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Citation for published version (APA):

Lox, E. S., Marin, G. B., Grave, de, E., & Bussière, P. (1988). Characterization of a promoted precipitated iron catalyst for Fischer-Tropsch synthesis. *Applied Catalysis*, 40(1), 197-218. [https://doi.org/10.1016/S0166-9834\(00\)80438-8](https://doi.org/10.1016/S0166-9834(00)80438-8)

DOI:

[10.1016/S0166-9834\(00\)80438-8](https://doi.org/10.1016/S0166-9834(00)80438-8)

Document status and date:

Published: 01/01/1988

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Characterization of a Promoted Precipitated Iron Catalyst for Fischer–Tropsch Synthesis

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(Received 12 October 1987, accepted 18 January 1988)

ABSTRACT

A commercial precipitated catalyst for Fischer–Tropsch synthesis has been characterized by temperature-programmed techniques, carbon monoxide chemisorption, X-ray photoelectron spectroscopy, X-ray diffraction and Mössbauer spectroscopy. The catalyst consists of non-porous iron particles with a diameter close to 10 nm. Textural promotion, i.e. maintenance of the particle diameter during exposure to reaction conditions, is achieved by the coverage of the iron particles by silica islands. Upon exposure of the fresh catalyst to hydrogen at 493 K according to the manufacturer's specifications 20% of the iron is reduced to the metallic state. Only 3% of the iron atoms are exposed to the gas phase. After more than 200 h exposure to reaction conditions similar to industrial ones, the iron phase consists of more than 75% non-stoichiometric iron carbides with $\text{Fe}_{2.23}\text{C}$ as the overall composition. The remaining iron atoms are either oxidized or present as carbides which show paramagnetic relaxation at 80 K. The iron atoms at the interface of the iron particles are oxidized. The pores of the catalyst pellets, i.e. the voids between the iron particles, are completely filled with liquid hydrocarbons during steady-state operation under industrial conditions.

INTRODUCTION

The Fischer–Tropsch synthesis is carried out industrially on promoted iron catalysts which are either precipitated or fused. Typical inlet reaction condi-

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tions are: 500–600 K, 20–30 bar and molar hydrogen to carbon monoxide ratios around 2 [1].

The activity and selectivity of iron-based Fischer–Tropsch catalysts is time-dependent during the first hours of reaction. It is generally accepted that this is caused by structural changes of the catalyst under the reaction conditions [1]. An intensive investigation of the solid state transformations occurring during reaction has been performed in the past ten years [2–12]. Most of the research has focused on the study of model catalysts, i.e. unpromoted supported iron, and this mainly at atmospheric pressure. In the present work a commercial, i.e. promoted, precipitated catalyst has been studied after exposure to reaction conditions close to the industrial ones.

Recently, the importance of the state of the catalyst prior to reaction has been emphasized [3,13]. In particular, higher stability and activity by precalcination at 773 K is claimed [13]. Most of the characterization work reported in the literature, however, has been performed on fully prereduced iron. Nevertheless, the presence of oxidized iron after reaction has been detected by surface-sensitive techniques [14,15]. The catalyst investigated here was prereduced at 493 K, according to the manufacturer's specifications. At such a temperature full reduction is not expected [16].

In this work information from Mössbauer spectroscopy, X-ray diffraction and X-ray photoelectron spectroscopy is combined to characterize a commercial catalyst for Fischer–Tropsch synthesis prior to, during and after reaction. Particular attention is paid to the state of the iron atoms in bulk as well as on the surface.

EXPERIMENTAL

Catalyst

A commercial catalyst of the Arge type was obtained from Ruhrchemie. The preparation of the catalyst is described by Frohning et al. [17]. The catalyst pellets were crushed and sieved to a diameter between 0.4 and 0.5 mm. The elemental composition was determined by atomic absorption spectrometry for iron, copper, potassium and sodium and gravimetrically for silicon. The following stoichiometries were assumed for calculation of the oxygen content: $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, SiO_2 , CuO , K_2O and Na_2O . The results are summarized in the first column of Table 1. The sodium content was below 0.1 wt.-%. X-ray fluorescence revealed traces of calcium, zinc, manganese, molybdenum and aluminium and sulphur.

The standard pretreatment of the catalyst was prescribed by the manufacturer and consisted of reduction for 3 h in an atmospheric flow of hydrogen at 493 K. After reduction, the carbon monoxide feed rate was adjusted until a molar hydrogen to carbon monoxide ratio of 3 was achieved. Next, the reactor

TABLE 1

Catalyst composition relative to iron (mol/mol)

Element	Before reduction		After reaction
	Bulk	Surface	Surface
Si	0.246	1.3	2.5
Cu	0.051	0.05	0.3
K	0.056	0.3	—
O	4.008	5.4	10
C	—	2.0	123

was pressurized to 11 bar and the carbon monoxide feed rate was slowly increased to a value for W/F_{CO} of 50 kg·s/mol. Finally, the reactor temperature was increased at 5 K/min to 623 K. Typically 5 g of catalyst was used. The catalyst was exposed over a period of 12 h to these reaction conditions. The carbon monoxide conversion decreased from 95 to 80% during the first three hours of reaction. Next, a study of the reaction kinetics was performed at molar hydrogen to carbon monoxide ratios between 3 and 6, temperatures between 553 and 573 K and pressures between 11 and 21 bar. Before unloading, the catalyst was quenched in an atmospheric flow of hydrogen and passivated by a flow of industrial nitrogen at room temperature.

The sample on which in situ Mössbauer spectroscopy has been performed was submitted to the standard reduction at 493 K followed by reaction at atmospheric pressure, 623 K, W/F_{CO} = 50 kg·s/mol and $(H_2/CO)^{\circ} = 3$. A wafer of 106 mg of catalyst, corresponding to 2 cm², was used without diluent.

Temperature-programmed reduction

Samples of 25 mg were reduced by either pure hydrogen or 5% hydrogen in argon at a heating rate of 10 K/min. Differential thermogravimetry (DTG) was performed in a Setaram MTB 10-8 microbalance. Differential thermoanalysis (DTA) was performed in a Setaram ATD-M4 calorimeter. The hydrogen consumption during reduction was determined by use of a calibrated thermal conductivity detector.

Texture

The pore diameter distribution was determined by a combination of nitrogen desorption isotherm and mercury penetration data. Prior extraction of the heavy hydrocarbon fraction with carbon tetrachloride was performed on the catalyst sample after reaction. All samples were outgassed at 372 K and 10⁻⁴

mbar. The skeletal density of the sample was determined picnometrically by immersion in water.

Carbon monoxide chemisorption

In situ carbon monoxide chemisorption was performed at room temperature with a pulse reactor set-up. It has been assumed that there are two surface iron atoms per molecule of chemisorbed carbon monoxide and that the surface area per iron atom amounts to $8.2 \cdot 10^{-20} \text{ m}^2$ [4].

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed with a Hewlett-Packard 59500A spectrometer without any treatment of the samples. Exposure to air after reaction during transfer from the reactor to the spectrometer was not considered to cause significant oxidation of metallic iron. This is supported by a comparison of in and ex situ Mössbauer spectroscopy data after reaction. Similar observations were made on partially or fully reduced unpromoted iron catalysts [2,3]. The binding energies were referenced against $\text{Cu } 2p_{3/2} = 934.0 \text{ eV}$. The catalyst sample investigated after reaction had been exposed to reaction for more than 200 h and showed a loss of carbon monoxide conversion of 10%.

X-ray diffraction

X-ray powder diffraction (XRD) patterns were obtained on a Philips PW diffractometer using $\text{Fe } K\alpha$ radiation and a diffracted beam monochromator. The spectra were recorded digitally with a resolution of $1/30^\circ$ (2θ) per channel and regressed with pseudo-Lorentzian lines, two for each reflection in order to account for the $K\alpha 1$ and $K\alpha 2$ wave lengths. Crystallite dimensions were estimated from the broadening of the reflection lines using the Scherrer formula with $K=0.9$.

Mössbauer spectroscopy

The ^{57}Fe Mössbauer spectra were obtained on a time-mode spectrometer with constant acceleration drive and a triangular reference signal. The gamma source was ^{57}Co in a rhodium matrix. The absorbers consisted of the powder compounds mixed with very pure carbon and spread out over the sample support in a uniform thickness. The spectrometer was calibrated either interferometrically or from the spectra recorded on a standard iron foil.

The spectra were analysed by least-squares regression of a sum of Lorentzian lines to the experimental data [18]. Corresponding lines within a particular sextet or doublet were forced to have the same intensity and line width.

The hyperfine parameters, i.e. the isomer shift, IS, the quadrupole splitting, QS, and the magnetic hyperfine field, H_{hf} , were obtained from the estimated line positions. The shifts are reported with respect to metallic iron at room temperature. The average standard deviations as evaluated from the error analysis by the regression program, are 0.01 mm/s for QS and IS, and 1 kOe for H_{hf} . The standard deviation for the calculated relative absorption areas of the different components is, on average, 2%. The estimations of compositions have been based on the assumption of equal recoilless fractions.

RESULTS

Temperature-programmed reduction

Fig. 1 compares the hydrogen consumption during a temperature-programmed reduction of a catalyst sample as prepared and after the standard reduction at 493 K.

The hydrogen consumption of the fresh sample presents three peaks corresponding to the transformations listed in Table 2. Differential thermogravimetry shows also three peaks at the same temperatures. On top of the mass decrease due to reduction, there is a continuous removal of hydrate water. The total mass loss at 1000 K amounts to 40.0%. If the hydrate water of the fresh catalyst is present in a stoichiometry given by $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, the theoretical mass loss corresponding to the transformations shown in Table 2 and the total removal of the hydrate water amounts to 41.9%. The differential thermoanalysis results are in agreement with the hydrogen consumption and thermogra-

Fig. 1. Hydrogen consumption during temperature-programmed reduction; (a) before standard reduction at 493 K; (b) after standard reduction at 493 K.

TABLE 2

Major transformations and corresponding hydrogen uptake during the temperature-programmed reduction of fresh catalyst

Temperature (K)	Transformation	Hydrogen uptake (mol/kg cat)	
		Theoretical*	Experimental
550-600	$\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$	0.05	0.2
600-650	$\text{Fe}_2\text{O}_3 + \frac{1}{3}\text{H}_2 \rightarrow \frac{2}{3}\text{Fe}_3\text{O}_4 + \frac{1}{3}\text{H}_2\text{O}$	1.25	2.7
650-1000	$\frac{2}{3}\text{Fe}_3\text{O}_4 + \frac{8}{3}\text{H}_2 \rightarrow 2\text{Fe} + \frac{8}{3}\text{H}_2\text{O}$	10.13	13.0

*Assuming $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ as the initial stoichiometry for the iron phase.

TABLE 3

Textural properties of the catalyst

	Surface area ($10^3 \text{ m}^2/\text{kg}$)	Pore volume ($10^{-3} \text{ m}^3/\text{kg}$)	Average mesopore diameter (nm)	Average particle diameter (nm)*
As prepared	318	0.543	7.2	7
Reduced at 493 K	168	0.508	9.9	10
After 212 h of reaction	80	0.368	12	11

*With respectively 2900, 3600 and 7000 kg/m^3 as skeletal density, ρ_m .

vimetric data. Moreover, several exothermic peaks are shown between 463 and 493 K. These can be ascribed to recrystallization.

After the standard reduction, the hydrogen consumption shows only one peak which occurs at the temperature at which Fe_3O_4 is reduced to metallic iron. The size of the peak is 20% smaller than before reduction. The standard reduction procedure of the catalyst results in full reduction of Fe_2O_3 to Fe_3O_4 and in partial reduction of the latter to metallic iron. The corresponding DTG results show that only half of the originally present hydrate water is removed during the standard reduction.

Texture

The textural properties of the catalyst are summarized in Table 3. The specific surface areas have been calculated from the pore diameter distribution, based on a cylindrical pore shape. The agreement with the BET surface areas is good. The fresh catalyst shows a unimodal pore distribution. After the standard reduction, macropores with a diameter of $3 \cdot 10^4 \text{ nm}$ are formed. This macroporosity is maintained after reaction. The decrease of the specific surface area after reduction and reaction is not primarily due to an increase of the size

of the non-porous aggregates making up the catalyst. This is evidenced by the stable size of the mesopores. Also, the average diameter of the non-porous aggregates constituting the catalyst can be calculated from:

$$d_p = 6 \frac{1}{\rho_m a_s} \quad (1)$$

for spherical particles. The resulting diameters are listed in Table 3 and confirm that the decrease of the specific surface area is basically caused by an increase of the density of the primary aggregates after reduction and reaction.

Exposed iron atoms

The interpretation of carbon monoxide chemisorption data on both unpromoted and promoted iron catalysts has been much debated in the literature [3,4,19]. Although carbon monoxide appears to chemisorb selectively on iron, it is not clear whether all zerovalent surface iron chemisorbs carbon monoxide at room temperature. Ionic surface iron is also claimed to chemisorb carbon monoxide [20,21]. After the standard reduction at 493 K, 120 mmol CO/kg of catalyst or 285 mmol CO/kg of iron was chemisorbed. This corresponds to only 3% of the iron being exposed, if all the exposed iron is thought to be involved in the chemisorption. The corresponding specific iron surface area amounts to 12 m²/g of catalyst or 28 m²/g of iron.

Bianchi et al. [4] reported similar results on an unpromoted 10% Fe/Al₂O₃ catalyst with 76% of the iron reduced to Fe⁰, the balance being Fe²⁺. The carbon monoxide chemisorption amounted to 200 mmol/kg of iron and the specific iron surface area to 19.7 m²/g of iron. Amelse et al. (2) derived an average iron crystallite diameter of 13 nm from X-ray line broadening on a fully reduced 4.94 wt.-% Fe/SiO₂ catalyst. The corresponding surface iron surface area amounts to 60 m²/g of iron. Dwyer and Hardenbergh [22] report a BET surface area of 16 m²/g of iron for unsupported and unpromoted iron powder which was totally reduced.

Methanation activity

At 573 K, 11 bar, a molar inlet hydrogen:carbon monoxide ratio of 3 and differential conversions a methane production rate of 8.2 mmol/s·kg of catalyst was measured. This corresponds to a turnover frequency of 3.4 10⁻² s⁻¹. The selectivity for methane amounted to 24%.

Satterfield et al. [10,11] obtained rates per unit mass on a promoted fused-magnetite catalyst at 518 K, 9.2 bar and a molar inlet hydrogen:carbon monoxide ratio of 0.93. Extrapolation to 573 K, assuming an activation energy of 80 kJ/mol leads to a rate of 9 mmol/s·kg of catalyst. The catalyst was reported to consist of a mixture of α -iron and carbides. The methane production rate

per unit surface area observed by Dwyer and Hardenbergh [22] on a fully carbided iron powder at 578 K, 7 bar and a molar inlet hydrogen:carbon monoxide ratio of 3 is a factor of 3 lower than on the catalyst studied in the present work.

Atmospheric experiments on unpromoted supported iron catalysts lead, after extrapolation to 573 K and assuming an activation energy of 80 kJ/mol, to turnover frequencies between 10^{-2} and 10^{-1} s^{-1} [2,4,7,23].

Hydrocarbon accumulation in the pores

The catalyst activity is, of course, not limited to methanation. A typical Schultz-Flory product distribution was observed. Depending upon the growth probability and the time of reaction, the catalyst pores can be completely filled with large hydrocarbons in the liquid state under the reaction conditions [24].

Fig. 2 shows a gas chromatographic analysis of the hydrocarbon mixture extracted with n-hexane under reflux conditions from the used catalyst. The mixture consists essentially of alkanes and 1-alkenes with a carbon number ranging from 20 to 60 forming a solid wax at room temperature. The amount of wax corresponds to complete pore filling.

The presence of a liquid hydrocarbon phase in the catalyst pores was confirmed by the observations shown in Fig. 3. Switching off the carbon monoxide feed but maintaining the other reaction conditions does not lead to an instantaneous reduction to zero of the methane production rate. The total quantity of hydrocarbons produced at these conditions amounts to $6 \cdot 10^{-2} \text{ mol/g}$ of iron. Assuming that this production originates solely from the hydrogenation of a carbonaceous deposit on the iron surface and taking into account the fraction of exposed iron atoms, leads to more than 100 mol of carbon per mol of exposed iron atoms. It is not clear how the iron surface could accommodate such an amount of carbon [4]. Hydrogenation of iron carbides is another source for the hydrocarbon production, but can account only for a minor fraction of it. It can be assumed that the observed production originates mainly from the liquid hydrocarbon phase in the pores. The amount produced then exceeds the amount corresponding to completely filled pores.

X-ray photoelectron spectroscopy

Table 4 summarizes the energies of the most important emission of each of the catalyst constituents. The reported concentrations take into account the cross sections for photoionization and the escape lengths of the electrons [25,26]. The Fe $2p_{3/2}$ peak before reduction corresponds to Fe^{3+} . The 1-eV shift to lower binding energies after reaction is consistent with a lowering of the oxidation state [27,28]. The O 1s signal at 531.6 eV can be assigned to the presence of hydroxyl groups [27] on the fresh catalyst. The 1-eV shift to lower

Fig. 2. Gas chromatographic analysis of the wax extracted from used catalyst.

Fig. 3. Hydrocarbon production rates by hydrogen at 573 K and 11 bar after reaction at a molar inlet ratio of hydrogen:carbon monoxide = 3 and interruption of the carbon monoxide flow.

TABLE 4

Binding energies of photoelectrons and surface concentrations of the corresponding elements

Electron	Before reduction		After reaction	
	Energy (eV)	Concentration (mass-%)	Energy (eV)	Concentration (mass-%)
Cu 2p _{3/2}	934.0	1	934.0	1
Fe 2p _{3/2}	712.3	26	711.3	3
O 1s	531.6	39	530.7	12
K 1s	294.3	5	—	—
C 1s	285.5	10	283.6	79
Si 2p	101.9	17	101.9	5

binding energies would then correspond to a disappearance of the hydroxyl groups after reaction. The C 1s carbon contamination peak on the sample before reduction is typical for non carbidic carbon [22,27,29].

Table 1 allows comparison of the surface composition of the fresh catalyst with the bulk composition. A pronounced surface enrichment of the silicon and potassium promoters can be deduced from the data, provided that the carbon contamination does not occur selectively on the iron atoms.

After reaction, the C 1s signal increases drastically. The decrease of the iron and potassium signals is much more pronounced than that of the copper, silicon and oxygen signals. The absolute intensity of the Fe 2p_{3/2} signal decreases by more than a factor of four. The high intensity of the C 1s signal causes a peak width which makes the determination of the corresponding binding energy and its interpretation difficult. The C 1s signal is mainly attributed to the hydrocarbon phase in the catalyst pores.

X-ray diffraction

The X-ray diffraction pattern of the catalyst does not exhibit qualitative differences before and after the standard reduction at 493 K. Four, poorly-defined, diffraction peaks correspond to the most intense lines of α -Fe₂O₃. Broad absorption bands occur around 45 and 80°, which is typical for a poorly crystalline iron oxide or oxyhydroxide such as ferrihydrite.

Fig. 4 shows the X-ray diffraction pattern after more than 200 h of reaction. A pattern obtained after 24 h of reaction looks similar. The diffraction peaks around 25° corresponds to oxides different from α -Fe₂O₃ with a crystallite size of 25 ($\pm$ 5) nm. The diffraction between 48 and 58° is due to carbides. The detailed patterns between these angles after 24 h and after more than 200 h of reaction are shown in Fig. 5. A comparison with literature data supports the coexistence of three carbides. The line positions and intensities corresponding

Fig. 4. X-ray diffraction pattern after 212 h of reaction; (a) oxides different from $\alpha\text{-Fe}_2\text{O}_3$; (b) carbides.

Fig. 5. Part of the X-ray diffraction pattern corresponding to iron carbides. Full lines: regression curves. Assignment of phases to the deconvoluted diffraction peaks: Fe_2C (1), $\chi\text{-Fe}_5\text{C}_2$ (2) and $\theta\text{-Fe}_3\text{C}$ (3). (a) After 24 h of reaction at a molar ratio of hydrogen:carbon monoxide=3, 573 K and 11 bar; (b) corresponding to Fig. 4.

TABLE 5

Deconvoluted X-ray diffraction data for angles between 50° and 58° corresponding to Fig. 5b

Fe _x C				χ-Fe ₅ C ₂			
Fig. 5b		Literature [5,30]		Fig. 5b		Literature [5,31]	
2θ (°)	I (%)	2θ (°)	I (%)	2θ (°)	I (%)	2θ (°)	I (%)
				50.1	72	50.1	35
				51.9	89*	52.0	64
52.8	23	52.8	23				
54.6	100	54.6	100	54.6	**	54.5	34
				55.6	100	55.4	100
				56.3	100*	56.4	134
				57.3	***	57.5	40

*Completely assigned to χ-Fe₅C₂, θ-Fe₃C diffracts at 52.0° and 56.0°.

**Completely assigned to Fe_xC.

***Completely assigned to θ-Fe₃C, which diffracts at 57.2° and 57.6°.

to the two phases with the highest carbon content are summarized in Table 5. The carbides with the highest carbon content are designated Fe_xC. They are often referred to as ε'-Fe_{2.2}C. In such carbides the iron atoms form a hexagonal or approximately hexagonal close-packed array while the carbon atoms occupy octahedral interstices. Hägg carbide, χ-Fe₅C₂, is monoclinic with the carbon atoms in the trigonal prismatic interstices of the iron atoms. The third phase can be assigned to cementite, θ-Fe₃C, with the most important diffraction angles at: 56.0, 57.2 and 57.6° [5,32]. Clearly, the importance of the Fe_xC phase increases with the length of time of the reaction. Also, the crystallite size of Fe_x increases from 10 to 18 nm between 24 h and more than 200 h of reaction. The crystallite sizes of χ-Fe₅C₂ and θ-Fe₃C are stable and amount to 15 resp. 5 nm.

Mössbauer spectroscopy

Fig. 6 compares the in situ Mössbauer spectra obtained at room temperature before and after the standard reduction at 493 K. The spectral parameters are summarized in the first part of Table 6. Spectrum (a) was regressed with two sets of doublets. The isomeric shifts are typical for Fe³⁺ in an octahedral oxygen or (oxygen, hydroxyl) environment. The doublet with the largest quadrupole splitting can be assigned to interface ferric ions [33,34]. No ferrimagnetic sextet is observed. A spectrum of the fresh catalyst taken at 80 K showed a sextet accounting for 8% of the spectral areas. Regression of this sextet with a

Fig. 6. In situ Mössbauer spectra at room temperature before and after reduction; (a) before standard reduction at 493 K; (b) after standard reduction at 493 K. Full lines: calculated with parameters of Table 6.

distributed magnetic field resulted in an average value of 518 kOe comparable to that of bulk α - Fe_2O_3 .

Magnetic splitting occurs already at room temperature when the catalyst has been exposed to hydrogen at 493 K, viz Fig. 6b. The value of the hyperfine field is again comparable to that of bulk α - Fe_2O_3 . The central part of spectrum b of Fig. 6 is fitted by a singlet and two doublets. The former corresponds to α Fe in a superparamagnetic state, the doublets to ferrous ions. The doublet with the lowest quadrupole splitting can be assigned to interface ferrous ions [34,35].

The first two spectra of Fig. 7 were recorded during reaction at atmospheric pressure and 623 K. Hence, no magnetic splitting was observed. These spectra were obtained during periods of 1.5 h to improve the statistics of the regression. The first spectrum was obtained at the beginning of the reaction, the second after 15 h of reaction. Taking into account the temperature dependency of isomer shifts, the isomer shifts of the doublets accounting for 71 and 95% of the spectral area correspond to shifts around 0.25 mm/s at room temperature. These are values typical for iron carbides. The second doublet corresponds to

TABLE 6

Mössbauer parameters corresponding to Figs. 6 and 7.

Spectrum	IS (mm/s)	QS (mm/s)	H_{hf} (kOe)	Rel. area (%)	Fe site
Fig. 6a (298 K)	0.41	1.04	—	25	Interface Fe^{3+}
	0.42	0.57	—	75	Bulk Fe^{3+}
Fig. 6b (298 K)	0.01	—	—	20	α -Fe
	0.40	-0.20	500	4	α - Fe_2O_3
	1.11	0.99	—	53	Interface Fe^{2+}
	1.17	1.84	—	23	Bulk Fe^{2+}
Fig. 7a (623 K)	0.05	0.520	—	71	Carbides
	1.00	0.725	—	29	Fe^{2+}
Fig. 7b (623 K)	0.07	0.594	—	95	Carbides
	0.87	1.384	—	5	Fe^{2+}
Fig. 7c (298 K)	0.22	-0.03	184	21	II' in χ - Fe_5C_2
	0.28	0.23	185	11	II in χ - Fe_5C_2
	0.29	0.21	110	19	III in χ - Fe_2C_2
	0.32	0.04	220	31	I in χ - Fe_5C_2
	0.57	0.55	—	5	Fe^{2+}
	0.92	1.80	—	13	Fe^{2+}

ferrous ions. The last spectrum of Fig. 7 has been obtained at room temperature and fitted with four sextets and two doublets. The estimated hyperfine fields are consistent with those of Hägg carbide, χ - Fe_5C_2 . Hägg carbide presents three types of iron atoms in a ratio I:II:III = 2:2:1. The relative spectral areas of the sites reported in Table 6 do not conform to this ratio. Similar deviations have been reported by Raupp and Delgass [6]. The two central doublets can mainly be ascribed to ferrous ions in superparamagnetic phases. There are no α -Fe nor superparamagnetic carbidic sites present.

The spectra reported in Fig. 8 were obtained after more than 200 h of exposure to conditions given in the experimental section. They can be regressed adequately by two sextets and a central doublet, with parameters shown in Table 7. The values of the hyperfine fields are consistent with the presence of carbides with higher carbon contents than χ - Fe_5C_2 . Pijolat et al. (9) have reported fields of 173 and 238 kOe at room temperature on Fe_xC with x between 2.0 and 2.4. The sites with a field of 238 kOe were attributed to iron atoms with 2 carbon neighbours, those with a field of 173 kOe to iron atoms with 3 carbon neighbours. The central doublet can either correspond to octahedral Fe^{3+} ions or to iron carbides in a superparamagnetic state. The decrease of the relative area occupied by the doublet with decreasing temperature coincides with an increase of the sextets. Hence, at least part of the doublet has to be attributed

Fig. 7. In situ Mössbauer spectra during reaction at 623 K, atmospheric pressure and a molar inlet ratio hydrogen:carbon monoxide=3; (a) first 1.5 h of reaction; (b) between 14.5 and 16 h of reaction; (c) after cooling down to room temperature. Full lines: calculated with parameters of Table 6.

to non-stoichiometric hexagonal carbides which are superparamagnetic at room temperature. This implies the existence of a distribution of the diameter of the carbides.

The average composition Fe_xC of the non-stoichiometric hexagonal carbides can be calculated from:

$$\frac{6}{x} = \sum_{n=0}^3 np_n \quad (2)$$

according to Le Caër et al. (37), where p_n is the fraction of iron atoms with n

Fig. 8. Ex situ Mössbauer spectra after 212 h of reaction; (a) room temperature; (b) 80 K. Full lines: calculated with parameters of Table 7.

TABLE 7

Mössbauer parameters corresponding to Fig. 8

Spectrum	IS (mm/s)	QS (mm/s)	H_{hf} (kOe)	Rel. area (%)	Fe site
Fig. 8a (298 K)	0.24	0.03	175	47	hcp Fe, 3 C neighbours
	0.26	0.09	217	12	hcp Fe, 2 C neighbours
	0.34	0.34	—	41	carbides and Fe^{3+}
Fig. 8b (80 K)	0.36	0.03	188	57	hcp Fe, 3 C neighbours
	0.38	0.11	244	18	hcp Fe, 2 C neighbours
	0.44	1.02	—	25	carbides and Fe^{3+}

carbon neighbours. Based on the sextets resolved at 80 K, a composition of $Fe_{2.23}C$ is obtained.

Mössbauer spectroscopy allows resolution of nuclei in a certain state as soon as 5% of the atoms belong to it. Hence, particles with at least 5% of the atoms at an interface – i.e. with particle diameters lower than 20 nm – are expected to exhibit Mössbauer spectra with significant contributions from the latter

behaviour of the catalyst with data reported in the literature, yields the ranges of particle diameters listed in Table 8. Also shown in Table 8 are the fractions of the different iron atoms in the catalyst.

DISCUSSION

Bulk of the iron particles

As prepared, the catalyst consists of a poorly crystalline ferric phase.

The standard reduction maintains this amorphous character although differential thermoanalysis indicates some crystallization. Mössbauer spectroscopy points to α -Fe₂O₃ as the crystallizing phase with a particle diameter of at least 14 nm after reduction. The amount of this phase is too low to allow unambiguous detection by X-ray diffraction. Temperature-programmed reduction indicates that the major part of the iron phase is reduced to oxides with Fe₃O₄ as stoichiometry. Both temperature-programmed reduction and Mössbauer spectroscopy indicate that about one fifth is reduced to metallic iron. As these phases do not diffract X-rays, their crystallite diameter must be lower than 3 nm. Mössbauer spectroscopy indicates that the particle diameter of the partially reduced phase lies around 2 nm.

Thermodynamically, magnetite and iron carbides are favoured relative to α -Fe or hematite at the conditions to which the catalyst was exposed. There is no spectroscopic nor X-ray diffraction evidence pointing to the existence of metallic iron after exposure to the reaction conditions.

An important fraction of the iron phase is still in an oxidized state after more than 200 h of reaction. The assignment of the X-ray diffraction peaks to oxide crystalline phases is not straightforward. Only α -Fe₂O₃ can be excluded. Mössbauer spectroscopy gives an upper limit of 25% for the contribution of the oxides relative to that of the carbides. The relative intensities of the corresponding X-ray diffraction peaks are not in contradiction with this ratio. The oxide crystallite diameter of 25 nm is one order of magnitude larger than the particle diameter of the partially reduced fraction of the iron phase prior to reaction but similar to that of the small amount of α -Fe₂O₃ originally present. The oxide crystallites present after reaction are probably the result of the partial reduction of the α -Fe₂O₃ crystallites as well as of a pronounced crystal growth of a fraction of the partially reduced part of the catalyst.

Exposure to reaction conditions converts the metallic iron and the major part of the partially reduced iron phase into carbides. For kinetic reasons, the carbiding of the latter occurs through metallic iron as an intermediate [13,14]. The lack of evidence for the presence of metallic iron then indicates that the reduction of the oxides is much slower than the subsequent carbiding [3]. The transformation of the oxides into carbides takes more than one hour. After 15 h a steady-state carbide concentration of at least 75% is reached but, even then,

the distribution of the carbide phases is still changing in favour of the most carbon rich phase. After more than 200 h of reaction at least 75% of the carbides are made up by a hexagonal close-packed phase with $\text{Fe}_{2.23}\text{C}$ as composition and a distribution of the particle diameter. Similar behaviour was observed when using model catalysts in Fischer–Tropsch synthesis at and below 523 K, as reviewed by Le Caër et al. [37] who proposed a reinterpretation of all the previous relevant bibliography. In the case of $\text{Fe}/\text{Al}_2\text{O}_3$ at 523 K, iron metal was totally converted into Fe_xC only and x varied from 2.23 at the beginning to 2.06 after 20 h, corresponding to a decrease in the activity for Fischer–Tropsch synthesis [47]. The fact that here, even after 200 h exposure to reaction conditions, a major fraction of the iron atoms has only 2 C neighbours indicates that at our conditions the diffusion of C in the particles is slow compared to the synthesis of hydrocarbons. In terms of the competition model [41] this means that hydrogenation of the surface carbidic C^* resulting from carbon monoxide dissociation occurs much faster than diffusion into the bulk. Since diffusion of carbon is much slower into iron oxide than into any other iron phase, the above is consistent with the presence of an oxide layer at the interface of the iron particles.

Interface of the iron particles

The Mössbauer spectrum obtained *in situ* after the standard reduction does not allow discrimination between surface and bulk sites of $\alpha\text{-Fe}$. Most of the Fe^{2+} sites are located at the interface of the iron particles, however. This suggests that the reduction to metallic iron starts from the bulk and not from the surface of the iron particles. Grzybek et al. [28] reached the same conclusion for the reduction of iron–manganese oxide catalysts for Fischer–Tropsch synthesis.

After reaction, the oxygen:silicon ratio at the surface of the catalyst particles is still twice that corresponding to silica. The excess oxygen must be present in the form of surface oxides of iron, copper and potassium. Chemisorbed molecular carbon monoxide would give a O 1s photo emission at 532.5 eV [27]. Most of the exposed iron atoms are in an Fe^{2+} oxidation state. Krebs et al. [27] report a binding energy of 711.3 eV for $\text{Fe}^{2+} 2p_{3/2}$. Pommier et al. [13] observed $\text{Fe}^{2+} 2p_{3/2}$ signals of 711.5 and 712.3 eV on a silica supported catalyst having been exposed at 523 resp. 563 K and $(\text{H}_2/\text{CO})^\circ = 9$ directly in the spectrometer. In the present work the catalyst was contacted with the atmosphere during the transfer from the reactor to the spectrometer. Significant oxidation was not caused by this contact, since this would have given rise to Fe^{3+} . The binding energy of $\text{Fe}^{3+} 2p_{3/2}$ is 1 eV higher than that observed after reaction [28].

Niemantsverdriet et al. [42] have shown the presence of iron oxides on the surface of unpromoted iron powder after reaction at 500 K and $(\text{H}_2/\text{CO})^\circ = 3$ for 3 h. The Mössbauer recoilless fraction of these surface iron sites was re-

ported to be low and to decrease with increasing temperature. The in situ Mössbauer spectral areas of the oxides observed in the present work increase also with decreasing temperature, as can be seen in Table 6 by comparing the spectra obtained at 623 and 298 K after 15 h of reaction. The assumption that the interface of the iron particles is exclusively composed of Fe^{2+} and that the Fe^{2+} fraction of the bulk can be neglected, leads to the conclusion that about 10% of the iron atoms are located at the interface. According to eqn. (3) a particle diameter around 10 nm is then obtained.

Location and function of the promoters

The particle dimensions derived from nitrogen sorption data, Mössbauer spectroscopy and X-ray diffraction lead, according to eqn. (3), to much higher values for the exposed fraction of iron atoms than the 3% obtained from carbon monoxide chemisorption. This can be explained by the coverage of two thirds of the interface of the iron particles by silicon and potassium oxides and is consistent with the pronounced surface enrichment of these promoters observed by X-ray photoelectron spectroscopy. Similar observations are reported on ammonia [43–45]. It is generally accepted that alumina is a textural promoter of fused iron catalysts [19,44–46] because refractory alumina islands on the iron interface prevent sintering by acting as spacers between the iron particles. The silica of the present catalyst is thought to behave in an equivalent way. Potassium oxide is usually considered as a chemical promoter for the synthesis of ammonia [43], i.e. it increases the synthesis rate. The available literature data on the activity for methanation of unpromoted and promoted iron catalysts show considerable scattering, even when the activities are expressed per unit iron surface area. No conclusions can be drawn concerning the effect of the potassium oxide promoter on the methanation activity.

CONCLUSIONS

The investigated Fischer–Tropsch catalyst consists of iron particles with an average diameter of 10 nm which is rather stable during reduction and exposure to reaction conditions close to industrial ones. This stability is a result of the textural promotion by silica. The silica islands on the iron particles prevent sintering of the latter.

Two thirds of the iron interface are covered by silicon and potassium oxides, which leaves only 3% of the iron exposed to the gas phase. The iron atoms at the interface of the particles are oxidized.

The bulk phase shows X-ray crystallinity only after exposure to reaction conditions. A standard reduction at 493 K results in 20% of the iron being reduced to metallic iron. After exposure to reaction conditions, no metallic iron is present. The dominant phase is a non-stoichiometric hexagonal closed packed

carbide with $\text{Fe}_{2.23}\text{C}$ as composition. The deviation from the Fe_2C stoichiometry indicates that carbon diffusion into the bulk is hindered.

LIST OF SYMBOLS

a_s	specific surface area	(m^2/kg)
D	fraction of iron atoms at the interface	
d_p	average particle diameter	(m)
F_{CO}	molar feed rate of carbon monoxide	(mol/s)
H_{hf}	magnetic hyperfine field, $1 \text{ kAm}^{-1} = 4\pi \text{ Oe}$	(kOe)
I	relative diffraction intensity	(%)
IS	isomer shift	(mm/s)
K	constant in the Scherrer formula	
n	number of carbon neighbours per iron atom	
p_n	fraction of iron atoms with n carbon neighbours	
QS	quadrupole splitting	(mm/s)
W	mass of catalyst	(kg)
x	stoichiometry of iron in Fe_xC , with $2.0 < x < 2.4$	

Greek symbols

ρ_m	skeletal density	(kg/m^3)
θ	diffraction angle	($^\circ$)

ACKNOWLEDGEMENTS

E. Lox gratefully acknowledges the "Diensten voor Programmatie van het Wetenschapsbeleid" for financial support during the period 1982–1986. E. De Grave acknowledges the National Fund for Scientific Research (NFWO–FNRS, Belgium) for a position as research associate.

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