

# Evaluation of re-oxidation thresholds for $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported cobalt catalysts under Fischer - Tropsch synthesis conditions

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**ABSTRACT:** Size dependent phenomena at the nanoscale influence many applications, notably in the science of heterogeneous catalysis. In cobalt based Fischer – Tropsch synthesis, the size of Co nanoparticles dictates to a high degree catalysts performance in terms of activity, selectivity and stability. Here, a highly dispersed Re/Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with high Co surface area per gram of catalyst was exposed to industrially relevant Fischer-Tropsch synthesis conditions and monitored *in situ* by synchrotron X-ray radiation. X-ray absorption near edge structure spectra were obtained on cobalt K edge and Re L<sub>3</sub> edge of the working catalyst. The experimental results demonstrate development of tetrahedrally coordinated Co<sup>2+</sup> forming at the expense of metallic Co<sup>(0)</sup>. The structure of the oxide resembles CoAl<sub>2</sub>O<sub>4</sub> and appears at the onset (first 5-10 h) of the reaction. Re-oxidation of Co<sup>(0)</sup> is more pronounced close to the outlet of the reactor, where higher p<sub>H<sub>2</sub>O</sub> is anticipated. The state of the Re promotor does not change during the FT process. We propose that re-oxidation of small Co nanoparticles is followed by spreading of Co oxide that leads to the formation of Co<sub>x</sub>Al<sub>y</sub>O<sub>z</sub> phases. Hence, in order to avoid irreversible loss of active phase during process start-up, catalyst design should be restricted to Co nanoparticles larger than 5.3 nm.

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## 1. Introduction

Properties of nanoparticles (NPs) often exhibit strong size dependency at the nanoscale and understanding such relations has significant impact on heterogeneously catalyzed processes<sup>1</sup>. Rational design of heterogeneous catalysts based on fundamental understanding of NP properties is necessary for improving efficiency of chemical processes<sup>2</sup>. A sound example of chemical process complexity that requires rational catalyst design for successful application is the Fischer–Tropsch synthesis (FTS). In FTS catalyzed by cobalt NPs, synthesis gas (a mixture of CO and H<sub>2</sub>) is converted into high quality hydrocarbons that can be further upgraded to ultra clean fuels and chemicals. In the recent years the process has attracted both academic as well as industrial interest due to the alternative that offers for production of hydrocarbons from non-petroleum feedstock's such as natural gas, coal, and biomass<sup>3,4</sup>.

Commonly, industrial FT catalysts consist of Co NPs dispersed on different refractory metal oxides, including TiO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, doped with structural and reduction promoters<sup>5</sup>. High surface area supports like  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are utilized for enhancing dispersion and maximizing available surface area of the active component. FTS has one of the most

complicated chemical reaction environments, counting hundreds of products and intermediates deriving from surface oligomerization of CH<sub>x</sub> building blocks, while high partial pressures of steam (p<sub>H<sub>2</sub>O</sub>) are co-produced, rendering the reaction chemistry a challenging topic.

Structure sensitivity of the reaction limits the dispersion of the Co<sup>(0)</sup> active phase up to a threshold where activity (6 nm)<sup>6-9</sup>, selectivity to higher hydrocarbons (8-9 nm)<sup>10</sup> and catalyst stability are not influenced<sup>11</sup>. In addition to the Co particle size sensitivity, the reaction is sensitive to the crystal structure of Co NPs<sup>12,13</sup> and the characteristics of the support<sup>14</sup>. Catalyst deactivation also appears more pronounced at high Co dispersions, while promoters may have a significant contribution to the observed deactivation rates<sup>15</sup>. Investigations of catalyst deactivation in such a complex and sensitive process have led to suggestions of different mechanisms<sup>11,16</sup>; the main ones being sintering, carbon formation and re-oxidation of Co. The latter has been a topic of scientific debate for the last 20 years<sup>15,17-20</sup>.

Former investigations on Co re-oxidation have been conducted primarily by comparison of the state of activated against spent catalysts<sup>11</sup>. However, the added uncertainty of *ex situ* experimentation, together with air sensitivity of the activated material and the FT-wax covering the spent

catalyst, creates a demanding catalyst characterization subject. Therefore, recent research has turned towards the equally challenging but more reliable *in situ* characterization at working conditions. The techniques that have been successfully applied for monitoring the state of Co *in situ* are X-ray absorption near edge structure (XANES), X-ray powder diffraction (XRPD), magnetic methods and Mössbauer Spectroscopy<sup>21–24</sup>. Among them, XANES is the most sensitive to the oxidation state and co-ordination geometry of the absorbing atom, and it can give quantitative estimations of the involved phases<sup>25</sup>.

In the present study, a highly dispersed Re/Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with known particle size distribution (PSD) and an average Co NP size of 6.2 nm has been exposed to common benchmarking FTS conditions similar to that encountered inside an industrial reactor. Synchrotron based X-ray radiation was utilized for *in situ* monitoring the state of the active phase and promoter of the working catalyst in order to shed light on to phase transformations occurring during start-up and first day on stream.

## 2. Experimental & Analysis protocols

The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported catalyst consists of 20 wt% Co and 0.5 wt% Re. It has been prepared by incipient wetness impregnation of a high surface area  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (186 m<sup>2</sup>/g, Puralox SCCa from Sasol GmbH) with a solution of cobalt nitrate and perrhenic acid in a mixture of H<sub>2</sub>O and ethylene glycol added in a ratio of 0.9. After impregnation, the catalyst was dried (110 °C) for 3 h and calcined (300 °C) for 16 h. Sieved catalyst fractions of 53–90  $\mu$ m were used for the experiment.

Transmission electron microscopy (TEM) measurements were performed with a JEOL 2010F instrument, operating at 200 kV accelerating voltage. The catalyst was reduced in a reactor cell at identical conditions to those applied in the *in situ* synchrotron experiment. The cell was purged with Ar transferred and opened in a glove box. Subsequently, the reduced catalyst was prepared by dispersion on a carbon supported Cu mesh grid and then transferred to the TEM using a dedicated transfer holder. Particle size measurements were performed by direct measurements on the annular dark field STEM images using ImajJ. The longest radius of the NPs on a sample of 222 Co NPs was measured to derive the particle size distribution. The contrast between nanoparticles and support was variable, due to differences in thickness of the crushed fragments and overlap of projected images of neighboring particles. Care was taken to measure catalyst particle where it was judged that they could be observed individually with good atomic number contrast, bright relative to the support.

The *in situ* XANES experiment was performed at Station BM01B of the Swiss-Norwegian Beamlines (SNBL) located at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. X-ray absorption spectra were recorded at the Co K edge ( $E_0 = 7709$  eV) and Re L<sub>3</sub> edge ( $E_0 = 10535$  eV) by using a double crystal Si (111) monochromator. Data collection was carried out in transmission mode. Gas filled ion chamber detectors at ambient temperature and pressure were used for measuring the intensities of the incident

( $I_0$ ) and transmitted ( $I_t$ ) X-rays. The Co K edge  $E_0$  is defined as 45% of the edge step, while the Re L<sub>3</sub> edge is defined as the maximum of the first derivative.

A quartz capillary based *in situ* cell was used in a set-up configuration similar to that described previously<sup>26,27</sup>, but modified to perform Fischer – Tropsch synthesis at realistic conditions. A detailed description of the set-up can be found elsewhere<sup>22,28</sup>. Initially, the calcined catalyst was diluted with one part of hexagonal boron nitride (h-BN) against three parts of catalyst and loaded into a quartz capillary (1 mm ID). High temperature epoxy glue was used to seal the capillary and the metallic parts of the cell. Prior to the experiment, the system was flushed with pure H<sub>2</sub> at 25 °C. Reduction of the catalyst followed at 400 °C with H<sub>2</sub> flow of 2.5 ml/min at pressure slightly above atmospheric. The heating rate was set to 3 °C/min. The temperature was held at the set-point for 4 h before returning to 180 °C under the flow of He (5 ml/min). At 180 °C the system was pressurized to 18 bar using He diluted synthesis gas (He:H<sub>2</sub>:CO = 1.5:2.1:1). When the pressure was reached, the flow rates were adjusted to reaction levels (He:H<sub>2</sub>:CO = 0.5:2.1:1). The temperature was then increased at 1 °C/min to 220 °C. The catalyst was kept on stream at the chosen conditions for more than 24 h, after which the synthesis gas feed was replaced by He. The system was cooled down to room temperature and depressurized where post mortem profile analysis was performed.

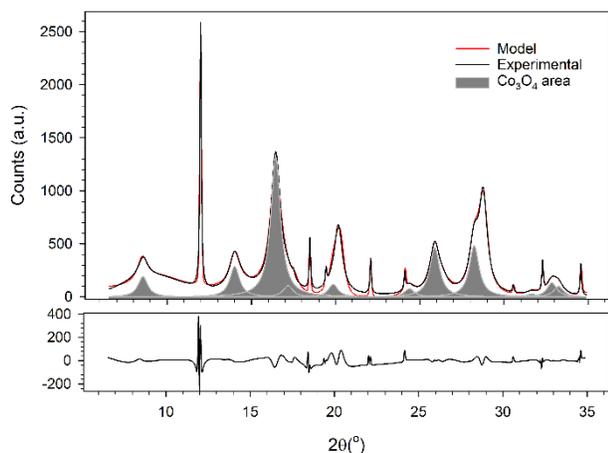
The Athena software from the Iffeffit software package (Version 1.2.9)<sup>29</sup> was used for the XAS (X-ray Absorption Spectroscopy) data analysis. Data sets were processed as a unit with the same background correction and normalization parameters. A rhenium foil (thickness 0.0125 mm) and ReO<sub>3</sub> powder were used as references for the Re L<sub>3</sub> edge. Spectrum from a cobalt foil (hcp) was used as Co<sup>(0)</sup> and powder samples of pure Co<sub>3</sub>O<sub>4</sub>, CoO (rock-salt type) and CoAl<sub>2</sub>O<sub>4</sub> were used as additional references. Co K edge XANES spectra were also simulated by the finite difference method and multiple scattering calculations. X-ray simulations were build using the finite difference method near-edge structure package FDMNES<sup>30</sup>. Identification and quantitative analysis of the Co phases has been done by a linear combination analysis (LCA) of first derivatives of normalized reference XANES spectra in the range -30 eV to +40 eV from the edge.

The commercially available Unscrambler X 10.2 software was used for the MCR-ALS (Multivariate Curve Resolution-Alternating Least Squares) data analysis. We have constrained the MCR analysis to non-negativity for normalized spectra and closure of concentration profiles. The number of pure components to be included in the MCR analysis was determined by PCA (Principal Component Analysis) analysis and examination of the S/N (Signal-to-Noise) and spectral structure of the components. A detailed description of application of MCR-ALS on full range XAS can be found elsewhere<sup>31</sup>.

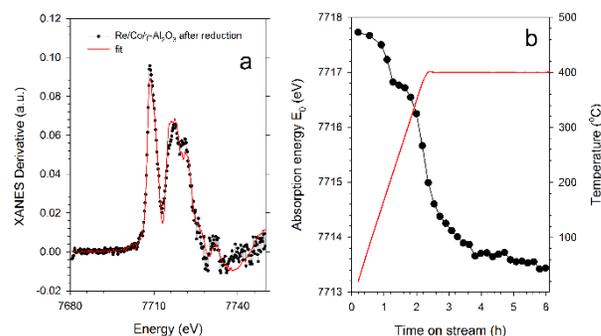
## 3. Results

Freshly calcined catalyst consists of  $\text{Co}_3\text{O}_4$  crystalline NPs, as detected by XRD (Figure 1), and Co K edge XANES (Figure 1s).  $\text{Co}_3\text{O}_4$  crystallites have an average size of 7 nm. The expected crystallite size of metallic Co NPs can be derived by taking into account shrinkage of the crystallites due to loss of oxygen from the lattice<sup>21</sup>, and it is estimated 5.6 nm. Lattice constants for cubic  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$  crystallites were found to be 7.9474 Å and 8.0939 Å, respectively. Particularly for the  $\gamma\text{-Al}_2\text{O}_3$  support, the unit cell appears significantly larger than that of the support before impregnation (7.9072 Å), suggesting that Co cation diffusion into the support is taking place during the calcination step<sup>32</sup>.

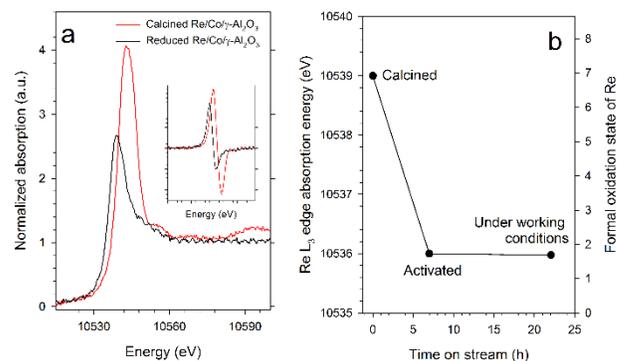
Co NP size analysis through  $\text{H}_2$  chemisorption on the reduced catalyst gave an average size of 5.2 nm (11.9% Co dispersion and 16  $\text{m}^2 \text{Co}^{(0)}/\text{g}$ ). The product of catalyst reduction was quantitatively evaluated by XANES at the Co K edge. Spectra obtained from the reference compounds were linearly combined in all possible combinations and the best fit obtained is depicted in Figure 2a. The final degree of reduction of the catalyst is 91 % (R-factor =  $2.20 \cdot 10^{-2}$ ,  $\chi^2 = 4.95 \cdot 10^{-3}$ ). During reduction the absorption edge ( $E_0$ ) drifts towards lower values, meaning that the average oxidation state is moving towards zero. The shift is initiated at relatively low temperatures, near 160 °C, and extends for 4.4 eV. The low reduction initiation temperature imply that in the present NPs the reduction process is initiated earlier, than for larger NPs for catalysts of similar composition<sup>22</sup>. In agreement with the TPR profiles of the two catalysts (Figure 1cS). A similar observation was made for Co NPs with bimodal size distribution supported on carbon based supports<sup>33</sup>.



**Figure 1:** Full profile fit of the diffraction pattern obtained from the h-BN diluted  $\text{Re}/\text{Co}/\gamma\text{-Al}_2\text{O}_3$  calcined catalyst (BM01A, ESRF  $\lambda=0.6978$  Å).



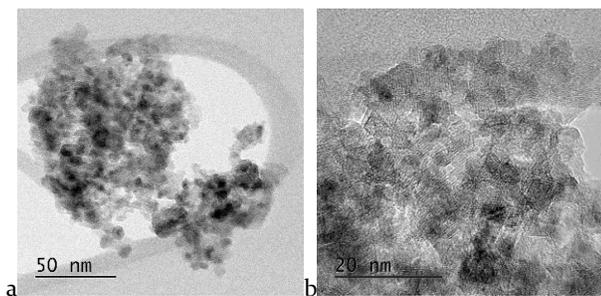
**Figure 2:** (a) LCA of the Co K edge XANES derivative spectra obtained at the end of reduction. (b) Shift in absorption edge  $E_0(t)$  throughout reduction under pure  $\text{H}_2$  (2.5 ml/min, 3 °C/min up to 400 °C and hold for 4 h).



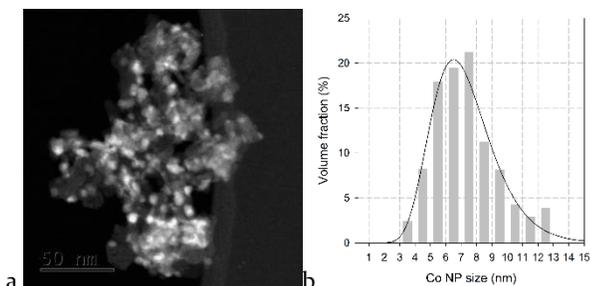
**Figure 3:** (a) Normalized XANES spectra at the Re  $L_3$  edge and their first derivatives (inset). (b) Shift in absorption edge  $E_0$  and average formal oxidation state of Re as evaluated from spectra obtained at different times on stream; before reduction (0 h, 25 °C), after reduction (7 h, 180 °C), during FTS at pseudo steady state (22 h, 220 °C)

In line with the known two-step reduction mechanism of  $\text{Co}_3\text{O}_4$  that passes through  $\text{CoO}$  intermediate phase, two distinct regions, with different reduction rates, can be seen (Figure 2b). In the first region the rate evens out at 250 °C ( $\text{Co}_3\text{O}_4$  to  $\text{CoO}$ ) and triggered again at 315 °C until it levels out after 2 h at 400 °C ( $\text{CoO}$  to  $\text{Co}^{(0)}$ ).

Comparison of rhenium  $L_3$  edge spectra obtained at the start and at the end of the reduction shows that the Re promoter has been partially reduced under the applied conditions Figure 3a. This is reflected in the decrease of “white line” intensity and simultaneous energy shift of approximately 3 eV that brings the  $E_0$  edge position very close to that of the reference foil. Combination of the two aforementioned spectral characteristics suggests that, although Re is predominantly metallic, part of it still poses a cationic nature, probably due to interaction with the support as has been demonstrated for monometallic  $\text{Re}/\gamma\text{-Al}_2\text{O}_3$  catalysts<sup>34</sup>. Since there is a linear relationship between the average formal oxidation state and the edge position<sup>35</sup>, an average oxidation state of +1.7 can derive. This value is maintained during the FTS reaction at the steady state; Figure 3b.



**Figure 4:** TEM image (a) and lattice resolution image (b) of the reduced catalyst after reduction at 400 °C for 4 h (3 °C/min).



**Figure 5:** (a) Annular dark-field scanning transmission electron microscopy image (ADF-STEM) of the catalyst after reduction at 400 °C for 4 h (3 °C/min). (b) volume-weighted Co NP size distribution of the activated catalyst together with a lognormal fit of the data.

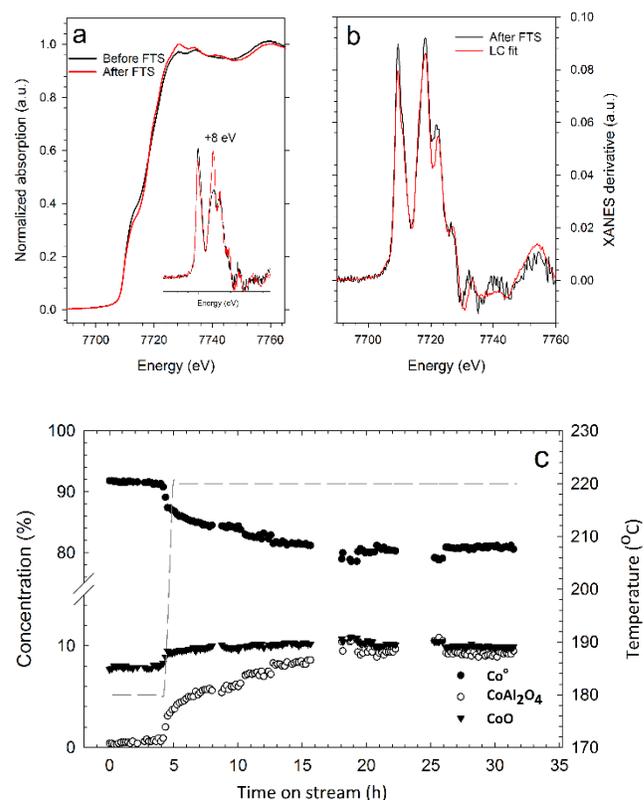
TEM analysis showed that Co NPs are finely distributed on the alumina support. The use of ethylene glycol during impregnation is known to allow a finer dispersion of Co on  $\gamma$ - $\text{Al}_2\text{O}_3$  inhibiting the formation of aggregates<sup>36</sup>. Such aggregates are absent in our standard TEM images; Figure 4a. Contrast consistent with a uniform distribution of Co particles is seen. Furthermore, the lattice resolution images show no evidence of any common crystallographic orientation of Co NPs after reduction (Figure 4b), that is usually seen in the  $\text{Co}_3\text{O}_4$  phase of the calcined catalyst<sup>37</sup>. Figure 5 shows an example of the ADF-STEM images used for particle size distribution measurements. The random distribution of the bright Co particles is evident in these images. The direct (number-weighted) particle size distribution was converted to its volume-weighted equivalent (Figure 10S). X-ray analysis gives a volume-weighted rather than a number-weighted or surface-weighted average<sup>38</sup>, Therefore a volume-weighted distribution is expected to better correlates with the obtained average values from XANES spectra representing more precisely the sample. It should be mentioned here that atomically dispersed Co phases are not visible in such electron microscopy images and thus are not included in the obtained PSD.

The activated catalyst combines a high degree of reduction (91 %) together with high dispersion of the active phase (11.9 %) at high Co loadings (20 wt%), utilizing most of the catalytically active component.

**Fischer – Tropsch synthesis.** After catalyst activation the system was cooled to 180 °C and pressurized. When the

set-point pressure was reached, flows were adjusted and the temperature was increased at a rate of 1 °C/min to 220 °C. Subsequently FTS was performed for several hours. Estimation of the conversion level and the average reactor environment was done by comparison of the  $\text{Re}/\text{Co}/\gamma\text{-Al}_2\text{O}_3$  catalyst with a reference catalytic material of the same composition that had been tested at identical conditions in lab-scale fixed bed reactor as well as in the *in situ* cell<sup>22</sup>. Despite their differences in dispersion (8.5% vs. 12%), the two catalysts exhibit similar activity ( $r_{\text{CO}} = 0.53 \text{ mol CO/g}^*\text{h}$ ) as demonstrated in fixed-bed reactor tests. Identical reaction conditions were chosen for the two catalytic materials and the results were extrapolated so as to estimate the conversion level (Figure 2S). Consequently, CO conversion at the applied conditions inside the *in situ* cell is expected to reach 60-65% at *pseudo* steady state.

At the onset of FTS the reactor environment changes gradually. The initial dry conditions are followed by a significant shift in chemical potential with the formation of liquid products and high  $p\text{H}_2\text{O}_{(g)}$ . The prolonged induction period is possibly related to the implications that the change in chemical environment has on stabilization of the cobalt surface<sup>39,40</sup> and the gradual changes in diffusivity of products and reactants due to the formation of FT liquids<sup>41</sup>. Phase transformations and temperature stabilization issues may also interplay<sup>22,33</sup>.



**Figure 6:** (a) Normalized XANES spectra and their corresponding first derivatives obtained before and after FTS. (b) First derivative spectrum after FTS and its fit by linear combination of the Co foil, CoO and  $\text{CoAl}_2\text{O}_4$  bulk references. (c)

LCA from the sequence of first derivatives of Co K edge XANES spectra obtained during reaction.

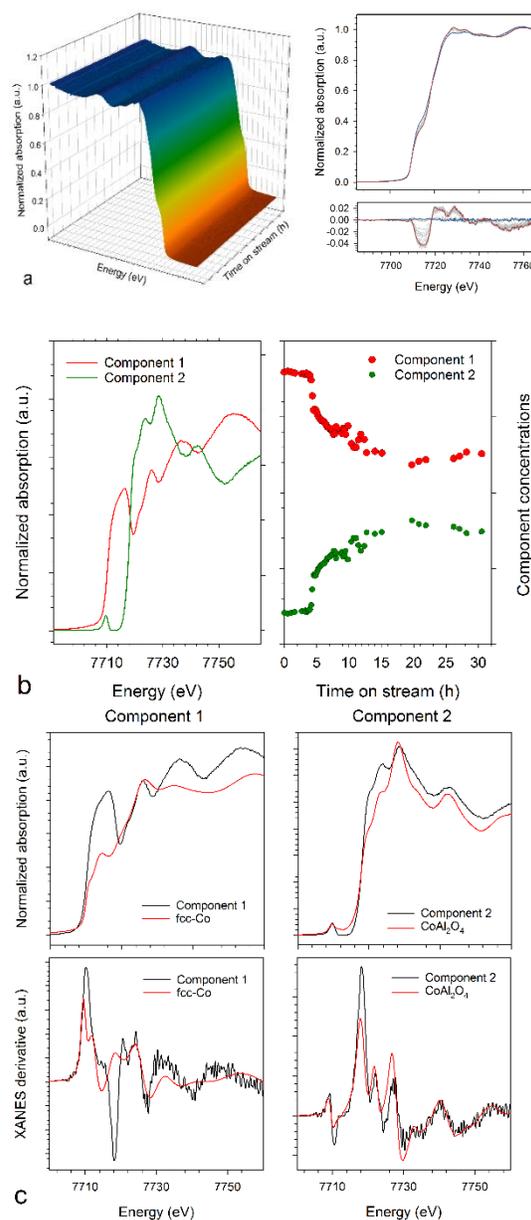
Comparison of Co K edge XANES spectra obtained before the start and at the end of FT reaction shows significant changes; see Figure 6a. In the normalized XANES spectra the “white line” formation together with suppression of the shoulder in the rising edge are evident. In the corresponding derivatives, a noticeable increase in the feature +8 eV (7717 eV) above the edge is seen. The observation suggests re-oxidation of cobalt into a phase rich in tetrahedrally co-ordinated ( $T_d$ ) divalent cobalt ( $Co^{2+}$ )<sup>42–44</sup>. Indeed, by observing the changes in absorption edge  $E_0$  a drift towards higher energies is observed (Figure 3S) supporting re-oxidation of  $Co^{(0)}$ . The drift during the onset period is intense and levels off approximately after 5 h, at the set-point temperature (220°C). Evidently, re-oxidation of Co NPs is taking place under the applied reaction conditions, but is limited only to the initial stages of the reaction.

Qualitative analysis by fitting and following representative features of the XANES derivatives for  $Co^{(0)}$  (7709 eV),  $CoAl_2O_4$  (7718 eV) and  $CoO$  (7722 eV) by Voigt functions shows significant changes of the derivative spectrum throughout FTS (Figure 3S). The growth of both features at 7718 and 7722 eV with time is demonstrated, while the feature corresponding to  $Co^{(0)}$  near the absorption energy (7709 eV) is decreasing. Results are in line with our previous observations<sup>22</sup> on a similar Co/Re/ $\gamma$ - $Al_2O_3$  catalyst with 10 nm average NP size, but much more pronounced, allowing a clear detection of the re-oxidation phenomenon. All characteristic features of the XANES spectra i.e.  $E_0$ , white line and resonances; point towards re-oxidation of  $Co^{(0)}$ .

Quantitative LCA utilizing Co K edge XANES spectra from bulk materials was used to reconstruct the derivative spectrum obtained after FTS (80%  $Co^{(0)}$ , 12%  $CoO$  and 8%  $CoAl_2O_4$ , R-factor =  $1.67 \cdot 10^{-2}$ ,  $\chi^2 = 3.00 \cdot 10^{-3}$ ); Figure 6b. Co foil,  $CoAl_2O_4$  and  $CoO$  were chosen as representative standards as derived from PCA in combination with target transformation (Figure 6S). In agreement with qualitative analysis, the output of the linear combination shows that 12% of  $Co^{(0)}$  is consumed in favor of the formation of a  $Co^{2+}$  oxide. Consequently, the concentrations of  $CoAl_2O_4$  and  $CoO$  increase during the FT process, with the first being the major developing phase (Figure 6c). LCA on the full data set describes the kinetics of the transformation, yet not all features of the derivative spectra could be reproduced during the fit. The difference between the formed compounds at the nanoscale against the bulk crystalline standards might explain the mismatch. Hence, a chemometric approach was applied in order to overcome this discrepancy.

Multivariate curve resolution-alternating least squares (MCR-ALS) has been used traditionally to treat vibrational spectroscopy data<sup>45,46</sup> and only recently on X-ray absorption spectroscopy data<sup>3</sup>. The MCR-ALS chemometric analysis has been applied to the acquired data-set combined with *ab initio* simulations of Co XANES spectra at K edge. Through MCR-ALS statistics of the fit and analysis time are

significantly improved since the full data matrix is analyzed as a unit, instead of analyzing single spectra. Thus, MCR is more suitable for large datasets providing faster output<sup>3</sup>, while the acquired components are allowed to relax within meaningful physicochemical constrains, such as non-negativity and closure (summation to 1 of the concentration profile), potentially supplying input on the mechanism and structure of the evolved phases. Both reference assisted (Figures 8S) and blind source analysis were used (Figures 9S).



**Figure 7:** (a) 3D plot of normalized Co K edge XANES spectra obtained during reaction and normalized Co K edge XANES spectra obtained during reaction and their difference ( $\Delta$ XANES). (b) MCR-ALS output with the corresponding extracted components of the blind source analysis and the dimensionless component concentrations. (c) Comparison of normalized and first derivatives of components 1 and 2 with

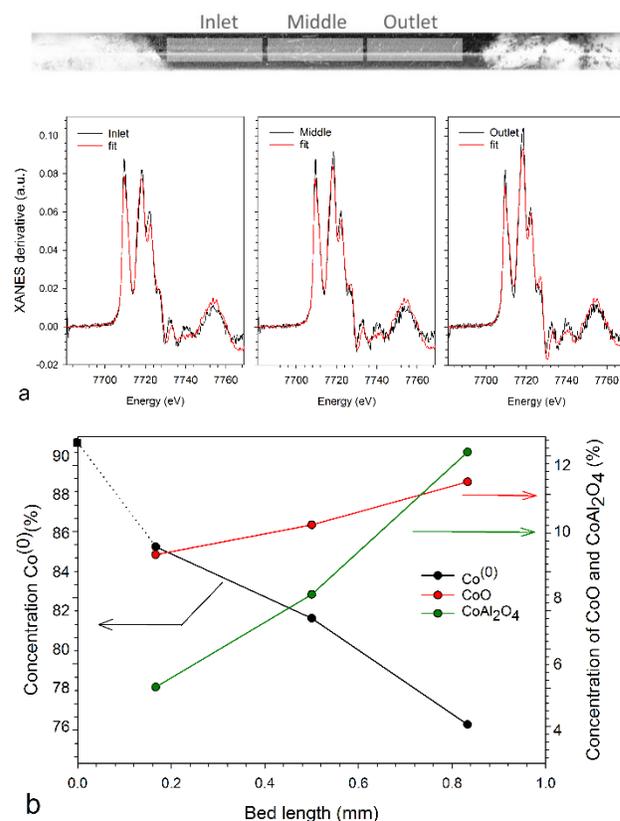
simulated spectrum of fcc-Co, by the finite difference method, and powder  $\text{CoAl}_2\text{O}_4$  reference, respectively.

Blind source analysis was applied to a matrix consisting of 163 spectra from pressurization, on-set and steady state FTS. The output of blind source analysis of the matrix is given in Figure 7. PCA analysis suggests that the data set can be decomposed into two main components. The contribution of a third component appears minor with increased noise levels (Figure 5S and Figure 6S). Comparison of the components with simulated and reference spectra shows strong similarities of the components with metallic Co and  $\text{CoAl}_2\text{O}_4$ . In particular, the first component shows spectral features similar to the ones found at  $\text{Co}^{(0)}$  in a face-centered cubic (fcc) configuration Figure 7c. It is well accepted, mainly from *in situ* XRD studies, that fcc-Co is the dominating crystal structure of Co NPs that have a size <20 nm and produced by  $\text{H}_2$  reduction of  $\text{Co}_3\text{O}_4$  NPs<sup>47</sup>. Contributions from other possibly existing phases like hcp-Co and rocksalt-CoO are probably part of the extracted component. For the second component, it becomes apparent that the formed phase clearly resembles in detail the  $\text{CoAl}_2\text{O}_4$  structure; see Figure 7c. Both characteristic features of the  $T_d$  coordination, i.e. the pre-edge peak that corresponds to  $1s \rightarrow 3d$  transition, and electron resonances after  $-8$ -9 eV are found in the component, with especially the second to be more pronounced<sup>25</sup>.

An equally good fit is obtained when the components are compared with the metal-support mixed oxide phases ( $\text{Co}_x\text{Al}_y\text{O}_z$ ) produced by the reduction of calcined  $\gamma\text{-Al}_2\text{O}_3$  impregnated with low loadings of Co (3 wt%). Comparison with the simulated wurtzite-CoO that is composed solely from  $\text{Co}^{2+}$  ( $T_d$ ), nor any other of the references (acquired or simulated) cannot describe the obtained component in such detail (Figure 7S). Absorption edges of components 1 and 2 are located at 7710 eV and 7718 eV, respectively. Blind source analysis of the data-set by the MCR-ALS provides a further proof of the formation of a  $\text{CoAl}_2\text{O}_4$  like compound ( $\text{Co}_x\text{Al}_y\text{O}_z$ ) during the initial stages of FTS as the final product of re-oxidation. Observation of the extracted component concentrations shows clear loss of component 1 in favor of component 2. In accordance with the aforementioned LCA analysis, this result illustrates the transformation of a fraction of the activated catalyst, consisting of  $\text{Co}^{(0)}$  and CoO phases into a final  $\text{Co}_x\text{Al}_y\text{O}_z$  product. Contributions to the  $\text{Co}_x\text{Al}_y\text{O}_z$  formation are from  $\text{Co}^{(0)}$  that re-oxidizes under FTS conditions and possibly from unreduced CoO reacting with the support as previously proposed<sup>48</sup>.

At the integral conditions applied (high conversions) the environment in a plug-flow reactor is position dependent (exhibits concentration gradient). As such the outlet has higher  $p\text{H}_2\text{O}_{(g)}$ , therefore it describes better the reaction environment inside widely applied slurry bubble column reactors (SBCR). An attempt was made to evaluate possible concentration gradients in the catalytic bed of the quartz capillary reactor. Thus, with the assistance of automated slits the width of the X-ray beam was reduced to  $\frac{1}{3}$  and the different positions in the reactor were scanned (Figure 8). The first derivatives of the obtained Co K edge XANES

spectra clearly demonstrate a more oxidized catalyst towards the outlet of the catalyst bed. The feature at +8 eV after the edge is more pronounced while the feature at the edge position (7709 eV) is suppressed.



**Figure 8:** Post mortem profile analysis of the catalyst bed by Co-XANES at the K edge. (a) The obtained first derivatives together with the LCA fit of the inlet, middle and outlet of the reactor are shown. (b) Quantitative results from the LCA.

Similarly, normalized Co K edge XANES spectra show the “white line” formation. Our observation verifies a correlation of  $p\text{H}_2\text{O}_{(g)}$  and formation of  $\text{Co}^{2+}$  compounds. Indeed, LCA shows that the degree of reduction after FTS is significantly lower at the reactor outlet (Figure 8b). In addition, by the spatially resolved analysis the existence and growth of a CoO intermediate phase is identified.

#### 4. Discussion

From Co K edge and Re  $L_3$  edge XANES it is found that Co and Re species after activation resemble their corresponding zero-valent states. However, a small fraction of both elements preserves a positive charge, possibly due to strong interaction with the support. Furthermore, the current data-set provides *in situ* evidence on the formation of  $\text{Co}^{2+}$  ( $T_d$ ) at the initial stages of FTS performed at 220°C, 18 Bar and CO conversion in the order of 60%-65% ( $\text{H}_2:\text{CO}=2.1$ ). The transformation of  $\text{Co}^{(0)}$  to  $\text{Co}^{2+}$  is clearly visualized in the onset of FTS (5-10 h) and levels off in the timescale where the system is expected to be in equilibrium (*pseudo* steady state). Since the re-oxidation phenomenon is rapid and occurs only in the initial stages it is proposed that re-oxidation should not be associated with

catalyst deactivation<sup>49–54</sup>. Analogous observations were recently reported by X-ray absorption studies on *ex situ* obtained samples after catalyst activation and after the onset of FTS<sup>55</sup>. In addition, *in situ* magnetic measurements supported by *in situ* XRD during co-feeding of H<sub>2</sub>O<sub>(g)</sub>, simulating CO conversions of 77%, showed re-oxidation of small Co NPs<sup>23</sup>. Similarly, the observed re-oxidation was fast, lasting only a few hours. However, in both previous cases re-oxidation led to the formation of cubic CoO. Here the re-oxidation of the catalyst leads primarily to the creation of a phase similar to the CoAl<sub>2</sub>O<sub>4</sub> compound comprised predominantly of Co<sup>2+</sup> in tetrahedral coordination (T<sub>d</sub>), as has been detected previously *ex situ* on Pt promoted Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with similar extent of Co dispersion (11%)<sup>56</sup>. A small part of the oxide in (O<sub>h</sub>) Co<sup>2+</sup> coordination, resembling cubic CoO, is also detected. The already existing CoO after reduction possibly participates in the observed formation of Co<sub>x</sub>Al<sub>y</sub>O<sub>z</sub><sup>48</sup>. The concentration of both oxides is higher towards the outlet of the reactor evidencing the profound effect of pH<sub>2</sub>O in this transformation. In accordance, Lögdberg et al. reported a rapid irreversible deactivation of small Co particles when high partial pressures of steam were externally introduced<sup>57</sup>.

Stabilization of the wurtzite-CoO phase, rich in Co<sup>2+</sup> (T<sub>d</sub>) at Co NPs < 4 nm under different environments has been reported recently by different research groups<sup>58–60</sup>. Authors argued the postulated Co-mixed compound formation during FTS to be related to wurtzite-CoO (Figure 7S). In the current dataset obtained under realistic FTS conditions neither the fit from linear combination analysis nor reference assisted MCR-ALS gave better results when the simulated XANES spectrum of wurtzite-CoO was used. Similarly, re-oxidation during the induction period by C obtained from CO dissociation, that leads to Co<sub>x</sub>C assemblies where C is covering step sites, cannot explain the extent of the present observations<sup>39</sup>. In addition, the XANES signal of the re-oxidation product is far from known Co<sub>x</sub>C structures (Figure 7S).

Based on our observations a valid mechanistic scenario should fulfill two conditions. First is that the oxidation state is increasing from 0 to +2. Second, the final product of re-oxidation is predominantly a Co<sub>x</sub>Al<sub>y</sub>O<sub>z</sub> structure. The magnitude of the observation suggests the existence of a mechanism that involves easy transfer of Co allowing the contact of cations with tetrahedral vacancies or other reactive sites in the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Four different scenarios are discussed below.

(a) Static diffusion of Co atoms into the support<sup>61</sup> through the interphase between support and NPs cannot alone describe the scale of the phenomenon. By assuming hemispherical Co NPs lying on the support the interfacial area between the NPs and the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> can be calculated by dividing the Co surface area obtained by H<sub>2</sub> chemisorption (i.e. the area of the hemisphere  $2\pi r^2$ , where  $r$  is the radius) in half (since the base of the hemisphere has area equal to  $\pi r^2$ ). Thus, only 6% of the Co atoms are at the interphase of NPs and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. In addition, already during catalyst calcination<sup>61</sup> and reduction<sup>62</sup> the loss of Co through diffusion into  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is known to occur. Current Co K edge XANES

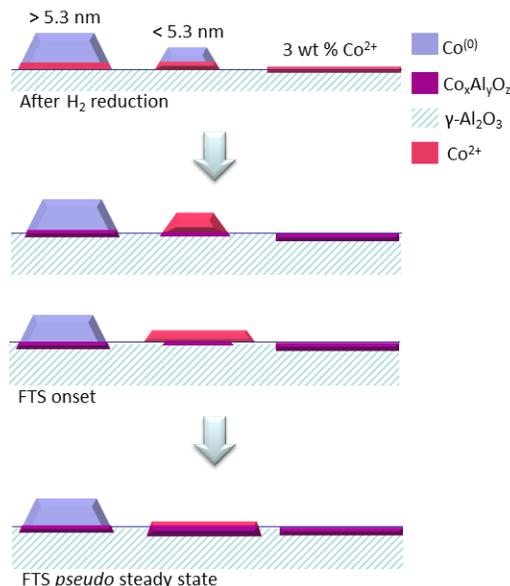
data show that the DOR of the activated catalysts is 91%, while lattice constants obtained by XRD show that  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the calcined Re/Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst has larger unit cell than of the material before the addition of Co. Both facts suggest that already in the activated catalyst there is a part of Co<sup>2+</sup> that strongly interacts with the support, setting the path of static diffusion inadequate to explain the extent of re-oxidation.

(b) Sole re-oxidation of cobalt surface can be ruled out since a catalyst with 12% dispersion (meaning surface Co atoms) would be completely inactive at such severe re-oxidation. This is not the case in the present catalyst, which exhibits similar activity to a catalyst with 8.5% dispersion. In addition, the final transformation of surface oxidized Co NPs into CoAl<sub>2</sub>O<sub>4</sub> is difficult to visualize.

(c) Ostwald ripening was proposed to occur at the first 10 h of FTS<sup>63</sup> on planar Co/SiO<sub>2</sub> model catalysts under dry syngas conditions. The authors demonstrated that particles < 5 nm decreased in size while the overall catalyst dispersion dropped. They suggested that Co forms sub-carbonyl monoatomic or small clusters that diffuse on the support and result in loss of total surface area. In such a scenario, especially for the initial reaction stage where  $p$ CO is at its maximum and temperature is comparably low to allow FT reaction ignition, sub-carbonyls could be favored. In addition, the highly defective surface of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support would be partially dehydrated and therefore very reactive. Co atoms or clusters diffusing over the surface of the support might be captured by the support forming a Co oxide or being re-oxidized by the conditions. This mechanism might contribute to the phenomenon, but profile analysis has shown that pH<sub>2</sub>O is more important than  $p$ CO, since the Co<sup>(o)</sup> loss is higher towards the end of the reactor where pH<sub>2</sub>O is maximized and  $p$ CO minimized accordingly.

(d) Finally, thermodynamic calculations have shown that bulk re-oxidation of Co NPs can occur at FTS relevant pH<sub>2</sub>O/ $p$ H<sub>2</sub> for Co NPs less than 4.4 nm in diameter<sup>64</sup>. In the current case conditions during the observed re-oxidation are milder (since steady state is not reached), yet dynamically capable of changing NPs energetics due to environmentally induced phenomena<sup>65,66</sup>.

In our view, the scenario of multilayer (bulk) re-oxidation followed by Co oxide spreading on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface, allowing ultimately the reaction of Co<sup>2+</sup> with the support, can explain the observations. Sub-carbonyl assisted diffusion, merely during the initial stages of FTS, cannot be excluded and might have a contribution until surface saturation of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with Co<sup>2+</sup>, while further ripening leads to particle growth<sup>67</sup>. Reaction-induced spreading is driven by the surface free energy difference of the NPs and support<sup>68–70</sup>. Spreading of CoO<sub>x</sub> species over TiO<sub>2</sub> support in relation to FTS has been discussed recently<sup>58,71</sup>. In our case, the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support in its partially dehydroxylated state after reduction has indeed higher surface energy<sup>72</sup>. The production of H<sub>2</sub>O<sub>(g)</sub> shifts the chemical potential inside the reactor and allows transformation of small metallic NPs to oxide forms.



**Figure 9:** Illustration of the proposed re-oxidation mechanism.

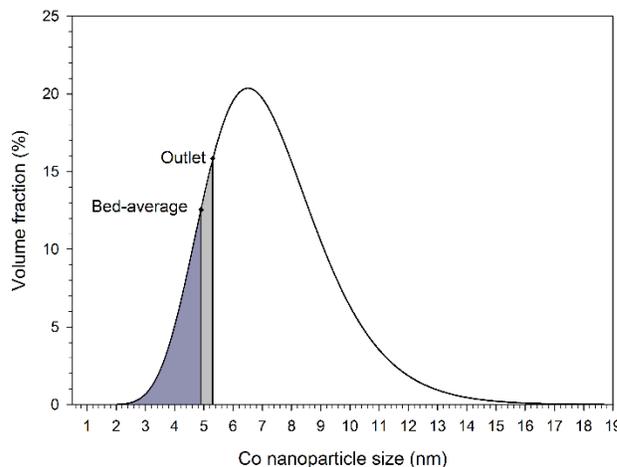
Provided that the surface energy of the oxide NPs is lower than that of the support, Co NPs may spread on the surface of  $\gamma\text{-Al}_2\text{O}_3$  and react forming sub-monolayers of mixed metal-support compounds  $\text{Co}_x\text{Al}_y\text{O}_z$  that resemble the  $\text{CoAl}_2\text{O}_4$  structure. Metal support interactions and strain are also known to affect the wetting/spreading properties<sup>68</sup>.

It is well accepted that  $\gamma\text{-Al}_2\text{O}_3$  catalysts with low Co loadings (3 %) lead to inactive materials<sup>73,74</sup>. Atomically dispersed Co shows epitaxial interactions with the support during aqueous impregnation that eventually leads to the formation of two-dimensional Co-Al oxide layered structures<sup>75,76</sup>. As already mentioned, highly dispersed Co-support phases are invisible by electron microscopic techniques meaning that they are not part of the Co PSD obtained by TEM. *In situ* X-ray diffraction has been used to probe them indirectly through the detection of their lattice expansion<sup>32,62</sup>. Here it is worth mentioning that an *in situ* XRD approach in the current case would give valuable input.

Based on the quantitative results that were obtained by the widely accepted LC fit, the establishment of a re-oxidation threshold can be structured as follows. In our case, it can be assumed that from the 9 % of cationic (+2) Co remaining in the reduced catalyst (from Co XANES) 6 % is due to interfacial interaction of the Co NPs with the support (from  $\text{H}_2$  chemisorption) and 3 % of Co is existing in monolayer form and therefore is not included in the PSD (following Refs. 71-74), as described in the previous paragraph. Accordingly, our XRD patterns of the reduced catalyst support the absence of standalone CoO particles (Figure 1S).

Therefore, it can be assumed that all the 91 % metallic  $\text{Co}^{(0)}$  is visible in TEM and by normalizing the continuous

PSD to 91 % the integrated area under the curve will correspond to the total number of TEM visible NPs. In our multilayer re-oxidation scenario the 12% loss of  $\text{Co}^{(0)}$  under benchmarking FTS conditions derives from the smallest  $\text{Co}^{(0)}$  NPs with size less than 4.9 nm (bed average) and less than 5.3 nm in the extreme outlet conditions (Figure 10). As such, the threshold for optimized design avoiding re-oxidation and Co-support compound formation  $\text{Co}_x\text{Al}_y\text{O}_z$  can be set close to 5.3 nm with a sharp PSD above that limit. The threshold might be underestimated for slurry bubble column reactor applications that perform under higher  $p\text{H}_2\text{O}$ , since the reaction environment is dictated by outlet conditions due to significant back mixing.



**Figure 10:** Re-oxidation of Co NPs supported on  $\gamma\text{-Al}_2\text{O}_3$  at the onset of FTS (220 °C, 18 bar, ~60% CO Conversion and  $\text{H}_2:\text{CO}=2.1$ ). Bed average re-oxidation threshold for Co NPs 4.9 nm (blue area) and re-oxidation threshold 5.3 nm for Co NPs at the outlet of the reactor (grey area).

## 5. Conclusions

We have provided experimental evidence on the re-oxidation of Co NPs by applying *in situ* synchrotron X-rays on a  $\text{Re}/\text{Co}/\gamma\text{-Al}_2\text{O}_3$  catalyst working at common FTS benchmarking conditions. Our data show that the highly dispersed Re promoted metallic Co NPs supported on  $\gamma\text{-Al}_2\text{O}_3$  partially re-oxidizes to  $\text{Co}^{2+}$  principally in the initial stages of the FT reaction. The formed  $\text{Co}^{2+}$  species adapt predominantly a  $\text{Co}_x\text{Al}_y\text{O}_z$  structure, while rocksalt-CoO species are detected to a minor extent. A positive correlation between  $\text{Co}^{2+}$  formation and  $p\text{H}_2\text{O}$  was observed after analysis of the reactor profile. It also becomes apparent that the reactivity of the  $\gamma\text{-Al}_2\text{O}_3$  support has a vital role in this phase transformation since the re-oxidation product is not the CoO structure, but a compound very similar to  $\text{CoAl}_2\text{O}_4$ . At the *pseudo* steady state FTS conditions neither metallic Co nor Re species are altered.

Finally, we have demonstrated that *in situ* X-ray spectroscopy significantly benefit from chemometric analysis like the MCR-ALS protocol applied here. The powerful combination of quantitative information obtained from a single *in situ* experiment and the size distribution obtained

by electron microscopy gives input to and assists in better catalyst design. In accordance, the minimum NP size in Co-based FTS catalysts, that are dispersed on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and contain a reduction promoter such as Re, has to be kept above 5.3 nm in order to avoid re-oxidation.

## ASSOCIATED CONTENT

**Supporting Information.** Contains additional experimental procedures, results from computations, Figures S1–S10, and Tables S1–S3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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