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Cobalt Fischer-Tropsch synthesis: Deactivation by oxidation?

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Abstract

Cobalt catalysts as used in the Fischer-Tropsch synthesis (FTS) are relatively expensive (as compared to iron) and need to have a high metal dispersion and long life to be able to offer a good balance between cost and performance. The oxidation of nano-sized metallic cobalt to cobalt oxide during Fischer-Tropsch synthesis has long been postulated as a major deactivation mechanism. However, to date there is no consistent picture. This paper presents an extensive overview of the literature on this topic of deactivation by means of oxidation for unsupported as well as silica-, alumina- and titania-supported cobalt catalysts. Furthermore, it presents results on the deactivation of an industrial Co/Al_2O_3 catalyst as obtained by pseudo in situ X-ray diffraction, magnetic measurements and X-ray absorption near-edge spectroscopy. These analyses were performed to study the oxidation state of spent industrial Co/Al_2O_3 catalyst samples withdrawn from a slurry reactor operating under realistic FTS conditions, and it was concluded that oxidation can be ruled out as a major deactivation mechanism. Finally, these data together with all relevant literature were used to create a common view on the oxidation behaviour of metallic cobalt during FTS. The apparent discrepancies in literature on the oxidation behaviour of cobalt are most likely due to the lack of direct characterisation of the cobalt oxidation state and due to the comparison of catalysts with varying cobalt crystallites sizes, compared at different reactor partial pressures of hydrogen and water (P_{H_2O}/P_{H_2}). It was shown that the oxidation of cobalt can be prevented by selecting the correct combination of the reactor partial pressures of hydrogen and water (P_{H_2O}/P_{H_2}) and the cobalt crystallite size.

Keywords: Fischer-Tropsch synthesis; Gas-to-liquids (GTL) process; Cobalt catalysts; Deactivation

1. Introduction

Supported cobalt catalysts are receiving widespread attention as the preferred Fischer-Tropsch synthesis (FTS) catalyst for the gas-to-liquids (GTL) process [1–4]. GTL on a global scale is making its mark with many of the multi national oil companies (ConocoPhillips, Exxon, Sasol-Chevron, Shell, Syntroleum) announcing to build GTL facilities in Qatar [2]. On a commercial scale, Shell is operating a supported cobalt catalyst in a fixed bed reactor, as part of their 12,000 barrels per day Shell middle distillate synthesis (SMDS) process in Bintulu, Malaysia [3]. Sasol has a 34000 barrels per day GTL plant in operation in Ras Laffan, Qatar, which is based on the Sasol Slurry Phase Distillate™ (Sasol SPD™) process [4]. Global growth for clean diesel fuel and the high crude oil price are the major drivers for GTL [2].

Cobalt catalysts as used in the FTS are relatively expensive (as compared to iron) and need to have a high metal dispersion and long life to be able to offer [5] a good balance between cost and performance. Hence, the development of economically attractive cobalt based FTS catalysts with a high stability requires detailed fundamental understanding of the deactivation mechanisms at play for supported nano-sized cobalt crystallites. The oxidation of cobalt metal to cobalt oxide or cobalt aluminate (for alumina supported cobalt catalysts) by the product water has long been postulated to be a major cause of deactivation of supported cobalt FTS catalysts [6–28]. In general, although a lot of research has been carried out with the aim of proving that oxidation is indeed a deactivation mechanism of cobalt based FTS catalysts, to date there is no consistent picture [6–41].

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The objective of this paper is to reconcile the apparent contradictions in literature with respect to oxidation as a deactivation mechanism for cobalt-based FTS catalysts. In this regard, the literature was reviewed extensively. Furthermore, oxidation as a deactivation mechanism for an industrially relevant Co/Al_2O_3 FTS catalyst that was operated at realistic industrial FTS synthesis conditions was investigated by means of pseudo in situ characterisation using X-ray diffraction (XRD), X-ray absorption near-edge spectroscopy (XANES), and Magnetic measurements. The literature together with the results on the industrial Co/Al_2O_3 catalyst are combined and consolidated so as to create a common view on the oxidation behaviour of cobalt catalysts during FTS.

2. Summary of open literature

2.1. Thermodynamic analysis of the oxidation of bulk cobalt metal

In order to understand the effect of water on the oxidation behaviour of cobalt based Fischer-Tropsch catalysts, a bulk phase thermodynamic evaluation (Fig. 1) was carried out by Van Berge et al. [6].

The Fischer-Tropsch synthesis region specified in Fig. 1, was based on realistic Fischer-Tropsch synthesis conditions assuming a gradientless slurry phase reactor: reactor pressure of 20 bar, reactor temperature of 170–240 °C, synthesis gas composition of 67 vol.% H_2 and 33 vol.% CO, and a %(H_2 + CO) conversion of 50–70. These Fischer-Tropsch conditions result in a hydrogen partial pressure between 6.5 and 9.2 bar, and a water partial pressure between 4.6 and 7.6 bar, thus a P_{H_2O}/P_{H_2} ratio between 0.5 and 1.2. The equilibrium constant (K_{eq}) versus temperature curves of equations (1) $Co + Al_2O_3 + H_2O \Leftrightarrow CoAl_2O_4 + H_2$ and (2) $Co + H_2O \Leftrightarrow CoO + H_2$ in Fig. 1 are in good agreement with previous publications, i.e. [42,43], respectively.

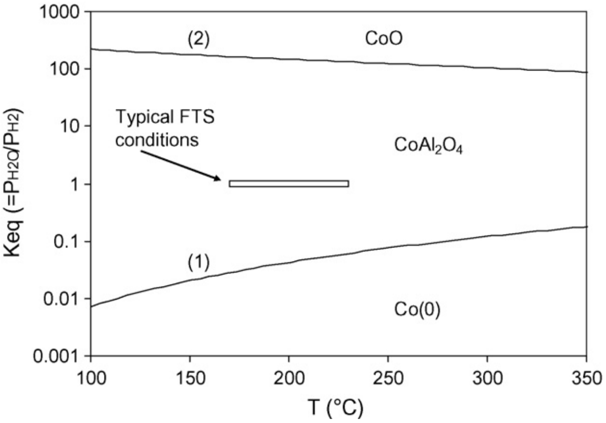

Fig. 1. Thermodynamic equilibrium constants K_{eq}, which is equal to P_{H_2}/P_{H_2O}, for two selected cobalt oxidation reactions, i.e. (1) $Co + Al_2O_3 + H_2O \Leftrightarrow CoAl_2O_4 + H_2$ and (2) $Co + H_2O \Leftrightarrow CoO + H_2$ (*Note*: The thermodynamic equilibrium for the oxidation of cobalt to Co_3O_4 is not shown as this is about four orders of magnitude higher than that of the oxidation to CoO) (adapted from Ref. [6]).

Seen that the thermodynamic equilibrium constants (K_{eq}) for the oxidation of cobalt metal to CoO is higher than typical P_{H_2O}/P_{H_2} ratios observed during Fischer-Tropsch synthesis conditions, it was concluded that the oxidation of bulk cobalt metal is not spontaneous. The thermodynamic equilibrium for the oxidation of cobalt to Co_3O_4 is not shown in Fig. 1 as this is about four orders of magnitude higher than that of the oxidation to CoO. However, according to Fig. 1, for Co/Al_2O_3 catalysts, the oxidation of cobalt to $CoAl_2O_4$-spinel is thermodynamically spontaneous. It was argued that the formation of $CoAl_2O_4$ is kinetically restricted [43]. This statement was supported by the observation [43] that relatively severe hydrothermal treatment (i.e. steam at 500–800 °C) of Co/Al_2O_3 is required for the formation of the $CoAl_2O_4$-spinel.

2.2. Thermodynamic analysis of nano-sized cobalt crystallites

Although oxidation of bulk cobalt metal is thermodynamically not favourable, a recent study showed that oxidation of nano-sized cobalt crystallites seems to be thermodynamically possible at realistic Fischer-Tropsch synthesis conditions [7]. This is due to the contribution of the surface energy of nano-sized cobalt crystallites to the overall oxidation process. The surface energy of a metal can be regarded to be proportional to the number of broken bonds. These broken bonds will increase as the metal crystallite becomes smaller and increases in curvature [44,45]. Hence, smaller cobalt crystallites will have a higher propensity to oxidize than larger ones. It should be noted that although in general the surface energy of small crystallites increases with decreasing diameter, exceptions have been observed for gold crystallites which deviate for closed shell structures [46].

The thermodynamic stability of nano-sized cobalt crystallites was calculated by taking the surface energy of Co(0) and Co(II)O into account [7]. It was assumed that no defects and stacking faults are present. The fact that cobalt oxide can react with the support and form, for example, cobalt aluminate was also not considered.

The following expression [7]:

$$\mu^0_{CoO(s)} + \mu^0_{H_2(g)} - \mu^0_{Co(s)} - \mu^0_{H_2O(g)} + RT\ln\left(\frac{p_{H_2}}{p_{H_2O}}\right) + \frac{6\gamma_{Co}}{\rho_{Co} d_{Co}}\left(\frac{\gamma_{CoO}}{\gamma_{Co}}\left(\frac{\rho_{Co}}{\rho_{CoO}}\right)^{2/3} - 1\right) > 0$$

was used to conclude that for spherical cobalt crystallites the reduced state, i.e. $Co + H_2O$, is energetically favoured over the state containing $CoO + H_2$ if the above sum is >0. From these calculations (Fig. 2) it was concluded that cobalt crystallites <4–5 nm will oxidise under FTS conditions, i.e. P_{H_2O}/P_{H_2} = 1–1.5. It was also reported [7] that these thermodynamic calculations were not very sensitive to the temperature changes in the FTS regime, i.e. increasing the temperature from 220 to 250 °C decreased the cobalt crystallite size that should oxidise from 4.4 to 4.3 nm (i.e. at P_{H_2O}/P_{H_2} ratio of 1.5).

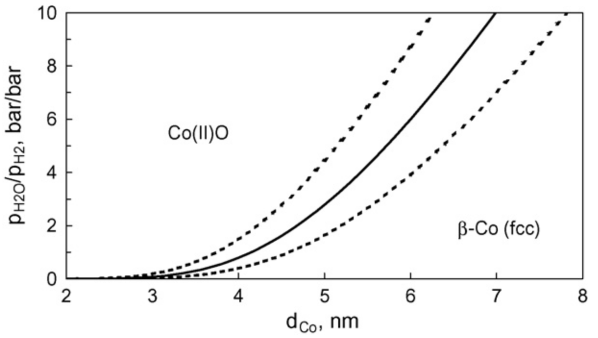

Fig. 2. Stability region of spherical β-Co (fcc) and Co(II)O crystals in H_2O/H_2 atmospheres at 220 °C as a function of the diameter of a spherical metallic Co crystallite (dotted line $\gamma_{\beta\text{-Co}} \pm 15\%$) (adapted from Ref. [7]).

2.3. Unsupported cobalt catalysts

Kim [29,30] showed that the addition of water to the syngas feed at low CO conversions increased the activity of unsupported cobalt based Fischer-Tropsch synthesis catalysts. Similarly, Das et al. [31] showed that the addition of water to the syngas feed increased the activity of an unsupported cobalt catalyst. Bertole et al. [32] concluded from isotopic labelling experiments that water partial pressures of 4 and 8 bar decrease the FTS activity of unsupported cobalt catalysts irreversibly. This was explained by sintering. For unsupported catalysts with large cobalt crystallites, i.e. >ca. 30 nm, it is generally agreed that the addition of water to the FTS feed at low CO conversions has a positive effect. Bertole et al. [32] concluded from isotopic labeling experiments that water increases the CO dissociation rate.

2.4. Alumina supported cobalt catalysts

Huffman et al. [33] showed using in situ XANES/EXAFS that a Co/Al_2O_3 catalyst did not oxidize during FTS (190–200 °C; 1 bar, $P_{H_2O} = 0.025$ bar, $H_2/CO = 3$).

Schanke et al. [18–20] reported that oxidation of cobalt to cobalt oxide can be regarded as a possible deactivation mechanism, as based on model experiments applying thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS) and water co-feeding experiments in a fixed bed reactor. They used cobalt on alumina catalysts with a cobalt loading between 18 and 30 wt.%. Water co-feeding during FTS in a fixed bed showed a rapid deactivation which was attributed to surface oxidation or oxidation of small cobalt crystallites. The TGA experiments performed on the 18 wt.% Co/Al_2O_3 catalyst (i.e. Co size of 25 nm) did not show oxidation [18] at the following conditions: 250 °C, $P_{H_2O} = 5.5$ bar, $P_{H_2} = 0.55$ bar, $P_{CO} = 0$ bar, $P_{tot} = 10$ bar. At the same conditions, TGA experiments on a 21 wt.% Co/1 wt.% Re/Al_2O_3 catalyst (i.e. Co size of 15 nm) did show oxidation of cobalt crystallites. It was mentioned that the oxidation is most likely surface cobalt oxidation or oxidation of small cobalt crystallites. In support of the TGA results XPS experiments [18] on the 21 wt.% Co/1 wt.% Re/Al_2O_3 catalyst did show oxidation of surface cobalt or of small cobalt crystallites at similar conditions, i.e. 200 °C, $P_{H_2O} = 5$ bar, $P_{H_2} = 15$ bar, $P_{CO} = 0$ bar, $P_{tot} = 20$ bar.

Hilmen et al. [21–23] studied, similarly to the Schanke et al. papers [18–20], the deactivation mechanism of unpromoted and Re promoted Co/Al_2O_3 catalysts under model conditions with XPS, TPR, TPD and gravimetry as well as by fixed bed reactor FTS experiments, using co-feeding of water. Both unpromoted and Re promoted Co/Al_2O_3 catalysts showed a decrease in the FTS activity when the water partial pressure was increased. The Re promoted 17 wt.%Co/Al_2O_3 catalyst was found to undergo slight oxidation as observed with TPR and gravimetry. TPD and pulse adsorption indicated a large decrease in cobalt metallic surface area. Surface oxidation of cobalt was also observed for the Re promoted Co/Al_2O_3 with XPS under model conditions ($H_2O/H_2 = 1$, 250 °C, 10 bar, $P_{H_2O} = 5$ bar). The oxidation of cobalt was found to increase with P_{H_2O} and the P_{H_2O}/P_{H_2} ratio. From these studies it was concluded that small cobalt crystallites or surface oxidation of cobalt was responsible for the deactivation during FTS. On the contrary for the unpromoted Co/Al_2O_3 catalyst a slight reduction was observed with XPS under model conditions ($H_2O/H_2 = 10$, 250 °C, 10 bar, $P_{H_2O} = 5$ bar).

Rothaemel et al. [24] and Hanssen et al. [25] studied the effect of water during FTS on the number of active sites on a Co/Al_2O_3 and $Co/Re/Al_2O_3$ catalyst using steady-state isotopic transient kinetic analysis (SSITKA). Co-feeding of water was shown to decrease the number of active sites during FTS. This loss of active sites was explained by surface oxidation of the metallic cobalt during water treatment.

Van Berge and co-workers [6,26–28] showed that for a 20 wt.% $Co/Pt/Al_2O_3$ catalyst the addition of 40% water under FTS conditions, i.e. 220 °C, 20 bar, 50–70% syngas conversion, in a laboratory micro CSTR brought about an irreversible deactivation. The negative effect of water was explained by the oxidation of small metallic cobalt crystallites. Kinetic inhibition due to competitive chemisorption of water was not observed. Model experiments (H_2O/H_2, $P_{H_2O} = 0.025$ bar, 150 °C) on a 9 wt.% $Co/Pt/Al_2O_3$ catalyst, prepared by incipient wetness impregnation, using Mössbauer emission spectroscopy and thermogravimetric analyses showed that the degree of oxidation of $Co/Pt/Al_2O_3$ catalysts depends on the P_{H_2O}/P_{H_2} ratio [6,27]. Model experiments at higher water partial pressures (i.e. $P_{H_2O} = 5.0$ bar, $H_2O/H_2 = 1.0$, 150 °C) on a 12 wt.% $Co/Pt/Al_2O_3$ catalyst, prepared by slurry impregnation, did not show any oxidation of the cobalt metal [28], on the contrary it reduced even further. Van Berge et al. further hypothesised that Co crystallites below 10 nm will oxidise during realistic FTS conditions [13].

Jacobs et al. [14] analysed wax coated spent $Co/Ru/Al_2O_3$ (Co size = 6 nm, H_2 chemisorption) catalysts following FTS (220 °C, $P = 18$–20 bar, $H_2/CO = 2$) with XANES and found oxidation of a fraction of the spent catalysts. They concluded that small cobalt crystallites oxidised during FTS to Co_3O_4 or cobalt aluminate, and were unable to differentiate between the two cobalt phases. The XANES analyses of spent catalysts protected in a blanket of FT wax was new in the field and allowed for the first time direct characterisation of the oxidation state of spent FTS catalysts. Similarly for unpromoted, Pt promoted and Ru promoted Co/Al_2O_3 catalysts (Co size = 6 nm, H_2 chemisorption) oxidation of a fraction of the catalyst to Co_3O_4 or cobalt aluminate was found with XANES following FTS testing (220 °C, $P = 18$ bar, $H_2/CO = 2$) [15]. Again it was concluded that the fraction that did oxidise is most likely the small cobalt clusters. Slight cobalt aluminate formation was also observed by Das et al. for a Re promoted Co/Al_2O_3 catalyst tested at 220 °C, $H_2/CO = 2$, $P = 20$ bar [16].

Li et al. [17] studied the influence of co-fed water on the deactivation of Pt promoted Co/Al_2O_3 catalysts (Co size = 6 nm, H_2 chemisorption) during FTS (210 °C, $P = 29$ bar, $H_2/CO = 2$). Water was shown to have a reversible effect at low amounts in the reactor, i.e <ca. $P_{H_2O}/P_{H_2} = 0.5$. However, with a $P_{H_2O}/P_{H_2} = 0.6$ in the reactor an irreversible deactivation of the Pt promoted Co/Al_2O_3 catalyst was observed. From this observed irreversible deactivation and an increase in the CO_2 selectivity it was suggested that the catalyst underwent oxidation to cobalt oxide or cobalt aluminate. Similarly for a Pt promoted Co/Al_2O_3 (Co size = 6 nm, H_2 chemisorption) catalyst Jacobs et al. [8] concluded using water co-feeding experiments during FTS that at $P_{H_2O}/P_{H_2} < 0.6$ in the reactor reversible deactivation takes place with no changes in the cobalt structure as observed with XANES. However when a higher P_{H_2O}/P_{H_2} ratio in the reactor was used, i.e. >0.6, irreversible deactivation of the catalyst takes place. From XANES analyses it was concluded that cobalt oxidation took place, including cobalt aluminate formation. Jacobs et al. also studied the oxidation behaviour of unpromoted alumina supported cobalt catalysts, containing 15 and 25 wt.% cobalt [9], using water co-feeding during FTS. The 25 wt.% Co/Al_2O_3 catalyst did not deactivate irreversibly under the conditions: 210 °C, $P_{tot} = 20$ bar; $P_{H_2O} = 7.7$ bar, $P_{H_2} = 6.2$ bar, and XANES analysis confirmed that oxidation did not occur. The 15 wt.% Co/Al_2O_3 catalyst did however show irreversible deactivation during FTS (conditions: 220 °C, $P_{tot} = 19.7$ bar; $P_{H_2O} = 7.4$ bar, $P_{H_2} = 8.1$ bar), which was explained by oxidation and the subsequent formation of cobalt–aluminate, as observed by XANES analyses.

In general, for alumina supported cobalt catalysts most authors postulate that surface oxidation or the oxidation of small cobalt crystallites is responsible for a significant part of the deactivation observed during FTS. However, there is no agreement on this threshold value above which cobalt is stable against oxidation. Furthermore, many postulate that this deactivation, i.e. oxidation, is dependant on the P_{H_2O}/P_{H_2} ratio and the total water partial pressure.

2.5. *Silica supported cobalt catalysts*

Kiss et al. [10] observed for a 44 wt.% $Co/Re/SiO_2$ catalyst with predominantly 5 nm cobalt crystallites (as measured with TEM) irreversible deactivation during Fischer-Tropsch synthesis (220 °C, $P_{tot} = 20$ bar; 94% syngas conversion; $P_{H_2O} = 13.1$ bar, $P_{H_2} = 2.1$ bar, $P_{CO} = 0.4$ bar). This irreversible deactivation was ascribed to oxidation of cobalt to a needle-like cobalt-silicate structure. Although cobalt silicate formation was observed, part of the deactivation could be ascribed to sintering. Similarly, Kogelbauer et al. reported [11] that a Co/SiO_2 catalysts formed cobalt silicates as determined with TPR following FTS (220–240 °C, $P_{tot} = 31$ bar, $H_2/CO = 2$). Also Huber et al. [12] reported that Co/SiO_2 catalysts deactivated irreversibly during Fischer-Tropsch synthesis, due to water induced formation of cobalt-silicates, which thus has to involve cobalt oxidation as a first step. Iglesia [39,40] mentioned that cobalt crystallites below 5–6 nm will oxidise and deactivate rapidly under realistic FTS conditions.

On the contrary, for a Co/SiO_2 catalyst Krishnamoorthy et al. [41] found no detrimental effect of the water partial pressure on the FTS activity. Similarly, Bian et al. [34] reported that Co/SiO_2 catalysts with cobalt crystallite sizes of 10 and 29 nm did not oxidise during FTS as measured with EXAFS and XRD under the following FTS conditions: 200–240 °C, $P = 10$ bar; 90% $H_2 + CO$ conversion. Ernst et al. [35] reported that a 25 wt.% Co/SiO_2 catalyst did not show any oxidation as measured with EXAFS/XRD during FTS (1 bar, 220 °C). Li et al. [36] reported that addition of water to silica supported catalysts increased the FTS activity, although high water partial pressures did have a negative effect on the FTS activity. Saib et al. [47] reported for planar $Co/SiO_2/Si(1\,0\,0)$ model catalysts with cobalt crystallites of 4–5 nm that surface oxidation did not occur under model FTS conditions ($P_{H_2O}/P_{H_2} = 1.0$; $P_{H_2O} = 0.2$ mbar), as studied in situ with NEXAFS.

The oxidation behaviour of silica supported cobalt catalysts, although not clear, seems to be related to the Fischer-Tropsch synthesis reaction conditions, especially the water partial pressure, and the cobalt crystallite size.

2.6. *Titania supported cobalt catalysts*

Kim [29,30] showed that the addition of water to the syngas feed at low CO conversions increased the activity of TiO_2 supported cobalt based Fischer-Tropsch synthesis catalysts. It was postulated that the positive effect of water is due to a reversal of the encapsulation of the cobalt crystal with titania [29,30]. Li et al. investigated the effect of water on the performance of titania supported ruthenium promoted cobalt based FTS catalysts [37], and found only reversible deactivation during Fischer-Tropsch synthesis at relatively mild conditions. At more severe FTS conditions permanent deactivation did occur. Bertole et al. [32] concluded from isotopic labelling experiments that water partial pressures of 2 bars increased the FTS activity of a TiO_2 supported rhenium promoted cobalt catalysts.

For titania supported cobalt catalysts the addition of water seems to improve the activity of the catalysts during FTS (low conversions) similar to unsupported cobalt catalysts and in many cases to silica supported cobalt catalysts. However, high water partial pressures are detrimental to the activity. Although it is postulated that the positive effect of water for Co/TiO_2 catalysts is due to a reversal of the encapsulation of the cobalt crystal with titania [29,30] it is also plausible that it is a crystallite size effect, which is in agreement with the results on unsupported bulk cobalt catalysts with large cobalt crystallites.

2.7. Comparisons between catalysts on different supports

Storæter et al. examined [38] the influence of water during FTS on unpromoted and Re promoted cobalt catalysts supported on alumina, silica and titania. Water was found to increase the deactivation of the unpromoted and Re promoted Co/Al_2O_3 catalysts. Whereas for the promoted and Re promoted Co/SiO_2 and Co/TiO_2 catalyst the activity was found to go through a maximum as a function of water partial pressure. This appears to be in agreement with most of research performed on supported cobalt catalysts.

Li et al. [37] mentioned that for the research results obtained in the group of Davis [8,9,14–17,36] the following trends seem to be valid: (i) for titania supported catalyst there is no effect of water addition, (ii) silica supported catalysts show an improvement when water is co-fed and (iii) alumina supported catalyst decrease in activity when water is added. It was also mentioned [37] that this so-called support effect might be a cobalt crystallite size effect, as the cobalt crystallite size decreases in the following order: SiO_2 (13.2 nm) > TiO_2 (8.5 nm) > Al_2O_3 (5.6 nm).

3. Experimental

A cobalt catalyst was prepared by means of aqueous slurry impregnation of a Puralox 5/150 gamma alumina support (Sasol Germany) with a cobalt nitrate solution, also containing ammonium platinum nitrate, followed by vacuum drying [48]. The dried intermediate was subjected to fluidized bed calcination at 250 °C, and was reduced in hydrogen at 425 °C [48]. The reduced cobalt catalyst contained 20 wt.% cobalt and 0.05 wt.% platinum, and had a cobalt crystallite size of maximum abundance of 6 nm [13].

The $Co/Pt/Al_2O_3$ catalyst was tested in a 100 barrel/day slurry bubble column reactor with a diameter of 0.9 m at commercially relevant FTS conditions, i.e. 230 °C, 20 bar ($H_2 + CO$) conversion between 50 and 70%, feed gas composition of ca. 50 vol.% H_2 and 25 vol.% CO, reactor partial pressure ratio P_{H_2O}/P_{H_2} = 1–1.5, reactor water partial pressure P_{H_2O} = 4–6 bar. No water co-feeding was performed during FTS. Direct comparison of catalyst performance can only be done at the same test conditions. As this is difficult to achieve experimentally, a kinetic model was developed using the Satterfield [49,50] equation, i.e. $\text{FT rate} = (kP_{H_2}P_{CO})/(1 + KP_{CO})^2$, in which the observed catalytic performance can be recalculated to exactly the same test conditions. For this study the relative intrinsic (Fischer-Tropsch) activity factor (RIAF) was reported relative to the intrinsic activity after 1 day on stream, which was normalized to 1.0 on day 1.

Representative slurry samples, containing a mixture of spent catalyst and Fischer-Tropsch synthesis wax, were taken directly from the reactor under a nitrogen blanket and were allowed to settle and congeal. The stability of these wax coated catalyst samples against artificial oxidation in air was demonstrated previously [51] using XANES. This method thus allows for analysis of spent catalysts outside the reactor without changing the properties of the spent catalysts, and is referred to as pseudo in situ.

X-ray absorption near edge spectroscopy (XANES) analyses were performed on spent wax coated cobalt catalyst samples, taken from the 100 barrel/day slurry bubble column reactor. Details about the XANES analyses can be found in Ref. [51].

X-ray diffraction (XRD) measurements were performed on spent wax coated cobalt catalyst samples, taken from the 100 barrel/day slurry bubble column reactor. XRD analyses were carried out with D-8 Bruker and URD-6 diffractometers on Cu Kα radiation. XRD patterns were registered in the range from 30° to 55° 2θ with a coupling time of 90 s at each point. Software ORIGIN-6.0 with a Voigt function as approximation was used for the deconvolution of the overlapped diffraction peaks of several phases.

Magnetic measurements were also performed on spent wax coated cobalt catalyst samples, taken from the 100 barrel/day slurry bubble column reactor. The amount of catalyst was determined by burning off the wax after the magnetic measurement. The magnetic measurements were performed by the Weiss extraction method in an electromagnet providing fields up to 21 kOe (2.1 T) at 25 °C. Information is generated about the amount of reduced cobalt present in the catalyst by comparing the saturation magnetization thus obtained with the specific saturation magnetization of bulk cobalt [52].

4. Results

A 20 wt.% $Co/Pt/Al_2O_3$ catalyst [48], having cobalt crystallite size of maximum abundance of 6 nm in the freshly reduced catalyst [13], was tested during Fischer-Tropsch synthesis in a 100-bbl/day slurry bubble column reactor operated at commercially relevant FTS conditions, i.e. 230 °C, 20 bar, ($H_2 + CO$) conversion between 50 and 70%, feed gas composition of ca. 50 vol.% H_2 and 25 vol.%, reactor water partial pressure P_{H_2O} = 4–6 bar, reactor partial pressure ratio P_{H_2O}/P_{H_2} = 1.1.5. The relative intrinsic catalyst activity profile (refer: experimental section for definition on relative intrinsic catalyst activity) is presented in Fig. 3. It can be seen from Fig. 3 that deactivation of the 20 wt.% $Co/Pt/Al_2O_3$ catalyst occurred during the first 30 days, after which the activity started to level off.

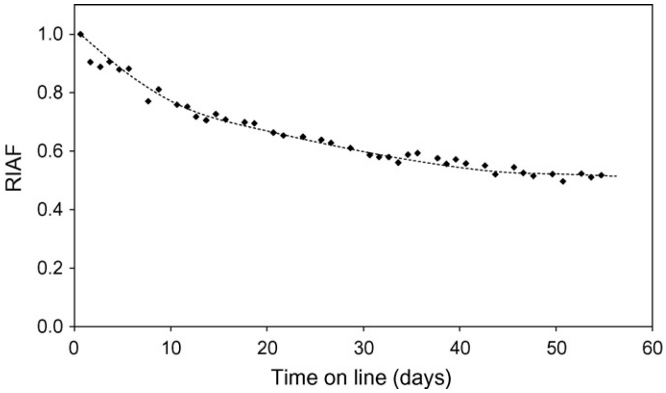

Fig. 3. Relative intrinsic activity factor (RIAF) for a $Co/Pt/Al_2O_3$ catalyst during realistic Fischer-Tropsch synthesis [59].

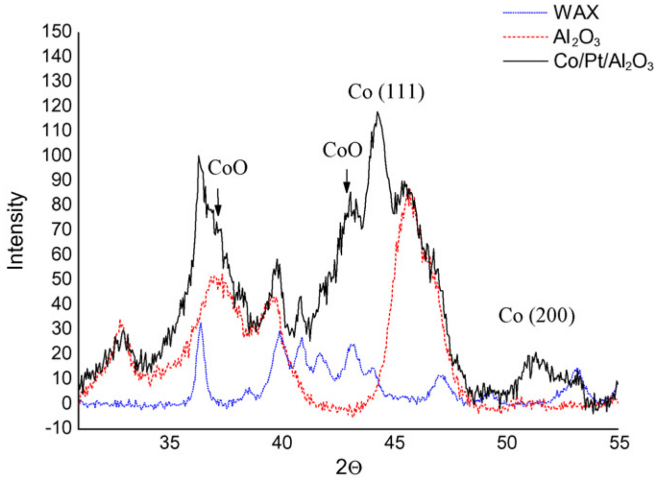

Fig. 4. Superimposed XRD pattern of the Al_2O_3 support, wax and freshly reduced cobalt catalyst.

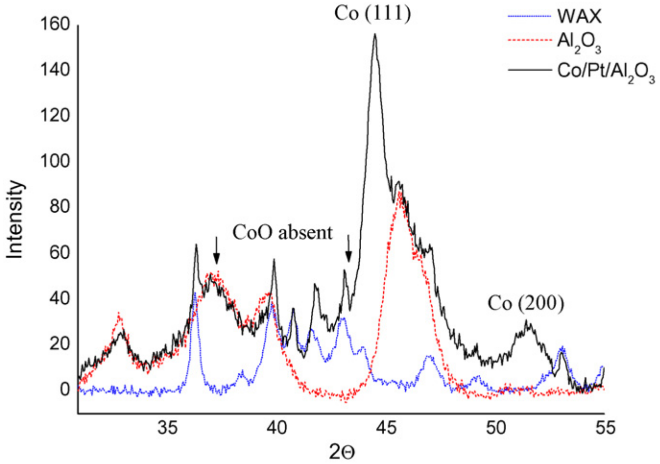

Fig. 5. Superimposed XRD pattern of the Al_2O_3 support, wax, and spent cobalt catalyst after 3 days of Fischer-Tropsch Synthesis.

To verify if oxidation was the primary cause of this deactivation spent wax coated cobalt catalyst samples were taken from the FTS run at different times on stream and studied by means of XRD, magnetic measurements, and XANES. The stability of wax coated samples, removed from the reactor, against artificial oxidation in air was demonstrated previously [51] using XANES.

XRD analyses of the freshly reduced wax coated Co/Al_2O_3 catalyst as well as a spent catalyst sample after three days of FTS are shown in Figs. 4 and 5. XRD analyses can distinguish between cobalt metal and cobalt oxides, as long as these phases are crystalline. In both Figs. 4 and 5, XRD peaks of the alumina support and the wax protective layer are present.

It can be seen from Fig. 4 that the fresh catalyst contained both cobalt metal and a fraction of CoO. In Fig. 5, it can be seen that the XRD peaks indicating CoO disappeared after 3 days of Fischer-Tropsch synthesis. The cobalt metal peaks as well as the alumina support peaks are still present. This shows that oxidation of cobalt metal to cobalt oxide did not occur, while it seems that the CoO present in the fresh catalyst reduced to cobalt metal.

Further support was obtained by performing magnetic measurements on the freshly reduced as well as spent wax coated cobalt catalyst samples from the above-mentioned FTS run. Magnetic measurements can easily determine the total amount of cobalt metal present in a sample.

The magnetic measurement on freshly reduced as well as spent Co/Al_2O_3 catalyst samples show a clear hysteresis (Fig. 6), which indicates the presence of both superparamagnetic cobalt (i.e. cobalt crystallites smaller than or equal to 15 nm) and ferro magnetic or non-superparamagnetic cobalt (i.e. larger than 15 nm) [52]. From the saturation magnetisation the degree of reduction or the amount of cobalt metal can be calculated, if the amount of catalyst is known. The amount of cobalt metal as a function of time on line during Fischer-Tropsch synthesis was calculated and is presented in Table 1. It can clearly be seen from Table 1 that the amount of cobalt metal did not decrease during time on line, but rather increased. This shows that during Fischer-Tropsch synthesis the cobalt catalyst did not oxidize, but rather reduced to a higher degree of reduction. Due to the small Co crystallite size in this catalyst (i.e. 6 nm), which results in a fairly high dispersion of 16%, it can even be concluded that surface oxidation did not occur.

To confirm the XRD and magnetic results, XANES analyses were performed on a series of wax coated samples and were reported previously in detail [51]. XANES analyses have atomic sensitivity and can distinguish between cobalt metal and

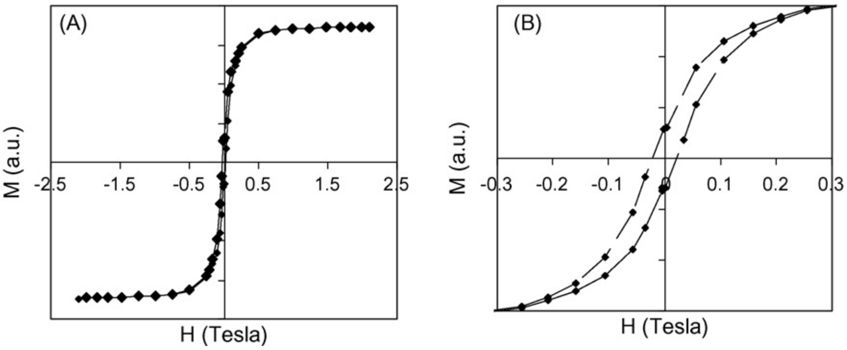

Fig. 6. Magnetic hysteresis (A) of a freshly reduced cobalt catalyst, i.e. magnetization M of catalyst as a function of the applied external magnetic field H. Enlarged section is presented in (B).

Table 1
Quantification of magnetic analyses of a series of spent $Co/Pt/Al_2O_3$ catalysts taken from FTS run

Sample	% Co^0
Freshly reduced	50
Day 1	58
Day 4	66
Day 10	69
Day 21	81
Day 41	71
Day 66	73
Day 90	67
Day 120	74
Day 150	88

different cobalt oxides (CoO, Co_3O_4 and $CoAl_2O_4$) quantitatively.

The XANES spectra are shown in Fig. 7 and the corresponding amount of cobalt metal and oxide following quantification is shown in Table 2. It can be seen from Fig. 7 that the XANES spectrum of the freshly reduced catalyst still has a cobalt oxide component in the spectrum, while the XANES spectrum of the spent catalyst after 140 days of FTS seems to be similar to cobalt metal. This notion is confirmed by the data in Table 2, which shows that this Co/Al_2O_3 catalyst does not oxidize to CoO or cobalt aluminate under realistic FTS conditions. To the contrary, the catalyst was found to reduce to a higher extent. Due to the high dispersion of this catalyst, i.e. 16%, it can again be concluded that surface oxidation did not occur for this catalyst with 6 nm crystals.

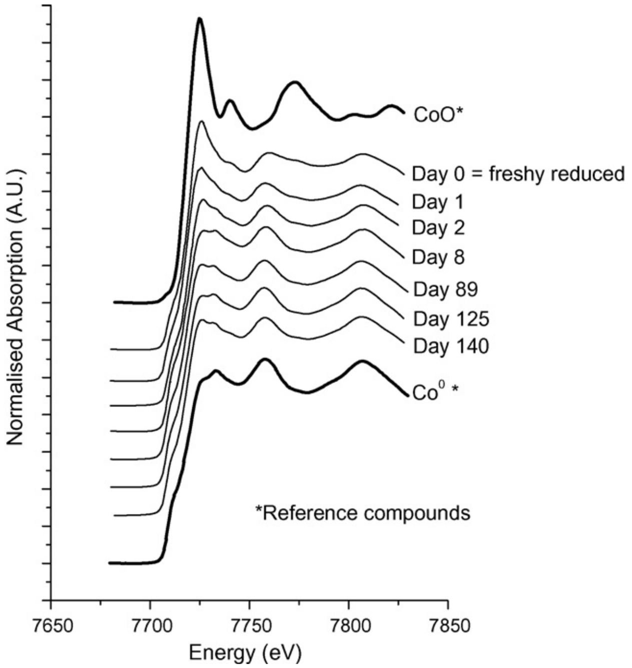

Fig. 7. XANES analysis of spent $Co/Pt/Al_2O_3$ catalyst samples taken from FTS run [59].

Table 2
Quantification of XANES analyses of a series of spent $Co/Pt/Al_2O_3$ catalysts taken from FTS run using a linear combination of reference compounds

Sample	% Co^0	% CoO^a
Freshly reduced	53	47
Day 1	69	31
Day 2	80	20
Day 8	85	15
Day 89	88	12
Day 125	89	11
Day 140	87	13

Error = 2–3%.

[a] This does not rule out any minor $CoAl_2O_4$, which is difficult to differentiate with XANES using the current data.

5. Discussion

5.1. Industrial Co/Al_2O_3 catalyst

A combination of the XANES and the magnetic analyses on spent industrial 20 wt.% $Co/Pt/Al_2O_3$ catalyst samples is presented in Fig. 8. The figure shows that the freshly reduced catalyst contains, besides the cobalt metal, also a CoO fraction, which are most likely small unreduced CoO crystals [51]. It can be seen that both techniques show that oxidation of cobalt metal during Fischer-Tropsch synthesis at realistic conditions, i.e. $P_{H_2O} = 4–6$ bar, $P_{H_2O}/P_{H_2} = 1–1.5$, did not occur for this Co/Al_2O_3 catalyst, containing cobalt crystallites of 6 nm. This is also confirmed by the XRD measurements. On the contrary, the catalyst reduced to a higher extent during FTS. The increase in the degree of reduction seems to occur during the first 10 days of Fischer-Tropsch synthesis, after which it levels off. Although there is a difference in the absolute level of cobalt metal in the spent cobalt catalyst between magnetic measurements (i.e. average of 75% Co(0)) and XANES analyses (i.e. average of 85% Co(0)) of about 10 percentage points, the agreement between the XANES and magnetic analyses results is considered reasonable. The explanation for the fact that the

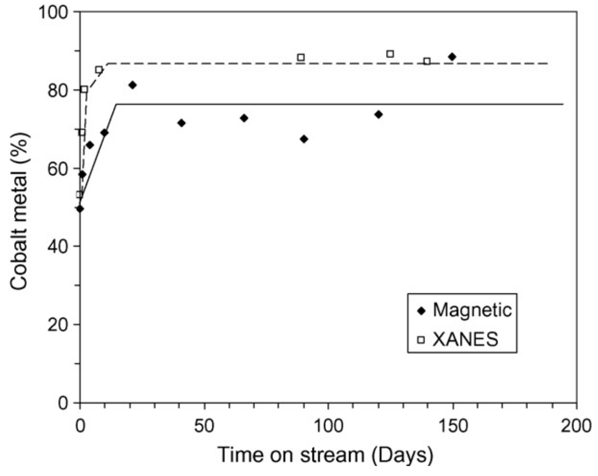

Fig. 8. Amount of cobalt metal as a function of time on line in spent cobalt catalyst samples taken from FTS run, as determined with magnetic measurements and XANES analyses.

catalyst reduced during Fischer-Tropsch synthesis is not clear yet, but it could be speculated that one of the following parameters is important in assisting the reduction of the unreduced small cobalt oxide crystallites: (i) the relatively high hydrogen partial pressure during Fischer-Tropsch synthesis, (ii) the presence of CO during Fischer-Tropsch synthesis, or (iii) sintering causing larger cobalt crystallites that can reduce easier.

These measurements clearly show that oxidation (bulk and surface) can be ruled out as a major deactivation mechanism for this Co/Al_2O_3 catalyst with Co crystallites of predominantly 6 nm during realistic Fischer-Tropsch synthesis. The notion of no surface oxidation is also supported by the cobalt flat model results reported by Saib et al. [47]. Furthermore, wax coated samples can be studied in a ‘‘pseudo in situ’’ mode with XRD, magnetic measurements and XANES, which allows for the characterization of spent catalyst samples that were subjected to realistic Fischer-Tropsch synthesis conditions.

The observed deactivation of the cobalt on alumina catalyst (i.e. refer Fig. 3) can thus not be explained by oxidation of (part of) the cobalt metal crystallites. The observed deactivation might be explained by other deactivation mechanisms as sintering, surface reconstruction, support migration and/or carbon deposition.

5.2. *Reconciliation of literature*

The apparent discrepancy in literature on the oxidation of cobalt as a deactivation mechanism is partly due to the comparison of FTS catalysts made up of different support materials (SiO_2, TiO_2 and Al_2O_3), different promoters and different preparation methods mostly compared at different FTS process conditions (temperature and pressure). These variables will affect amongst others, the reactor ratio of the P_{H_2O}/P_{H_2} and the cobalt crystallite size distribution, which will therefore affect the tendency of the catalyst to oxidise [7]. Furthermore, the complexity of the influences of water on cobalt supported catalysts, i.e. oxidation of Co to CoO [6,7], oxidation of existing CoO in contact with the support to cobalt support compounds [6], sintering [10], support migration [53–56], surface reconstruction and/or oxidation of the defects which are known to significantly enhance activity [57,58] also contributes to the apparent discrepancy. All of the above mentioned deactivation mechanisms could occur during the addition of water and would vary from system to system. Hence, reported oxidation of cobalt based on indirect techniques that does not monitor the oxidation state of the cobalt directly will overestimate the degree of oxidation.

In an attempt to consolidate the current data (i.e. Section 4) with the open literature data (Section 2), it was decided to compare all available data to the thermodynamic data, on the stability of nano-sized cobalt crystallites, as reported by van Steen et al. [7]. According to these ‘‘surface’’ thermodynamics the tendency of the cobalt crystallites to oxidise is related to the combination of the cobalt crystallite size and the ratio of the reactor partial pressures of water and hydrogen, i.e. P_{H_2O}/P_{H_2}.

Only literature data where the oxidation state of cobalt was directly measured were used [8–10,14,15,18,21,34,40,47,51].

Table 3
Summary of the open literature as well as current data on the effect of the water/hydrogen reactor ratio combined with the cobalt crystallite size on the occurrence of oxidation during FTS. (P_{H_2O}/P_{H_2} data in ‘‘*italics*’’ were re-calculated; cobalt sizes in ‘‘*italics*’’ were estimated)

Author	Support	Cobalt size (nm)	Cobalt size measurement technique	P_{H_2O}/P_{H_2} in reactor	Oxidation (yes/no)	Oxidation analysis technique
Schanke et al. [18]	Alumina	25	H_2 TPD	0.33	No	XPS
		15		0.33	No	XPS
		<15		0.33	Yes	XPS
Hilmen et al. [21]	Alumina	16	H_2 chemisorption	10	No	XPS
		10		10	No	XPS
		<10		10	Yes	XPS
Iglesia [40]	Silica	4	–	*0.74*	Yes	–
Jacobs et al. [14]	Alumina	6	H_2 TPD	*0.16*	No	XANES
		<6		*0.16*	Yes	XANES
Jacobs et al. [8]	Alumina	6	H_2 TPD	0.56	No	XANES/EXAFS
		6		0.60	Yes	XANES/EXAFS
Jacobs et al. [15]	Alumina	6	H_2 TPD	*0.38*	No	XANES
		<6		*0.38*	Yes	XANES
Jacobs et al. [9]	Alumina	6	H_2 TPD	0.91	Yes	XANES/EXAFS
		12		1.24	No	XANES/EXAFS
Kiss et al. [10]	Silica	5[a]	TEM	6.55	Yes	TEM
Bian et al. [34]	Silica	10	H_2 chemisorption	6.11	No	EXAFS/XRD
		29		6.11	No	EXAFS/XRD
Saib et al. [47]	Silica	4.5	AFM	1.0	No	NEXAFS
Saib et al. [51]	Alumina	6	TEM	1.0–1.5	No	XANES
This paper	Alumina	6	TEM	1.0–1.5	No	XANES/XRD/magnetic

[a] Although reported as oxidation of 5–6 nm Co crystallites from TEM it is not clear whether only the small cobalt crystallites were oxidised to cobalt silicate.

For the open literature results, it was sometimes necessary to calculate hydrogen and water reactor partial pressures from the data available in the literature (e.g. syngas conversion, total pressure, feed composition). Furthermore, on a few occasions where oxidation to cobalt aluminate was observed it was only reported that this oxidation is due to a fraction of small cobalt crystallites. In this case a crystallite size band was used [14,15,18,21]. Since, there is no direct evidence that the observed oxidation was due to oxidation of this fraction of small cobalt crystallites, it is also plausible that the observed oxidation is due to cobalt aluminate formation at the interface of the cobalt crystallite and alumina support. This could also be assisted by defects in the support. The data used for this consolidation are shown in Table 3. Although data only on silica and alumina supported cobalt catalysts are reported, the general perception for titania supported cobalt catalysts is that it does not oxidize during FTS [29,30,32,37]. The data that were re-calculated and estimated are shown in *italics* in Table 3. Note that the temperature at which the experiments were performed varied between 200 and 250 °C [8,14–17]. Van Steen et al. [7] showed only a small change in the ''surface'' thermodynamic data between 220 and 250 °C. Therefore, no large changes between 200 and 250 °C are expected in the experimental results. It was also assumed that sintering is either not occurring in catalysts that were reported in the ''oxidation'' literature or that sintering is slow compared to the (surface) oxidation rate of cobalt crystallites and does not play a role of significance in the observed oxidation.

A combination of the open literature data where the oxidation of cobalt was directly measured and the current results are presented in Fig. 9. It can be seen that there is a good agreement between the reported data on oxidation and the ''surface'' thermodynamics data, especially for the region of ''no oxidation''. The reason that there is not complete agreement between surface thermodynamics and results, as presented in Fig. 9, could possibly be due to the fact that, although often average cobalt crystallite sizes are reported in literature, supported catalysts normally do have a crystallite size distribution. The fraction of small cobalt crystallites might thus behave different than the expected behaviour of cobalt crystallites of the average reported crystallite size.

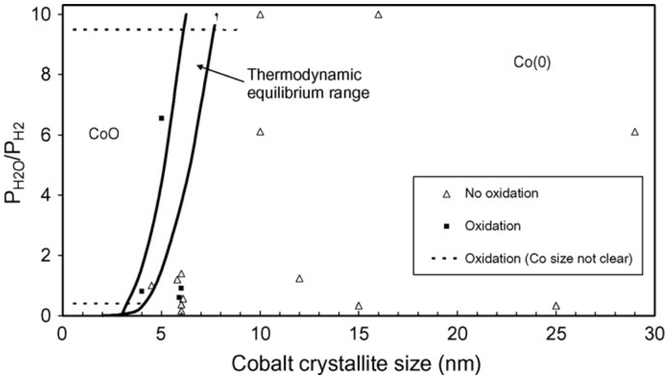

Fig. 9. Summary of the open literature (Section 2) as well as current data (Section 4) on the effect of the water/hydrogen reactor ratio as a function of cobalt crystallite size on the oxidation behaviour of cobalt. All the data are superimposed on the thermodynamic equilibrium data range (solid lines) generated by Van Steen et al. [7] for nano-sized cobalt crystallites.

Fig. 9 shows that the literature reported data, which seem to be in contradiction with each other, are in better agreement if only the results are compared where oxidation was directly observed by a suitable characterization technique and when viewed as a function of cobalt crystallite size and the ratio of reactor partial pressures of hydrogen and water (P_{H_2O}/P_{H_2}). From Table 3 and Fig. 9 there also appears to be no effect of the support, i.e. silica versus alumina.

6. Conclusions

This study on an industrial Co/Al_2O_3 catalyst (i.e. containing cobalt crystallites of 6 nm) showed, using XRD, XANES and magnetic measurements, that oxidation is not a deactivation mechanism during realistic Fischer-Tropsch synthesis. The large discrepancies in literature on the oxidation behaviour of cobalt are likely due to the lack of direct characterisation of the cobalt oxidation state and due to the comparison of catalysts with varying cobalt crystallites compared at different reactor partial pressures of hydrogen and water (P_{H_2O}/P_{H_2}). A better agreement of all the data (literature and current study) was obtained when only the results where oxidation was directly observed by a suitable characterization technique were viewed as a function of cobalt crystallite size and the ratio of reactor partial pressures of hydrogen and water (P_{H_2O}/P_{H_2}). Hence, the oxidation of cobalt can be prevented by the correct combination of the reactor partial pressures of hydrogen and water (P_{H_2O}/P_{H_2}) and the cobalt crystallite size and appears to be independent of the support.

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