

Supporting Information for:

Catalytic consequences of platinum deposition order on cobalt-based Fischer-Tropsch catalysts with low and high cobalt oxide dispersion

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S.1 List of the techniques and procedures used for the characterization of the catalysts:

- BET and ICP-MS: The BET surface area (S_{BET}) and the specific pore volume of the calcined catalysts are estimated from the N_2 adsorption isotherms measured at $-196\text{ }^\circ\text{C}$ with a Micromeritics Tristar 3000 instrument. Prior to the measurement, the samples are heated at $120\text{ }^\circ\text{C}$ and evacuated for 3 h under vacuum (0.1 Torr). The total amount of Co and Pt loaded on each catalyst is determined by inductively coupled plasma mass spectrometry (Thermo Electron, X series 2 ICP-MS) on the samples dissolved in ultrapure concentrated nitric acid (Sigma Aldrich, 70%).
- TG/DTA: Thermogravimetric/differential thermal analyses (TG/DTA) in air are carried out on the unpromoted samples obtained after the first impregnation step with and without DEG and drying at room temperature for 12 h. The samples are named as $\text{CoDEG}^{\text{ld}}/\text{Al}_2\text{O}_3^{(\text{s})}$ and $\text{Co}^{\text{ld}}/\text{Al}_2\text{O}_3^{(\text{s})}$, respectively. TG/DTA analyses are also performed on $\text{Pt}^{\text{ld}}/\text{CoDEG}/\text{Al}_2\text{O}_3^{(\text{s})}$ and $\text{CoDEG}^{\text{ld}}/\text{Pt}/\text{Al}_2\text{O}_3^{(\text{s})}$. The first one is prepared as the $\text{Pt}/\text{CoDEG}/\text{Al}_2\text{O}_3^{(\text{s})}$ catalyst, but without calcining the catalyst after the Pt-impregnation step. The second one is prepared as the $\text{CoDEG}/\text{Pt}/\text{Al}_2\text{O}_3^{(\text{s})}$ sample, but stopping the synthesis procedure after the first Co-impregnation step, before the calcination step. During TG/DTA, the sample is heated in synthetic air ($1833\text{ cm}^3(\text{STP})/\text{min}/g_{\text{cat}}$, Sapio) from ambient temperature to $700\text{ }^\circ\text{C}$ at $2\text{ }^\circ\text{C}/\text{min}$ in an Exstar 6000 instrument from Seiko Instruments.

- In-situ XRD: XRD measurements are carried out with an X-ray diffractometer (Bruker D8 Advanced) equipped with a Co-K α radiation source ($\lambda = 1.78897 \text{ \AA}$) and a position sensitive detector (VÅNTEC-2000, Bruker AXS). The in-situ XRD reaction cell developed at the University of Cape Town is used in these experiments.^{1,2} The sample (15 mg) is placed in a borosilicate capillary reactor with a 1 mm outer diameter and 0.01 mm wall thickness (Hilgenberg GmbH, Germany). Then, it is exposed to a H₂ gas stream of 5000 cm³(STP)/h/g_{cat} (Afrox, 99.999 mol.%) at atmospheric pressure and 400 °C for 17 h (heating rate: 2 °C/min). The temperature of the bed is directly monitored via an internally mounted thermocouple, while the reactor is heated with two infrared heaters (Elstein MSH) in series. The powder diffractograms of both the calcined (before the reduction treatment, T.o.R.= 0 h) and reduced (at the end of the reduction process, T.o.R.≈ 20 h) catalysts are collected over a 2 θ range of 20-120° at a scan time of 1 s/step. The powder diffraction patterns during the whole in-situ reduction process are collected over a narrower 2 θ range of 40-62° at a scan time of 0.5 s/step (step size of 0.0616), so as to minimize the time required to perform each scan and to maximize temporal resolution. The observed reflexes are identified based on entries in the International Centre for Diffraction Data PDF-2 database is used to identify all the peaks/phases in the diffractograms.

XRD spectra are analyzed with full pattern fitting via the Rietveld refinement approach using the TOPAS 4.1 software (Bruker AXS), to determine crystallite sizes and composition of the cobalt phase of the catalysts. The Sasol Puralox[®] Al₂O₃ material used in this work has an unknown crystallite structure and hence it is not considered in the refinement. Its reflexes are described as two distinct peaks at 53.71 and 79.47° modeled according to the fundamental parameters profile function. Accordingly, the quantitative results are normalized to the sum of Co⁰, CoO, Co₃O₄ and CoAl₂O₄.

- In-situ magnetic measurements: The reduction of the catalysts at 400 °C for 17 h (heating rate: 2 °C/min) in H₂ (5000 cm³(STP)/h/g_{cat}, Afrox, 99.999 mol.%) at atmospheric pressure is also studied using the in situ magnetometer developed by Claeys et al. in collaboration of the University of Cape Town and Sasol.³ The reactor consists of a 1/2" stainless steel tube with a non-magnetic brass frit to support the catalyst bed. A non-magnetic temperature detector (Pt100 RTD) is placed with the tip in the bed while two infrared heaters supply uniform heat the reactor. The setup is

based on the Weiss extraction method and uses a field-controlled electromagnet that provides field strengths up to 20 kOe. This instrument allows monitoring the amount of metallic cobalt, i.e. the only ferromagnetic phase present, and therefore the degree of reduction of the catalyst during the entire activation step. In addition, magnetic measurements can give insight on the Co^0 particle size distribution if the crystallites present in the catalyst are mostly relatively small and therefore display superparamagnetic behavior. A description of the set-up and examples of its use can be found in⁴⁻⁶. A full M-H curve from -20 to 20 kOe is also measured at 400 °C on the reduced catalysts under Ar flow (Afrox, 99.999 mol.%). By fitting Langevin functions, this test allows obtaining a crystallite size distribution of the superparamagnetic Co^0 nanoparticles.⁴ However, the Langevin function can only be applied with samples containing predominantly superparamagnetic crystallites, i.e. a very low amount of larger crystallites which display remnant magnetization upon the removal of an external field ($\gamma < 10\%$).

- H_2 -TPR analyses: H_2 -Temperature Programmed Reduction (H_2 -TPR) analyses are carried out both on the calcined and reduced catalysts using a Micromeritics Thermoquest TPDRO1100 instrument. The instrument is equipped with a thermal conductivity detector (TCD) located downstream the reactor after a soda lime steam trap. In all the experiments the sample is heated from 40 to 1050 °C (heating rate: 15 °C/min) under a flow of 5.15 vol.% H_2 in Ar (600 $\text{cm}^3(\text{STP})/\text{min}/g_{\text{cat}}$, Sapiro). The reduction of the sample is carried out in situ at 400 °C (heating rate: 2 °C/min) for 17 h using 83 $\text{cm}^3(\text{STP})/\text{min}/g_{\text{cat}}$ of pure H_2 (Sapiro, 99.995 mol.%) and then it is cooled to 40 °C in Ar (Sapiro, 99.999 mol.%). Then, the reactor is purged with a stream of 5.15 vol.% H_2 in Ar, and further heated to 1050 °C (heating rate: 15 °C/min). H_2 consumption in this latter heating step correlates with the amount of cobalt which remains unreduced after the treatment in H_2 at 400 °C.

H_2 -chemisorption: Information on the amount of Co^0 dispersed at the catalytic surface is collected by running H_2 -chemisorption experiments using the same TPDRO instrument which is used to run TPR experiments. To this end, 300 mg of sample are placed in a quartz reactor and reduced in situ at 400 °C (heating rate: 2 °C/min) and atmospheric pressure for 17 h under a flow of pure H_2 (5000 $\text{cm}^3(\text{STP})/\text{h}/g_{\text{cat}}$, Sapiro, 99.995 mol.%). After flowing Ar (Sapiro, 99.999 mol.%) at 400 °C and atmospheric pressure for 2 h and cooling to 100 °C, successive

pulses of H₂ (264 μL/pulse) are passed over the catalyst. The total amount of chemisorbed hydrogen ($\text{mol}_{\text{H}_2}^{\text{chemi}}/\text{g}_{\text{cat}}$) was calculated from the difference between the peak area obtained during the saturation experiment and the areas of the peaks in the absence of a chemisorption event. Then, by assuming a chemisorption stoichiometry of Co:H equal to 1, the cobalt metal dispersion (D, [%]) was calculated as per eq. (S1)

$$D [\%] = \frac{(\text{mol}_{\text{H}_2}^{\text{chemi}}/\text{g}_{\text{cat}}) \cdot 2}{\text{mol}_{\text{Co}^0}^{\text{TPR}}/\text{g}_{\text{cat}}} \cdot 100 \quad (\text{S1})$$

where $\text{mol}_{\text{H}_2}^{\text{chemi}}/\text{g}_{\text{cat}}$ is the total amount of H₂ chemisorbed in the experiment and $\text{mol}_{\text{Co}^0}^{\text{TPR}}/\text{g}_{\text{cat}}$ is the amount of metallic cobalt on the reduced catalysts.

The average cobalt metal crystallite size ($d\text{Co}_{\text{chemi}}^0$) was estimated from the Co⁰ dispersion measurements using eq. (S2):⁷

$$d\text{Co}_{\text{chemi}}^0 [\text{nm}] = \frac{96}{D [\%]} \quad (\text{S2})$$

S.2 Procedures adopted for the reactivity experimental tests:

Once diluted with 300 μm α-Al₂O₃ pellets so as to prevent local hot-spots (catalyst: α-Al₂O₃ = 1:4 v/v), The prepared catalysts are tested for FTS using a lab-scale tubular fixed-bed reactor (1.1 cm ID). More details on the reactor and on the adopted lab-scale apparatus can be found in⁸ and references therein. Prior to exposing the samples to syngas, the catalyst is reduced in situ at 400 °C (heating rate 2 °C/min) for 17 h using 5000 cm³(STP)h⁻¹g_{cat}⁻¹ of H₂ (Sapio, 99.995 mol.%). Catalytic runs are carried out at relevant process conditions: T = 210 °C, P = 25 bar, H₂/CO inlet molar ratio = 2.0, GHSV = 6410 cm³(STP)h⁻¹g_{cat}⁻¹, inerts (N₂+ Ar) in the feed = 24 vol.%.

The unconverted reactants and the full spectrum of products are measured by on-line and off-line gas-chromatographic analyses. Details on product collection and analytical procedures can be found elsewhere.⁹ In order to check that steady state conditions are achieved, multiple data at the same experimental condition are collected for more than 48 h.

References:

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6. N. Fischer, M. Claeys, *Catal. Today*, 2016, **275**, 149-154
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8. C. G. Visconti, M. Mascellaro, *Catal. Today*, 2013, **214**, 61-73
9. C. G. Visconti, L. Lietti, P. Forzatti, R. Zennaro, *Appl. Catal. A-Gen.*, 2007, **330**, 49-56

S.3 List of the figures:

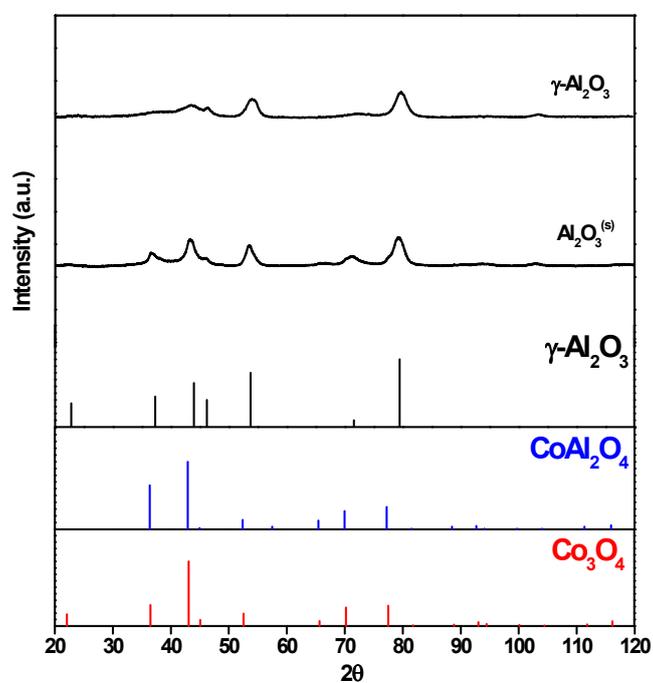


Figure S1. XRD scans of (a) the $\gamma\text{-Al}_2\text{O}_3$ pellets and (b) the stabilized alumina. Reference patterns of $\gamma\text{-Al}_2\text{O}_3$, CoAl_2O_4 and Co_3O_4 phases are also shown.

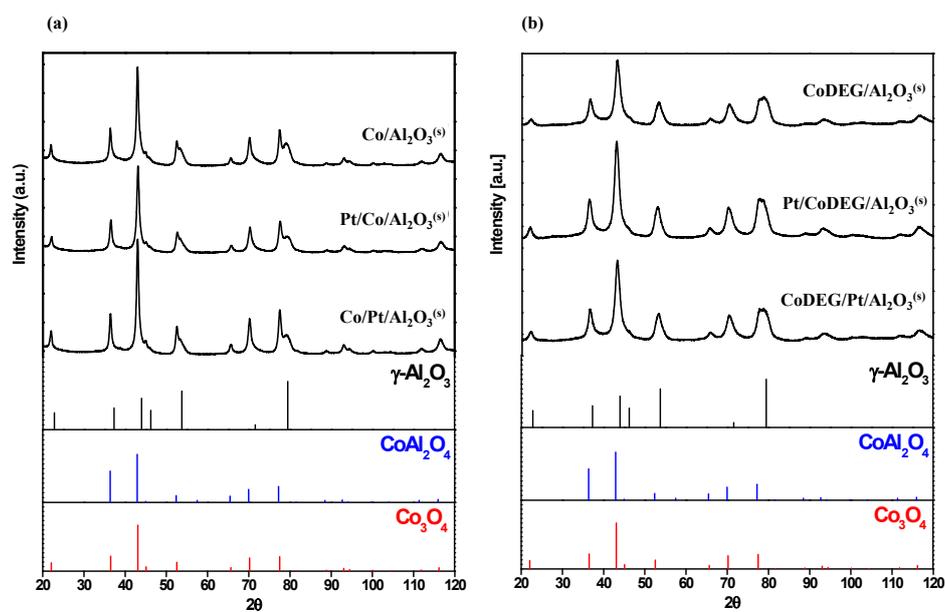


Figure S2. XRD scans of the calcined catalysts prepared (a) without and (b) with DEG. Reference patterns of $\gamma\text{-Al}_2\text{O}_3$, CoAl_2O_4 and Co_3O_4 phases are also shown.

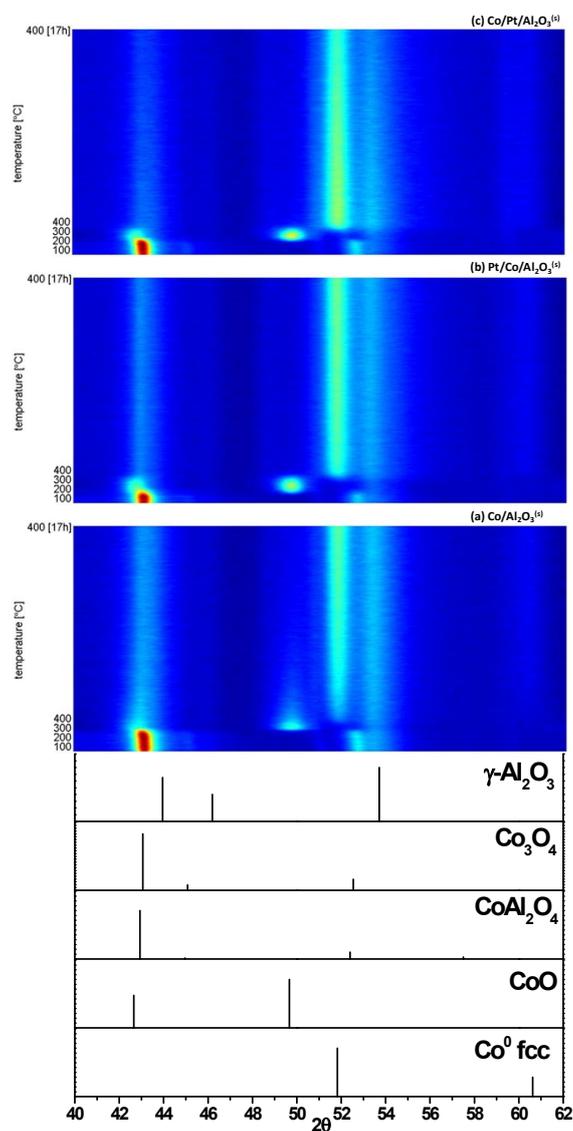


Figure S3. Reduction of the catalysts prepared without DEG (a) Co/Al₂O₃^(s), (b) Pt/Co/Al₂O₃^(s), (c) Co/Pt/Al₂O₃^(s). Scans collected at a temperature ramp of 2 °C·min⁻¹ and a holding time of 17 h at 400 °C (atmospheric pressure, hydrogen flow) with a Bruker D8 Advance diffractometer equipped with a Co source ($\lambda = 1.792850 \text{ \AA}$) and a position sensitive detector (Bruker Vantec). Reference patterns of Co₃O₄, CoAl₂O₄, CoO, Co⁰ fcc and γ -Al₂O₃ are given.

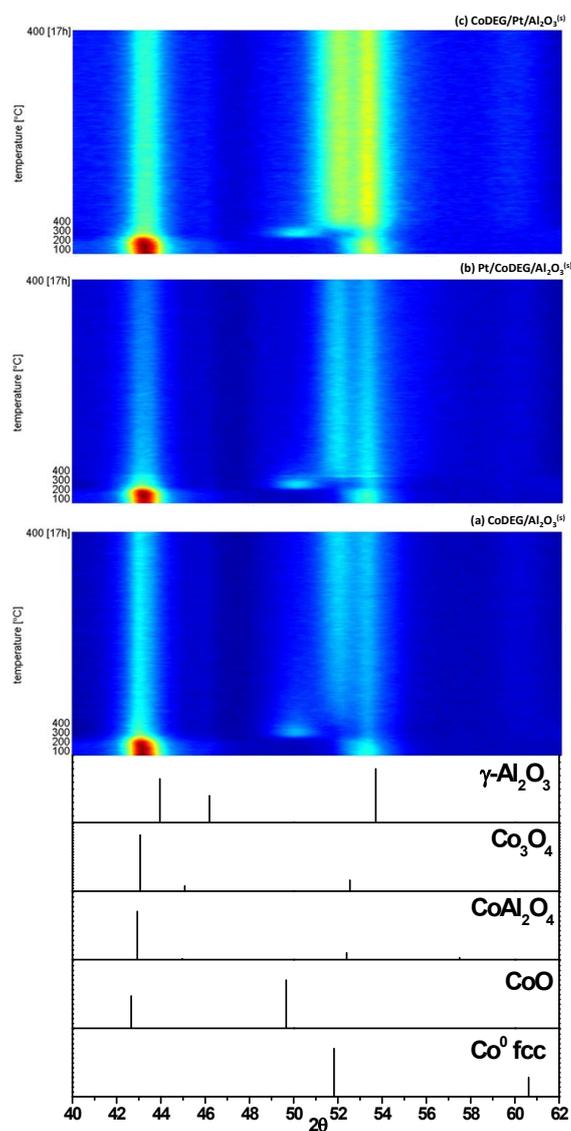


Figure S4. Reduction of the catalysts prepared with DEG (a) CoDEG/Al₂O₃^(s), (b) Pt/CoDEG/Al₂O₃^(s), (c) CoDEG/Pt/Al₂O₃^(s). Scans collected at a temperature ramp of 2 °C·min⁻¹ and a holding time of 17 h at 400 °C (atmospheric pressure, hydrogen flow) with a Bruker D8 Advance diffractometer equipped with a Co source ($\lambda = 1.792850 \text{ \AA}$) and a position sensitive detector (Bruker Vantec). Reference patterns of Co₃O₄, CoAl₂O₄, CoO, Co⁰ fcc and γ -Al₂O₃ are given.

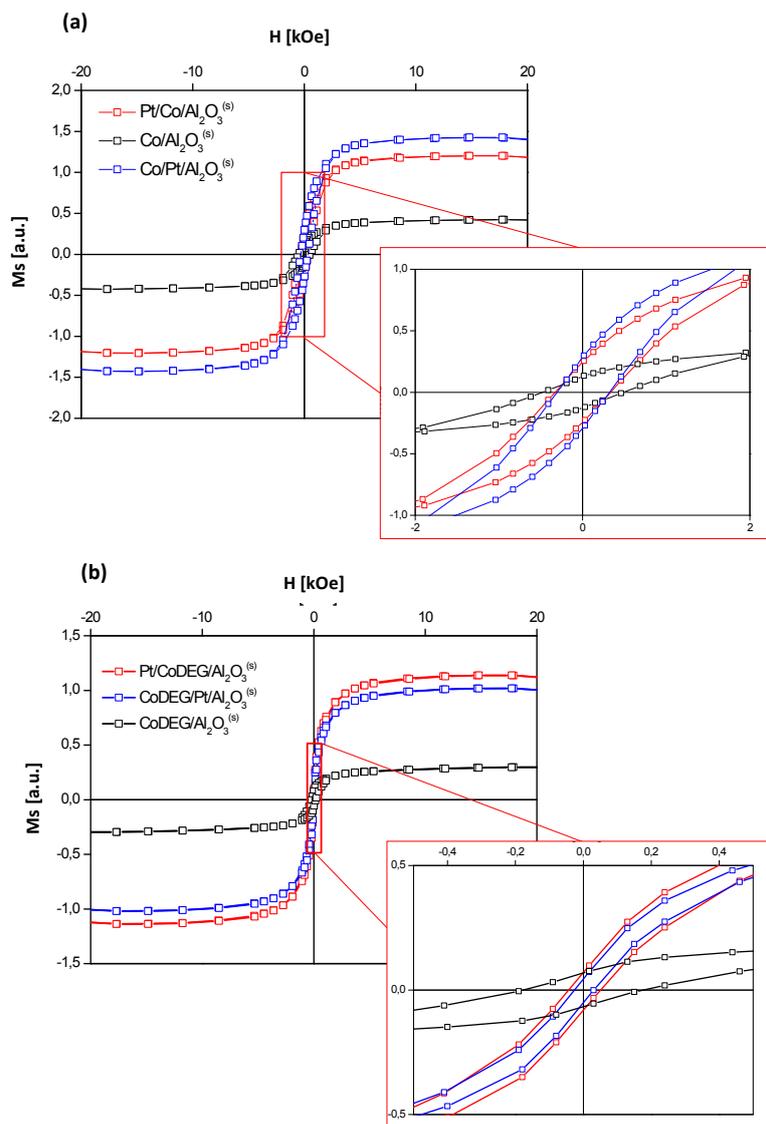
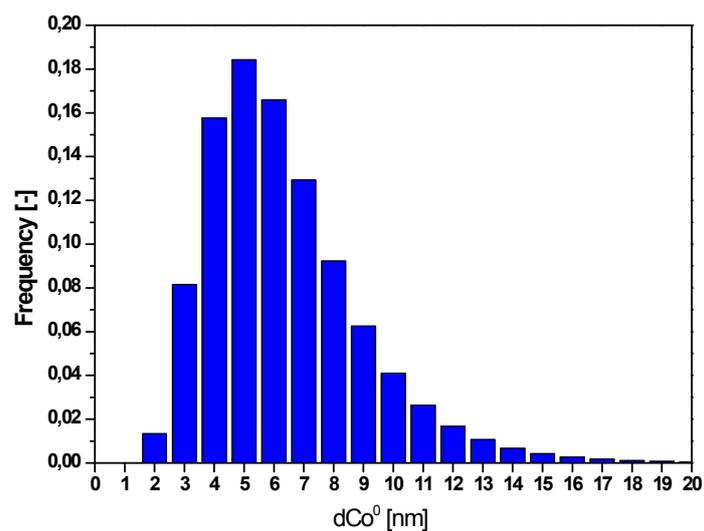


Figure S5. The full hysteresis of the reduced catalysts prepared (a) without DEG: Co/Al₂O₃^(s) (black), Pt/Co/Al₂O₃^(s) (red) and CoPt/Al₂O₃^(s) (blue) catalysts and (b) with DEG: CoDEG/Al₂O₃^(s) (black), Pt/CoDEG/Al₂O₃^(s) (red), and CoDEG/Pt/Al₂O₃^(s) (blue) catalysts. An expansion of the plot around the origin is also shown.



FigureS6. Co⁰ Particle size distribution of CoDEG/Pt/Al₂O₃^(s) catalyst obtained by applying Langevin function to its hysteresis shown in Figure S5.

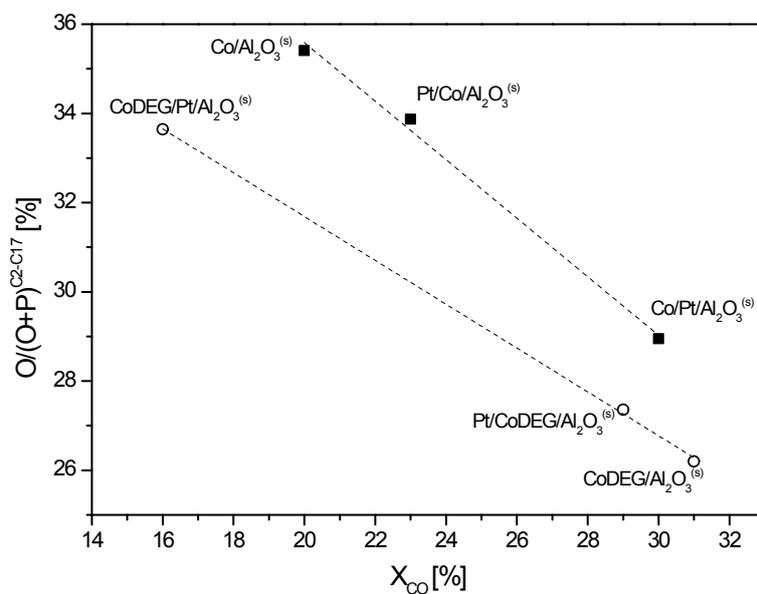


Figure S7. Olefins fraction with respect to the sum of olefins and paraffins calculated for the hydrocarbons with carbon number C₂-C₁₇ as a function of the CO conversion.