

Cobalt Catalyzed Fischer-Tropsch Synthesis with O₂-Containing Syngas

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Appendix

The in-situ XRD measurements show the formation of only CoO in case of reoxidation of the Co-catalyst at near FTS conditions (5 bar, 230 °C). (Figure S1).

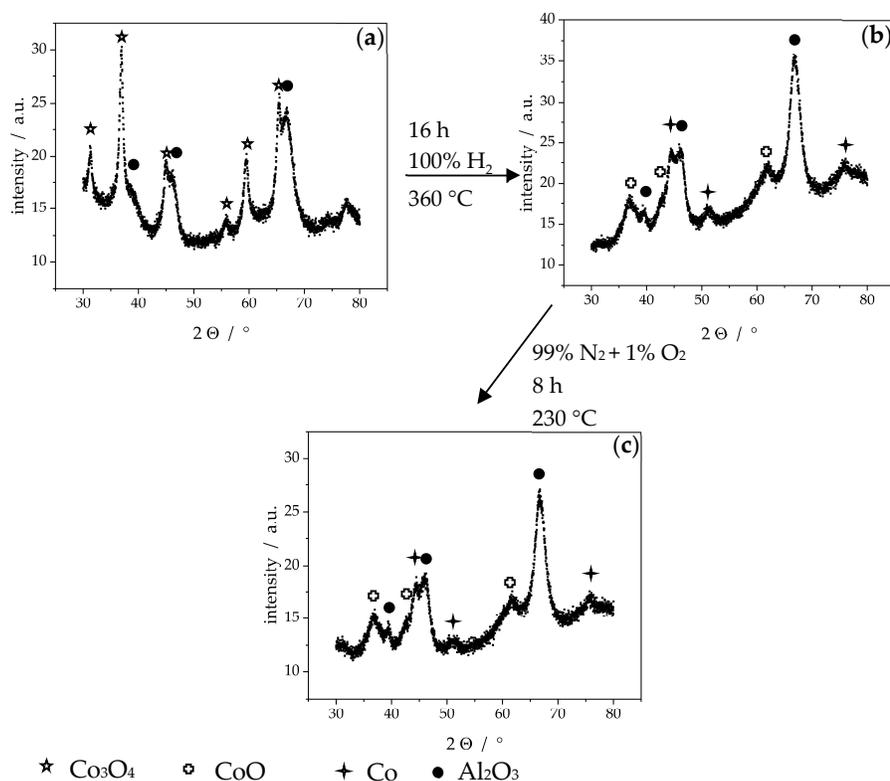


Figure S1. (a) X-Ray Diffractogram of fresh Co/Pt/Al₂O₃ catalyst. (b) Diffractogram of reduced Co/Pt/Al₂O₃ catalyst. (c) Diffractogram of re-oxidized Co/Pt/Al₂O₃ catalyst. Conditions: $T = 230\text{--}360$ °C; $p = 5$ bar; $V_{total} = 7$ l/h (NTP); $p_{H_2} = 0\text{--}5$ bar, $p_{N_2} = 0\text{--}4.95$ bar; $p_{O_2} = 0\text{--}0.05$ bar; m_{cat} (Co/Pt/Al₂O₃) = 0.5 g.

The fresh catalyst shows the characteristic reflexes of the Co₃O₄ phase (at 31.1°, 36.7°, 44.7°, 59.1° and 65° (Figure S1a)). A mixture of metallic Co and CoO is left after reduction at 360 °C in hydrogen for 16 h. The XRD results show the corresponding reflexes for CoO at 36.5°, 42.3 and 61.3° and at 44.2°, 51.7° and 75.9° for metallic Co (case b). After reoxidation at 230 °C for 8 h the peaks for metallic Co decrease and for CoO increase but no reflections for Co₃O₄ are measured (case c). This suggests that at elevated temperature the oxidation of Co is to CoO only.

To compare the effect of the catalyst reduction treatment on the O₂-product selectivity the reduction degree of a pure Co catalyst was monitored to see if cobalt was reduced without Pt added to the active catalyst with regard to molecular oxygen (Figure S2).

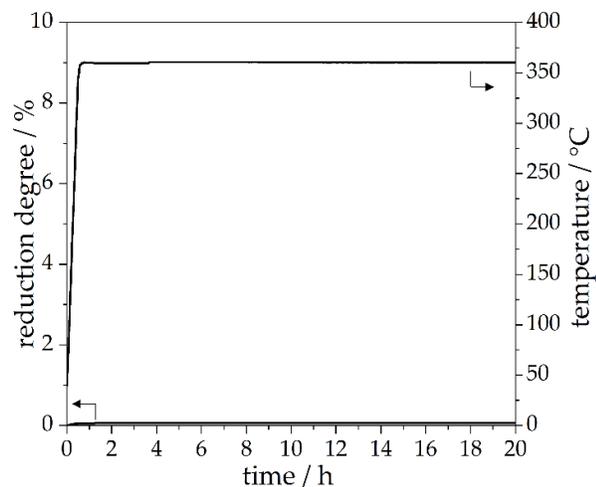


Figure S2. Reduction degree of Co/Al₂O₃ catalyst over time in H₂ atmosphere. Conditions: $p = 1$ bar; $\dot{V}_{total} = 30$ l/h (NTP); m_{cat} (Co/ Al₂O₃) = 0.1 g; $T = 0 - 360$ °C.

As shown in Figure S2 cobalt is still in its oxidized form on Al₂O₃ in pure H₂ atmosphere at 360 °C. This is expected as a typical FTS catalyst has a reduction enhancement promoter added because metallic cobalt is formed only at very high temperature (> 500 °C) without such a promoter.