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

Nikolaos E. Tsakoumis, Eleni Patanou, Sara Lögberg, Rune E. Johnsen, Rune Myrstad, Wouter van Beek, Erling Rytter, Edd A. Blekkan

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

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

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

SINTEF Materials and Chemistry, NO-7465 Trondheim, Norway.

The 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 Co$_2$C 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 Co$_2$C 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, H$_2$ 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/ignorable (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 size$^3$. Similarly, crystallographic structure and particle shape have an analogous impact. Molecular level understanding at the nanoscale is needed for the establishment of structure performance relationships$^4$ 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 H$_2$) into linear hydrocarbons$^{11,12}$. FTS follows a polymerization mechanism where a C$_2$ unit is added to a growing chain. As such, the products follow the Anderson–Schultz–Flory (ASF) distribution and the polymerization probability $\alpha$ 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 CO$_2$ and H$_2$O$^{13}$. 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; activity$^{10}$, selectivity$^{12}$ and stability$^{23}$. Co crystallizes in three different phases; face-centered cubic (fcc), hexagonal closed packed (hcp), and epsilon$^{24}$. FTS sensitivity over the last two phases is less studied since at the nanoscale (< 20 nm) Co NPs stabilize into an
intergrown structure with fcc-Co as the major phase. Production of hcp rich Co NPs can be achieved from decomposition of cobalt carbide precursors (produced by carburization of the metallic NPs) under H₂. This alternative multistep activation was first studied by Hofer and Peebles and reinvestigated, leading to uncover of phase sensitivity in FTS by Ducrèux et al. The differences in rate and selectivity between NPs of fcc-Co and hcp-Co structures, although challenging to interpret, appear clear.

Support effects are more difficult to study since many parameters are affected from one support to the other in terms of acidity, metal-support interactions, porous network and Co particle size. For Al₂O₃ based supports, the fcc rich Co NPs deriving from the commonly applied H₂ reduction of Co₃O₄ precursor are hybrid fcc-hcp structures with high concentration of stacking faults that are support dependent. As mentioned above, predominately hcp-Co NPs can be prepared when a reduction – carburization – reduction (RCR) activation protocol is followed. However, to achieve the best catalytic properties, carbon produced during the carburization (CO disproportionation) step has to be minimized.

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

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

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, Sₐₘ = 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)₂·6H₂O 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 μm. More details on catalyst synthesis can be found in a different source.

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 surface and that rhenium does not contribute to the amount of hydrogen adsorbed. Re acts as a promoter increasing the exposed surface area of Co. The average cobalt metal particle size (d(Co₄⁺)) nm was calculated from the Co metal dispersion (D%) by assuming spherical, uniform Co metal nanoparticles with a site density of 14.6 atoms/μm².

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.

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 °C.
°C for the final measurement of X-ray diffractogram and X-ray absorption spectra.

X-ray absorption spectra were recorded at the Co K-edge (E = 7709 eV) using a double crystal Si (111) monochromator. The data collection was carried out in the transmission mode. Ion chamber detectors with their gases at ambient temperature and pressure were used for measuring the intensities of the incident (I₀) and transmitted (Iₜ) X-rays. Spectra from a cobalt foil (hcp) was used as Co¹⁰ reference. The energy calibration was done by measuring the spectrum of the cobalt foil with the energy of the peak of the first derivative as the edge energy (7709 eV). The Demeter software (0.9.24) from the Iffefit software package (Version 1.2.11) was used for the XAS data analysis.

X-ray diffractograms were obtained using two independent Si (111) monochromators. XRD data were collected using a wavelength of 0.505 Å. A Si (111) standard was used for beam calibration. 2D images were obtained from a Drexel 2923 two-dimensional CMOS X-ray detector and converted to normal diffraction patterns using the program FIT2D. An estimation of the mean cobalt crystallite size was obtained using the Scherrer formula on the average FWHM. Pattern decomposition by Le Bail method was applied with TOPAS v4.2 software.

**Fischer – Tropsch Synthesis**

The activation procedure and FTS were performed in a 10 mm i.d. steel tube fixed-bed reactor. One gram of calcined catalyst was diluted with twenty parts per weight of SiC (75–150 μm), in order to reduce the temperature gradients throughout the catalyst bed. Aluminium blocks were fixed around the steel tube reactors to improve the heat distribution in the axial direction, and the reactors were placed in a furnace. Three thermocouples along the catalyst bed were used for temperature monitoring and control. Calcined catalyst followed a multistep activation procedure consisting of the following steps. A primary H₂ reduction (R) was performed at 350°C for 10 h with a ramping rate of 60 °C/h. The first reduction step was identical for all samples. It is noted that the reference sample (REF) underwent only the first reduction step in H₂ before FTS. A carburization step (C) of the metallic nanoparticles followed. During carburization the reduced catalyst was exposed to pure CO (250 mL·min⁻¹·gcat⁻¹), at 230 °C. The reactor was first pressurized with Ar to 14 bar. Then CO was introduced by replacing the Ar flow gradually, in order to keep the temperature increase in the catalyst bed below 2 °C during the carburization. Carburization lasted 3 hours with the exception of the 350° catalyst that was exposed at 14 bar CO for 6 hours. Finally, prior to catalyst exposure at FTS conditions, a secondary H₂ reduction (R) was performed at different temperatures of 200 °C, 250 °C, 350 °C and 450 °C. The samples were treated with H₂ 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 air. FTS was performed at 210 °C and 20 bar pressure with a H₂/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% N₂, 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 ± 5% CO conversion in order to record selectivity data at a fixed conversion level. The selectivity data reported here are collected at similar conversion levels (46-48%) based on the analysis of C₃–C₅ hydrocarbons in the gas phase. Since the desired products are higher hydrocarbons, the selectivity is reported as C₃, and CH₄ selectivity.

**Data analysis and interpretation**

The selectivity results are discussed both in terms of absolute selectivities (C-atom based) and in terms of αCₙ values (i.e. chain-growth probabilities of Cₙ⁺ intermediates on the catalyst surface). The αCₙ values have been calculated according to the procedure reported elsewhere. The αCₙ values provide more comprehensive information regarding the FT mechanism, while the absolute selectivities are of more practical use. In the supporting information one can find a brief discussion on αCₙ values interpretation based on the knowledge obtained from conventional Co-based catalysts, as well as detailed information on TOF calculations.
3. Results and Discussion

The Co₃C/γ-Al₂O₃ precursor was decomposed at four different temperatures under H₂ atmosphere; 200°C (R200), 250°C (R250), 350°C (R350) 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)²⁰. 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 α₃ 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 temperatures 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 CO₂.⁴⁶ Apparently, there is similar FTS performance of the Co NPs with lattice carbon observed here and Co₂C. αC₁ and αC₄ probabilities show minimum values for these catalysts, as well as the C₄ selectivity (SC₄). 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) and R350B. Our previous thermogravimetric investigations on these carburized samples have shown negligible amount of carbon resistant to H₂ at 350°C.²⁹ 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, d₀₀₂ and c/a ratio in Figure 2 and Figure S2. Furthermore, the Co surface area of the R350B 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 αC₂ to αC₄ values above 0.9, which are the highest values for all the γ-Al₂O₃ supported catalysts (Table 1), resulting in the highest SC₄.
Table 1. FTS performance indicators: reaction rate (TOF), product selectivities (C\textsubscript{2}, CH\textsubscript{4}, C\textsubscript{2}-C\textsubscript{6}, CO\textsubscript{2}), olefin-to-paraffin ratios (α/p) and chain growth probabilities of C\textsubscript{n} (αC\textsubscript{n}, n = 1 - 4) for carbide decomposed at 200°C to 450°C together with conventional catalyst (REF, Co\textsubscript{3}O\textsubscript{4} activated by H\textsubscript{2}). FTS was performed at 210°C, 20 bar and H\textsubscript{2}/CO ratio of 2.1. Reaction started at 15000 Nm\textsuperscript{3}/gcat and adjusted to give 50±1 % CO conversion after 24 h; selectivity C\textsubscript{2} was measured at 47±1 % CO conversion after approximately 48 h on stream. Hydrocarbon selectivities are reported on a CO\textsubscript{2}-free basis.

<table>
<thead>
<tr>
<th>Samples</th>
<th>n mol CO\textsubscript{2}·mol\textsuperscript{-1}H\textsubscript{2}</th>
<th>TOF s\textsuperscript{-1}</th>
<th>TOF XRD based on \textsuperscript{[17]}</th>
<th>Cr\textsubscript{2}</th>
<th>CH\textsubscript{4}</th>
<th>C\textsubscript{2}-C\textsubscript{6}</th>
<th>CO\textsubscript{2}</th>
<th>α/p</th>
<th>αC\textsubscript{1}</th>
<th>αC\textsubscript{2}</th>
<th>αC\textsubscript{3}</th>
<th>αC\textsubscript{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>REF</td>
<td>0.044</td>
<td>0.049</td>
<td>0.062</td>
<td>82.1</td>
<td>8.6</td>
<td>9.3</td>
<td>0.18</td>
<td>0.10</td>
<td>2.32</td>
<td>1.38</td>
<td>1.09</td>
<td>0.73</td>
</tr>
<tr>
<td>R200</td>
<td>0.047</td>
<td></td>
<td>0.059</td>
<td>79.9</td>
<td>10.2</td>
<td>9.9</td>
<td>0.27</td>
<td>0.14</td>
<td>2.87</td>
<td>1.77</td>
<td>1.46</td>
<td>1.02</td>
</tr>
<tr>
<td>R250</td>
<td>0.046</td>
<td></td>
<td>0.058</td>
<td>81.1</td>
<td>9.8</td>
<td>9.1</td>
<td>0.22</td>
<td>0.15</td>
<td>3.07</td>
<td>1.92</td>
<td>1.70</td>
<td>1.25</td>
</tr>
<tr>
<td>R350\textsuperscript{*}</td>
<td>0.083</td>
<td>0.090</td>
<td>0.104</td>
<td>87.8</td>
<td>6.8</td>
<td>5.5</td>
<td>0.11</td>
<td>0.19</td>
<td>3.06</td>
<td>1.89</td>
<td>1.64</td>
<td>1.11</td>
</tr>
<tr>
<td>R450</td>
<td>0.065</td>
<td></td>
<td>0.081</td>
<td>85.2</td>
<td>7.9</td>
<td>6.9</td>
<td>0.16</td>
<td>0.18</td>
<td>3.18</td>
<td>1.91</td>
<td>1.63</td>
<td>1.19</td>
</tr>
</tbody>
</table>

\textsuperscript{*R350\textsuperscript{*} has a doubled carburization duration of 6 hours in comparison to other samples.}

\[\text{Crystallite size [nm]}\]

\[\text{Particle size [nm]}\]

\[\text{DOR XANES [%]}\]

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

<table>
<thead>
<tr>
<th>Samples</th>
<th>Crystallite size [nm]</th>
<th>Particle size [nm]</th>
<th>DOR XANES [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>REF</td>
<td>13.2\textsuperscript{*}</td>
<td>13.0 nm</td>
<td>-</td>
</tr>
<tr>
<td>R200</td>
<td>13.1</td>
<td>-</td>
<td>89±3</td>
</tr>
<tr>
<td>R250</td>
<td>13.5</td>
<td>-</td>
<td>92±3</td>
</tr>
<tr>
<td>R350</td>
<td>14.0</td>
<td>12.8 nm</td>
<td>95±3</td>
</tr>
<tr>
<td>R450</td>
<td>14.4</td>
<td>-</td>
<td>98±3</td>
</tr>
</tbody>
</table>

\textsuperscript{*from Co\textsubscript{3}O\textsubscript{4} due to theoretical oxygen loss d(Co) = 0.8 x d(Co\textsubscript{3}O\textsubscript{4}).}

\textsuperscript{**evaluated from H\textsubscript{2} chemisorption dispersion (D) measurements according to d(Co)=96.2/D%\textsuperscript{[20]}.}

In addition, transmission electron microscopy (TEM) studies on reduced Re/Co/γ-Al\textsubscript{2}O\textsubscript{3} FTS catalysts activated by H\textsubscript{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 NPs\textsuperscript{[23]}. 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 kink\textsuperscript{[9]}. FTS performance indicators for the R450 catalyst are approaching the ones for the R350 catalysts, yet with reduced value of SC\textsubscript{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.

\[\text{Figure 2. Structural evolution obtained from refinement of in situ TPR-XRD (a) d spacing of 013 hcp-Co reflection and (b) c/a lattice parameters ratio from Le Bail refinement during TPR.}\]
Overall performance indicators \( (I_{\text{CO}}, SC_{\text{r}}, \alpha/p \text{ and chain growth probabilities } \alpha C_{\alpha}) \) of the catalysts originating from the Co\(_2\)C 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 phases\(^{54}\), 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 layer\(^{55}\). 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 H\(_2\)O are assisting the CO scission process\(^{59-61}\) and therefore adjacency is needed. On a different perspective, if the reaction mechanism involves merely the highly coordinated surfaces\(^{62}\) a less disrupted surface will as well be of benefit for the reaction.

Figure 3. SC\(_{\text{r}}\), related performance indicators in comparison with relevant literature. Co and CoRe NPs prepared by IWI on γ-Al\(_2\)O\(_3\), δ-Al\(_2\)O\(_3\) and α-Al\(_2\)O\(_3\) at (210 °C, 20 bar, \(H_2/CO\) ratio of 2.1 and 47.5±2 % CO conversion) obtained from reference therein.

Selectivities to higher hydrocarbons of the category B and C catalysts deriving from the Co\(_2\)C precursor are comparable to selectivities that are achieved by less interacting and low surface area supports such as α-Al\(_2\)O\(_3\), TiO\(_2\) and partly SiO\(_2\)\(^{64}\). A comparison of the obtained data with respect to performance of conventionally prepared (i.e. by \(H_2\) reduction of Co\(_2\)O\(_4\) precursors) Al\(_2\)O\(_3\) 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 \(\alpha C_{\alpha}\) values as well as SC\(_{\text{r}}\) (Figure S3, Table S1). Similar correlations have been found for conventional catalysts\(^{64}\) and suggest that the concentration of the monomer on the cobalt surface, the \(CH_x\) pool (\(\theta_{CH_x}\),
dictates the higher $\alpha_{C_n}$ values via a monomer surface-crowding mechanism\textsuperscript{65}. Furthermore, the data from REF (higher $\alpha_{C_n}$ values vs. TOF) fall more or less on the same trendlines, suggesting Co phase independent relationships. In addition, RCR catalysts show significantly lower $\alpha_{C_1}$ values ($\sim 0.52 – 0.57$) compared to the higher $\alpha_{C_2}$ values ($> 0.8$) just as conventional Co-based FT catalysts do so \textsuperscript{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$_2$ (Figure 3a) that has been previously found for conventional Co-FTS catalysts \textsuperscript{67}. 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 (±2σ, see supporting information) and actual differences in $\alpha_{C_1}$ ranging from 0.52 to 0.57\textsuperscript{44}. Here, values from B and C category catalysts with the $\alpha_{C_1}$ 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 $\alpha_{C_1}$ (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 $C_2$ to $C_6$ hydrocarbons are reaching very high values (Figure 4a), higher than normally observed even with less interacting large-pore supports\textsuperscript{21,44}. In particular, the R350 catalysts have twice as high $C_2$ o/p ratio compared to the REF, while the $C_2$ hydrocarbons at 47% CO conversion reach remarkable o/p values above 3, rarely seen in γ-Al$_2$O$_3$ supported catalysts\textsuperscript{48} at such conversion levels and then only after H$_2$O addition \textsuperscript{22,64} (Figure 4b). Since $C_2$ and $C_1$ o/p ratios are fair indicators of the relative hydrogen coverage ($\theta_H$) on the cobalt surface\textsuperscript{69}, we propose that the catalysts with hcp-Co NPs have a lower $\theta_H$ than the conventionally activated catalyst. A further indication of this is seen in the relatively high $\alpha_{C_2}$ and $\alpha_{C_3}$ values of the category A catalysts. Despite having lower SC$_5$, and similar TOF as the REF, the $\alpha_{C_2}$ and $\alpha_{C_3}$ values are markedly higher than those of the REF. The connection between $\alpha_{C_2}/\alpha_{C_3}$ and $\theta_H$ is explained in Supporting Information.

Exceptions from the observed improved performance of the hcp-Co NPs are found for the $\alpha_{C_1}$ 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 $\alpha_{C_n}$ values ($n > 1$) and $\alpha_{C_1}$ has been found\textsuperscript{44}. 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. $\alpha_{C_n}$, and TOF), while $\alpha_{C_1}$ is invariant (the exception is category A catalysts that exhibit a reduction in $\alpha_{C_1}$). The fact that $\alpha_{C_1}$ does not follow an inverse relationship with higher $\alpha_{C_n}$ values, but rather stays the same, could possibly be explained by a counteracting effect of a lowered $\theta_H$.

Figure 3b shows the effect of conversion level on SC$_5$. It appears that indigenous H$_2$O$_(g)$ has a stronger positive influence on SC$_5$, for the catalysts reduced at moderate temperatures (Category A), when compared with literature values\textsuperscript{22,61}. $\alpha_{C_1}$ to $\alpha_{C_4}$ chain growth probabilities on these catalysts increase significantly at higher conversions (Table 2S). From the above and the observed reduction in CO$_2$ production with time on stream (Figure 5S) a partial removal of carbon by H$_2$O 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 surface\textsuperscript{55}. Lattice carbon residues appear to interact and alter the properties of the Co surface resulting in a surface with the lowest $\alpha_{C_1}$ and $\alpha_{C_4}$ probabilities. The low $\alpha_{C_4}$ can be related to the lower apparent TOF, compared to the other RCR catalysts, resulting in a lower coverage of CH$_x$. The $\alpha_{C_4}$ is the single chain growth probability that is most affected by: changes in operating conditions \textsuperscript{67,69,70}, the presence of mass transfer limitations on reactant arrival\textsuperscript{72}, and the presence of “pure methanation” sites\textsuperscript{67}. A high $\theta_H$ mass transfer limitations and “pure methanation” sites would generally result in a lowered $\alpha_{C_1}$. All catalysts in the present study have particle size less than 90 μm and are subjected to identical conditions. In addition, judging from their high o/p ratios and high $\alpha_{C_2}$ and $\alpha_{C_3}$ values, high $\theta_H$ does not seem probable. Instead, “pure methanation” sites can be postulated and are indeed supported by the high CH$_4$ 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.
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 NPs. 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 reactions. 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 steps. 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 stress. 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. We speculate that part of the additionally formed cus is poisoned by strong CO adsorption while a portion is providing H₂ dissociation increasing δs. The additional supply of H is expected to negatively affect the propagation rates as seen in αC₂ and αC₃ for the R450 catalyst. Furthermore, creation of planar defects may divide the NP in such a way that mobility of the CH₄ monomer is hindered. Previous STM studies have shown that Co surface reconstructs under syngas exposure 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 addition 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 αC₁ 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 SC₃ (7%) and C₃ o/p ratio (10%) is apparent followed by a slight increase in higher alpha values (αC₃), (Figure 6S). Similarly to the γ-Al₂O₃ analogue, suppression of the CH₄ and CO₂ is also observed (Figure S6).
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 Co_NPs 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) Formation of catalysts with high Co loadings for maximizing catalyst productivity, minimizing process volume and potentially facilitating intensified process applications¹⁶,⁷⁸.

- 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 (αC₅). This is ascribed to a higher population of CH₄ that might derive from a higher intrinsic activity or accommodation of higher number of active sites.
- Apparently, chain growth over Co NPs follows a CH₄ monomer surface-crowding mechanism independently of the nanoparticle crystalline phase, with evidenced, to a first approximation, relationships between higher αC₅ and TOF.
- The exposed Co surfaces on hcp-Co NPs seem to have a lower relative hydrogen coverage θₜ than their highly faulted fcc-Co counterparts, resulting in higher o/p ratios and in lower relative termination rates of C₂* - C₄*- 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 αC₅ and selectivity toward CH₄.
- Structural faults have a negative impact on SC₅, and TOF. The results point to an enhanced capacity of the CH₂ 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 CO may explain part of the increased relative propagation rates of lower carbon number surface intermediates.

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:

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4. Conclusions

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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 SCα, 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 Cn* surface intermediates (the αCn values) together with figures on structural similarity, structural changes during TPR, TOF, change of performance indicators from period of similar GH5W to similar conversion level, comparison of RCR response on Re/CoAl2O3 and Co/Al2O3 and deactivation with time on stream are given in supporting information.

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