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The application of Mössbauer emission spectroscopy to industrial cobalt based Fischer–Tropsch catalysts

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Abstract

^{57}Co-Mössbauer emission spectroscopy (MES) has been used to study the oxidation of cobalt as a deactivation mechanism of high loading cobalt based Fischer–Tropsch catalysts for the gas-to-liquids process. It was reported previously [Catal. Today 58 (2000) 321; Proceedings of the International Symposium on the Industrial Applications of the Mössbauer Effect, 13–18 August, 2000, Virginia Beach, VA] that oxidation was observed at atmospheric pressure under conditions that were in contradiction with the bulk cobalt phase thermodynamics. A high-pressure MES cell was designed and constructed, which created the opportunity to study the oxidation of cobalt based Fischer–Tropsch catalysts under realistic synthesis conditions. The cobalt catalyst preparation procedure was investigated by means of ^{57}Fe-Mössbauer absorption spectroscopy, applying ^{57}Fe as a probe atom. Initial results indicate, although not yet conclusive, that a ^{57}Co-MES catalyst can be prepared from the industrial prepared standard Co catalyst by an additional simple incipient wetness impregnation procedure. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Mössbauer emission spectroscopy; Fischer–Tropsch catalyst; Gas-to-liquid process

1. Introduction

The Fischer–Tropsch synthesis forms an integral part of the gas-to-liquids (GTL) process, which is currently receiving serious attention as a way of exploiting remote gas fields and/or associated gas at crude oil production fields, i.e. gas that is currently being flared or reinjected. The GTL process consists of three main process steps [3–5]. First, natural gas is converted into synthesis gas by means of a reforming process, e.g. autothermal reforming or partial oxidation. The second step is the Fischer–Tropsch synthesis, i.e. the conversion of the synthesis gas into a waxy syncrude. Finally, a hydroprocessing step converts the waxy syncrude into a mixture of gas-oil (80%) and naphtha (20%) [6]. The gas-oil can be sold at a potential premium as an environmentally friendly diesel [4] and the aromatics free naphtha is an excellent cracker feedstock to produce light olefins like ethylene and propylene [4].

The Fischer–Tropsch process (i.e. coal based) has commercially been applied for several decades, using precipitated and fused Fe-catalysts. However, the lifetime of the Fe-catalysts is limited and only low conversions per pass seem feasible. To overcome these problems, supported cobalt has received widespread attention as the preferred catalyst [3–5] in the GTL process. High-per-pass synthesis gas conversions can be achieved and the water gas shift reaction does not play a major role in this cobalt based process. The relative high cost of cobalt demands stable catalyst performance to ensure extended Fischer–Tropsch synthesis runs. Supported cobalt based Fischer–Tropsch catalysts, however, may deactivate during extended

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periods of continuous operation under realistic synthesis conditions. This deactivation is ascribed to sulphur poisoning [7], ammonia and hydrogen cyanide poisoning [8], surface condensation of hydrocarbons [9], as well as oxidation [10] of the metallic cobalt. The oxidation of bulk cobalt metal to cobalt oxides, i.e. CoO and Co_3O_4, is thermodynamically not favoured under realistic Fischer–Tropsch synthesis conditions [11]. The formation of $CoAl_2O_4$, in the case where Al_2O_3 is the selected support material, is thermodynamically spontaneous, but it is reported that this does not occur at temperatures up to $T = 773\,K$ [12,13].

Literature support does exist in favour of oxidation of cobalt catalysts [10,14,15]. However, the analytical techniques used in these studies were always ex situ. As the validity of ex situ studies can be questioned, there is still a need for a feasible in situ technique that can determine: (i) the extent of oxidation under realistic Fischer–Tropsch reaction conditions, and (ii) the type of oxide species that may be produced.

Mössbauer emission spectroscopy (MES) is one of the few techniques that can be considered for in situ characterisation studies of supported cobalt based Fischer–Tropsch catalysts. In previous studies [1,2], it was shown that MES can be used to study cobalt based Fischer–Tropsch catalysts at atmospheric pressure conditions.

The present study reports on the cobalt catalyst preparation procedure by probing the cobalt with ^{57}Fe and ^{57}Co, and on the oxidation by means of water of industrial cobalt based Fischer–Tropsch catalysts through experiments at atmospheric pressure and low water partial pressures, up to real industrial conditions (P_{H_2} and P_{H_2O} up to 5 bar each). For these last MES experiments, a reactor has been designed and constructed to perform long-term (deactivation) studies at pressures up to 20 bar and at temperatures up to $T = 773\,K$.

2. Experimental

2.1. Mössbauer emission and absorption spectroscopy

The ^{57}Co-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 nitroprusside, $Na_2(Fe(CN)_5NO){\cdot}2H_2O$, obtained with a ^{57}Co:Rh source, and the zero of the velocity scale was relative to the single line position of the $K_4Fe(CN)_6{\cdot}3H_2O$ absorber, measured with the ^{57}Co:Rh source.

The ^{57}Fe-Mössbauer absorption spectroscopic (MAS) measurements were also recorded with a constant acceleration spectrometer in a triangular mode, using a ^{57}Co:Rh source at room temperature. Positive velocities corresponded to the source moving towards the absorber and the velocities are given relative to the sodium nitroprusside at room temperature.

The overall spectra were deconvoluted with calculated sub-spectra that consisted of Lorentzian-shaped lines. In the case of quadrupole doublets, the line widths and the absorption areas of the constituent peaks were constrained equal. The MES measurements were carried out in a new developed Mössbauer in situ high-pressure reactor described in more details in Section 3.4, using oxygen purified gases. Mössbauer emission spectra were obtained at room temperature or at the treatment temperatures.

2.2. Co/Al_2O_3 slurry phase Fischer–Tropsch catalysts

A 15 gCo/0.025Pt/100 gAl_2O_3 standard catalyst was prepared according to a proprietary recipe [16]. The catalyst was prepared by the application of a single aqueous slurry phase $Co(NO_3)_2$-impregnation step (spiked with a specific amount of ammonium–platinum–nitrate) of pre-shaped spherical alumina, followed by a calcination step (directly performed after the impregnation/vacuum drying step), carried out at $T = 523\,K$. The calcined catalyst was reduced at $T = 653\,K$ for 16 h in pure hydrogen, at atmospheric pressure, using a heating rate of 1 K/min.

3. Results and discussion

3.1. Catalyst preparation

The question whether or not oxidation causes deactivation of cobalt based Fischer–Tropsch catalysts has been studied previously [1]. In this previous study, the incipient wetness impregnation method was applied to prepare the 'look-alike' catalyst for the MES experiments instead of the preferred 'standard' slurry phase impregnation method. Oxidation experiments showed that the 'look-alike' catalyst oxidised slower than the 'standard' one, which could be explained by the lower dispersion of the former as determined from hydrogen chemisorption results [1].

To overcome this hypothesised difference in cobalt-crystallite size between the 'look-alike' and 'standard' catalysts, the possibility to apply the addition of the radioactive ^{57}Co to the already prepared 'standard' catalyst was investigated. Whenever this procedure would turn out to be successful, it would not be necessary to design and construct a new micro-catalyst preparation unit to simulate a slurry phase impregnation procedure using radioactive ^{57}Co. As a first approach it was decided to use enriched ^{57}Fe as a probe molecule. Two Fe containing cobalt catalysts were prepared. Catalyst A, $30Co/1.5Fe/0.075Pt/100Al_2O_3$, containing enriched ^{57}Fe, was prepared by slurry phase impregnation and the Fe was introduced by means of co-impregnation. Catalyst B, $30Co/1.5Fe/0.075Pt/100Al_2O_3$, containing enriched ^{57}Fe, was also prepared by a two-step slurry phase impregnation, but the Fe was added in an additional incipient wetness impregnation step. MAS experiments were performed at $T = 300$, 77, and 4.2 K, and the results obtained at $T = 4.2$ K are presented in Fig. 1. The spectra measured at $T = 300$ and 77 K consist of only a central quadrupole doublet ($T = 300$ K, isomer shift (IS) $= 0.56$ mm/s, quadrupole splitting (QS) $= 0.80$ mm/s for sample A and IS $= 0.56$ mm/s, QS $= 0.88$ mm/s for sample B). IS is given relative to sodium nitroprusside at room temperature.

The spectrum obtained for catalyst B at $T = 4.2$ K still shows a larger contribution of a doublet in the centre of the spectrum than the spectrum obtained for catalyst A at $T = 4.2$ K. This may imply that the Fe-crystallites in catalyst B are smaller than in catalyst A, but it is also possible that the Fe-crystallites in sample B show a faster superparamagnetic relaxation

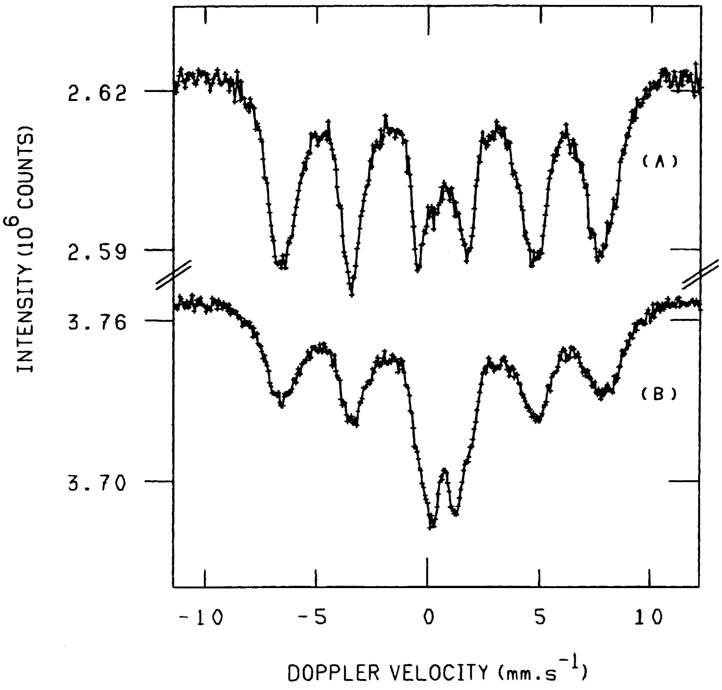

Fig. 1. Mössbauer absorption spectra at $T = 4.2$ K of ^{57}Fe containing cobalt catalysts prepared by slurry phase impregnation—(a) catalyst A: ^{57}Fe added by co-impregnation; (b) catalyst B: ^{57}Fe added by sequential impregnation.

due to a different location of these Fe-crystallites in or on the Co-crystallites. This could be due to a separation of the cobalt and iron crystallites in the catalyst prepared by sequential impregnation (catalyst B), while in catalyst A (prepared by co-impregnation), the cobalt and iron phase were intimately mixed. From the observed quadrupole splittings in the spectra obtained at $T = 77$ and 300 K, it can be concluded that the Fe-ions in both catalysts are not located on the crystallographic sites of Co_3O_4 [17], the phase in which the Co-ions are observed to be located, after the calcination treatments [1]. Furthermore, it can be concluded that the Fe-ions are not forming Fe_3O_4 [18], but an Fe(III)-oxide phase.

In addition to the study of the oxidic precursors of the Fe-containing cobalt catalysts A and B, the Mössbauer spectra of samples A and B were measured after a reduction treatment for 16 h in H_2 at $T = 653$ K. The measured spectra at room temperature are presented in Fig. 2.

For reasons of comparison, the spectrum of a sample with only Fe supported on alumina (Fe/Al_2O_3, incipient wetness impregnation) after the reduction treatment is also included in Fig. 2. It is clear that the spectra of the samples A and B are rather similar after the reduction treatment, but both are completely different from that of Fe/Al_2O_3. This indicates that the Fe- and Co-atoms might be intimately mixed in

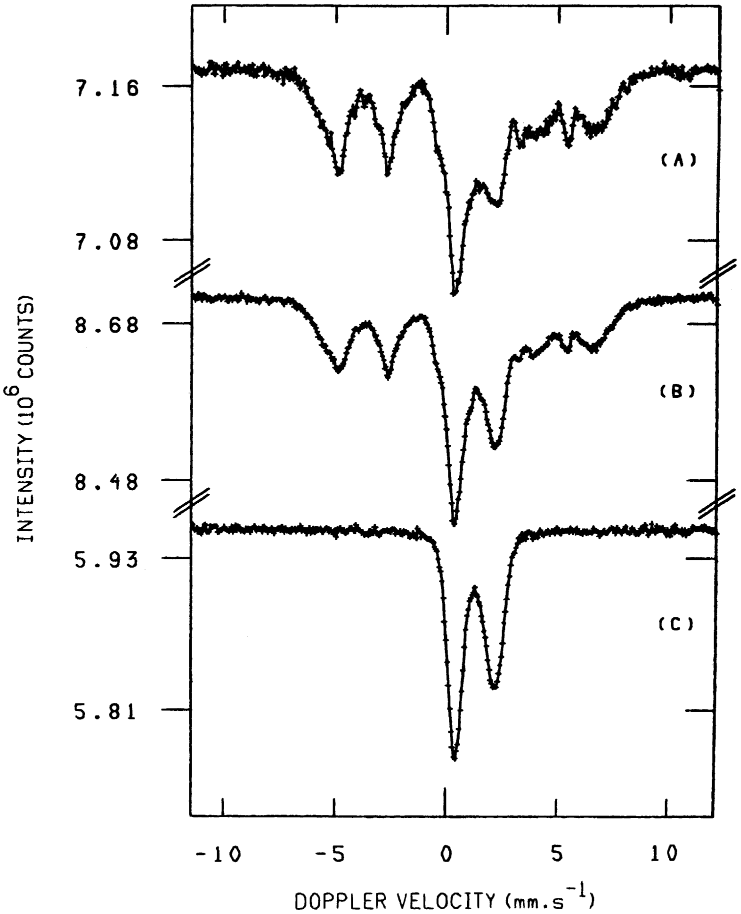

Fig. 2. Mössbauer absorption spectra at $T = 300$ K of ^{57}Fe containing cobalt catalysts prepared by slurry phase impregnation and of an only Fe containing catalyst Fe/Al_2O_3 after reduction at $T = 653$ K—(a) catalyst A: ^{57}Fe added by co-impregnation; (b) catalyst B: ^{57}Fe added by sequential impregnation; (c) Fe/Al_2O_3 by incipient wetness impregnation.

both samples A and B after reduction. This implies that the reduction treatment has taken away the differences observed between these samples after calcination, most probably due to the diffusion of the $Co^{(0)}$-atoms. It thus seems that it might be possible to prepare the catalyst for ^{57}Co-MES measurements by just adding ^{57}Co to the industrial prepared standard catalyst by a simple incipient wetness impregnation step.

Besides this rather promising result, Fig. 2 also shows that in the case of the Co-based catalysts, rather complex spectra are observed. From Table 1 and Fig. 2, one can see that, additional to the magnetically split spectral component of Fe in the metallic Co lattice ($H_{\mathrm{eff}} = 317/312$ kOe, IS $= 0.32/0.35$ mm/s), a spectral contribution with $H_{\mathrm{eff}} = 374/369$ kOe and IS $= 0.72/0.72$ mm/s is found. This last contribution was not found in the case of the Fe/Al_2O_3 catalysts (see Fig. 2), and may be ascribed to the influence of 'N' atoms in the metallic lattice [19]. In the case of the Co-catalyst prepared by industrial slurry phase impregnation, the presence of residual 'N' atoms after calcination, indeed is observed.

Table 1
The MAS and MES fitted parameters of the different catalyst samples, after different treatments[a]

Sample	Temperature (K)	IS (mm/s)	QS (mm/s)	Hyperfine field (kOe)	Spectral contribution (%)
Ex reduction (^{57}Fe: A)	300	0.32	0.00	317	15
		0.72	0.00	374	46
		1.42	1.56	–	30
		0.28	–	–	9
Ex reduction (^{57}Fe: B)	300	0.35	0.00	312	15
		0.72	0.00	369	40
		1.38	1.68	–	37
		0.28	–	–	8
Ex reduction (^{57}Co-MES)	300	−0.08	0.00	320	70
		0.32	0.96	–	17
		1.12	1.55	–	13
Ex passivation—1% O_2 (^{57}Co-MES)	300	−0.07	0.00	320	37
		0.26	0.85	–	54
		1.14	1.75	–	9
Ex passivation—air (^{57}Co-MES)	300	−0.08	0.00	317	26
		0.24	0.82	–	65
		1.13	1.78	–	9
Ex re-reduction (^{57}Co-MES)	300	−0.09	0.00	319	71
		0.26	1.31	–	15
		0.97	1.65	–	14
Ex $H_2/H_2O = 1$, 150 °C, 1 bar (^{57}Co-MES)	423	−0.17	0.00	311	76
		0.04	0.96	–	14
		0.96	1.55	–	10
Ex $H_2/H_2O = 1$, 150 °C, 5 bar (^{57}Co-MES)	423	−0.17	0.00	311	78
		0.05	0.96	–	12
		0.92	1.73	–	10
Ex $H_2/H_2O = 1$, 150 °C, 10 bar (^{57}Co-MES)	423	−0.17	0.00	315	86
		−0.01	0.83	–	7
		1.00	1.56	–	7

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

3.2. Reduction, passivation and re-reduction of ^{57}Co-MES catalyst

Following the above-mentioned postulation, a ^{57}Co-MES catalyst (i.e. LA-3) was prepared by adding radioactive ^{57}Co (about 1000 ppm) through an additional incipient wetness impregnation step to a 15Co/0.025Pt/100Al_2O_3 catalyst prepared by a single step slurry phase impregnation step as described previously [1]. After this incipient wetness impregnation step, the sample was dried at $T = 300$ K in flowing air and subsequently calcined at $T = 523$ K.

The calcined ^{57}Co-MES catalyst was reduced in a pure H_2 atmospheric pressure environment at $T = 653$ K for 16 h. The spectra obtained for the dried and calcined catalyst samples are similar to those presented in the previous study [1]. The measured spectrum of the reduced catalyst sample is shown in Fig. 3 and the analysis results are given in Table 1.

The degree of reduction of this ^{57}Co-MES catalyst was about 70%, which is in good agreement with the reported range 70–85% for the 'standard' cobalt catalyst and the previously investigated 'look-alike' catalysts [1]. The fact that the 1000 ppm of ^{57}Co can be reduced to a degree of reduction of 70%, indicates that this ^{57}Co is in direct contact with the original cobalt crystallites, because if the ^{57}Co would have been in direct contact with the alumina support, the expectation would have been that metal–support interaction would have lowered the cobalt oxide reducibility. This relative high degree of reduction is thus a strong indication that the ^{57}Co is present on the cobalt crystallites. The reduced catalyst was subsequently passivated for 18 h in an Ar-flow containing 1 vol.% O_2 and subsequently exposed to ambient air for 7 days. The measured spectra, after these different treatments were performed, are also presented in Fig. 3, while the analysis results are included in Table 1. Finally, this air-exposed sample was re-reduced in a pure H_2-flow at atmospheric pressure at $T = 653$ K for 18 h and the spectrum is included in Fig. 3 and the analysis results are given in Table 1.

It is obvious that the reduced catalyst was only partly oxidised by the passivation treatment (i.e. the degree of reduction decreased from 70 to 37%), indicating that only an outer shell of the metallic Co-particles was oxidised, and that the inner core of these particles remained metallic. From the re-reduced catalyst results, it can be concluded that the catalyst particles will not change whenever they are passivated carefully.

3.3. Model oxidation study of ^{57}Co-MES catalyst

In a previous study, where oxidation as a deactivation mechanism of cobalt based Fischer–Tropsch catalysts was shown [1], it was found that co-feeding of water during a Fischer–Tropsch slurry phase CSTR synthesis run (causing an increase of about 40% in the observed reactor water partial pressure), led to an enhanced decline of the activity during ca 3 days, after which period relative stable operation was again recorded. In addition, the activity did not recover upon the termination of water co-feeding. These observations provided strong arguments in favour of increased catalyst oxidation to be exclusively responsible for the observed enhancement in catalyst deactivation. ^{57}Co-MES oxidation experiments, performed at atmospheric pressure at a temperature of $T = 423$ K, using an Ar/H_2/H_2O gas mixture with $P_{H_2}/P_{H_2O} = 1.0$, i.e. a ratio similar to that during realistic Fischer–Tropsch synthesis, and a water partial pressure of 0.025 bar, did not show any oxidation of the reduced cobalt catalyst. This result was in agreement with the bulk cobalt thermodynamics. However, a rapid oxidation of part of the metallic cobalt phase was observed after increasing the oxidative nature of the environment by decreasing the P_{H_2}/P_{H_2O} ratio from 1.0 to 0.3 [1], which result is in contradiction with bulk phase cobalt thermodynamics. This oxidation did not proceed until extinction but levelled off, which might be due to selective oxidation of small Co-crystallites, or due to surface oxidation. Schanke et al. [10] deduced from model experiments that cobalt oxidises, but that the extent of oxidation depends on the P_{H_2}/P_{H_2O} ratio as well as on the absolute water partial pressure. The previously reported ^{57}Co-MES experiments [1] were insufficient to conclude that oxidation will not occur during realistic Fischer–Tropsch synthesis when a P_{H_2}/P_{H_2O} ratio of ca 1.0 is used, and the absolute water partial pressure is between 4.6 and 7.6 bar.

Therefore, ^{57}Co-MES experiments were performed using a H_2/H_2O gas mixture with $P_{H_2}/P_{H_2O} = 1.0$ up to a total pressure of 10 bar (i.e. P_{H_2O} up to 5 bar).

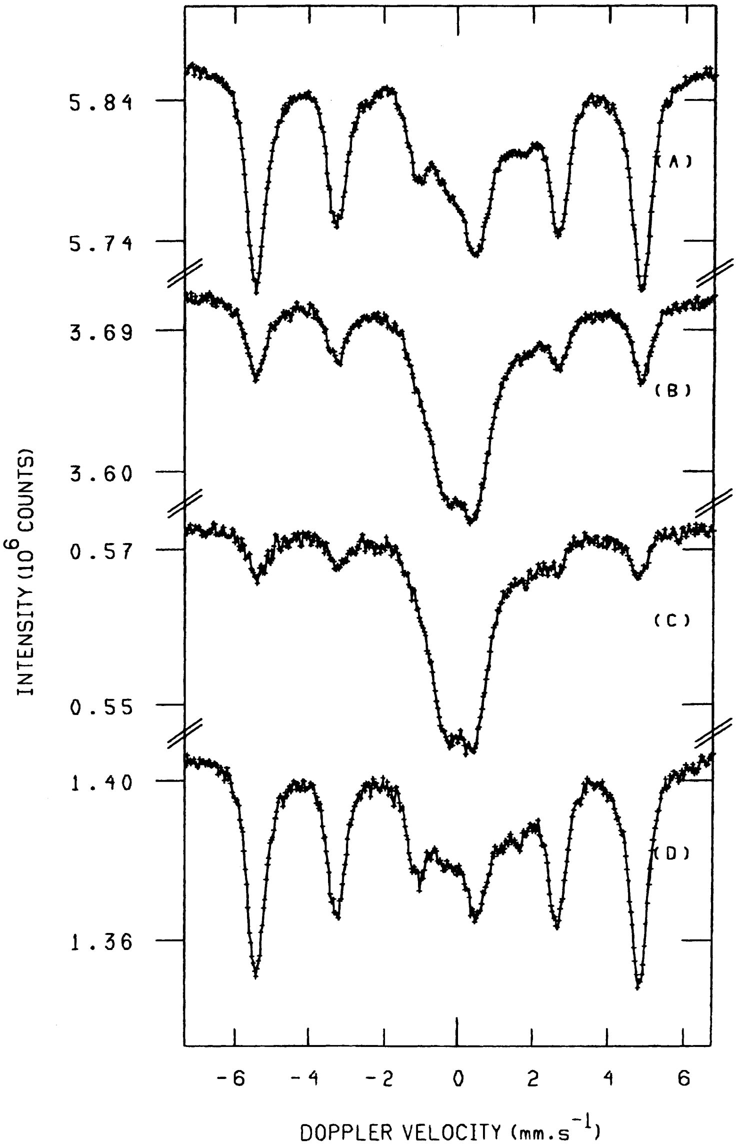

Fig. 3. ^{57}Co-Mössbauer emission spectra at $T = 300$ K of ^{57}Co-MES catalyst after—(a) reduction in H_2 at $T = 653$ K; (b) passivation in Ar-flow containing 1 vol.% O_2 at room temperature; (c) exposure to ambient air at room temperature; (d) re-reduction in H_2 at $T = 653$ K.

To be able to perform such ^{57}Co-MES measurements on cobalt based catalysts a high-pressure Mössbauer in situ reactor and additional infrastructure was designed and built. This in situ reactor is described in Section 3.4.

In Fig. 4, the spectra obtained at $T = 423$ K of the re-reduced ^{57}Co-MES catalyst are shown (see Fig. 3) during subsequent treatments in a H_2/H_2O gas mixture with $P_{H_2}/P_{H_2O} = 1.0$ at 1, 5 and 10 bar of total pressure (i.e. a P_{H_2O} of 0.5, 2.5, and 5 bar). From the spectral analyses, it follows that the amount of metallic Co increased from 71% after the re-reduction treatment to about 86% after the treatment at $T = 423$ K, in a H_2/H_2O gas mixture with $P_{H_2}/P_{H_2O} =$

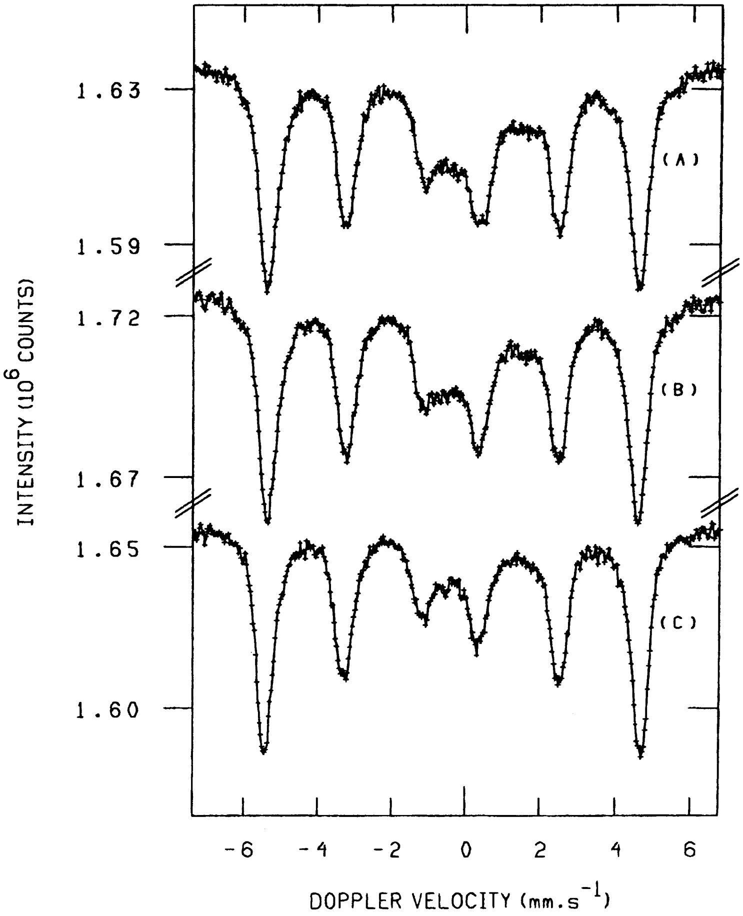

Fig. 4. ^{57}Co-Mössbauer emission spectra at $T = 423$ K of ^{57}Co-MES catalyst during a treatment in a H_2/H_2O gas mixture with $P_{H_2}/P_{H_2O} = 1.0$ and: (a) 1 bar of total pressure; (b) 5 bar of total pressure; (c) 10 bar of total pressure.

1.0 and 10 bar total pressure. It follows that at $T = 423$ K, the catalyst becomes more reduced during the treatment with H_2/H_2O ($P_{H_2}/P_{H_2O} = 1.0$) at 10 bar, in accordance with Hilmen et al. [15] who did not observe oxidation under these type of conditions for an unpromoted Co/Al_2O_3 catalyst, whilst oxidation was observed for a $Re/Co/Al_2O_3$ catalyst. The difference was ascribed to: (i) a difference in cobalt dispersion or (ii) the influence of the Re on the oxidation behaviour.

This model oxidation study of the ^{57}Co-MES catalyst will subsequently be continued with experiments at the industrial applied Fischer–Tropsch synthesis temperature of $T = 503$ K in a H_2/H_2O gas mixture with $P_{H_2}/P_{H_2O} = 1$ and at total pressures of 1, 5 and 10 bar.

3.4. High-pressure Mössbauer emission spectroscopy cell

To be able to study the oxidation behaviour of cobalt based catalysts under realistic Fischer–Tropsch conditions, MES at high pressure is required. A system has been designed and built that consists of a high-pressure Mössbauer in situ reactor with some additional infrastructure.

Requirements for the high-pressure MES reactor on process conditions, safety and Mössbauer

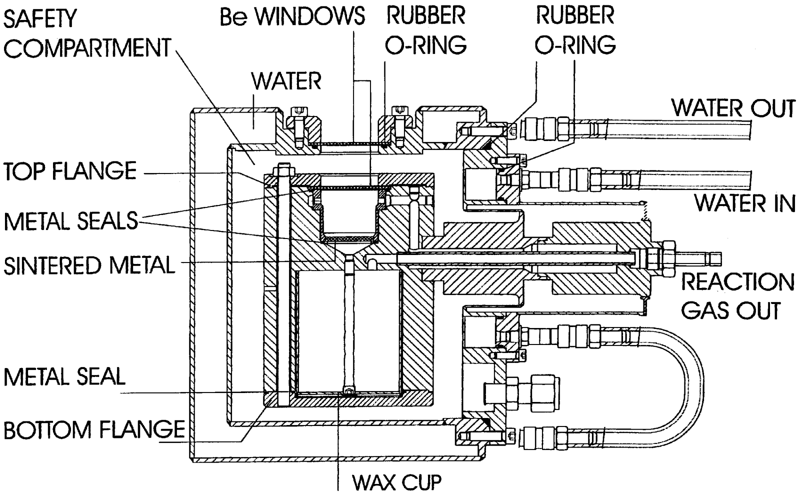

Fig. 5. Schematic representation of the high-pressure MES cell.

Fig. 6. Photograph of the high-pressure MES cell.

spectroscopic aspects, were laid down. The main process conditions decided on, were, (i) temperatures up to $T = 723\,\mathrm{K}$, (ii) pressures up to 20 bar, (iii) 10 bar steam injection, which implies that all tubing must have a heat tracing (up to $T = 473\,\mathrm{K}$), (iv) handling of wax production, (v) continuous Fischer–Tropsch synthesis test runs up to 2 months, (vi) use of argon, air, hydrogen, synthesis gas, (vii) gas flow through the catalyst sample, (viii) the reactor should be constructed of stainless steel. To enable 10 bar steam injection, a commercially available system has been installed. The steam is produced from demineralised water. To get gas flow through the catalyst bed, the catalyst was placed onto a sintered metal filter (pore diameter of 5 μm), and gas flows from top to bottom have been effected. The filter thus allows the produced wax to drain downwards into a collecting compartment.

To fulfil all safety aspects the following provisions were made: (i) the cell had to consist of two pressure compartments, the inner chamber for the high-pressure and high-temperature experiments and an outer compartment to trap the radioactive ^{57}Co in case the inner compartment (e.g. window) would fail, (ii) the volume of the high-pressure compartment should be as small as possible, (iii) the temperature of the outside of the cell is exposed to the laboratory and therefore had to be below $T = 333\,\mathrm{K}$, (iv) the applied Be windows were optimised for strength and not for low iron content (which is not a problem in MES), (v) it should be easy to change the catalyst sample.

The main demands on the reactor for Mössbauer spectroscopy reasons were: (i) the catalyst sample had to be in a horizontal position, (ii) the transmittance of the beryllium windows should be optimised within the demands of the strength of the windows (thickness versus diameter), (iii) the distance between the catalyst sample and the detector was minimised which implies that also the amount of reaction gas between the sample and the detector was minimised.

The high-pressure MES cell and additional infrastructure were designed and built according to the process conditions and safety requirements (Figs. 5 and 6) and is used for the model oxidation experiments described in Section 3.3. This unique high-pressure MES cell has proven to create the opportunity to perform in situ experiments under realistic Fischer–Tropsch synthesis conditions.

4. Conclusions

Initial results show that it might be possible that ^{57}Co-containing catalysts, representative of the Sasol proprietary cobalt slurry phase Fischer–Tropsch catalyst, can be prepared from the industrial ‘standard’ Co-catalyst by an additional simple incipient wetness impregnation procedure.

It was also shown that a reduced Co-catalyst is only partly oxidised by a carefully applied passivation treatment and that in this case the catalyst particles will not change.

A high-pressure MES cell has been developed and built, and it has proven to create the opportunity to perform in situ experiments under realistic Fischer–Tropsch synthesis conditions.

From the first in situ experiments in a H_2/H_2O gas mixture with $P_{H_2}/P_{H_2O} = 1.0$ at $T = 423\,\mathrm{K}$ and at pressures up to 10 bar, it followed that the catalyst becomes more reduced with increasing total pressure at this temperature.

References

[1] P.J. van Berge, J. van de Loosdrecht, S. Barradas, A.M. van der Kraan, Catal. Today 58 (2000) 321–334.
[2] J. van de Loosdrecht, P.J. van Berge, M.W.J. Crajé, A.M. van der Kraan, in: Proceedings of the International Symposium on the Industrial Applications of the Mössbauer Effect, 13–18 August, 2000, Virginia Beach, VA, Hyperfine Interactions, in press.
[3] B. Eisberg, R.A. Fiato, Stud. Surf. Sci. Catal. 199 (1998) 961–966.
[4] M.M.G. Senden, A.D. Punt, A. Hoek, Stud. Surf. Sci. Catal. 199 (1998) 943–948.
[5] P.J. van Berge, S. Barradas, E.A. Caricato, B.H. Sigwebela, J. van de Loosdrecht, in: Proceedings of Worldwide Catalyst Industry Conference CatCon2000, 12–13 June 2000, Houston, USA.
[6] R.L. Espinoza, A.P. Steynberg, B. Jager, A.C. Vosloo, Appl. Catal. A 186 (1999) 13–26.
[7] P.J. van Berge, R.C. Everson, Stud. Surf. Sci. Catal. 107 (1997) 207.
[8] S. Leviness, C.J. Mart, W.C. Behrmann, S.J. Hsia, D.R. Neskora, WO 98/50487.
[9] E. Iglesia, S.L. Soled, R.A. Fiato, G.H. Via, J. Catal. 141 (1993) 345.

[10] D. Schanke, A.M. Hilmen, E. Bergene, K. Kinnari, E. Rytter, E. Adnanes, A. Holmen, Catal. Lett. 34 (1995) 269.
[11] R.B. Anderson, in: P.H. Emmett (Ed.), Catalysis, Vol. IV, Reinhold, New York, 1956.
[12] H. Bolt, Ph.D. Thesis, University of Utrecht, Utrecht, The Netherlands, 1994.
[13] A. Hoff, E.A. Blekkan, A. Holmen, D. Schanke, in: Proceedings of the 10th International Congress on Catalysis, 19–24 July, 1992, Budapest, Hungary, Elsevier, Amsterdam, 1993, p. 2067.
[14] E. Iglesia, Stud. Surf. Sci. Catal. 107 (1997) 153.
[15] A.M. Hilmen, D. Schanke, K.F. Hanssen, A. Holmen, Appl. Catal. A 186 (1999) 169–188.
[16] R.L. Espinoza, J.L. Visagie, P.J. van Berge, F.H. Bolder, US Patent 5,733,839 (1998).
[17] C.D. Spencer, D. Schroerr, Phys. Rev. B 9 (1974) 3658.
[18] S. Mørup, H. Topsøe, J. Lipka, J. de Physique, Colloque C6 (1976) 287.
[19] P. Rochegude, J. Foct, Phys. Stat. Sol. (a) 98 (1986) 51.