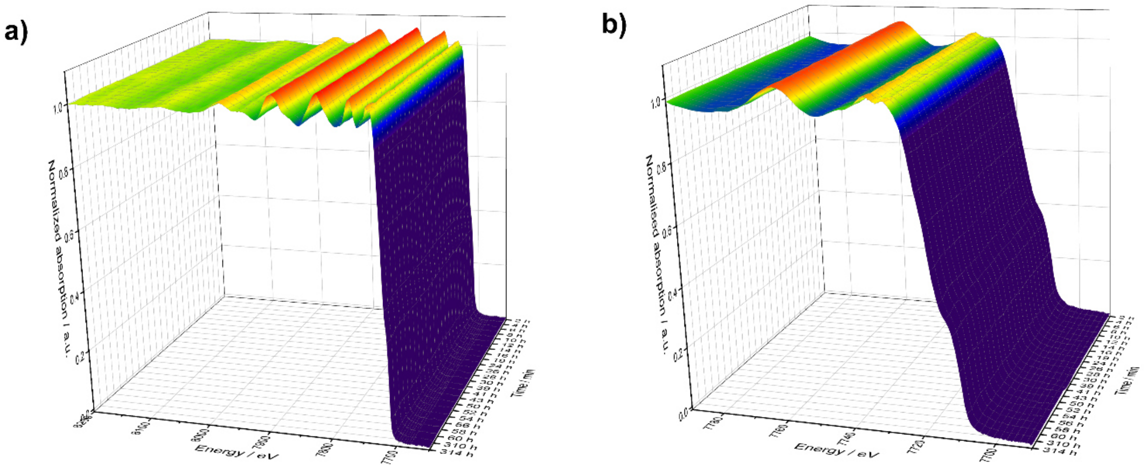

Figure S3: Operando (a) EXAFS and (b) XANES with high-resolution at the Co K edge of the Ni-Co-Re/Al_2O_3 catalyst at different time on stream (TOS) at 250 °C and 30 bar in 15 ml min^{-1} H_2:CO = 2:1.

4.3 *Operando* XRD

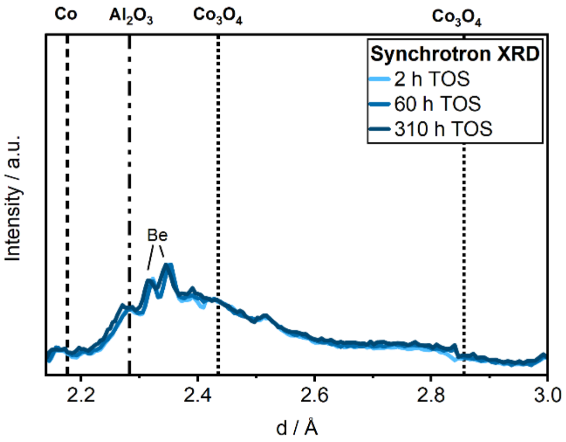

Figure S4: Operando XRD of the Co-Ni-Re/γ-Al_2O_3 catalyst after 2 h TOS (dark blue), 60 h TOS (blue) and 310 h (light blue) in the Fischer-Tropsch synthesis.

4.4 EXAFS Fitting

The amplitude factor was determined by fitting the Co-reference foil to a structural Co reference[2] and set to 0.767 for the following fits of the spectra during the 310 h long-term Fischer-Tropsch study. A first shell fit was performed with a k-range chosen from 2.7 to 12 $Å^{-1}$ in an R-range from 1.3-2.8 Å.

Table S2: EXAFS fitting results (first shell) of the Co-Ni-Re/γ-Al_2O_3 catalyst.

Conditions	**Atom**	**N**	**R / Å**	**σ^2*10^{-3} / $Å^2$**	**E_0 / eV**	**R Factor*10^{-2} / a.u.**
After H_2-TPR	Co	9.1 ± 0.6	2.50 ± 0.02	7.0 ± 0.6	7.9 ± 0.7	0.44
2 h TOS	Co	8.8 ± 0.8	2.49 ± 0.04	11.0 ± 0.9	5.9 ± 0.8	0.75
60 h TOS	Co	8.7 ± 0.8	2.49 ± 0.03	11.0 ± 0.9	6.4 ± 0.8	0.61
310 h TOS	Co	8.3 ± 1.2	2.49 ± 0.04	10.5 ± 1.5	6.4 ± 1.4	1.88

5 References

1. A. Sadezky, H. Muckenhuber, H. Grothe, R. Niessner and U. Pöschl, *Carbon*, 2005, **43**, 1731-1742.