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In-situ X-ray Raman Scattering Spectroscopy of the Formation of Cobalt Carbides in a Co/TiO₂ Fischer-Tropsch Synthesis Catalyst

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KEYWORDS

X-ray Spectroscopy • Fischer-Tropsch Synthesis • Heterogeneous Catalysis • Cobalt Carbide • Catalyst Deactivation

ABSTRACT

We present *in-situ* experiments to study the possible formation of cobalt carbides during Fischer-Tropsch synthesis (FTS) in a Co/TiO₂ catalyst at relevant conditions of pressure and temperature. The experiments were performed using a combination of X-ray Raman scattering (XRS) spectroscopy and X-ray diffraction (XRD). Two different experiments were performed: (1) a Fischer-Tropsch Synthesis (FTS) reaction of a ~ 14 wt.% Co/TiO₂ catalyst at 523 K and 5 bar under H₂-lean conditions (i.e., a H₂:CO ratio of 0.5) and (2) carburization of pure cobalt (as reference experiment). In both experiments, the Co L₃-edge XRS spectra reveal a change in the oxidation state of the cobalt nanoparticles, which we assign to the formation of cobalt carbide (Co₂C). The C K-edge XRS spectra were used to quantify the formation of different carbon species in both experiments.

INTRODUCTION

Fischer-Tropsch Synthesis (FTS) technology enables the production of long-chain hydrocarbons as synthetic fuels from fossil (e.g., coal and natural gas) and renewable feedstock (e.g., biomass and municipal waste). In the FTS process, a mixture of carbon monoxide (CO) and hydrogen (H₂) is converted into different hydrocarbons by a catalytic surface polymerization reaction [1]. Iron and cobalt-based FTS catalysts are the most relevant for industrial applications, where Co-based catalyst is more used for processing syngas derived from natural gas and possesses a higher selectivity towards liquid hydrocarbons (C₅₊) [2,3]. However, the gradual deactivation of Co-based FTS catalyst materials is one of the main concerns in FTS research. The deposition of carbon species, typically called coke (e.g., graphitic, aliphatic or aromatic) onto the catalyst surface as well as the sintering of supported cobalt nanoparticles are the most significant aspects of

deactivation [4,5]. In addition, the formation of cobalt carbides (e.g., bulk, sub-surface and surface) derived from the carbon deposition is a controversial topic. Some studies correlate its formation with the deactivation process of the catalyst [6-8], while other groups relate it with a higher selectivity towards lower olefins [9,10], as an intermediate species during the FTS reaction [11,12], and an active species for the water-gas shift (WGS) reaction and oxygenate selectivity [13,14]. Clearly, more research is needed to resolve this debate in literature.

Advances of various *in-situ* and *operando* synchrotron techniques have resulted in comprehensive studies on the coke formation over TiO₂-supported cobalt catalyst during FTS reaction [15], the influence of Mn and Re as promotor elements on Co/TiO₂ and Co/Zr/SiO₂ FTS catalysts [16-18], the effect of the particle size and the formation of carbides on Al₂O₃-supported Co FTS catalysts [19], among others. Additionally, *in-situ* studies on carbide formation, using laboratory and synchrotron-based set-ups have been performed on different cobalt-based catalysts [20-25]. Despite these advances and the characterization studies performed, our fundamental understanding of the effect of carbide species on the performance of FTS catalyst still remains rather limited [1,4,5]. Hence, other characterization methods should be called in.

X-ray Raman scattering (XRS) spectroscopy is a photon-in/photon-out probe where inelastic scattering of hard (~ 10 keV) X-rays is used to probe core-level electron excitations. Using this X-ray energy-loss method, information equivalent to soft X-ray absorption spectroscopy can be obtained [26-30], allowing to measure the spectroscopic fingerprints of the Co L_{2,3}-edges and C K-edge, which are relevant for the study of Co/TiO₂ FTS catalysts. The principle is the same as in electron energy-loss near-edge spectroscopy (ELNES), but since hard X-rays are used as a probe, most constraints on sample environments are lifted and experiments can be done under *in-situ* conditions such as those required during the FTS reaction. Hence, we present here an *in-situ* study

that combines XRS and X-ray diffraction (XRD) to study the FTS reaction at relevant conditions of pressure and temperature (i.e., 5 bar and 523 K). This new analytical approach was used to elucidate the formation of cobalt carbides during FTS reaction within an unpromoted Co/TiO₂ catalyst.

RESULTS AND DISCUSSION

The experiments described were performed at the ID20 beamline of the European Synchrotron Radiation Facility (ESRF), which hosts an end-station dedicated for XRS [31]. The used spectrometer has 72 spherically bent crystal analyzers with the Si(660) reflection, organized in 6 modules with 12 analyzers each [31]. For the XRD data collection, a Pilatus 300K-W detector was used. The photon energy at the zero loss line was 9.7 keV. The *in-situ* configuration of the combined XRS and XRD experiments is illustrated in Figure 1.

First, we measured the Co L_{2,3}-edges of metallic Co, CoO, CoTiO₃ and Co₃O₄, as reference cobalt materials. They were used to identify the different cobalt species (i.e., during the activation process of cobalt, Co₃O₄ → CoO → Co⁰) formed at different stages of the *in-situ* reactions. Figure 2 depicts the spectra of the different cobalt references.

The first experiment performed was an *in-situ* carburization reaction (control experiment) of pure cobalt nanoparticles at 523 K and 5 bar of CO. At the end of the experiment the sample was re-hydrogenated (1 ml/min of H₂ for ~ 1 h) and the Co₂C formed was back-converted to metallic Co. This experiment was done in order to identify the main features of the spectra of the carburized sample. We expect the Co L_{2,3}-edges to change shape owing to the change of oxidation state upon the formation of cobalt carbide (Co₂C). The normalized and background subtracted *in-situ* Co L_{2,3}-edges spectra obtained during the carburization reaction are presented in Figure 3. During the

carburization reaction, a distinct change in the Co L_{2,3}-edges spectrum can be identified. Upon carburization, the spectral weight shifts toward higher energies and the L₃ edge at 780 eV becomes broader. This can be attributed to the changing oxidation state of Co, most likely in this experiment owing to the formation of Co₂C, which is considered to be the most stable cobalt carbide under FTS conditions.

A second experiment performed was an *in-situ* FTS reaction of a ~ 14 wt.% Co/TiO₂ catalyst at 523 K and 5 bar, using a H₂:CO ratio of 0.5 (0.5 ml/min of H₂ and 1 ml/min of CO). The latter represent H₂-lean reaction conditions to enhance the deactivation process of the catalyst (the FTS reaction is performed normally at a H₂:CO ratio of 2). The FTS reaction was performed for 15 h. Figure 4 shows the different Co L₃-edges of the Co metal reference and the carburized samples obtained in the *in-situ* experiment, compared to the spectrum collected during FTS for 15 h. We report here only the Co L₃-edge because this edge presents the characteristic shift produced by the Co₂C. Instead, the Co L₂-edge did not provide sufficient information about the oxidation state of the samples. The full spectrum obtained during FTS is presented in Figure S1 of the Supporting Information.

From the Co L_{2,3}-edge analysis it was confirmed that the catalyst was reduced to metallic cobalt (the active phase of cobalt for the FTS reaction) after the activation process [4,16,21]. During the FTS reaction at 523 K and 5 bar, we obtained a Co L₃-edge spectrum that presents similar characteristics to that obtained during the carburization reaction (i.e., no further re-oxidation into CoO and subsequent Co₃O₄ was observed during the reaction). This was taken as a conclusive *in-situ* evidence of the formation of Co₂C also during the FTS reaction, which agrees with previous work performed in our research group [3,22].

In the case of the C K-edge measurements, graphite powder, pyrene, as well as SX-70 and SX-100 (FTS waxes) were measured as carbon standard materials. Figure 5 shows the spectra of these reference samples. Also electron energy loss spectra from amorphous graphite [32] and carbon monoxide [33-35] are included and broadened via a convolution by a Gaussian for the total linewidth to match our 0.7 eV energy resolution. In case of the *in-situ* carburization reaction, Figure 6.I illustrates the *in-situ* carbon spectrum collected at the beginning and during 10 h of carburization.

The spectrum at the beginning of the carburization shows no relevant intensity as expected from this carbon-free material. However, a distinct spectrum of the C K-edge is clearly visible after 10 h of carburization. The C K-edge is expected to reveal the formation of a number of carbonaceous condensed-phase products, e.g. coke, in addition to the CO_2C formed. From the spectrum of the carburized sample, an absorption band can be observed at ~ 285 eV that correspond to the $1s \rightarrow \pi^*$ transition, which evidences the presence of aromatic rings (C=C) [36-39]. The absorption band observed at ~ 287 eV corresponds to the $1s \rightarrow \pi^*$ transition, assigned to C=O that could be ascribed to the carbon monoxide from the gas phase [40]. In addition, an absorption band at ~ 292 eV was detected, corresponding to the $1s \rightarrow \sigma^*$ transition in aromatic C-C [36,38,39,41]. From the analysis of the C K-edge spectrum, one can establish that the carburized sample exhibits characteristics of graphitic carbon. By integrating over the C K-edge spectra between 280 and 310 eV, it was possible to quantify the amount of carbon formed as a function of the reaction time. The result of this analysis is given in Figure 6.II. The last time step corresponds to the beginning of the re-hydrogenation step, where the amount of carbon was expected to decrease, which indeed is evidenced by the data obtained.

A similar trend was observed for the *in-situ* FTS reaction. Figure 7 presents the C K-edge spectrum acquired during 15 h of FTS reaction and the amount of carbon formed during the FTS reaction at 523 K and 5 bar. As in the case of the C K-edge spectrum from the carburization experiment, absorption bands were observed at ~ 285 eV, $1s \rightarrow \pi^*$ transition [36-39], at ~ 287 eV, $1s \rightarrow \pi^*$ transition [40], and at ~ 292 eV, $1s \rightarrow \sigma^*$ transition [36,38,39,41]. From the analysis of the data obtained, it was established that during the FTS reaction, graphitic species were deposited on the active phase of the Co/TiO₂ catalyst. The relative intensity at ~ 287 eV (i.e., CO in the gas phase) was more pronounced than in the case of the carburization experiment because of the reduced amount of carbon species formed and deposited during the FTS reaction.

Finally, to identify and quantify the different carbon species presented during the carburization and FTS reactions, the C K-edge spectra were fitted to the measured reference components using the least-squares method. The fit was done using the area-normalized spectra of graphite, carbon monoxide, pyrene, amorphous graphite, and SX-70 in the case of the FTS reaction, while for the carburization reaction the SX-70 and pyrene were left out from the fit as their formation is not possible in that reaction. The area normalization was done for the range 280-310 eV. The spectra of SX-70 and SX-100 (see Fig. 5) were so similar that using both of them in the fit was not justified, hence SX-70 represents the total waxes contribution for the purpose of the least-squares fit. The aim of the fits is to represent the area-normalized experimentally observed C K-edge spectrum $S(E)$ as a linear combination of individual components spectra $S_i(E)$ with weight fractions c_i , i.e., $S(E) = \sum_i c_i S_i(E)$. The fit results are shown in Figure 8. Overall, using these carbon reference species produces an excellent agreement with the fit and the experimental C K-edge spectra. The spectral weight compositions c_i obtained for the carburization reaction were 66% amorphous graphite, 30% crystalline graphite with 4% carbon monoxide present owing to the gas

flow. In the case of the FTS reaction the composition obtained was: 34% amorphous graphite, 23% SX waxes, 17% crystalline graphite, 15% pyrene, and with a spectral contribution of 11% of carbon monoxide.

Interestingly, certain level of disagreement between the fit and both experiments at ~288 eV energy transfer region remains, with an apparent spectral weight observed in the experiment at that energy not explained by the fit. In order to model if this disagreement could be assigned to the formation of Co₂C we calculated the expected C K spectrum of Co₂C using the FEFF software [42-44]. The results of the FEFF calculation for C K-edge spectra of Co₂C and calculation for graphite using the same method are shown in Figure 9. The energy scale of the calculated spectra is shifted rigidly so that the 1st peak of the graphite spectrum is at the experimentally observed energy (285 eV). Interestingly, the spectrum of Co₂C shows a strong peak close to the energy region that exhibits the disagreement between the experiment and the fit in Figure 8. We thus assign the remaining spectral weight at 288 eV in the spectrum obtained from the experiment to the formation of Co₂C. The agreement between the calculated and measured spectra of graphite does not warrant to use the calculated spectra in the fit as a spectral component, but the qualitative agreement of the experimental and calculated spectra is satisfactory. Most notably, the calculated spectra would need effectively an energy scale condensation as the π^* and σ^* peaks of the graphite spectrum are further apart from each other than in the experimental spectra. Based on this note and comparing the calculated and experimental C K-edge spectra qualitatively, gives confidence to the assignment of the 288 eV spectral region to originate from the formation of Co₂C.

Additionally, *in-situ* XRD patterns were collected during the carburization reaction of Co nanoparticles to determine the cobalt species present in the distinctive steps of the reaction. Figure 10.I shows the *in-situ* XRD patterns collected at different reaction times. From the XRD analysis

it can be confirmed that at the beginning of the reaction the cobalt was presented as metallic cobalt and during the execution of the experiment it was gradually converted to cobalt carbide. At the end of the carburization reaction, the sample was re-hydrogenated. During the reaction, the hcp-Co phase was faster transformed into Co_2C , while a fraction of the fcc-Co phase remained metallic during the course of the experiment. This agrees with information previously reported in literature [22]. Figure 10.II presents the ratio between the specific intensities of Co_2C , fcc-Co and hcp-Co peaks, and the intensity of BN reference peak at $\sim 34^\circ$, called normalized relative intensity, during the *in-situ* carburization reaction. The data confirms the fast transformation of hcp-Co into Co_2C , and the more stable fcc-Co phase during the reaction.

In addition, a relation was found between the conversion of the cobalt metal into Co_2C and the spatial position along the reactor. Figure 11 shows an image of the capillary reactor and XRD measurements performed at different positions in the reactor bed during 6 h of carburization reaction [45]. It can be concluded that a larger conversion rate was observed at the beginning of the catalyst bed of the reactor, and the conversion gradually decreased with increasing distance from the gas inlet. Figure 12 shows the normalized relative intensity of the Co_2C , fcc-Co and hcp-Co species at different positions along the reactor bed.

The distinct cobalt species presented during the different stages of the FTS reaction were confirmed by *in-situ* XRD over Co/TiO_2 (Figure 13.I). From the XRD analysis, it could be corroborated that cobalt was present as a mixture of fcc-Co and hcp-Co after the activation process ($\text{Co}_3\text{O}_4 \rightarrow \text{CoO} \rightarrow \text{Co}^0$). And, a very small fraction of CoTiO_3 (i.e., an inactive phase of cobalt for FTS reaction and related to the metal-support effect) was detected after the reduction process, performed at 673 K and 1 bar [4,5]. The presence of hot-spots in the catalyst bed of the reactor could contribute to the formation of this inactive phase [46]. Additionally, the evolution of Co_2C

(crystalline phase) during FTS reaction was observed. Figure 13.II shows the normalized relative intensity of the Co_2C , fcc-Co and hcp-Co species during the *in-situ* FTS reaction, where the instability of the Co_2C phase formed during the reaction was confirmed.

Stable cobalt carbide species were expected to be observed during the reaction. Those species could reduce the amount of exposed active cobalt metallic sites for the FTS reaction, which would contribute to the deactivation of the catalyst. Therefore, it is concluded that no direct and conclusive evidence that relates to the unstable Co_2C formed, during 15 h of FTS at H_2 -lean reaction conditions, can be correlated to the deactivation process of the Co/ TiO_2 catalyst. In the case of olefins selectivity and intermediate species during FTS reaction, the instability of the carbide formed do not provide enough evidence, and more experiments are needed to corroborate those hypothesis [3,18-22].

It is important to note that the gradient along the reactor bed length, as seen in Figure 12, is typical for the plug-flow reactors, and such gradients should be taken into account before to draw conclusions about the different phenomena that take place during FTS catalyst experiments under reaction conditions.

Summarizing, we have provided evidence that cobalt carbide can be formed during FTS at 5 bar and 523 K, but there is no direct proof that its formation relates to increased olefins selectivity, catalyst deactivation or either that it is an intermediate species of the FTS reaction, because of its instability during the reaction [3,18-22].

CONCLUSION

By using a unique combination of *in-situ* X-ray Raman scattering (XRS) spectroscopy and X-ray diffraction (XRD), it was possible to study cobalt carbide (Co_2C) formation in pure cobalt nanoparticles. By analyzing the spectra obtained from the carburization reaction, the characteristic features were obtained for the Co L-edges and C K-edge spectra for Co_2C . During FTS reaction under H_2 -lean conditions (i.e., a $\text{H}_2:\text{CO}$ ratio of 0.5) of a Co/ TiO_2 catalyst at 523 K and 5 bar, a change in the oxidation state of the cobalt was observed during 15 h of reaction, which was related to the formation of cobalt carbides. The formation of Co_2C was confirmed by *in-situ* XRD. Additionally, the Co L_{3} -edge and C K-edge XRS spectral analysis exhibits features that can be assigned to the carbide formation.

From the analysis, we could conclude that the instable Co_2C formed, which degrades to metallic Co and graphite [7,8,12], cannot be correlated to the deactivation process of the Co/ TiO_2 catalyst, olefins selectivity or intermediate species of FTS reaction [6-11]. The results obtained demonstrate that XRS is a powerful technique that allows measuring the Co $\text{L}_{2,3}$ -edges and C K-edge (edges present in the soft X-rays range) at high pressure and high temperature by using hard X-rays; which represents an advantage for the *in-situ* study of a wide range of reactions over supported metal and metal oxide catalysts.

EXPERIMENTAL SECTION

The Co/ TiO_2 catalyst under study was synthesized by incipient wetness impregnation (IWI). For this purpose, a TiO_2 P90 support (Evonik, 90% anatase and 10% rutile) was impregnated with a solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Acros Organics, 99+%). The support was subsequently impregnated until the catalyst reached a final loading of 14.1 wt.%, which was confirmed by Inductively

Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). After impregnation, the catalyst powder was dried overnight at 333 K in a static air atmosphere, and then calcined for 4 h at 673 K under a N₂ flow of 100 ml/min (Linde, N₂ ≥ 99.999%). Cobalt was present in the calcined catalyst in the form of Co₃O₄ nanocrystallites with an average size of ~ 14 nm. The average crystallite size was obtained by X-ray Diffraction (XRD) analysis and confirmed by using Scanning Transmission Electron Microscopy-Energy Dispersion X-ray Spectroscopy (STEM-EDX). An in-depth characterization of the catalyst under study has been reported in previous work [46], see section S3 and S4 of the supplementary information. The *in-situ* set-up consists of a plug-flow reactor (capillary) horizontally mounted, with an outer diameter of 1 mm and inner diameter of 0.98 mm [47,48]. The catalyst (with a particle size range of 150-90 μm) was placed and held by quartz wool in the isothermal zone of the plug-flow reactor. The capillary was heated by two IR heaters and the temperature was controlled by a thermocouple placed on the bed of the plug-flow reactor. Section S5 presents the set-up mounted in the XRS spectrometer and a schematic of the plug-flow reactor. This type of reactors presents a more temperature homogeneous distribution compare to other set-ups systems that have been used and studied in our research group [49]. During the *in-situ* XRS/XRD experiments, two different types of experiments were performed: a) a FTS reaction at 523 K and 5 bar, over the Co/TiO₂ FTS catalyst, and b) a carburization reaction of pure cobalt nanoparticles (i.e., Co₃O₄, Sigma-Aldrich 99.5%) at 523 K and 5 bar. The *in-situ* experiments contained two parts: i) reduction (activation process, Co₃O₄ → CoO → Co⁰) of Co in H₂ atmosphere (Air Liquid, H₂>99.9995%) by heating up to 673 K for 2 h, and ii) FTS/carburization reaction. Before reduction, Co L_{2,3}-edge and C K-edge spectra as well as XRD patterns were measured (at room temperature) to identify the different species presented in the catalyst before the activation process started. After the reduction of cobalt was achieved, a second set of

measurements (i.e., Co L_{2,3}-edge and C K-edge spectra as well as XRD patterns) were acquired to establish the changes experienced by the catalyst during the reduction process. Then, the reactor was cooled down from 673 K (reduction temperature) to room temperature (RT), and was exposed to a pure CO flow (1 ml/min, Air Liquid, CO>99.997%) in the case of the carburization reaction, and to a mixture of H₂:CO (ratio of 0.5, 0.5 ml/min of H₂ and 1 ml/min of CO) in the case of FTS reaction, followed by the pressurization of the system to 5 bar. After the pressurization process was finished, the temperature in the reactor was increased with a heating rate of 5 K/min for both reactions. The measurements were performed at reaction conditions. The FTS and carburization reactions were completed after 15 h and 10 h, respectively. Additionally, *ex-situ* measurements of Co and C reference materials were performed; Co₃O₄, CoO (Acros Organics, 99+%), CoTiO₃ (Alfa Aesar, 99.8%), Co (Co foil, 99.9%), pyrene (Sigma-Aldrich, 98%), graphite (Sigma-Aldrich), SX-70 (Shell) and SX-100 (Shell), SX-70 and SX-100 are FTS products (waxes). The catalytic activity of the Co/TiO₂ FTS catalyst was previously tested by using a fixed-bed reactor [15], see supporting information section S6. Finally, the graphite and Co₂C carbon K-edge XANES spectra were calculated using FEFF9 [42] using input and Crystallographic Information Files (CIF)'s from materialsproject.org [43,44]. In both cases the calculations were done in the reciprocal space, with core-hole taken into account within the random phase approximation and Hedin–Lundqvist exchange-correlation potential. A constant Gaussian broadening of 1 eV was applied to the computed spectra to account for a combined effect of core-hole lifetime broadening and the experimental resolution (the latter one being the dominant one). The k-space grid was 13x9x9 for Co₂C and 15x15x5 for graphite.

FIGURES

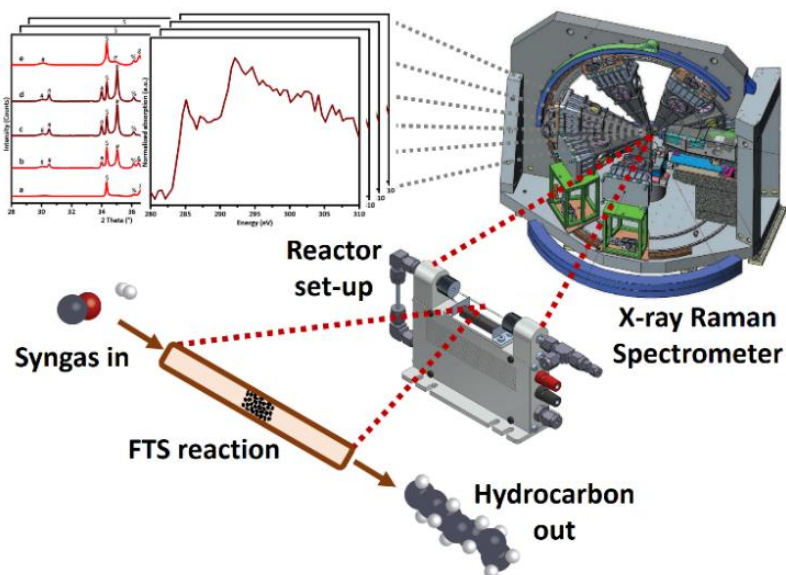


Figure 1. Schematic of the *in-situ* configuration used for combined X-ray Raman scattering (XRS) spectroscopy and X-ray diffraction (XRD) experiments on a Co/TiO₂ Fischer-Tropsch synthesis catalyst [26].

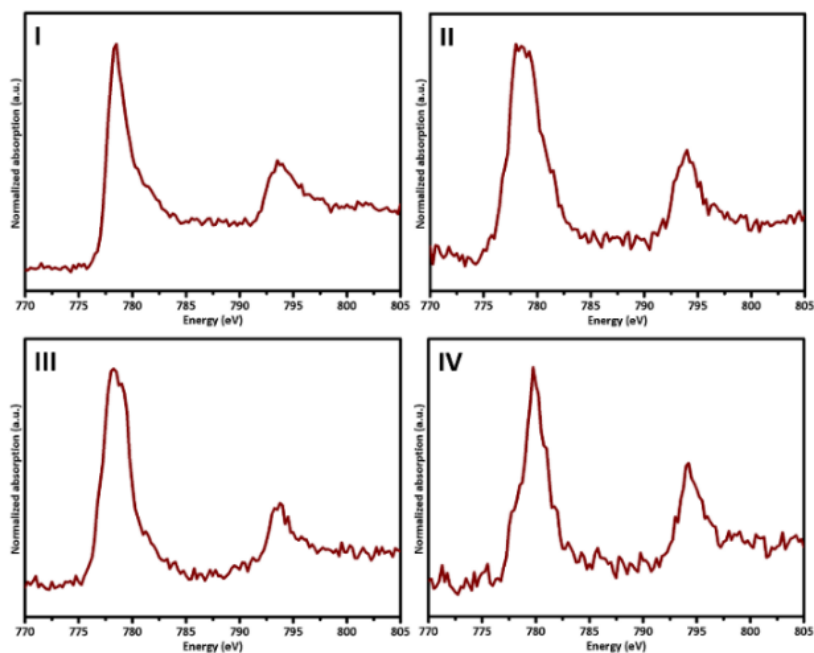


Figure 2. Co L_{2,3}-edges spectra for various reference samples: I) Co foil, II) CoO, III) CoTiO₃ and IV) Co₃O₄.

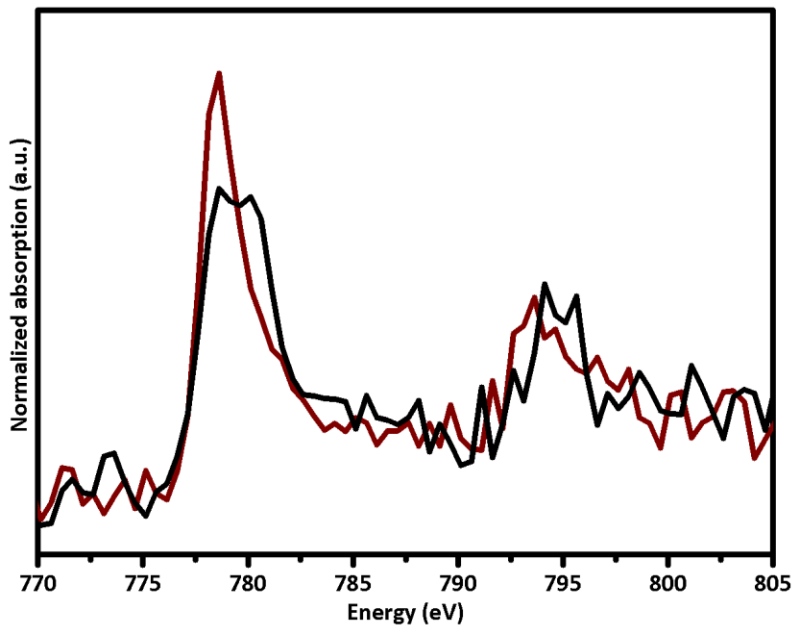


Figure 3. *In-situ* Co L_{2,3}-edges for the carburization reaction of pure Co nanoparticles at 523 K and 5 bar, the spectrum of reduced cobalt oxide (metallic Co) in red and the spectrum after carburization in black.

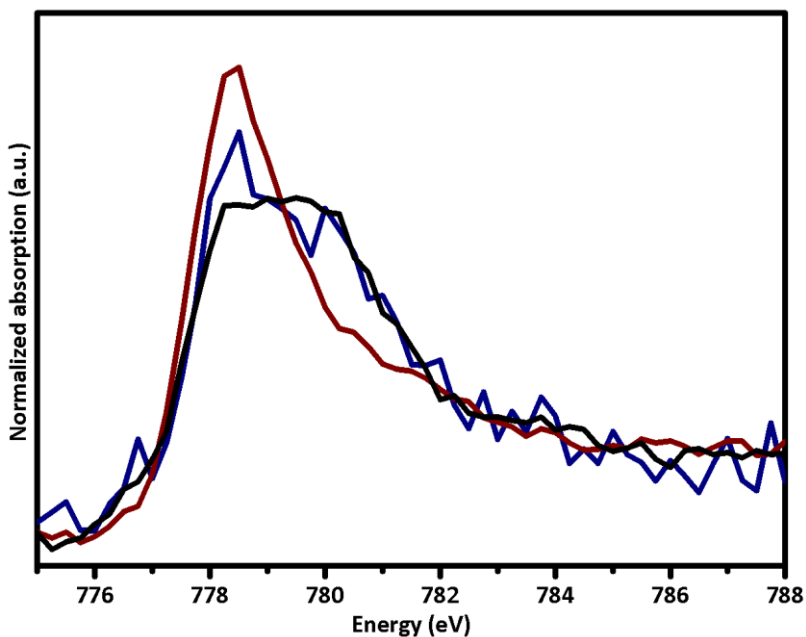


Figure 4. *In-situ* Co L₃-edge for the FTS reaction over a Co/TiO₂ catalyst at 523 K and 5 bar (with a H₂:CO ratio of 0.5) compared to the spectra of Co metal reference and carburized sample. FTS sample: blue; Co metal reference: dark red; carburized sample: black.

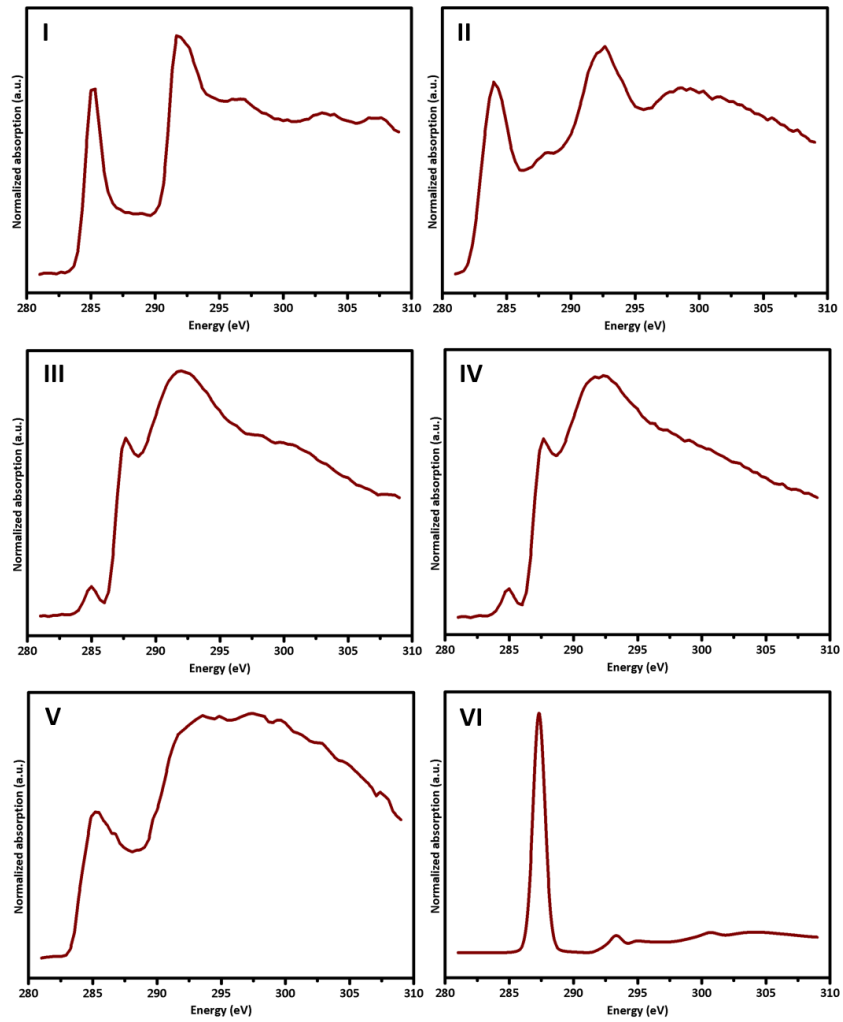


Figure 5. C K-edge spectra for reference samples: I) graphite, II) pyrene, III) SX-70, IV) SX-100, V) amorphous graphite and VI) carbon monoxide [32-35].

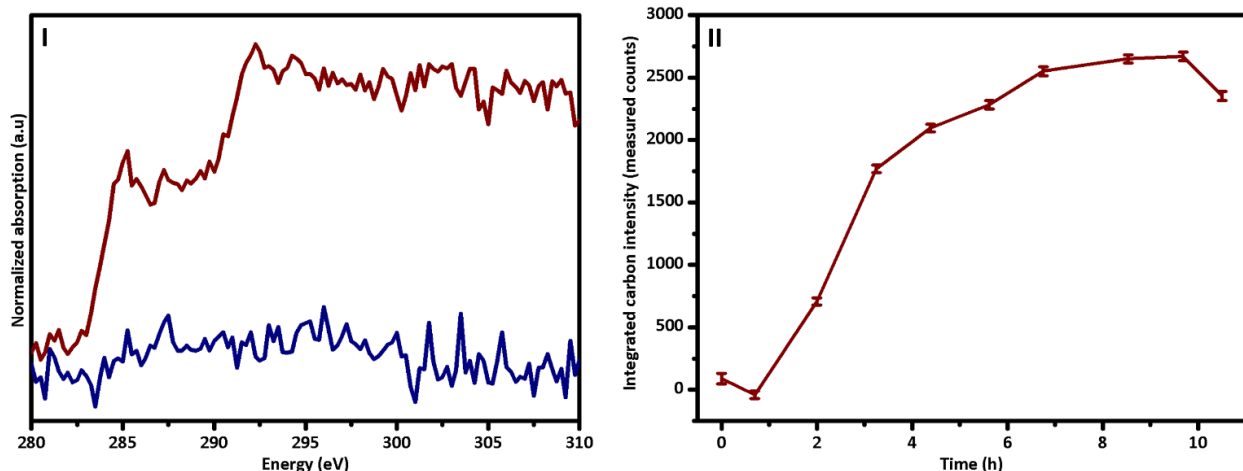


Figure 6. I) *In-situ* C K-edge for the carburization reaction of pure Co nanoparticles at 523 K and 5 bar, spectrum at the beginning of the carburization reaction in blue and carburized spectrum in dark red. II) Carbon evolution during the carburization reaction (the last point correspond to the re-hydrogenation step). Error bars are based on the statistical uncertainties, see section S2 of the supporting information.

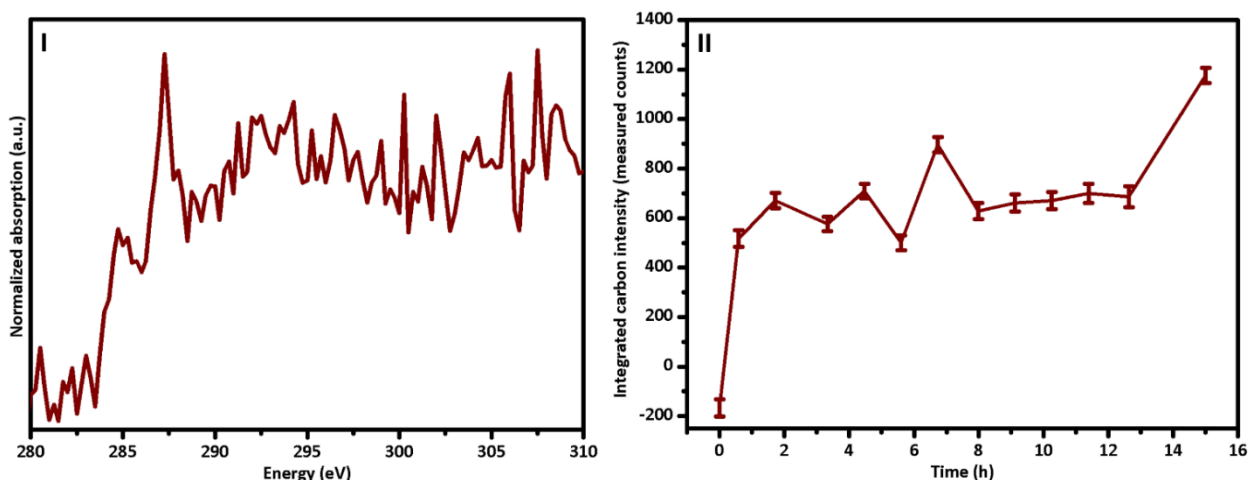


Figure 7. I) *In-situ* C K-edge for the FTS reaction over a Co/TiO₂ catalyst at 523 K and 5 bar, and for 15 h of reaction with a H₂:CO ratio of 0.5. II) amount of carbon evolved during the FTS reaction. Error bars are based on the statistical uncertainties. Further systematic uncertainty arises especially below the FTS onset due to Compton background subtraction, but it is not included in the error bars, see section S2.

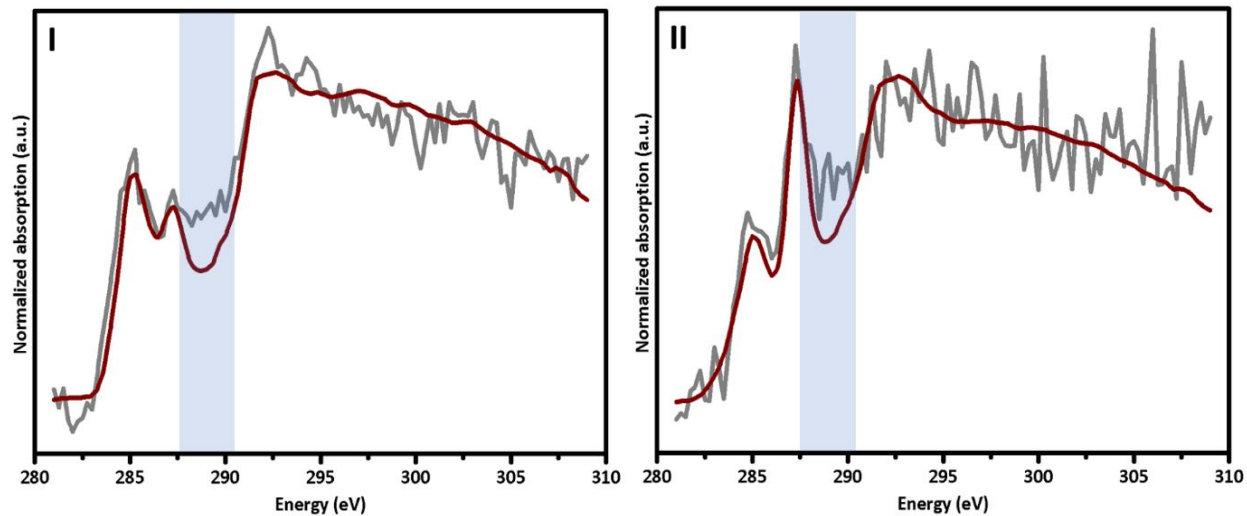


Figure 8. I) Carburization reaction C K-edge data and calculated fit, and II) FTS reaction C K-edge data and calculated fit. The details of the fit and the resulting spectral compositions are explained in the main text. Experimental spectrum in grey and fitting data in dark red. The shaded region marks the energy where the agreement between the fit and the experiment are not explained by the used reference standards.

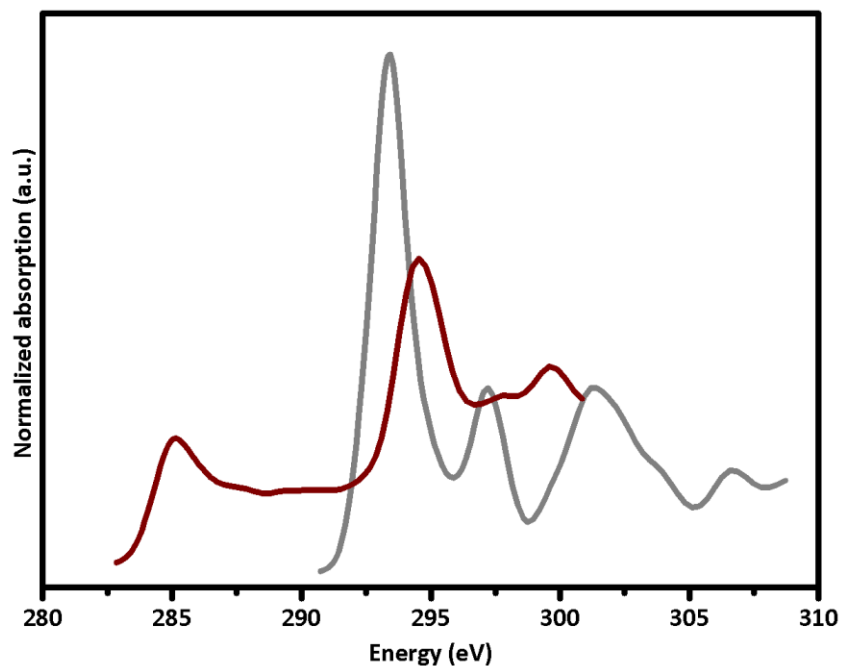


Figure 9. Calculated XANES spectra of graphite and Co_2C using FEFF. Co_2C in gray and graphite in dark red.

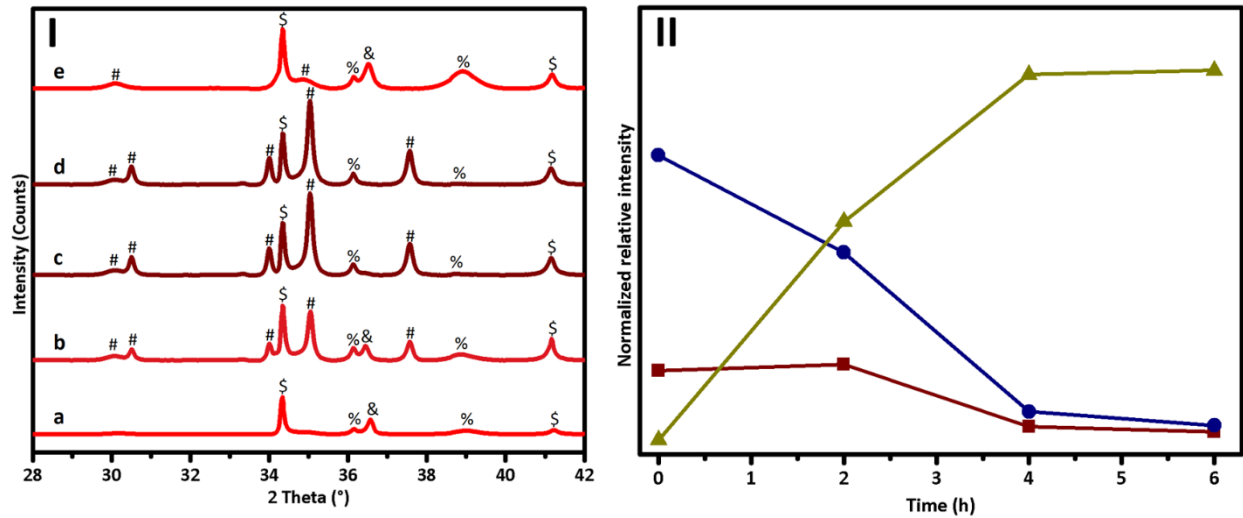


Figure 10. I) *In-situ* XRD patterns collected during carburization reaction of pure cobalt nanoparticles at 523 K and 5 bar, using a pure CO flow: a) reduced cobalt, b) 2 h of carburization, c) 4 h of carburization, d) 6 h of carburization and e) re-hydrogenation of cobalt. Diffraction peaks of fcc-Co are marked with ‘%’ and hcp-Co with ‘&’, Co₂C peaks are marked with ‘#’ and boron nitride peaks are marked with ‘\$’. II) Normalized relative intensity of the Co₂C (35°), fcc-Co (36.1°) and hcp-Co (36.5°) species during in-situ carburization reaction. Co₂C in yellow, fcc-Co in red and hcp-Co in blue.

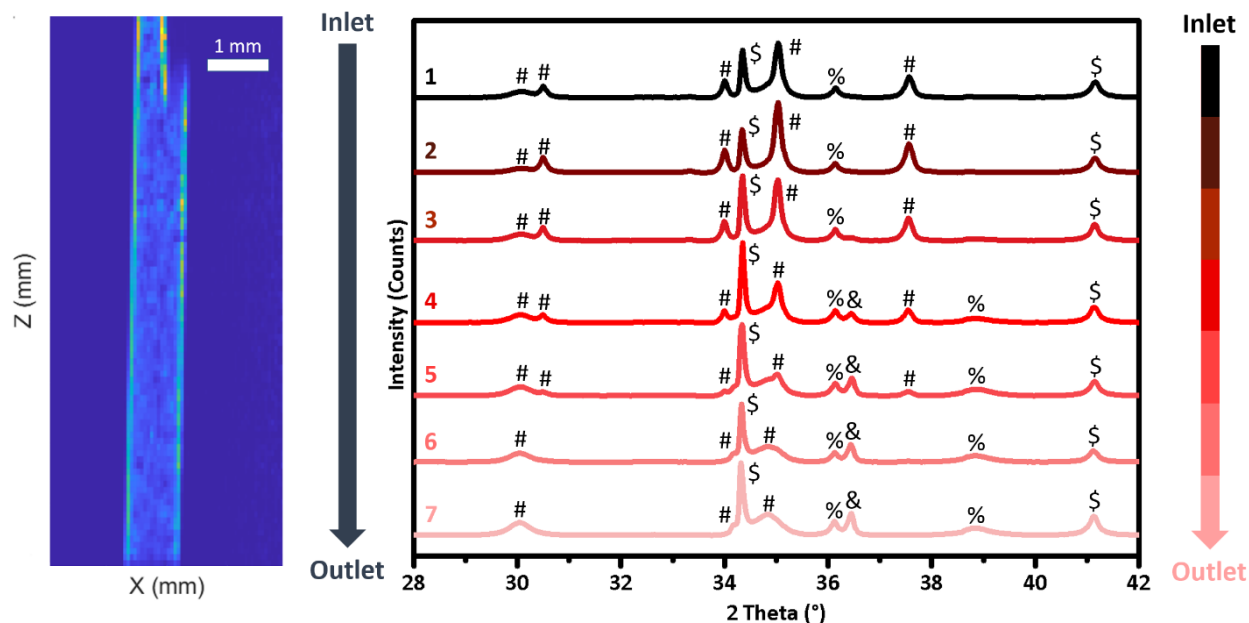


Figure 11. On the left, an image of the capillary reactor recorded during the *in-situ* XRS experiments using the spectrometer’s imaging capability [37]. The probing x-ray beam propagates along the X-axis and Z is along the cylindrical reactor bed axis. Each pixel color represents the intensity of elastic scattering as seen by one of the point-to-point focusing spherically bent analyzer crystals of the XRS spectrometer. The 10- μm thick glass wall is seen as a bright scattered on the left and the intensity of scattering decreases toward the positive X-direction because of attenuation by the sample. The thermocouple can be seen on the top to the reactor. On the right, XRD measurements performed at different position of the bed of the capillary reactor during 6 h of carburization reaction, diffraction peaks of fcc-Co are marked with ‘%’ and hcp-Co with ‘&’, Co_2C peaks are marked with ‘#’ and boron nitride peaks are marked with ‘\$’.

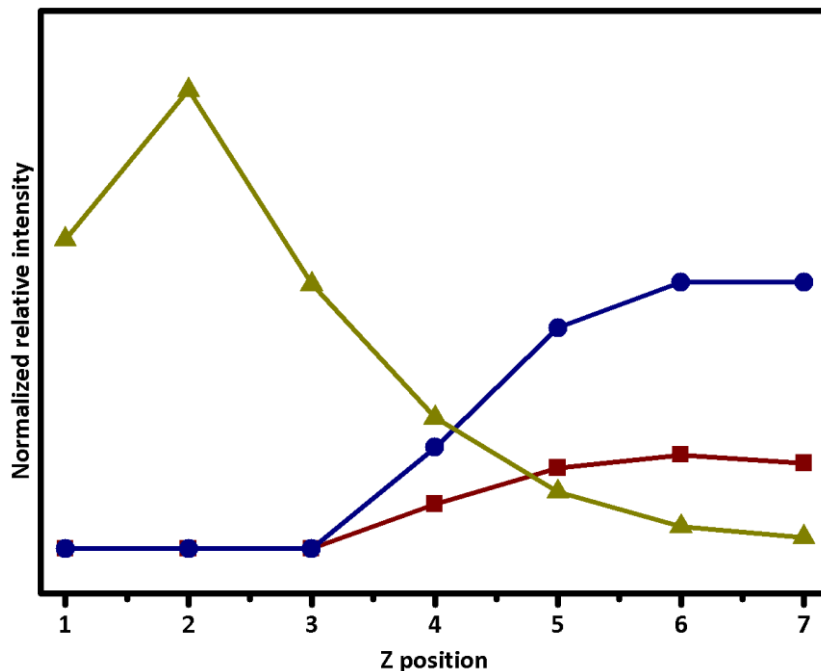


Figure 12. Normalized relative intensity of the Co₂C (35°), fcc-Co (36.1°) and hcp-Co (36.5°) species during 6 h of *in-situ* carburization reaction at different positions along the reactor bed. Co₂C in yellow, fcc-Co in red and hcp-Co in blue. Z position 1 corresponds to the measurement closer to the inlet.

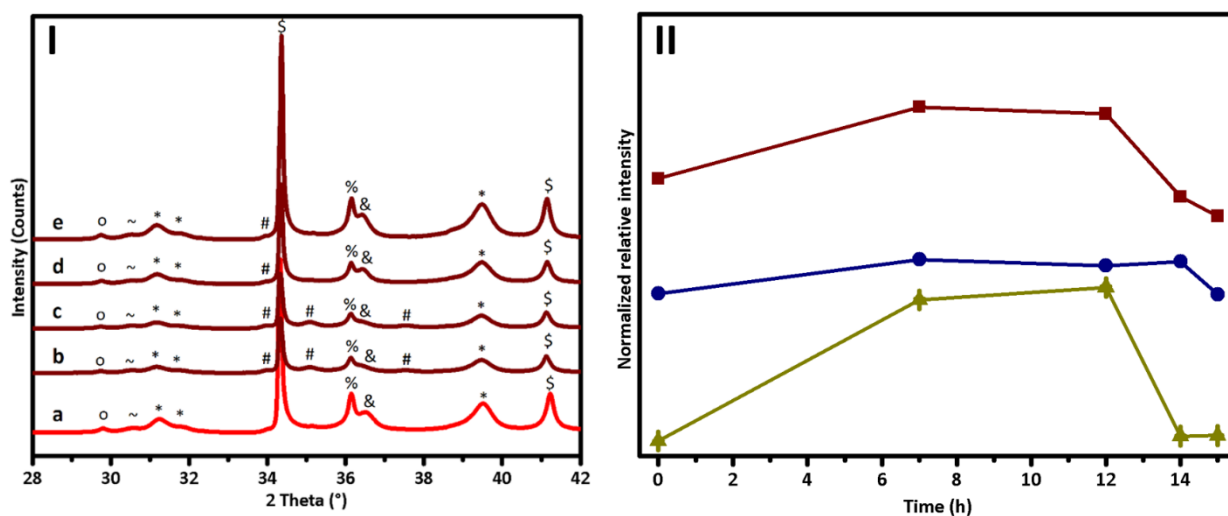
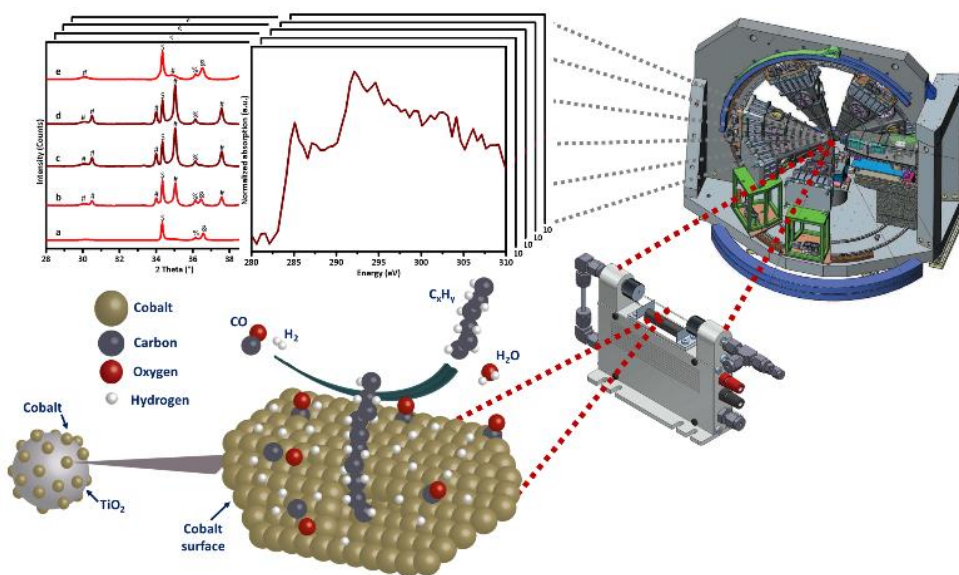


Figure 13. I) *In-situ* XRD patterns collected during FTS reaction onto unpromoted Co/TiO₂ FTS catalyst at 523 K and 5 bar, using a H₂:CO ratio of 0.5: a) reduced catalyst, b) 7 h of reaction, c) 12 h of reaction, d) 14 h of reaction and e) 15 h of reaction. Diffraction peaks of fcc-Co are marked

with ‘%’ and hcp-Co with ‘&’, Co₂C peaks are marked with ‘#’, boron nitride peaks are marked with ‘\$’, TiO₂ rutile peaks are marked with ‘o’, TiO₂ anatase peaks are marked with ‘*’ and CoTiO₃ peaks are marked with ‘~’. II) Normalized relative intensity of the Co₂C (35°), fcc-Co (36.1°) and hcp-Co (36.5°) species during *in-situ* FTS reaction. The instability of the carbide formed, and the relative stability of the different cobalt metallic species presented during the reaction are confirmed. Co₂C in yellow, fcc-Co in red and hcp-Co in blue. Error bars are included in the plot for Co₂C.



TOC Figure

ASSOCIATED CONTENT

Supporting Information

In the Supporting Information file can be found the error calculation, the full XRS spectrum for the FTS experiment, the characterization of the Co/TiO₂ ~14 wt.% catalysts and the catalytic test at different reaction conditions.

AUTHOR INFORMATION

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Author Contributions

Frank de Groot, Simo Huotari and José Moya-Cancino formulated the idea and wrote the proposal for beamtime at the European Synchrotron Radiation Facility (ESRF). José Moya-Cancino prepared the catalyst used in this research and designed the experiments. Simo Huotari, José Moya-Cancino, Ari-Pekka Honkanen, Ad van der Eerden, Ramon Oord and Matteo Monai performed the different experiments. Simo Huotari and José Moya-Cancino analyzed the obtained data. José Moya-Cancino, Simo Huotari, Frank de Groot wrote the manuscript. Florian Meirer and Bert Weckhuysen made revisions and corrections to the manuscript.

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ABBREVIATIONS

FTS, Fischer-Tropsch synthesis; XRS, X-ray Raman scattering spectroscopy; XRD, X-ray diffraction; ELNES, Electron energy-loss near-edge spectroscopy; ESRF, European Synchrotron Radiation Facility; hcp, Hexagonal close-packed; fcc, Face-centered cubic; IWI, Incipient wetness impregnation; ICP-AES, Inductively coupled plasma-atomic emission spectrometry; STEM-EDX, Scanning transmission electron microscopy-energy dispersion X-ray spectroscopy; RT, Room temperature; GC, Gas chromatograph.

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SYNOPSIS

An *in-situ* X-ray Raman scattering spectroscopy and X-ray diffraction study is presented. The characteristic features of Co L_{2,3}-edges and C K-edge spectra were obtained for cobalt carbide. During Fischer-Tropsch synthesis reaction under H₂-lean conditions, C₂C formation was detected.