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Oxidation of cobalt based Fischer–Tropsch catalysts as a deactivation mechanism

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Abstract

The oxidation of supported cobalt based slurry bed Fischer–Tropsch catalysts by means of water was studied. Water is one of the Fischer–Tropsch reaction products and can probably cause oxidation and deactivation of a reduced cobalt catalyst. Model experiments using Mössbauer emission spectroscopy and thermogravimetry as well as realistic Fischer–Tropsch synthesis runs were performed. It was demonstrated that Mössbauer emission spectroscopy can successfully be applied to the investigation of high cobalt loading Fischer–Tropsch catalysts. Strong indications were found that oxidation of reduced cobalt catalysts occurs under realistic Fischer–Tropsch conditions. Mössbauer emission spectroscopy and thermogravimetry results showed that the oxidation depends on the P_{H_2}/P_{H_2O} ratio, and that oxidation proceeds to less than complete extents under certain conditions. The formation of both reducible and less reducible cobalt oxide species was observed, and the relative ratio between these species depends on the severity of the oxidation conditions.

Keywords: Fischer–Tropsch; Cobalt catalyst; Oxidation; Mössbauer emission spectroscopy

1. Introduction

Cobalt based Fischer–Tropsch is an alternative to iron [1], but the relative high cost of cobalt demands increased catalyst stabilities in order to ensure extended runs. The development of a stable cobalt catalyst, however, requires an improved fundamental understanding and quantification of the various deactivation mechanisms. Supported cobalt catalysts deactivate during extended periods of continuous Fischer–Tropsch synthesis [1,2]. This deactivation can be due to surface condensation [3], sulphur poisoning [1], and oxidation [2].

In order to obtain an impression of the feasibility of cobalt oxidation during Fischer–Tropsch synthesis, a thermodynamic evaluation was conducted. This was done to substantiate the published claim that the formation of cobalt oxide from metallic cobalt is thermodynamically not favoured under Fischer–Tropsch synthesis conditions [4]. Fig. 1 was constructed in accordance with basic thermodynamic considerations, and provides support for this earlier published conclusion. The FT region specified in Fig. 1 was based on the following supposition of what is to be understood as typical Fischer–Tropsch conditions (i.e. assuming a gradientless slurry phase reactor): a reactor pressure of 20 bar, a reactor temperature of 170–240°C, a synthesis gas composition of 67 vol.% H_2 and 33 vol.% CO, and a %(H_2+CO) conversion of 50–70. These typical FT 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_2}/P_{H_2O} ratio between 0.86 and 2.00. The equilibrium constant versus temperature curves of $Co+Al_2O_3+H_2O \leftrightarrow CoAl_2O_4+H_2$

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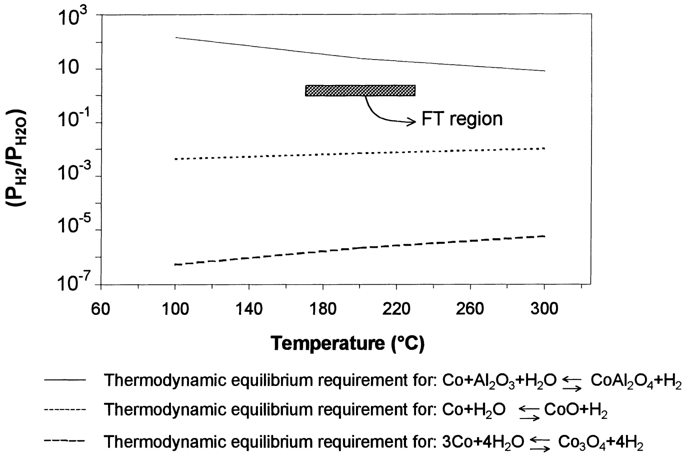

Fig. 1. Thermodynamic equilibrium constants for three selected cobalt oxidation reactions: (—) thermodynamic equilibrium requirement for $Co+Al_2O_3+H_2O$ $CoAl_2O_4+H_2$, (- - -) thermodynamic equilibrium requirement for $Co+H_2O$ $CoO+H_2$, (– – –) thermodynamic equilibrium requirement for $3Co+4H_2O$ $Co_3O_4+4H_2$.

and $Co+H_2O \leftrightarrow CoO+H_2$ in Fig. 1 agrees well with previous publications, i.e. [4,5], respectively. Typical P_{H_2}/P_{H_2O} ratios observed during low temperature Fischer–Tropsch conducted in a slurry phase "gradientless" reactor at realistic synthesis conditions, are higher than the thermodynamic equilibrium constants of $Co+H_2O \leftrightarrow CoO+H_2$ and $3Co+4H_2O \leftrightarrow Co_3O_4+4H_2$ (i.e. depicted in Fig. 1). Seeing that the thermodynamic equilibrium constants for both these chemical equilibria are smaller than typical P_{H_2}/P_{H_2O} ratios observed during Fischer–Tropsch synthesis, it can be concluded that the reduction of either CoO or Co_3O_4 by hydrogen will be spontaneous during the slurry phase Fischer–Tropsch synthesis under realistic conditions. In the case of Co/Al_2O_3 catalysts, the oxidation of Co to the $CoAl_2O_4$-spinel is thermodynamically spontaneous. It could be postulated that the conversion of Co/Al_2O_3 to $CoAl_2O_4$-spinel needs to proceed via CoO as an intermediate product, thus: $Co+H_2O \rightarrow CoO+H_2$ followed by $CoO+Al_2O_3 \rightarrow CoAl_2O_4$. The standard Gibbs energy changes for these two reactions are superimposed in Fig. 2, clearly illustrating the nonspontaneous nature of the reaction: $Co+H_2O \rightarrow CoO+H_2$,

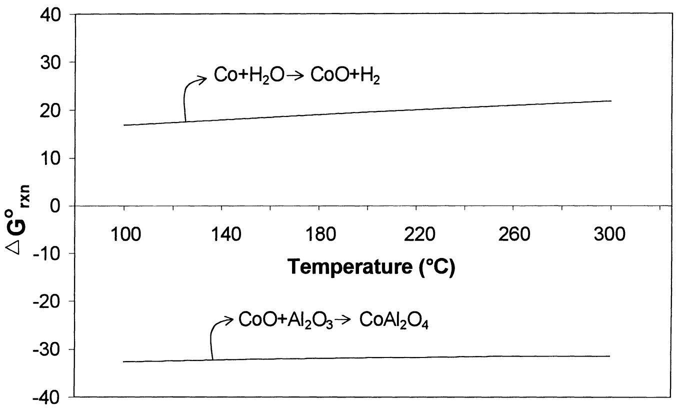

Fig. 2. Standard Gibbs energy change for the "kinetically coupled" reactions.

at typical Fischer–Tropsch temperatures. If however, the consecutive reaction ($CoO+Al_2O_3 \rightarrow CoAl_2O_4$ with $\Delta G_{rxn}<0$, i.e. spontaneous) should also prove to be kinetically facile, the overall conversion of $Co+Al_2O_3+H_2O$ to $CoAl_2O_4+H_2$ could not be ruled out. It is, however, reported that $CoAl_2O_4$ does not form, to any appreciable extent, during catalyst calcination of $Co(NO_3){\cdot}6H_2O$ impregnated Al_2O_3 supported catalysts at temperatures up to 500°C [6], which argues against the above-mentioned hypothesis of kinetic coupling. This statement is further supported by the published observation [5] that relatively severe hydrothermal treatment of Co/Al_2O_3 (i.e. steam at 500–800°C) is required for the formation of the $CoAl_2O_4$-spinel. This means that although the conversion of Co and Al_2O_3 to $CoAl_2O_4$ is thermodynamically favoured at typical Fischer–Tropsch temperatures, it is highly unlikely that it would take place. In summary, it can therefore be stated that, from a pure thermodynamic point of view, the oxidation of bulk phase metallic cobalt to either CoO or Co_3O_4 is unlikely, whilst the oxidation to $CoAl_2O_4$ is kinetically restricted during typical Fischer–Tropsch synthesis conditions.

Strong literature support does, however, exist in favour of cobalt catalyst oxidation during Fischer–Tropsch synthesis. Iglesia [7] concluded that rapid catalyst deactivation, as a result of cobalt oxidation, is to be anticipated in the case of supported cobalt catalysts with cobalt dispersions in excess of 15%. Schanke et al. [2] and Schanke and coworkers [8,9] deduced from model experiments performed on Co/Al_2O_3 catalysts, as analysed via the methods of gravimetry and XPS, that oxidation occurs to reducible Co_xO_y as well as less reducible Co-aluminate-like species, and that the high extents of oxidation were correlated with relative low H_2/H_2O ratios, high absolute values of P_{H_2O} and high cobalt dispersions. These observed deviations from bulk phase thermodynamics were ascribed to metal:support and metal:metal-oxide interactions at high cobalt dispersions. Whilst Iglesia [7] postulated a cobalt dispersion of 15% as the optimum with respect to maximising stabilised cobalt catalyst Fischer–Tropsch activities, Schanke et al. [2] observed oxidation of up to 16% (with respect to the initial total amount of reduced cobalt) in the case of catalysts with a cobalt dispersion of 10%. In an apparent contradiction to the above-mentioned published work of Iglesia [7] and Schanke et al. [2], Goodwin and coworkers [10] demonstrated that a 9% Co/Al_2O_3 catalyst did not oxidise during Fischer–Tropsch synthesis at 200°C, as observed with X-ray absorption fine structure spectroscopy (i.e. XAFS). Only minor traces of CoO were observed.

The present study was undertaken to test the hypothesis that under certain conditions (i.e. gas environment and temperature), cobalt catalyst oxidation levels off, and does not continue until the extinction of all reduced cobalt.

2. Experimental

2.1. Spectroscopy of choice to complement model gravimetry studies

Gravimetry was proven [2] to be successful in the quantification of extents of cobalt catalyst oxidation under the influence of modelled environments, i.e. H_2+H_2O+ an inert gas (e.g. N_2 or Ar). The prerequisite is that changes in catalyst weight should only be a result of cobalt oxidation and perhaps the physical adsorption of water, which can be quantified separately. Gravimetry, however, cannot be used in a Fischer–Tropsch synthesis environment, because it would be impossible to ascribe weight changes exclusively to catalyst oxidation.

The objective is thus to identify a suitable spectroscopic method, that will have the capacity of complementing gravimetry as the preferred cobalt catalyst fingerprinting/characterisation method, the latter being limited to model environments.

Mössbauer emission spectroscopy was selected on the strength of four characteristics [11,12]. Firstly, Mössbauer is an in situ technique applicable to real synthesis conditions because of its ability to reflect for a single element, in a complex system, oxidation state, details of chemical bonding, symmetry of the atomic environment, magnetic ordering and lattice dynamical properties. A possible complication might, however, be the need to obtain the spectrum at temperatures below 25°C in the case of highly dispersed particles [13]. Secondly, Mössbauer is a bulk technique, because it detects all the Mössbauer nuclei in a given sample. Thirdly, Mössbauer absorption spectroscopy (MAS), where the recoil free emission of a

γ-ray, produced in the source by the decay of radioactive ^{57}Co isotopes, is absorbed by the ^{57}Fe isotope (i.e. a natural abundance of ca. 2%), has been successfully applied to a Fe/TiO_2 Fischer–Tropsch catalyst [14,15]. Finally, Mössbauer emission spectroscopy (MES) is, however, required in the case where cobalt catalysts are to be investigated. The implication of this requirement is that the source (i.e. the radioactive ^{57}Co isotope) should be incorporated into the catalyst. This may place restrictions on the selected catalyst preparation method, and although not yet applied to high loading cobalt based Fischer–Tropsch catalysts, MES has already been successfully demonstrated on Co–Mo hydro-desulphurisation (HDS) catalysts [16,17] as well as model 1–2% Co/Al_2O_3 catalysts [18].

MES measurements were carried out using a constant acceleration spectrometer in a triangular mode with a moving single line absorber of $K_4Fe(CN)_6{\cdot}3H_2O$ enriched in ^{57}Fe. Positive velocities corresponded to the absorber moving away from the source. The velocity was calibrated with the Mössbauer spectrum of sodium nitro-prusside $Na_2(Fe(CN)_5NO){\cdot}2H_2O$ obtained with a ^{57}Co:Rh source, and the zero of the velocity scale was relative to the single position of the $K_4Fe(CN)_6{\cdot}3H_2O$ absorber measured with the ^{57}Co:Rh source [19]. An option that was also explored was the deconvolution of the overall spectra with calculated sub-spectra that consisted of Lorentzian-shaped lines. In the case of quadruple doublets the line widths and the absorption areas of the constituent peaks were constrained equal. The measurements were carried out in a Mössbauer in situ atmospheric pressure reactor previously described [20], using oxygen-purified gasses. Mössbauer emission spectra were obtained at 25°C under a static pure hydrogen environment of slight overpressure. This condition was reached after the in situ atmospheric pressure reactor was first flushed for ca. 1 h with pure argon at the specific treatment temperature, cooled down to 25°C, under a pure argon flow, whereafter Ar was replaced with H_2.

The interpretation of MES spectra may be hampered by the so-called chemical effects. The transition from ^{57}Co to ^{57}Fe occurs via electron capture whereby the electronic structure of the atom is changed, followed by a reshuffling of the electrons. In particular, if the atom is incorporated in an insulating material (for instance Co_3O_4), this may take a relatively long time. If the required time is longer than the lifetime of the excited state, the electronic structure, and so the energy levels, may have changed. In case of ^{57}Co: Co_3O_4, it is found that ^{57}Fe, produced by the decay, is Fe^{3+} for the tetrahedral as well as octahedral sites, irrespective of the valence state of the parent cobalt [21,22]. In case of ^{57}Co: Co-metal, the ^{57}Fe is also in the metallic state. This makes a direct interpretation of the MES spectra difficult. Therefore, in this investigation MES has been applied as a fingerprint technique. This means that spectra of catalysts are compared with those of reference compounds.

2.2. Co/Al_2O_3 slurry phase Fischer–Tropsch catalysts used during this investigation

2.2.1. A 30 g Co/0.075 g Pt/100 g Al_2O_3 standard catalyst

This catalyst was prepared according to a proprietary recipe [23]. The catalyst was prepared by the application of two aqueous slurry phase $Co(NO_3)_2$ impregnation steps (spiked with a specific amount of ammonium-platinum-nitrate) of pre-shaped spherical alumina, followed by a 250°C calcination step directly performed after each of the two impregnation/vacuum drying steps. The calcined catalyst was reduced at 380°C for 16 h in pure hydrogen using a heating rate of 1°C/min. Degrees of reduction of ca. 75%, with a typical cobalt dispersion of 15%, were obtained. The degree of reduction was determined by means of oxygen titration at 380°C, while the dispersion was calculated from hydrogen chemisorption experiments. These static hydrogen chemisorption measurements were performed on a Micromeritics ASAP 2010 equipment at a temperature of 100°C. Prior to the chemisorption experiments, the catalyst sample was reduced in situ in hydrogen at 380°C for 16 h. This catalyst is referred to as the standard catalyst in this study, and was used in gravimetric experiments, temperature programmed reductions (TPR) as well as in slurry phase CSTR Fischer–Tropsch synthesis evaluations.

2.2.2. A look-alike 10 g Co/0.025 g Pt/100 g Al_2O_3 catalyst

A similar preparation method as that described in Section 2.2.1 cannot be used easily to prepare a catalyst doped with radioactive ^{57}Co isotope, as is required for an MES investigation. A simplified single step incipient wetness impregnation procedure was therefore used in order to prepare a “look-alike” catalyst. After this incipient wetness impregnation step of the preferred pre-shaped Al_2O_3 with a ^{57}Co isotope containing aqueous cobalt nitrate solution (also spiked with a specific amount of ammonium-platinum-nitrate), the sample was dried at 25°C in flowing air, and subsequently calcined at 250°C. Reduction of this catalyst was effected in a pure H_2 atmospheric pressure environment at 380°C for 16 h. The radioactive ^{57}Co was obtained from I.D.B. Holland B.V. as $^{57}Co(NO_3)_2$ in 1 mol HNO_3.

2.3. Fischer–Tropsch slurry phase CSTR synthesis run

Fischer–Tropsch synthesis tests were performed in a slurry CSTR with a reactor volume of 670 ml. The catalyst samples (i.e. 20–30 g) were pre-reduced at 380°C for 16 h in pure hydrogen at 1 bar, using a heating rate of 1°C/min, and suspended (under an argon blanket) in 300 ml molten Fischer–Tropsch hydrogenated wax (Schumann-Sasol H1 hard wax) inside the reactor. Typical conditions were employed, i.e. 220°C, 20 bar, feed of composition: 50 vol.% H_2, 25 vol.% CO and 25 vol.% inerts, and syngas conversion levels of 50–70% were maintained. The synthesis gas flows were regulated by Brooks mass flow controllers, and use was made of the ampoule-sampling-technique as the selected on-line synthesis performance monitoring method [24]. This technique is based on the quantitative transfer of all volatile overhead compounds (i.e. inlet or outlet) into pre-evacuated glass ampoules of ca. 2 ml, which were subsequently analysed on a gas chromatograph.

2.4. Temperature programmed reduction experiments

The TPR experiments were performed on a conventional Perkin Elmer TGA-7 thermogravimetric analyser, using 15 mg of catalyst sample. A gas mixture of 90% hydrogen in nitrogen was used, and a heating rate of 10°C/min from 25 to 1050°C was employed.

3. Results and discussion

The objectives with respect to further exploring the feasibility of MES to study industrially attractive cobalt based Fischer–Tropsch catalysts were to illustrate the quantitative application of MES, as well as to test the hypothesis that, under certain conditions (i.e. gas environment and temperature), catalyst oxidation will level off and will not continue until the extinction of all reduced cobalt. The results published by Bartholomew et al. [18] provided an indication of success, but the Co/Al_2O_3 systems investigated in this particular study could not be considered as industrially attractive (i.e. too low cobalt loading and too low degree of reductions).

Fig. 3 clearly illustrates the differences between the MES spectra of calcined and freshly reduced look-alike catalyst samples. These spectra were obtained at room temperature. The fitted MES parameters are presented in Table 1. The MES spectrum of the calcined look-alike catalyst sample is likely to be the combination of a singlet due to Co^{2+} and a doublet due to Co^{3+}, as per Co_3O_4-spinel. This is in agreement with results reported by Wivel et al. [21]. The sextet present in the MES spectrum of the freshly reduced look-alike catalyst in Fig. 3 clearly illustrates that this sample contained a significant amount of metallic cobalt. The overall degree of reduction of this particular sample LA2, as reflected by the relative area under the deconvoluted sextet, was 75%.

In total two ^{57}Co-doped look-alike catalysts were prepared (labelled as: LA1 and LA2), and analysed with in situ MES after different model treatment steps. Table 2 summarises the experimental program.

Gravimetry was used to verify the extents of reduction as derived from MES (i.e. mass% metallic cobalt as reflected by the relative area under the deconvoluted sextet of the overall MES spectrum). For this purpose the oxidation behaviour of a freshly reduced sample of the standard catalyst was monitored under a set of conditions (i.e. 150°C, an atmospheric pressure N_2+H_2O environment with $P_{H_2O}=0.025$ bar(a) and $P_{H_2}/P_{H_2O}=0$) that should lead to complete oxidation to Co_3O_4 as dictated by thermodynamics. Fig. 4 depicts the results of this endeavour. As shown in Fig. 4, the freshly reduced catalyst was first subjected to a H_2+H_2O atmospheric pressure environment, that was highly enriched in hydrogen (i.e. $H_2/H_2O=33$).

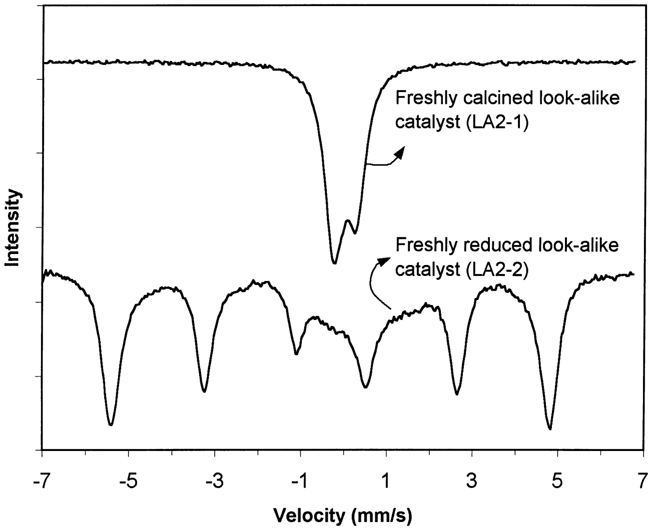

Fig. 3. Representative Mössbauer spectra of catalyst sample LA2.

According to the data presented in Table 2 (e.g. LA2-10) a H_2/H_2O ratio as low as 1 should also prevent oxidation at 150°C. The reason for this intermediate treatment step was to determine the potential weight increase due to any physical adsorption of water, as was indeed observed by Schanke et al. [2], who operated at much higher water partial pressures. In this particular situation, i.e. P_{H_2O}=0.025 bar(a) at 150°C, no measurable amount of water did adsorb. It appears (Fig. 4) that up to 85% of the total cobalt inventory was oxidised. This estimated degree of reduction of ca. 85% for the standard catalyst agrees well with the degree of reduction from MES for the look-alike catalyst LA2 of 79% (LA2-3 in Table 2). Having confirmed similar degrees of reduction of both the standard catalyst and the second look-alike catalyst (i.e. LA2-3), the oxidation profiles of these two catalysts under the oxidative environment described in Fig. 4, were compared (see Fig. 5). The data reported in Table 2 (i.e. labelled LA2-3 as representative for zero time, and LA2-4) were used in the construction of the oxidation profile of the freshly reduced look-alike catalyst as studied with MES (Fig. 5). Both these profiles clearly show oxidation to extinction, which is in agreement with bulk phase thermodynamics as applied to a (Ar or N_2)+H_2O environment at 150°C.

Table 1
The MES fitted parameters of look-alike catalyst LA2, after calcination and reduction[a]

Sample	Isomer shift (mm/s)	Quadrupole splitting (mm/s)	Hyperfine field (kOe)	Spectral contribution (%)
LA2-1 (ex calcination)	0.21	0.58	–	77
	0.11	–	–	23
LA2-2 (ex reduction)	−0.09	–	318	75
	0.29	0.97	–	13
	1.11	1.18	–	12
LA2-4 (ex oxidation 150°C)	0.22	0.59	–	94
	0.90	1.80	–	6
LA2-12 (ex 850°C)	0.08	0.67	–	49
	0.82	1.58	–	51

[a] Experimental uncertainties IS and QS ±0.03 mm/s, hyperfine field ±2 kOe, spectral contribution ±5%.

Table 2
Atmospheric pressure treatment steps applied to the two ^{57}Co-doped look-alike catalysts investigated with Mössbauer emission spectroscopy (MES)[a]

Catalyst label	Treatment	MES analysis	
		Analysis temperature (°C)	Metallic cobalt (mass%)
LA1-1	Ex calcination	25	0
LA1-2	Ex reduction	25	58
LA1-3	Ex 20 h under Ar+H_2O (P_{H_2O}=0.025 bar(a)) at 200°C	25	42
LA1-4	Ex 20 h under Ar+H_2O (P_{H_2O}=0.025 bar(a)) at 250°C	25	23
LA1-5	Ex 20 h under Ar+H_2O (P_{H_2O}=0.025 bar(a)) at 300°C	25	0
LA1-6	Ex re-reduction	25	35
LA1-7	Ex 160 h under Ar+H_2O+H_2 (P_{H_2O}=0.025 bar(a); H_2O/H_2=1) at 300°C	25	40
LA2-1	Ex calcination	25	0
LA2-2	Ex reduction	25	75
LA2-3	Ex 8 days under Ar+H_2O+H_2 (P_{H_2O}=0.025 bar(a); H_2O/H_2=1) at 300°C	25	79
LA2-4	Ar+H_2O with P_{H_2O}=0.025 bar(a) at 150°C		
	Ex 26 h	25	52
	Ex 50 h	25	20
	Ex 100 h	25	0
LA2-5	Ex re-reduction	25	76
LA2-6	Ar+H_2O+H_2 with P_{H_2O}=0.025 bar(a) and H_2/H_2O=0.1 at 150°C		
	Ex 72 h	150	50
	Ex 126 h	150	23
LA2-7	Ex re-reduction	25	71
LA2-8	Ar+H_2O+H_2 with P_{H_2O}=0.025 bar(a) and H_2/H_2O=0.1 at 150°C		
	Ex 20 h	150	39
LA2-9	Ex re-reduction	25	74
LA2-10	Ar+H_2O+H_2 with P_{H_2O}=0.025 bar(a) and H_2/H_2O=1.0 at 150°C		
	Ex 98 h	150	75
LA2-11	Ar+H_2O+H_2 with P_{H_2O}=0.025 bar(a) and H_2/H_2O=0.3 at 150°C		
	Ex 12 h	150	41
	Ex 35 h	150	35
	Ex 70 h	150	33
	Ex 95 h	150	32
LA2-12	Air at 850°C for 4 h	25	0

[a] All of the treatment steps listed in Table 2 followed each other consecutively (i.e. LA1-1→LA1-2→LA1-3, etc.), and the water partial pressure of 0.025 bar(a) was accomplished by having passed the carrier gas (i.e. pure Ar or a selected Ar+H_2 mixture) through a water saturation column that operated at a temperature of 21°C.

The principal difference between the oxidation profiles of the freshly reduced standard catalyst and the freshly reduced look-alike catalyst samples, is the slower oxidation rate associated with the look-alike catalyst. This observation could be explained by a lower dispersion for the look-alike catalyst, which could provide a higher resistance to oxidation. From Table 2, it can also be deduced that the cobalt oxide

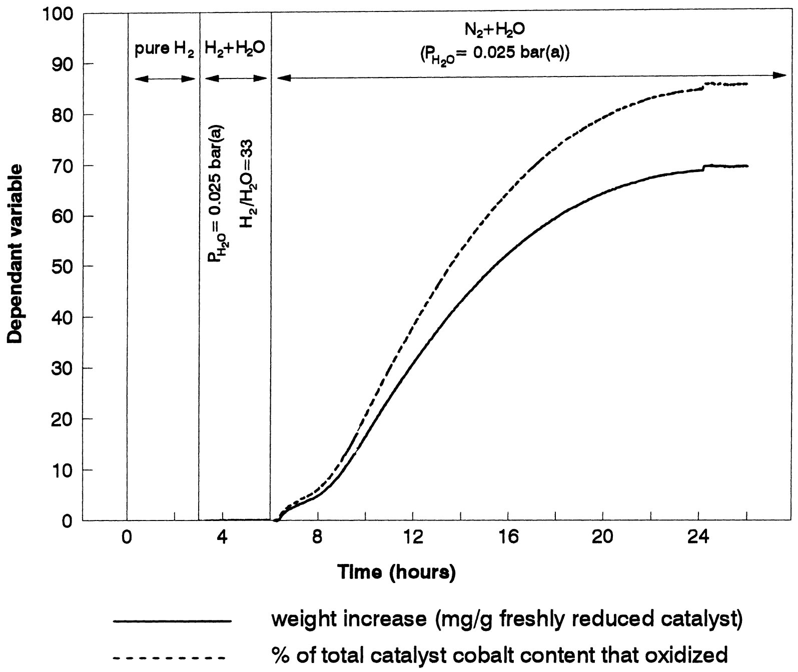

Fig. 4. Gravimetric analysis of a freshly reduced standard catalyst at 150°C and 0.84 bar(a): (—) weight increase (mg/g freshly reduced catalyst, (- - -) % of total catalyst cobalt content that oxidised.

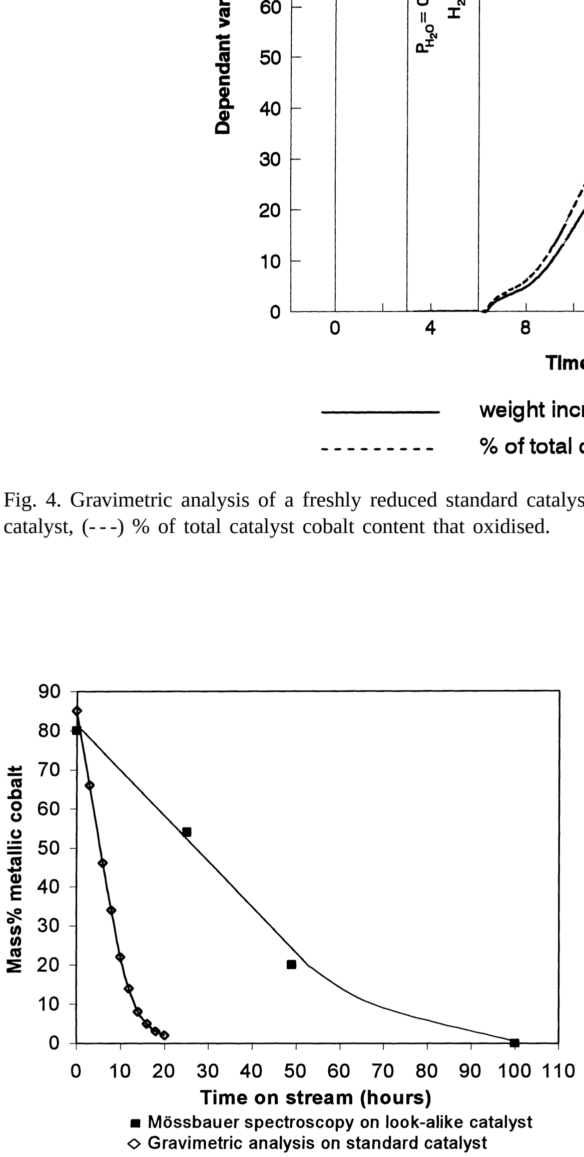

Fig. 5. Direct observation of the oxidation behaviour of freshly reduced catalyst at the conditions: 150°C; atmospheric pressure; (Ar or N_2)+H_2O environment; P_{H_2O}=0.025 bar(a): ■ Mössbauer spectroscopy on look-alike catalyst, ◇ gravimetric analysis on standard catalyst.

species formed upon catalyst oxidation at 150°C in an Ar+H_2O environment (i.e. P_{H_2O}=0.025 bar(a)), are completely reducible at 380°C (refer: catalyst label LA2-5). The spectral parameters of sample LA2-4 are very much like those of Co_3O_4 (Table 1).

The influence of the addition of a little hydrogen to the Ar+H_2O environment at 150°C on the oxidation behaviour of a re-reduced sample (i.e. LA2-5), was investigated. This was done with the aim of demonstrating deviations from bulk phase thermodynamics, as well as to determine whether catalyst oxidation always proceeds to extinction once it has been initiated. The model oxidation environment first investigated, was 1 bar(a) Ar+H_2+H_2O with P_{H_2O}=0.025 bar(a) and H_2/H_2O=0.1 at 150°C, i.e. labelled as LA2-6 and LA2-8 in Table 2. The catalyst oxidation profiles that were observed during these MES analyses of the look-alike catalyst are depicted in Fig. 6. Although analysis number LA2-6 (Table 2) was not allowed to run to completion, an impression of a linear decline of the degree of reduction until extinction was created. Upon the re-reduction of this

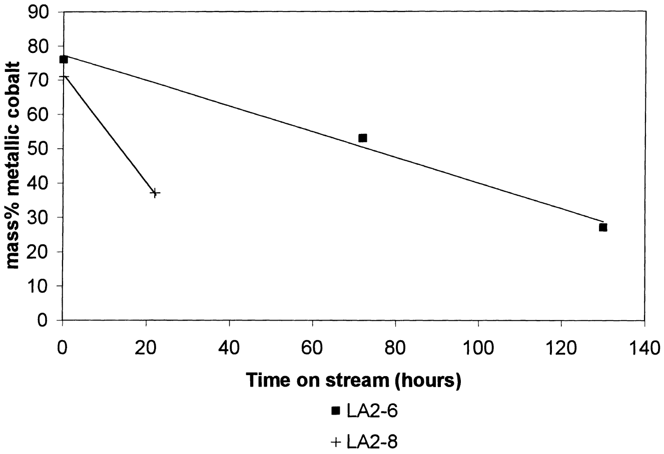

Fig. 6. Repeat oxidation profiles of the look-alike catalyst as observed with MES at the conditions: (150°C; 1 bar(a); Ar+H_2+H_2O environment, P_{H_2O}=0.025 bar(a) and H_2/H_2O=0.1): (■) LA2-6, (+) LA2-8.

look-alike catalyst sample (i.e. LA2-7), a repeat of the same oxidation experiment was followed for the first 20 h on stream (i.e. analysis number LA2-8). During the repeat run an increased oxidation rate was registered. The above-mentioned increased oxidation rate can possibly be interpreted in terms of the observation [25,26] that a *reduction→controlled oxidation→re-reduction* catalyst pretreatment cycle is to be associated with an enhancement of cobalt dispersion.

In view of the oxidation behaviour of the look-alike catalyst under the influence of 1 bar(a) Ar+H_2+H_2O with P_{H_2O}=0.025 bar(a) and H_2/H_2O=0.1 at 150°C, i.e. apparent oxidation to extinction in violation of bulk phase thermodynamics, it was decided to decrease the severity of the oxidative treatment, to test the validity of the earlier stated hypothesis that catalyst oxidation will not always proceed to extinction once it has been initiated. It was thus decided to increase the H_2/H_2O ratio to 1.0, whilst keeping the rest of the conditions fixed, i.e. 1 bar(a) Ar+H_2+H_2O with P_{H_2O}=0.025 bar(a) at 150°C. This analysis was labelled LA2-10 in Table 2. Based on the results listed in Table 2, it can indeed be concluded that this environment did not result in catalyst oxidation, even after ca. 100 h of exposure of the re-reduced sample (i.e. LA2-9). This experiment was immediately followed-up by a lowering of the hydrogen content to such an extent that the H_2/H_2O ratio decreased to 0.3 (i.e. analysis number LA2-11 of Table 2). This downward adjustment in the H_2/H_2O ratio initiated catalyst oxidation, and a levelling-off in the extent of oxidation was observed (Fig. 7).

From the above-presented results, it can be concluded that under the influence of 1 bar(a) Ar+H_2+H_2O with P_{H_2O}=0.025 bar(a) at 150°C, a fully re-reduced sample of the look-alike catalyst will not oxidise at all at H_2/H_2O=1.0, which is in agreement with bulk phase thermodynamics. The catalyst will oxidise only to a degree of reduction of ca. 30%

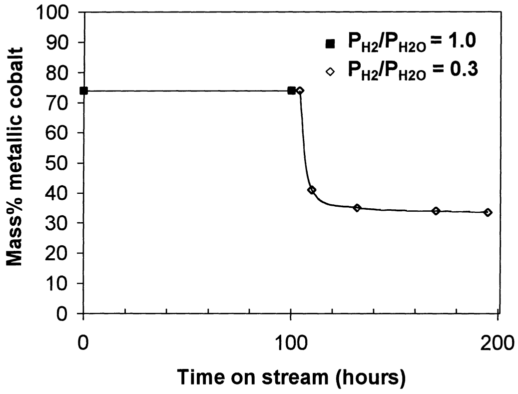

Fig. 7. Catalyst oxidation as directly observed with Mössbauer spectroscopy (150°C; 1 bar(a) Ar+H_2+H_2O environment; P_{H_2O}=0.025 bar(a)).

at $H_2/H_2O=0.3$, which is in violation of bulk phase thermodynamics, and the catalyst will apparently oxidise to extinction at $H_2/H_2O=0.1$, also in violation of bulk phase thermodynamics (refer: analysis number LA2-6).

The fact that no oxidation of the re-reduced look-alike catalyst was observed at a H_2/H_2O ratio of 1.0 (i.e. also a representative H_2/H_2O ratio of realistic slurry phase Fischer–Tropsch synthesis), does not imply that catalyst oxidation is to be ruled out in the case of the standard catalyst under typical Fischer–Tropsch synthesis conditions. Reasons for this are that (i) the MES analyses were all performed at $P_{H_2O}=0.025$ bar(a), which is much lower than typical synthesis water partial pressures (i.e. 4.5–7.5 bar(a)). Schanke et al. [2] have clearly stated that catalyst oxidation is not only a function of the H_2/H_2O ratio, but also of the absolute water partial pressure, and (ii) the cobalt crystallite size distribution of the standard catalyst might still be significantly smaller than that of the reduced→oxidised→re-reduced (i.e. treated) look-alike catalyst.

All of the oxidation environments so far considered in this section were maintained at a temperature of 150°C. Although oxidation to extinction was observed in a number of experiments, in no instance was the subsequent reducibility of the resultant cobalt oxide species influenced. In all instances complete recovery was accomplished through the application of a standard re-reduction procedure (i.e. atmospheric pressure pure hydrogen at 380°C). Schanke et al. [2], however, observed that catalyst oxidation might also produce a less reducible cobalt-aluminate-like species. In order to test this hypothesis, the look-alike catalyst was also oxidised at a more severe temperature of 200–300°C (i.e. analyses: LA1-3, LA1-4, and LA1-5). The corresponding gas environments consisted of 1 bar(a) Ar+H_2O with a fixed water partial pressure of 0.025 bar(a). Complete oxidation was eventually registered, and the application of a standard re-reduction at 380°C only effected a 60% recovery (i.e. analysis number LA1-6 of Table 2). The corresponding Mössbauer emission spectra are depicted in Fig. 8, which also contains superimposed spectra for comparative purposes, i.e. LA2-4 and LA2-5 as an example of a completely re-reducible situation, as well as LA2-12 (which was treated at 850°C in air to form the blue-coloured $CoAl_2O_4$-spinel). The

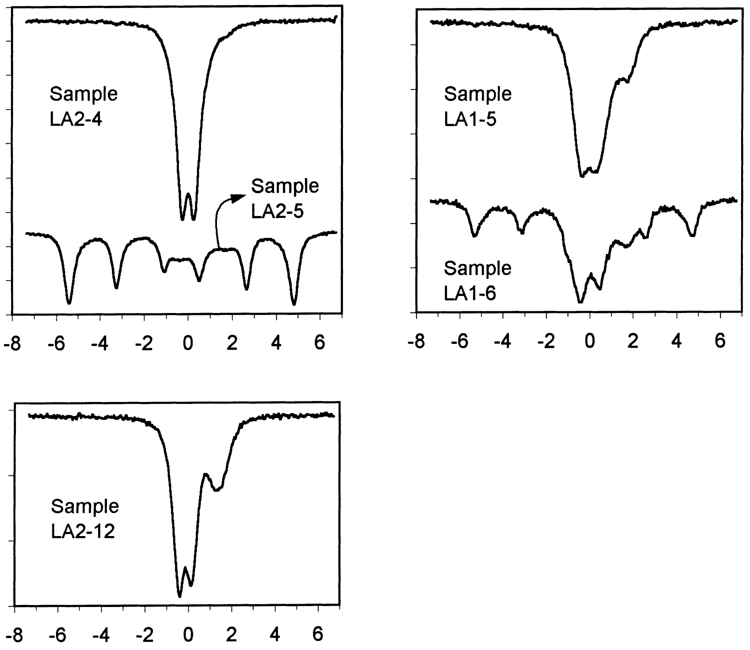

Fig. 8. Mössbauer spectra of completely oxidised (1 bar(a) Ar+H_2O; $P_{H_2O}=0.025$ bar(a)) and re-reduced look-alike catalysts.

data obtained for LA2-12, i.e. $CoAl_2O_4$-spinel are in agreement with literature reports [21]. Qualitatively speaking, it is observed in Fig. 8 that a pronounced peak was detectable at a velocity of ca. 2 mm/s in the spectra of the catalyst oxidised at 300°C (LA1-5), the re-reduced catalyst (LA1-6), as well as the $CoAl_2O_4$-spinel. This peak at ca. 2 mm/s was not that pronounced in either of the spectra of the catalyst oxidised at 150°C (LA2-4) and the re-reduced catalyst (LA2-5). It can thus be concluded that this peak at 2 mm/s, combined with the quadruple doublet, is unique to the less reducible cobalt oxide species, qualitatively indistinguishable from $CoAl_2O_4$-spinel.

It thus appears that MES might proved to be inadequate in conclusively characterising this observed less reducible cobalt oxide species, even with the application of spectrum deconvolution. Because of this perceived shortcoming, it was decided to resort to the conventional method of temperature programmed reduction, as detected through gravimetry. The following four standard catalyst samples were prepared for this purpose:

1. freshly calcined catalyst;
2. freshly reduced standard catalyst which was subjected to a controlled complete oxidation performed in the following environment: atmospheric pressure $Ar+H_2O$ with $P_{H_2O}=0.025$ bar(a) at 150°C;
3. freshly reduced standard catalyst which was subjected to a complete oxidation performed in the following environment: 10 bar(a) $Ar+H_2O$ with $P_{H_2O}=5$ bar(a) at 300°C;
4. freshly calcined catalyst, additionally calcined at 800°C, which proved successful (as confirmed with XRD) in quantitatively converting cobalt into $CoAl_2O_4$-spinel.

The TPR profiles of these four treated catalyst samples were obtained, and are illustrated in Fig. 9. The re-reduction profile of the standard catalyst that was oxidised in the environment of $Ar+H_2O$ with $P_{H_2O}=0.025$ bar(a) at atmospheric pressure and 150°C, is in complete accord with the earlier MES results (e.g. analysis LA2-5, Table 2), i.e. complete recovery is effected with a standard re-reduction procedure. This TPR profile is very similar to the TPR pattern of the untreated calcined catalyst. The reduction profile of $CoAl_2O_4$-spinel indicates a reduction temperature of >800°C, as compared to a literature quoted figure of ca. 930°C [2,27]. The reduction profile of the standard catalyst that was oxidised under a more severe environment (i.e. 10 bar(a) $Ar+H_2$ with $P_{H_2O}=5$ bar(a) at 300°C) does indeed substantiate the formation of less reducible cobalt oxide species, to be distinguished from $CoAl_2O_4$-spinel. This species is described in literature [2,27] as highly dispersed amorphous Co^{2+} and Co^{3+} overlayers interacting with Al_2O_3, associated with reduction temperatures evenly spread out over the range between 430 and 730°C.

3.1. Fischer–Tropsch slurry phase CSTR synthesis runs

Two synthesis runs (i.e. numbers 29F and 151$) were performed on 30 g Co/0.075 g Pt/100 g Al_2O_3 catalysts, both prepared according to the method of slurry phase cobalt impregnation of spray-dried and pre-shaped Al_2O_3 as support [23]. The aim of this discussion is to obtain information on the influence of an artificially increased reactor water partial pressure (i.e. brought about by the co-feeding of water to run 151$ during a selected period, viz.: ca. 7–23 days on stream) on the deactivation profile. A relative activity factor that allows for the direct comparison of the intrinsic Fischer–Tropsch activities of different cobalt catalysts and/or synthesis runs, not clouded by discrepancies in synthesis conditions (i.e. temperature, pressure, space velocity, etc.) was used for this comparison. Having applied the previously selected Satterfield and coworkers [28,29] Fischer–Tropsch kinetic equation (i.e. $r_{FT}=(kP_{H_2}P_{CO})/(1+KP_{CO})^2$), the Arrhenius derived pre-exponential factors of k were individually estimated for each catalyst as function of time on stream. The relative activity factor was defined as: (*observed pre-exponential factor*)/(*pre-exponential factor of an arbitrarily selected conditioned base-line catalyst*). During both Fischer–Tropsch synthesis runs (i.e. 29F and 151$) realistic conditions were maintained (i.e. 220°C, 20 bar, and 50–70% syngas conversion levels), as listed in Table 3. Fig. 10 depicts the superimposition of the Fischer–Tropsch synthesis performances observed during both these runs. The co-feeding of water during run 151$ was initiated after ca. 1 week of standard operation, which allowed for catalyst conditioning. Fig. 10 clearly illustrates that

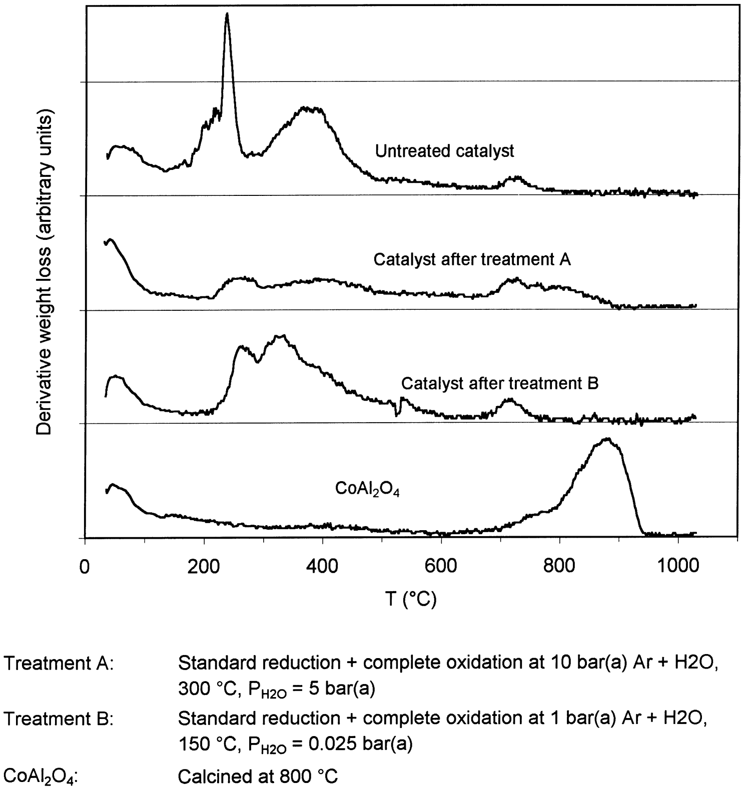

Fig. 9. Superimposed TPR patterns of differently pretreated Co/Al_2O_3 catalyst samples, as followed by atmospheric pressure TGA: carrier gas=90 vol.% H_2 in N_2; heating rate=10°C/min. Treatment A: standard reduction+complete oxidation at 10 bar(a) $Ar+H_2O$, 300°C, P_{H_2O}=5 bar(a). Treatment B: standard reduction+complete oxidation at 1 bar(a) $Ar+H_2O$, 150°C, P_{H_2O}=0.025 bar(a). $CoAl_2O_4$: calcined at 800°C.

Table 3
Synthesis conditions maintained during the Fischer–Tropsch slurry phase CSTR runs as performed on standard 30 g Co/100 g Al_2O_3 catalysts

	Run 29F	Run 151$
Temperature (°C)		221
Pressure (bar(a))	20	20
Catalyst mass (g)	20.0	23.7
Feed gas flow rate (dm^3_n/min)	1.02	1.14
Feed composition (vol.%)		
H_2	51.3	50.9
CO	27.4	28.6
Inerts	21.3	20.5
%(H_2+CO) conversion	75–65	75–55

the synthesis performances of both runs were very comparable during the first week of catalyst conditioning under the specified set of realistic synthesis conditions. Upon the co-feeding of water to run 151$, in order to bring about a ca. 40% increase in the observed reactor water partial pressure, the measured relative activity factor declined for ca. 3 days, after which relative stable operation was again recorded. The following four observations are all regarded to provide strong arguments in favour of increased catalyst oxidation to have been exclusively responsible for this observed enhancement in catalyst deactivation. The proposed kinetic equation of Satterfield and coworkers [28,29], was also recently confirmed by Bartholomew et al. [30], implies that the decline in catalyst activity was not due to a water inhibition effect of the kinetics. Secondly, the fact that the activity

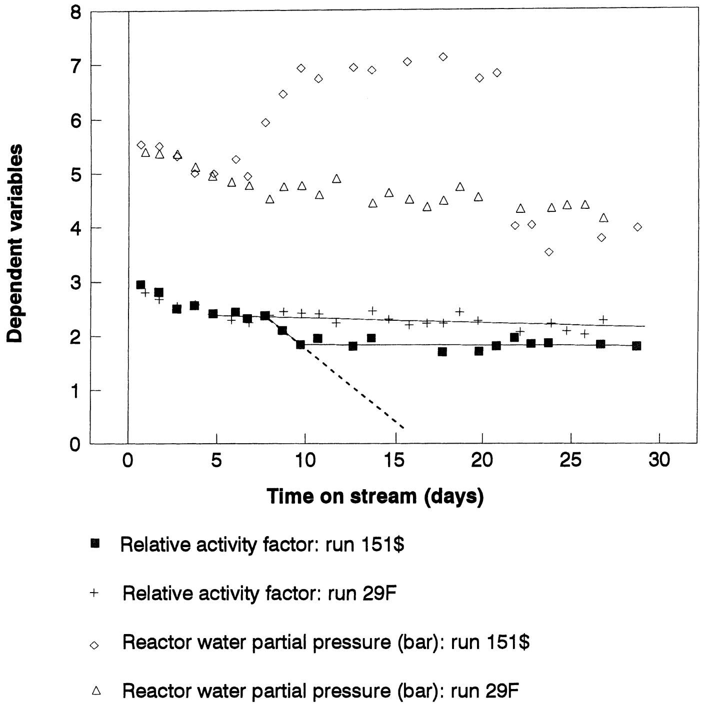

Fig. 10. Superimposition of the defined relative activity factors and reactor water partial pressures of the slurry phased Fischer–Tropsch synthesis runs 29F and 151$ — (■) relative activity factor: run 151$, (+) relative activity factor: run 29F, (◇) reactor water partial pressure (bar): run 151$, (△) reactor water partial pressure (bar): run 29F.

did not automatically recover upon the termination of water co-feeding at period 23, provides further support for this notion, i.e. kinetic inhibition of water due to competitive chemisorption. Thirdly, the qualitative similarity between the activity profile of run number 151$, the initiation of water co-feeding, and that of the oxidation profile depicted in Fig. 7, is striking. Finally, the deactivation rate of the activity profile of run 151$, ex 10 days on stream, did not differ statistically significantly from zero, whilst the deactivation rate as observed during run 29F (ex 5 days on stream) was estimated as 0.0129 units per day. This observation is thus not reconcilable with the hypothesis that the deactivation of a conditioned catalyst (i.e. ex 1 week on stream in a realistic synthesis environment) is exclusively caused by low level feed gas poisoning, a notion that would have implied comparable deactivation rates (ex period 10 days) for both runs, which was not observed with statistical significance.

4. Conclusions

It was demonstrated that MES can indeed be successfully applied to the investigation of high cobalt loading Fischer–Tropsch catalysts, i.e. bulk phase metallic cobalt contents (i.e. degree of reduction) could be obtained as function of time on stream during model oxidation experiments in good agreement with the established method of gravimetry.

The fact that the catalysts that were marked for Mössbauer analyses required doping with the radioactive ^{57}Co isotope, placed a restriction on the representativeness of these look-alike catalysts. This look-alike catalyst was prepared according to the method of aqueous phase incipient wetness impregnation, and the slower oxidation rates observed for these catalysts were seen as evidence for the anticipated lower cobalt dispersions.

MES results obtained during this investigation were limited to atmospheric pressure, and only model studies were performed for the oxidation behaviour of look-alike catalysts, under the influence of a gas environment consisting of a mixture of Ar, H_2 and H_2O at a specific temperature. These results can be summarised as follows:

Oxidation behaviour at 150°C with a fixed water partial pressure of 0.025 bar(a):

$H_2/H_2O=1.0$: No oxidation in accordance with bulk phase thermodynamics.
$H_2/H_2O=0.3$: Limited oxidation to fully reducible oxides in violation of bulk phase thermodynamics.
$H_2/H_2O=0$: Oxidation to extinction to fully reducible oxides, in accordance with bulk phase thermodynamics.

Oxidation behaviour at 300°C with a fixed water partial pressure of 0.025 bar(a):

$H_2/H_2O=0$: Oxidation to extinction to a mixture of reducible and less reducible oxides, in accordance with bulk phase thermodynamics.

The presence of less reducible cobalt oxides, after water treatment at 300°C, was also observed with TGA experiments, and is in agreement with the MES observations.

The increased deactivation in laboratory CSTR Fischer–Tropsch synthesis runs, as a result of the addition of water under realistic Fischer–Tropsch conditions, can be explained in terms of oxidation of cobalt, as was directly observed in the model MES experiments.

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