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Complete List of Authors:	Tsakoumis, Nikolaos; Norges teknisk-naturvitenskapelige universitet, Chemical Engineering Patanou, Eleni; Norges teknisk-naturvitenskapelige universitet, Chemical Engineering Lögberg, Sara ; Kungliga Tekniska Hogskolan Johnsen, Rune; Technical University of Denmark Myrstad, Rune ; SINTEF van Beek, Wouter; Università del Piemonte Orientale 'Amedeo Avogadro', DISTA Rytter, Erling; Norges teknisk-naturvitenskapelige universitet, Department of Chemical Engineering Blekkam, Edd Anders; Norges teknisk-naturvitenskapelige universitet, Department of Chemical Engineering

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Structure-performance relationships on Co based Fischer – Tropsch synthesis catalysts: The more defect free the better

Nikolaos E. Tsakoumis^{a,*}, Eleni Patanou^a, Sara Lögdberg^b, Rune E. Johnsen^c, Rune Myrstad^d, Wouter van Beek^e, Erling Rytter^{a,d}, Edd A. Blekkan^a

^aDepartment of Chemical Engineering, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway.

^bChemical Technology, KTH (Royal Institute of Technology), Teknikringen 42, SE-100 44 Stockholm, Sweden.

^cDepartment of Energy Conversion and Storage, Technical University of Denmark, DK-4000 Roskilde, Denmark.

^dSINTEF Materials and Chemistry, NO-7465 Trondheim, Norway.

^eThe Swiss-Norwegian Beamlines (SNBL) at ESRF, Grenoble F38043, France

ABSTRACT Understanding and utilizing structure-performance relationships in catalytic nanomaterials is the epitome of catalysis science. Knowledge at the atomic level can potentially allow rational design of more selective and energy efficient catalytic materials. Fischer – Tropsch synthesis on cobalt is an example of a complicated system that operates in a narrow process regime, and the nature of the reaction product is governed by numerous parameters. On an industrial model catalyst, we have simplified the structure of the active, metallic nanoparticles into predominantly hexagonal close packed structure via the use of a Co₂C precursor. By varying the final reduction temperature, we could mildly modify catalyst microstructural properties at the nanoparticle (NP) level. Catalytic materials, although with minimal structural differences, showed significantly different performance. Evidently there is a narrow window for complete utilization of the hexagonal close packed Co crystallites that lays between removal of lattice carbon, that remains from the Co₂C precursor, and the initiation of stacking disorder, due to transition to the face centered cubic Co structure. Fischer – Tropsch synthesis performance indicators show that Co NPs with minimum number of crystal defects outperform catalysts with lattice defects, either due to the existence of lattice carbon or stacking faults. Therefore, catalyst preparation and activation procedures probably should be designed targeting defect free Co crystallites.

KEYWORDS: Fischer–Tropsch synthesis, Cobalt, hcp, fcc, structure-performance relationships, stacking faults, lattice carbon, H₂ coverage.

1. Introduction

Chemical reactions catalyzed by supported metal nanoparticles (NPs) exhibit variations in reaction kinetics that depend on the exposed surface structures. This structure sensitivity comes in different degrees, from minor/negligible (structure insensitive) to orders of magnitude (structure sensitive)^{1,2}. For the structure sensitive reactions catalyst performance strongly

depends on NP size, since the relative ratio of terraces, steps and kinks changes with NP size³. Similarly, crystallographic structure and particle shape have an analogous impact. Molecular level understanding at the nanoscale is needed for the establishment of structure performance relationships⁴ that may lead to rational catalyst design. Such understanding has been previously obtained by theoretical^{5,6} and/or experimental methods^{7–10}.

Fischer - Tropsch synthesis (FTS) is a process that converts synthesis gas (mixtures of CO and H₂) into linear hydrocarbons^{11,12}. FTS follows a polymerization mechanism where a C₁ unit is added to a growing chain. As such, the products follow the Anderson–Schultz–Flory (ASF) distribution and the polymerization probability α can be derived if one knows hydrocarbon selectivities. The process has found application in conversion of natural gas into value added fuels and chemicals. In recent years, FTS is seen as an attractive option for production of ultraclean hydrocarbon mixtures from non-fossil feedstocks such as biomass and CO₂ and H₂O¹³. However, the complexity of the reaction is rendering FTS as one of the most challenging heterogeneous catalyzed systems.

In FTS, structure-performance relationships have been in the focus of research for many decades^{14–17}. Several structural parameters appear to affect intrinsic performance and these include Co NP size, Co crystal phase, Co-support interaction and porous network/support variables. The size effect on Co NPs rich in face-centered cubic configuration has been extensively studied^{10,18–21}. It was shown that the size of Co NPs is influencing performance in all aspects; activity¹⁰, selectivity²² and stability²³. Co crystallizes in three different phases; face-centered cubic (*fcc*), hexagonal closed packed (*hcp*), and epsilon²⁴. FTS sensitivity over the last two phases is less studied since at the nanoscale (< 20 nm) Co NPs stabilize into an

1
2
3 intergrown structure with *fcc*-Co as the major phase.
4 Production of *hcp* rich Co NPs can be achieved from
5 decomposition of Co carbide precursors (produced by
6 carburization of the metallic NPs) under H₂. This
7 alternative multistep activation was first studied by
8 Hofer and Peebles¹⁴ and reinvestigated, leading to
9 uncover of phase sensitivity in FTS by Ducreux *et al.*²⁵.
10 The differences in rate and selectivity between NPs of
11 *fcc*-Co and *hcp*-Co structures, although challenging to
12 interpret, appear clear^{26–29}.

13
14 Support effects are more difficult to study since many
15 parameters are affected from one support to the other
16 in terms of acidity, metal-support interactions, porous
17 network and Co particle size^{30–32}. For Al₂O₃ based
18 supports³³, the *fcc* rich Co NPs deriving from the
19 commonly applied H₂ reduction of Co₃O₄ precursor are
20 hybrid *fcc-hcp* structures with high concentration of
21 stacking faults that are support dependent^{25,34,35}. As
22 mentioned above, predominately *hcp*-Co NPs can be
23 prepared when a reduction – carburization – reduction
24 (RCR) activation protocol is followed. However, to
25 achieve the best catalytic properties, carbon produced
26 during the carburization (CO disproportionation) step
27 has to be minimized²⁹.

28
29 Regardless of differences in FTS performance, *hcp*-Co
30 NPs produced by RCR appear as a better model system
31 (in terms of crystallite purity) since they lack the
32 intensely intergrown complex structures seen after H₂
33 reduction of Co₃O₄. This allows the construction of
34 model systems with controlled differences solely at NP
35 level.

36
37 In the present study, an industrial model Re/Co/ γ -Al₂O₃
38 FTS catalyst was prepared by aqueous incipient wetness
39 co-impregnation of cobalt and rhenium salts on γ -Al₂O₃
40 to give 20 wt.% Co and 0.5 wt.% Re. The catalyst was
41 dried (100°C) and calcined (300°C), resulting in a
42 precursor containing Co₃O₄ NPs. H₂ reduction at 350°C
43 followed before carburization under CO at 14 bar and
44 230°C²⁹. The prepared γ -Al₂O₃ supported Co₂C NPs were
45 decomposed under H₂ at different temperatures
46 forming *hcp* rich metallic Co NPs. Their kinetic
47 performance in FTS and microstructural properties of
48 the active catalytic materials were evaluated by fixed-
49 bed reactor tests and synchrotron X-ray based
50 characterization, respectively. A reference analogue
51 (REF), where the Co₃O₄ precursor was reduced under H₂
52 and tested in FTS without any other treatment, was
53 used for benchmarking²⁹. By tuning preparation
54 conditions, specifically the final reduction temperature,
55 the catalysts gain their main properties, only differing in
56 the microstructure of the Co NPs.
57
58
59
60

2. Experimental Section

Catalyst synthesis

The γ -alumina supported catalyst was prepared by incipient wetness (IW) co-impregnation of cobalt and rhenium salts. In detail, a γ -Al₂O₃ (Puralox SCCa, S_{BET} = 170 m²/g, pore volume of 0.73 cm³/g and 12 nm average pore size) support was impregnated with an aqueous solution of Co(NO₃)₆·6H₂O and HReO₄ to give a loading of 20 wt. % Co and 0.5 wt. % Re. Subsequently, the catalyst was dried in an oven at 120 °C for 4 h and calcined in flowing air at 300 °C for 16 h with a ramping rate of 120 °C/h. For operation in diffusion limitation free regime, the catalyst samples were sieved to a particle diameter of 53–90 μ m. More details on catalyst synthesis can be found in a different source²⁹.

Catalyst characterization

Hydrogen chemisorption was performed using a Micromeritics 2020 unit at 40 °C. Prior to the analysis, the reference and carburized samples were reduced under H₂ flow at 350 °C for 10 h. The cobalt dispersion was calculated by assuming dissociative adsorption of H₂ on the cobalt metal surface³⁶ and that rhenium does not contribute to the amount of hydrogen adsorbed. Re acts as a promoter increasing the exposed surface area of Co³⁷. The average cobalt metal particle size (*d*(Co⁰), nm) was calculated from the Co metal dispersion (D%) by assuming spherical, uniform Co metal nanoparticles with a site density of 14.6 atoms/nm²³⁶.

Synchrotron X-ray based characterization was performed at the Swiss-Norwegian Beamlines (SNBL) located at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Station BM01B was used for the combined XANES and XRD. For the measurements, a quartz capillary (0.7 mm o.d.) based *in situ* cell was used. A detailed description of the set up can be found elsewhere^{34,38}.

In situ X-ray diffraction - Temperature programmed reduction (XRD-TPR). The carburized catalyst was inserted in the quartz capillary and temperature was increased from 30 °C to 700 °C at a heating rate of 3 °C/min under a flow of 2.5 ml/min pure hydrogen at ambient pressure. X-ray diffractograms were recorded throughout the TPR run. For *in situ* reduction experiment, similarly to XRD-TPR, the same setup and TPR profile configuration was used but different set-point temperatures i.e. 200 °C, 250 °C, 350 °C and 450 °C. The temperature was held at set point for 1 h (R250, R350 and R450) or 1.5 h (R200) before returning to 50

1
2
3 °C for the final measurement of X-ray diffractogram and
4 X-ray absorption spectra.

5
6 X-ray absorption spectra were recorded at the Co K-
7 edge ($E = 7709$ eV) using a double crystal Si (111)
8 monochromator. The data collection was carried out in
9 the transmission mode. Ion chamber detectors with
10 their gases at ambient temperature and pressure were
11 used for measuring the intensities of the incident (I_0)
12 and transmitted (I_t) X-rays. Spectra from a cobalt foil
13 (*hcp*) was used as $\text{Co}^{(0)}$ reference. The energy calibration
14 was done by measuring the spectrum of the cobalt foil
15 with the energy of the peak of the first derivative as the
16 edge energy (7709 eV). The Demeter software (0.9.24)
17 from the Iffit software package (Version 1.2.11)³⁹, was
18 used for the XAS data analysis.

19
20 X-ray diffractograms were obtained using two
21 independent Si (111) monochromators. XRD data were
22 collected using a wavelength of 0.505 Å. A Si (111)
23 standard was used for beam calibration. 2D images
24 were obtained from a Dexela 2923 two-dimensional
25 CMOS X-ray detector and converted to normal
26 diffraction patterns using the program FIT2D⁴⁰. An
27 estimation of the mean cobalt crystallite size was
28 obtained using the Scherrer formula⁴¹ on the average
29 FWHM. Pattern decomposition by Le Bail method⁴² was
30 applied with TOPAS v4.2⁴³ software.

31 32 33 Fischer – Tropsch Synthesis

34
35 The activation procedure and FTS were performed in a
36 10 mm i.d. steel tube fixed-bed reactor. One gram of
37 calcined catalyst was diluted with twenty parts per
38 weight of SiC (75–150 μm), in order to reduce the
39 temperature gradients throughout the catalyst bed.
40 Aluminium blocks were fixed around the steel tube
41 reactors to improve the heat distribution in the axial
42 direction, and the reactors were placed in a furnace.
43 Three thermocouples along the catalyst bed were used
44 for temperature monitoring and control. Calcined
45 catalyst followed a multistep activation procedure
46 consisting of the following steps. A primary H_2 reduction
47 (R) was performed at 350°C for 10 h with a ramping rate
48 of 60 °C/h. The first reduction step was identical for all
49 the samples. It is noted that the reference sample (REF)
50 underwent only the first reduction step in H_2 before FTS.
51 A carburization step (C) of the metallic nanoparticles
52 followed. During carburization the reduced catalyst was
53 exposed to pure CO (250 $\text{mL}\cdot\text{min}^{-1}\cdot\text{gcat}^{-1}$), at 230 °C. The
54 reactor was first pressurized with Ar to 14 bar.²⁹ Then
55 CO was introduced by replacing the Ar flow gradually, in
56 order to keep the temperature increase in the catalyst
57 bed below 2 °C during the carburization. Carburization
58 lasted 3 hours with the exception of the 350^B catalyst

that was exposed at 14 bar CO for 6 hours. Finally, prior
to catalyst exposure at FTS conditions, a secondary H_2
reduction (R) was performed at different temperatures
of 200 °C, 250 °C, 350 °C and 450 °C. The samples were
treated with H_2 at 1 bar for 10 h with a ramping rate of
60 °C/h.

Fischer – Tropsch Synthesis was carried out in the same
tubular fixed-bed reactor as activation for avoiding any
exposure of the catalyst in air²⁹. FTS was performed at
210 °C and 20 bar pressure with a H_2/CO ratio of 2.1.
After the final activation step the catalyst was cooled to
170 °C and pressurized with He to 20 bar before the
syngas feed of 250 NmL/min was introduced. Heating to
the target temperature was done gradually. The sample
was heated first to 190 °C with a ramping rate of 30
°C/h, then to 200 °C with a ramping rate of 5 °C/h, and
finally to the target temperature of 210 °C with a ramp
rate of ~6 °C/h. To collect wax and liquid products, one
hot trap at ~85 °C and a cold trap at ambient
temperature were used. Gas-phase products (after the
traps) were fed into an HP 6890 gas chromatograph
equipped with a thermal conductivity detector (TCD),
and a flame ionization detector (FID). The synthesis gas
contained 3% N_2 , which served as an internal standard
for quantification of the products. FTS was performed in
two periods: Period A which is a period of 24 h time on
stream (TOS) at a fixed space velocity and period B
where the space velocity of the feed gas was adjusted
to obtain $50 \pm 5\%$ CO conversion in order to record
selectivity data at a fixed conversion level²². The
selectivity data reported here are collected at similar
conversion levels (46–48%) based on the analysis of
 C_1 – C_4 hydrocarbons in the gas phase. Since the desired
products are higher hydrocarbons, the selectivity is
reported as C_{5+} and CH_4 selectivity.

39 40 41 Data analysis and interpretation

42
43 The selectivity results are discussed both in terms of
44 absolute selectivities (C-atom based) and in terms of α_{C_n}
45 values (i.e. chain-growth probabilities of C_n^*
46 intermediates on the catalyst surface). The α_{C_n} values
47 have been calculated according to the procedure
48 reported elsewhere⁴⁴. The α_{C_n} values provide more
49 comprehensive information regarding the FT
50 mechanism, while the absolute selectivities are of more
51 practical use. In the supporting information one can find
52 a brief discussion on α_{C_n} values interpretation based on
53 the knowledge obtained from conventional Co-based
54 catalysts, as well as detailed information on TOF
55 calculations.

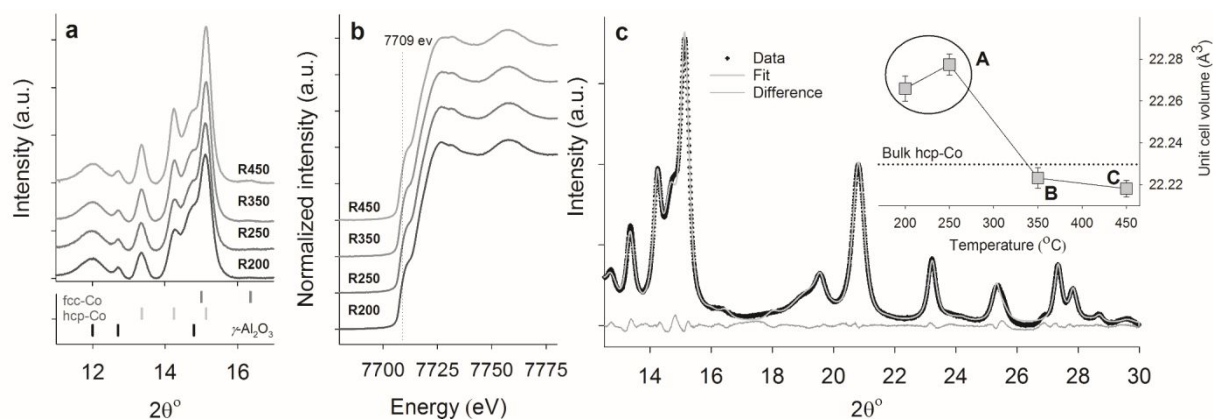


Figure 1. Diffraction and absorption X-ray signal of the activated catalytic materials after H₂ reduction at 200 (R200), 250 (R250), 350 (R350) and 450°C (R450) (a) X-ray diffraction patterns obtained at 50°C (b) K-edge Co-XANES spectra measured during cooling (c) fit of the diffraction pattern for R450 together with volume (inset) of the unit cell obtained from Le Bail refinement against bulk hcp-Co (dotted line).

3. Results and Discussion

The Co₂C/γ-Al₂O₃ precursor was decomposed at four different temperatures under H₂ atmosphere; 200°C (R200), 250°C (R250), 350°C (R350^A and R350^B) and 450°C (R450). All four catalysts share similar properties (same support, similar crystallite sizes and extent of reduction, see later in text). The active catalysts were characterized and evaluated for their reaction performance at realistic FTS conditions (210 °C, 20 bar, H₂/CO ratio = 2.1, 50% CO conversion), Table 1. FTS performance for the four treatments differ significantly, taking into account the narrow range of the applied reduction temperatures and correspondingly small structural differences as visualized by synchrotron X-rays (Figure 1a). Apparently, all catalysts have relatively similar average crystallite sizes (Table 2), far from the size sensitivity regime (reported for fcc-Co NPs)¹⁰. In addition, all Co-XANES spectra of the reduced catalysts resemble bulk cobalt to a high degree (Figure 1b, Figure S1), meaning that a high reduction extent is achieved. Structural analysis at the nanoscale allows grouping of the catalysts in three categories. **The first category A** consists of the two catalysts R200 and R250, both reduced at moderate temperatures. The higher lattice volume of these two catalysts (Figure 1c) is probably due to the presence of carbon inside the lattice of the hcp-Co NPs. Refined *in situ* TPR-XRD data (Figure 2, Figure S2), show that in the temperature range up to 250 °C there is a shrinking unit cell and reduction in the d-spacing of the (013) hcp-Co reflection. The minimum at around 250 °C indicates that lattice carbon is removed at approximately this temperature. However, the relatively fast heating rate (3°C/min) and the dynamic nature of TPR analysis may lead to temperature deviations. In terms of catalytic performance, R200 and R250 catalysts exhibit signs of simultaneously high (low

α_{C1} and high CH₄ selectivity) and low hydrogenation activity (high olefin-to-paraffin ratios (o/p) for C₂ to C₆ hydrocarbons). In particular, the application of low reduction temperature gives more CH₄ and CO₂ than any other catalyst. Indeed, it has been shown that Co₂C species are stable under FTS conditions⁴⁵ giving higher selectivities to CH₄ and CO₂⁴⁶. Apparently, there is similar FTS performance of the Co NPs with lattice carbon observed here and Co₂C. α_{C1} and α_{C4} probabilities show minimum values for these catalysts, as well as the C₅₊ selectivity (SC₅₊). Reaction rates are at levels similar to that of the REF catalytic material. **Lattice carbon free Co crystallites, category B**, are obtained after H₂ reduction at 350°C (R350^A and R350^B). Our previous thermogravimetric investigations on these carburized samples have shown negligible amount of carbon resistant to H₂ at 350°C²⁹. From *in situ* XRD it can be concluded that all lattice carbon has been removed at this temperature as well. This is evident from the changes in unit cell volume, d₀₁₃ and c/a ratio in Figure 2 and Figure S2. Furthermore, the Co surface area of the R350^A is very close to that of the REF catalyst, with the dispersion (H₂ chemisorption) estimated to be 7.5% and 7.4%, respectively. The FTS performance in terms of activity and selectivity is however, exceptional. Particularly, in comparison with the REF catalyst the CO turnover rate is nearly doubled reaching 0.0903 s⁻¹, a value comparable to previously reported TOF value obtained at higher temperature (220°C) for a Pt promoted Co/γ-Al₂O₃ catalyst²⁸, when a similar RCR activation protocol was followed. Here it has to be noted that TOF values of structure sensitive reactions are indicative (see supporting information). The selectivity parameters are also influenced, with α_{C2} to α_{C4} values above 0.9, which are the highest values for all the γ-Al₂O₃ supported catalysts (Table 1), resulting in the highest SC₅₊.

Table 1. FTS performance indicators; reaction rate (r_{CO}), turn over frequency (TOF), product selectivities (C_{5+} , CH_4 , C_2-C_4 , CO_2), olefin-to-paraffin ratios (α/p) and chain growth probabilities of C_n^* surface intermediates (αC_n , $n = 1 - 4$) for carbide decomposed at 200°C to 450°C together with conventional catalyst (REF, Co_3O_4 activated by H_2). FTS was performed at 210°C, 20 bar and H_2/CO ratio of 2.1. Reaction started at 15000 Nm/gcat and adjusted to give 50±1 % CO conversion after 24 h; selectivity C_{5+} was measured at 47±1 % CO conversion after approximately 48 h on stream. Hydrocarbon selectivities are reported on a CO_2 -free basis.

	r_{CO} mol CO·g _{Cat} ⁻¹ ·h ⁻¹	TOF s ⁻¹	TOF XRD based, s ⁻¹	C_{5+} C%	CH_4 C%	C_2-C_4 C%	CO_2 C%	o/p					alpha			
								C_2	C_3	C_4	C_5	C_6	αC_1	αC_2	αC_3	αC_4
REF	0.044	0.049	0.062	82.1	8.6	9.3	0.18	0.10	2.32	1.38	1.09	0.73	0.543	0.956	0.865	0.869
R200	0.047		0.059	79.9	10.2	9.9	0.27	0.14	2.87	1.77	1.46	1.02	0.511	0.961	0.878	0.853
R250	0.046		0.058	81.1	9.8	9.1	0.22	0.15	3.07	1.92	1.70	1.25	0.513	0.962	0.880	0.862
R350 ^A	0.083	0.090	0.104	87.8	6.8	5.5	0.11	0.19	3.06	1.89	1.64	1.11	0.542	0.969	0.908	0.901
R350 ^B	0.088		0.110	88.3	6.6	5.0	0.11	0.22	3.31	2.09	1.84	1.33	0.539	0.972	0.914	0.904
R450	0.065		0.081	85.2	7.9	6.9	0.16	0.18	3.18	1.91	1.63	1.19	0.532	0.967	0.892	0.886

^AR350^B has a doubled carburization duration of 6 hours in comparison to other samples.

αC_1 , on the contrary, is similar to that of the reference catalyst. Another important observation is that the o/p ratios for C_2 to C_6 products are high, in particular the C_2 o/p ratio is about twice the value observed for the REF (around 0.2, compared to 0.098). CO_2 formation is suppressed with the lowest obtained values of all the samples tested.

The third category C, consists of catalyst R450 and is characterized by increase in the fraction of *fcc*-Co. Exposure of bulk *hcp*-Co to temperatures above ~420°C has been shown to initiate/trigger transformation to *fcc*-Co^{47,48}. The topic is still a matter of scientific debate and various deviations from this transformation temperature have been reported and related to various factors such as NP size, metal-support interactions and pre-existing concentration of stacking faults^{49–51}. Here, with *in situ* TPR-XRD, the transformation from *hcp*-Co to *fcc*-Co is followed. During the transition, atomic diffusion creates *fcc* domains and dislocations that lead to increased disorder that is visualized by changes in c/a (Figure 2) and d_{010}/d_{011} ratios (Figure S2), starting around 350°C in the TPR experiment. After the atomic relocations, and when adequate long-range order of *fcc*-Co forms, reflections of *fcc* planes become XRD visible. This is seen at temperatures above 470°C (Figure S2). Obviously, the phenomenon occurs in the bulk, however, secondary electron imaging studies on Co single crystals have shown that the transformation is initiated in the bulk and proceeds to the surface with a delay⁵².

Table 2. Size and degree of reduction (DOR) of the metallic Co NPs.

	Crystallite size [nm]	Particle size** [nm]	DOR XANES [%]
Ref	13.2*	13.0 nm	-
R200	13.1	-	89±3
R250	13.5	-	92±3
R350	14.0	12.8 nm	95±3
R450	14.4	-	98±3

* from Co_3O_4 due to theoretical oxygen loss $d(Co) = 0.8 \times d(Co_3O_4)$.

** evaluated from H_2 chemisorption dispersion (D) measurements according to $d(Co) = 96.2/D\%$ ³⁶.

In addition, transmission electron microscopy (TEM) studies on reduced Re/Co/ γ - Al_2O_3 FTS catalysts activated by H_2 (containing *fcc*-*hcp* hybrid Co NPs) have shown a high concentrations of planar defects including twins, grain boundaries, edge dislocations, stacking faults and *hcp* lamellae in Co NPs⁵³. A similar observation has been obtained on fault-rich Cu NPs, where it was found that there is a high probability of termination of a twin boundary as a surface kink⁹. FTS performance indicators for the R450 catalyst are approaching the ones for the R350 catalysts, yet with reduced value of SC_{5+} and a substantial 26% decrease in the reaction rate compared to category B, despite the structural similarity (Figure 1 and Figure S2). The magnitude of the activity drop cannot be explained by the minor (3%) reduction in Co surface area due to sintering.

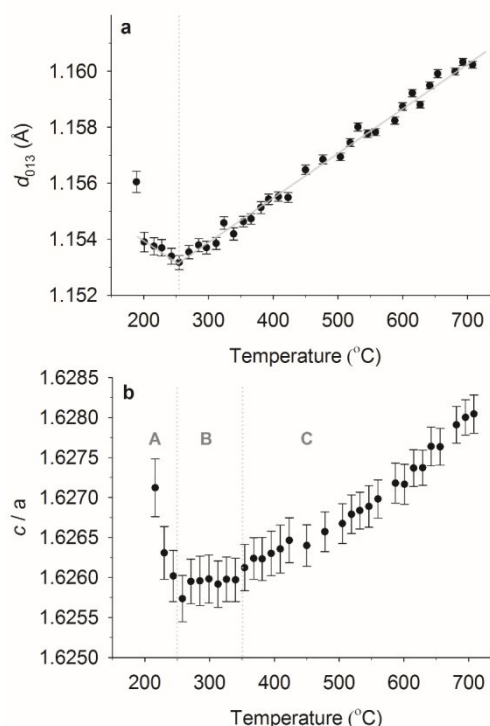


Figure 2. Structural evolution obtained from refinement of in situ TPR-XRD (a) d spacing of 013 *hcp*-Co reflection and (b) c/a lattice parameters ratio from Le Bail refinement during TPR.

Overall performance indicators (r_{CO} , SC_{5+} , o/p and chain growth probabilities αC_n) of the catalysts originating from the Co_2C precursor, show that the RCR protocol can potentially outperform conventional catalyst activation, provided that carbon is efficiently removed (Figure 3).

The reaction rates are at least equal to that of the REF catalytic material showing almost a doubling for the optimized category B catalysts, in spite of the very similar Co dispersion. The higher apparent CO turnover rates can be attributed to differences in electronic structure of the two Co polymorphs or to a larger number of active sites that can be accommodated. Regarding the electronic structure, DFT calculations have shown differences in the electron distribution density of the two phases⁵⁴, that might result in stronger CO adsorption over *hcp*-Co and subsequently higher reaction rates. Nevertheless, the most stable surfaces with highly coordinated Co atoms for the two polymorphs, i.e. *hcp*-Co (001) and *fcc*-Co (111), have the same surface geometry only differing in the third Co layer⁵⁵. As such, electronic differences might have an impact only for less abundant surfaces. In terms of sites for CO dissociation, the size, the shape and phase of the NP dictate the number of B5 sites that are exposed (and/or *in situ* formed) capable of dissociating CO^{56,57}. Theoretical molecular dynamic studies of *fcc*-Co and *hcp*-Co NPs have shown that differences between the two phases exist in terms of relative ratio of the exposed surfaces and the distribution of B5 sites. In particular, *hcp*-Co NPs have a slightly higher ratio of terraces to steps/kinks. Additionally, besides the common B5-A and B5-B sites, *hcp*-Co NPs show two more B5 site configurations with different properties (B5-B' and B5-C)⁵⁸. A combination of the two might explain the differences in performance, however it should again be stressed that the theoretical calculated values on ideal NPs or model surfaces may significantly differ from the experimentally measured rates since Co NPs regularly exist in hybrid *fcc-hcp* structures. In addition to the reasons stated above, an enhancement of the rate could derive from changes in the proximity of preferential adsorption sites of surface species since it has been suggested that H, OH or H₂O are assisting the CO scission process⁵⁹⁻⁶¹ and therefore adjacency is needed. On a different perspective, if the reaction mechanism involves merely the highly coordinated surfaces⁶² a less disrupted surface will as well be of benefit for the reaction.

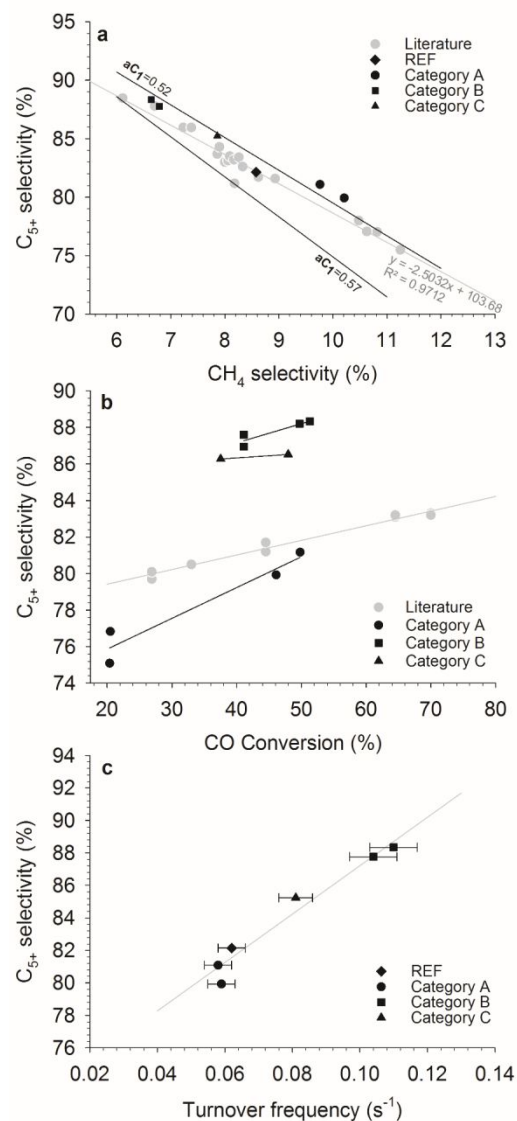


Figure 3. SC_{5+} related performance indicators in comparison with relevant literature. Co and CoRe NPs prepared by IWI on $\gamma-Al_2O_3$, $\delta-Al_2O_3$, $\vartheta-Al_2O_3$ and $\alpha-Al_2O_3$ at (210 °C, 20 bar, H_2/CO ratio of 2.1 and $47.5 \pm 2\%$ CO conversion) obtained from^{22,63,64} and references therein.

Selectivities to higher hydrocarbons of the category B and C catalysts deriving from the Co_2C precursor are comparable to selectivities that are achieved by less interacting and low surface area supports such as $\alpha-Al_2O_3$, TiO_2 and partly SiO_2 ⁴⁴. A comparison of the obtained data with respect to performance of conventionally prepared (i.e. by H_2 reduction of Co_3O_4 precursors) Al_2O_3 supported Co and CoRe NPs reported in the literature is presented in Figure 3. Figure 3c reveals a positive correlation between the apparent TOF (based on crystallite sizes obtained by XRD) and the higher αC_n values as well as SC_{5+} (Figure S3, Table S1). Similar correlations have been found for conventional catalysts⁴⁴ and suggest that the concentration of the monomer on the cobalt surface, the CH_x pool (ϑ_{CHx}),

dictates the higher α_{C_n} values via a monomer surface-crowding mechanism⁶⁵. Furthermore, the data from REF (higher α_{C_n} values vs. TOF) fall more or less on the same trendlines, suggesting Co phase independent relationships. In addition, RCR catalysts show significantly lower α_{C_1} values ($\sim 0.52 - 0.57$) compared to the higher α_{C_n} values (> 0.8) just as conventional Co-based FT catalysts do so^{66,67}. These observations indicate that the mechanism(s) of forming methane and higher hydrocarbons are similar and in their essence irrespective of the crystalline phase of cobalt and based on a common CH_x monomer. Further support of the existence of a common monomer is found in the linear relationship between SC_{5+} and SC_1 (Figure 3a) that has been previously found for conventional Co-FTS catalysts⁶⁷. Figure 3a compares the SC_{5+} vs. SC_1 values for the RCR catalysts with literature data for conventional catalysts with Co NPs > 6 nm at the same experimental conditions and conversion level. The scattering in the literature data is due to both experimental error ($\pm 2\sigma$, see supporting information) and actual differences in α_{C_1} ranging from 0.52 to 0.57⁴⁴. Here, values from B and C category catalysts with the α_{C_1} values in the range (0.53 to 0.54) are following the trendline of the literature data, suggesting that the surface-crowding mechanism is valid. Exceptions are category A catalysts that with the lowest α_{C_1} (0.51) fall outside the range and drift upwards and will be discussed in more detail later.

For all RCR catalysts it is striking to see that **o/p ratios for C₂ to C₆ hydrocarbons** are reaching very high values (Figure 4a), higher than normally observed even with less interacting large-pore supports^{31,44}. In particular, the R350 catalysts have twice as high C₂ o/p ratio compared to the REF, while the C₃ hydrocarbons at 47% CO conversion reach remarkable o/p values above 3, rarely seen in γ -Al₂O₃ supported catalysts⁶⁸ at such conversion levels and then only after H₂O addition^{22,64} (Figure 4b). Since C₂ and C₃ o/p ratios are fair indicators of the relative hydrogen coverage (ϑ_H) on the cobalt surface⁶⁹, we propose that the catalysts with *hcp*-Co NPs have a lower ϑ_H than the conventionally activated catalyst. A further indication of this is seen in the relatively high α_{C_2} and α_{C_3} values of the category A catalysts. Despite having lower SC_{5+} and similar TOF as the REF, the α_{C_2} and α_{C_3} values are markedly higher than those of the REF. The connection between $\alpha_{C_2}/\alpha_{C_3}$ and ϑ_H is explained in Supporting Information.

Exceptions from the observed improved performance of the *hcp*-Co NPs are found for the **α_{C_1} values, which appear invariant**. On a big sample of selectivity data from conventional Co-based FT catalysts that share support and have been measured at identical process

conditions, an inverse relationship between higher α_{C_n} values ($n > 1$) and α_{C_1} has been found⁴⁴. Here, comparing with the FT results of the REF catalyst it is apparent that the change from fcc rich hybrid *fcc/hcp*-Co to *hcp*-Co NPs increases most performance indicators (i.e. $\alpha_{C_{2+}}$ and TOF), while α_{C_1} is invariant (the exception is category A catalysts that exhibit a reduction in α_{C_1}). The fact that α_{C_1} does not follow an inverse relationship with higher α_{C_n} values, but rather stays the same, could possibly be explained by a counteracting effect of a lowered ϑ_H .

Figure 3b shows the **effect of conversion level** on SC_{5+} . It appears that indigenous H₂O_(g) has a stronger positive influence on SC_{5+} for the catalysts reduced at moderate temperatures (Category A), when compared with literature values^{22,63}. α_{C_1} to α_{C_4} chain growth probabilities on these catalysts increase significantly at higher conversions (Table 2S). From the above and the observed reduction in CO₂ production with time on stream (Figure S4) a partial removal of carbon by H₂O could be assumed.

Comparison between RCR produced catalysts. **Category A** catalysts exhibit poor FTS performance regarding selectivity. DFT calculations have shown that subsurface carbon modifies the electronic structure of the Co surface⁵⁵. Lattice carbon residues appear to interact and alter the properties of the Co surface resulting in a surface with the lowest α_{C_1} and α_{C_4} probabilities. The low α_{C_4} can be related to the lower apparent TOF, compared to the other RCR catalysts, resulting in a lower coverage of CH_x . The α_{C_1} is the single chain growth probability that is most affected by: changes in operating conditions^{67,69,70}, the presence of mass transfer limitations on reactant arrival⁷¹, and the presence of "pure methanation" sites⁶⁷. A high ϑ_H , mass transfer limitations and "pure methanation" sites would generally result in a lowered α_{C_1} . All catalysts in the present study have particle size less than 90 μ m and are subjected to identical conditions. In addition, judging from their high o/p ratios and high α_{C_2} and α_{C_3} values, high ϑ_H does not seem probable. Instead, "pure methanation" sites can be postulated and are indeed supported by the high CH₄ selectivity as compared with the reference material at very similar rates (Figure 3a). We propose that the existence of strong primary hydrogenation function is rather localized (few sites producing methane at high rates) since these catalysts retain high o/p ratios.

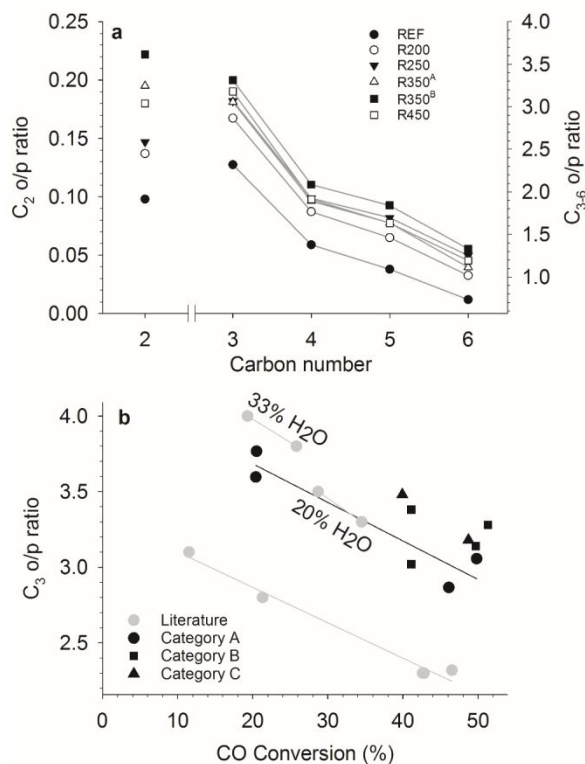


Figure 4. Olefin-to-paraffin ratio related performance indicators. Comparison with relevant literature of Co and CoRe NPs prepared by IWI on γ -Al₂O₃, δ -Al₂O₃, θ -Al₂O₃ and α -Al₂O₃ at (210 °C, 20 bar, H₂/CO ratio of 2.1 and 47.5±2 % CO conversion) obtained from ^{22,63,64} and references therein.

The **B category** catalysts outperform the other tested materials in all performance indicators (Table 1) and can be compared with the superior performance of α -Al₂O₃ and TiO₂ supported Co NPs⁴⁴. Following this pretreatment, the Co crystallites are rich in *hcp*-Co, with indications of stacking disorder and small contributions from *fcc*-Co (Figure S2). We propose that these materials possess minimum disorder of all the tested samples (Figure 2). The higher turnover rates achieved allow a significant increase in space velocity and consequently lower bed residence times, which result in minimization of secondary reactions¹⁶. In accordance, the relative CO₂ formation is at a minimum, demonstrating further suppression of the secondary water-gas-shift reaction.

Category C; the R450 catalyst shows an increase in lattice disorder due to initiation of phase transformation and increase in the *fcc* concentration. This structural change, although small, is accompanied by a significant drop in reaction rate, corresponding to a reduction in the amount and/or reactivity of sites that can dissociate CO. A decrease in selectivity indicators is also apparent.

Previous TEM studies on similar catalysts demonstrated that stacking faults appear to terminate in the surface of the nanoparticle as coordinatively unsaturated sites (cus) at edges and steps⁵³. In fact, even without termination to a cus the creation of lattice mismatch leads to the creation of strained overlayers and thus more reactive (in terms of adsorption/dissociation) sites due to change in the d-band induced by stress⁶. This implies that the stacking disorder seen in the bulk may negatively influence sites in the surface of the Co NP. We interpret the present results of increased lattice disorder coupled with a reduction in reaction rate as a structure sensitivity issue, where high concentration of cus has a negative effect on activity and selectivity in an analogue way to the particle size sensitivity described by den Breejen *et al.*⁷². We speculate that part of the additionally formed cus is poisoned by strong CO adsorption while a portion is providing H₂ dissociation increasing ϑ_H . The additional supply of H is expected to negatively affect the propagation rates as seen in αC_2 and αC_3 for the R450 catalyst. Furthermore, creation of planar defects may divide the NP in such a way that mobility of the CH_x monomer is hindered. Previous STM studies have shown that Co surface reconstructs under syngas exposure^{56,73}. In light of recent data from *in situ* STM the importance of terraces is highlighted^{74,75} particularly for their ability to form nano-islands and therefore their ability to provide additional step sites capable of CO dissociation. Provided that stacking faults formed during the *fcc* transition are terminated as cus, terrace sites will be disrupted rendering the surface unable to reconstruct forming nano-islands to the same extent. Inhibition of surface reconstruction has been found on Co surfaces after ppm alkali addition⁷⁶ that results in reaction rate loss in similar levels to the current study.

An un-promoted Co/ α -Al₂O₃ responded with a performance enhancement when an identical RCR activation procedure was followed (Table 3), especially with regard to selectivity. Although the activity and αC_1 practically remain on the same levels after treatment and o/p ratios are not boosted in comparable levels to the γ -Al₂O₃ analogue, a similar boost in SC₅₊ (7%) and C₃ o/p ratio (10%) is apparent followed by a slight increase in higher alpha values (αC_{2+}) (Figure 6S). Similarly to the γ -Al₂O₃ analogue, suppression of the CH₄ and CO₂ is also observed (Figure S6).

Table 3. FTS performance indicators for unpromoted α -Al₂O₃ supported catalyst; reaction rate r_{CO} , product selectivities, olefin-to-paraffin ratios (o/p) and chain growth probabilities of C_n^* surface intermediates (αC_n , $n = 1 - 4$) for carbide decomposed at 350 °C and conventional catalyst (α -REF, Co₃O₄ activated by H₂). FTS was performed at 210°C, 20 bar and H₂/CO ratio of 2.1. Reaction started at 14500 Nml/gcat and adjusted to give 30±1 % CO conversion after 24 h; selectivity C_{5+} was measured at 28±1 % CO conversion). Hydrocarbon selectivities are reported on a CO₂-free basis.

Co/ α -Al ₂ O ₃	r_{CO}	C_{5+}	CH ₄	C_{2-} C ₄	CO ₂	o/p					alpha			
						C ₂	C ₃	C ₄	C ₅	C ₆	αC_1	αC_2	αC_3	αC_4
α -REF	0.0066	81.9	7.9	10.2	0.52	0.13	2.66	1.71	1.55	1.32	0.572	0.933	0.849	0.871
α -R350	0.0070	88.0	6.3	5.7	0.41	0.17	2.92	1.93	1.85	1.45	0.560	0.953	0.893	0.906

It has to be noted that carbon diffusion during carburization and/or reduction steps of the RCR protocol might exhibit a size sensitivity and therefore the formed Co₂C on α -Al₂O₃ may not be as crystalline, or more stable carbon is produced not allowing a full utilization. Nevertheless, the selectivity enhancement is demonstrated and provides evidence for the significance of the NP phase on the FTS performance, suggesting that impact of support and promoter are of a secondary nature. Our data on the unpromoted Co/ α -Al₂O₃ catalyst demonstrates the relevance and universality of our results to other systems. More importantly, the presented structural modification of Co NPs towards defect free nano-crystallites with maximum FTS performance could be applied on high surface area and highly interacting porous supports giving two major advantages: (a) The inhibition of NP sintering, the primary deactivation cause, through maximization of interparticle distances⁷⁷ and metal-support interaction (b) Formulation of catalysts with high Co loadings for maximizing catalyst productivity, minimizing process volume and potentially facilitating intensified process applications^{16,78}.

4. Conclusions

In our approach we decouple the microstructure of (Re promoted) Co NPs from other structural parameters that affect FT catalysis (particle size, support, porous network) through an RCR activation protocol. This protocol delivers a simpler, in terms of crystal purity, model catalyst allowing the study of minor differences at the Co nanoparticle level due to the simplification of the crystal structure to predominantly *hcp* compared to the complex intensely intergrown system seen after H₂ activation of Co oxides. In summary our findings indicate that:

- Al₂O₃ supported *hcp*-Co NPs outperform the highly faulted *fcc*-Co NPs commonly obtained by H₂ reduction, in agreement with previous studies. Yet there is a narrow window of utilization of the benefits that lays between carbon removal (>250°C) and initiation of stacking disorder (<450°C).
- The catalyst with highest concentration of *hcp*-Co and minimum number of defects, has the highest TOF and, accordingly, the highest SC₅₊ and chain-growth probability (αC_{2+}). This is ascribed to a higher population of CH_x that might derive from a higher intrinsic activity or accommodation of higher number of active sites.
- Apparently, chain growth over Co NPs follows a CH_x monomer surface-crowding mechanism independently of the nanoparticle crystalline phase, with evidenced, to a first approximation, relationships between higher αC_n and TOF.
- The exposed Co surfaces on *hcp*-Co NPs seem to have a lower relative hydrogen coverage ϑ_H than their highly faulted *fcc*-Co counterparts, resulting in higher o/p ratios and in lower relative termination rates of C_{2*} - C_{3*} surface intermediates.
- Residual carbon from the carburization step is present in the lattice of Co NPs with final reduction temperature lower than 350°C (R200 and R250). This lattice carbon significantly increases the methanation function of the catalysts as visualized from changes in αC_1 and selectivity toward CH₄.
- Structural faults have a negative impact on SC₅₊ and TOF. The results point to an enhanced capacity of the CH_x pool on the defect free *hcp*-Co NP surface, possibly by allowing reconstruction and formation of sites highly active for CO dissociation. Suppression of H supplied from cus may explain part of the increased relative propagation rates of lower carbon number surface intermediates.

Apparently, the size sensitivity of the FTS has to be re-established with respect to Co phase and faults. Our results pave the way for Co based FTS catalyst design

with optimized activity and selectivity to higher hydrocarbons through avoidance of microstructural defects. With the optimized Co NPs it is possible to achieve high SC_{5+} with a high productivity per gram catalyst on high interacting/high surface area supports that allow higher Co loadings to be obtained and simultaneous reduction of sintering rates.

Supporting Information

A more detailed description on the basis of the interpretation of the chain growth probabilities of the C_n^* surface intermediates (the α_{C_n} values) together with figures on structural similarity, structural changes during TPR, TOF, change of performance indicators from period of similar GHSW to similar conversion level, comparison of RCR response on $Re/Co/Al_2O_3$ and Co/Al_2O_3 and deactivation with time on stream are given in supporting information.

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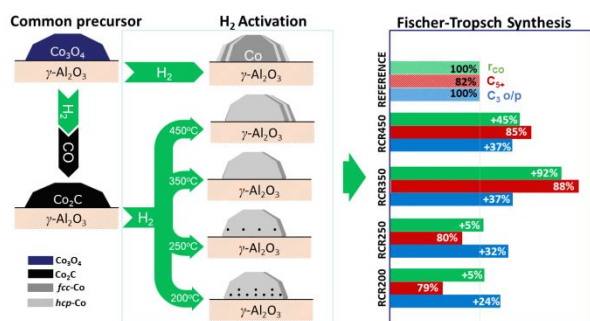
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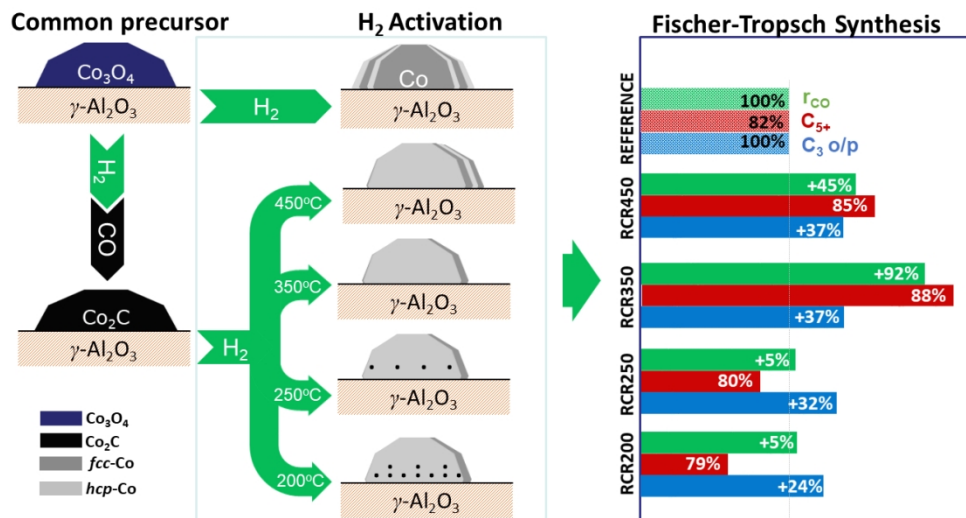


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