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Iron Sulphide Containing Hydrodesulphurization Catalysts

Mössbauer Study of the Sulphidibility of α -Iron(III) Oxide

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ABSTRACT

As a first step in the study of the sulphidation of carbon-supported iron oxide catalyst systems the sulphiding of a well-characterized, unsupported model compound, viz. α -Fe₂O₃ (mean particle diameter ca. 50 nm) was investigated using in-situ Mössbauer spectroscopy and the temperature-programmed sulphiding technique. Sulphidation was carried out in a flow of 10% hydrogen sulphide in hydrogen. At room temperature and atmospheric pressure no bulk sulphidation of the α -Fe₂O₃ particles was observed. However, as the sulphidation temperature increased a direct transformation of bulk α -Fe₂O₃ into iron sulphides took place. The iron-to-sulphur ratio of the iron sulphides formed during the sulphidation process was initially 2 and decreased to 1 with increasing sulphidation time and/or temperature.

INTRODUCTION

Hydrotreating catalysts are important within the oil-refining industry. Treatment with 5–15 MPa hydrogen at 600–700 K in the presence of alumina-supported Co-Mo and Ni-Mo sulphide catalysts removes carbon-bonded impurities such as sulphur, nitrogen, oxygen, nickel and vanadium via so-called hydrodesulphurization (HDS), hydrodenitrogenation (HDN), hydrodeoxy-

genation (HDO) and hydrodemetallization (HDM) reactions. Recently, it was shown that sulphided Fe_2O_3 well dispersed on a carbon support, has promising properties as a hydrotreating catalyst [1,2].

In the preparation of these catalysts, sulphidation of the oxidic catalyst precursor is a crucial step because it results in the formation of the actual active catalyst. Therefore, it is important to know how this sulphidation proceeds and whether the final result (type of sulphide and its dispersion) depends upon the sulphiding conditions applied. In general, the sulphiding process of oxidic catalyst precursors has hardly been studied so far. Recently, a temperature-programmed sulphiding (TPS) technique was developed and successfully applied [3-8]. In the case of iron- [9] or cobalt- [10,11] containing HDS catalysts, in-situ Mössbauer spectroscopy was shown to be an excellent technique for the study of the transition of oxide catalyst precursors to their sulphided state.

As a first step in our study of the sulphidation of carbon-supported iron oxide catalyst systems the present paper describes the sulphiding of a well-characterized, unsupported, model compound, viz. $\alpha\text{-Fe}_2\text{O}_3$. The techniques applied were in-situ Mössbauer spectroscopy and TPS.

During sulphiding of $\alpha\text{-Fe}_2\text{O}_3$ the iron sulphides Fe_{1-x}S (pyrrhotites) and FeS_2 (pyrite) were formed. However, in the former a wide range of solid solutions existed between $x=0$ and $x=0.18$. The non-stoichiometry of the iron sulphide system was attributed to the presence of iron vacancies [12]. It was reported that due to variations in the ordering of the iron vacancies different stable phases could exist at room temperature. This is reviewed briefly in the following section.

THE IRON MONOSULPHIDE SYSTEM

Besides the minerals troilite (FeS) and pyrrhotite (Fe_7S_8), the iron monosulphide system also includes artificially prepared Fe_{1-x}S compounds with $-0.02 \leq x \leq 0.18$.

Above about 400 K the stoichiometric mineral troilite and the near stoichiometric Fe_{1-x}S compounds with $-0.02 \leq x \leq 0.04$ have the regular NiAs structure, which is called the 1C-type structure. Below 400 K these compounds show a hexagonal superstructure [13] derived from the NiAs structure in such a way that the length of the crystallographic c -axis is twice as large as that of the 1C-type structure and is therefore called the 2C-type structure. In the temperature range 200 to 400 K the 1C-type structure, as well as the 2C-type structure, can exist for these compounds. In the basic crystallographic structure the relatively large sulphur ions are hexagonally close-packed, while the smaller iron ions preferentially occupy the octahedral sites and are arranged in layers.

It is obvious that, due to the close packing of the sulphur ions, the non-stoichiometry of the iron monosulphide system has to be attributed to the pres-

ence of iron vacancies [12]. These vacancies are randomly distributed in the range $0 < x < 0.09$. In this range the compounds show the 1C-type structure above 200 K and the 2C-type structure below 200 K. When $x > 0.09$, ordering of the iron vacancies leads to stable phases at room temperature which differ with respect to the stacking sequence of iron-deficient layers. Since a clearly defined and generally accepted convention does not exist, the name troilite will be used for all phases exhibiting vacancy disorder, while the term pyrrhotite will be used for all phases exhibiting vacancy order. So, both the 1C- and 2C-type structures will be called troilite like the stoichiometric mineral FeS. In the composition range where the iron vacancies are ordered, the 3C- and 4C-type structure are observed at room temperature [14–17]. The nominal composition of these stable phases corresponds to Fe_7S_8 which means $x = 0.125$. The difference between 3C- and 4C-type structures lies in the stacking sequence of the iron-deficient layers.

The troilite–pyrrhotite system has been extensively studied by various techniques in order to determine its magnetic as well as electrical properties. As the effective magnetic hyperfine field at an iron nucleus is dependent on the number of surrounding iron atoms, their distances and configurations, Mössbauer spectroscopy was used by Igaki et al. [18] to investigate the iron vacancy distribution in single crystals of Fe_{1-x}S in the range $0.083 \leq x \leq 0.125$. These authors took the iron vacancies within the third-nearest neighbouring positions into account and the iron sites were designated by the number of vacancies in each of the nearest, second-nearest and third-nearest neighbouring positions, labelled C, A and B, respectively.

In the region of vacancy order, Thiel [19] investigated by means of Mössbauer spectroscopy, the pyrrhotite Fe_7O_8 in the 3C-type structure as well as the 4C-type structure. The temperature dependence of hyperfine interactions in the near-stoichiometric Fe_{1-x}S (troilite) in the 1C-structure region as well as the 2C-structure region was studied by Thiel and Van den Berg [20].

EXPERIMENTAL

Experiments were carried out on a mixture of 75 mg $\alpha\text{-Fe}_2\text{O}_3$ (BASF, mean particle size = 50 nm) and 225 mg SiO_2 (Aerosil 300V) which was pressed into self supporting wafers with a diameter of 22 mm, using a pressure of 8–10 MPa.

Sulphidation of the $\alpha\text{-Fe}_2\text{O}_3$ was carried out in an in-situ Mössbauer reactor similar to the one described previously [21,22], the only difference being that the reactor used in the present investigation was made of stainless steel. Sulphiding took place in a 10% hydrogen sulphide, in hydrogen gas mixture at a flow-rate of 1 cm³/s. Before sulphidation was started, the reactor was flushed with argon, 1 cm³/s for 30 min at room temperature. During the sulphiding procedure the following temperature program was applied: 30 min at room temperature, linear increase to the desired maximum reaction temperature in 1 h,

holding at this temperature for a certain time and cooling (in the hydrogen sulphide–hydrogen flow) to room temperature. The samples used for Mössbauer analysis were denoted either by $\text{Fe}_2\text{O}_3(\gamma \text{ K})$ where γ is the maximum sulphiding temperature which, in all cases, was reached within 1 h or by $\text{Fe}_2\text{O}_3(\gamma \text{ K}, z \text{ h})$ with z being the time during which the sample was additionally kept at the maximum sulphiding temperature.

While the reactor was still filled with the sulphiding gas mixture the Mössbauer experiments were performed at room temperature with a constant acceleration spectrometer using a ^{57}Co in rhodium source. The spectra shown were not corrected for the varying distance between source and absorber and hence the curved background in the spectra was of instrumental origin. Isomer shifts are given relative to sodiumnitroprusside (SNP) at room temperature. Magnetic fields were calibrated with the 51.5 T field of $\alpha\text{-Fe}_2\text{O}_3$ at 293 K. The Mössbauer spectra were deconvoluted by computer with calculated subspectra consisting of Lorentzian-shaped lines, whereas the curved background was accounted for by a parabola.

A detailed description of the TPS equipment and procedure was given elsewhere [3,5]. At the start of the TPS experiment the reactor containing 38 mg $\alpha\text{-Fe}_2\text{O}_3$ was flushed with argon. Then, the sulphiding gas mixture (3.3% hydrogen sulphide, 29.1% hydrogen and 68.6% argon) was led through the reactor at about 293 K. The composition of the gas leaving the reactor was continuously monitored. Hydrogen sulphide was detected using an UV detector set at 215 nm, hydrogen was detected by a thermal conductivity detector after water and hydrogen sulphide had been trapped in molecular sieves. When the hydrogen sulphide uptake at room temperature was completed the temperature of the TPS reactor was increased to about 1270 K at a rate of 10 K/min.

RESULTS

Mössbauer spectrometry

First, the effect of hydrogen sulphide–hydrogen treatment at room temperature was studied. The Mössbauer spectrum obtained after 6 h exposure of the $\alpha\text{-Fe}_2\text{O}_3$ particles to the hydrogen sulphide–hydrogen gas mixture was not changed by this exposure.

Fig. 1a shows room temperature Mössbauer spectra of the samples $\text{Fe}_2\text{O}_3(423 \text{ K})$, $\text{Fe}_2\text{O}_3(473 \text{ K})$, $\text{Fe}_2\text{O}_3(523 \text{ K})$, $\text{Fe}_2\text{O}_3(573 \text{ K})$ and $\text{Fe}_2\text{O}_3(673 \text{ K})$, respectively. It is obvious that the spectral contribution of the $\alpha\text{-Fe}_2\text{O}_3$ sextuplet decreased as the final sulphiding temperature increased and that this coincided with the appearance of several newly-formed six-line patterns with much smaller magnetic hyperfine splittings. Besides these patterns of magnetically

Fig. 1. (a) In-situ Mössbauer spectra at 293 K of sulphidized Fe_2O_3 (γ K, 0 h). (b) In-situ Mössbauer spectra at 293 K of sulphidized Fe_2O_3 (γ K, 4 h). See Experimental for details of the sulphidation procedure and sample notation.

split components an electric quadrupole doublet was also observed in the centre of the spectra of the samples sulphided up to either 473 K or 523 K.

In order to follow how the sulphidation of $\alpha\text{-Fe}_2\text{O}_3$ proceeded we also continued the treatment in hydrogen sulphide–hydrogen for 4 h at the selected final sulphiding temperatures. In Fig. 1b the corresponding room temperature Mössbauer spectra are shown. Comparison of the spectra presented in Figs. 1a and 1b clearly shows that the $\alpha\text{-Fe}_2\text{O}_3$ contribution decreased as with the sulphiding temperature and sulphiding time increased. It is also evident that the doublet present in the centre of the spectra Fe_2O_3 (423 K), Fe_2O_3 (473 K) and Fe_2O_3 (523 K) in Fig. 1a and the Fe_2O_3 (423 K, 4 h), Fe_2O_3 (473 K, 4 h) spectra in Fig. 1b could be ascribed to a compound which was formed at the beginning of the sulphiding process at temperatures below 473 K. When the sulphiding process at 473 K was continued for 4 h the central doublet almost disappeared. It follows from the isomer shift (IS) and quadrupole splitting (QS) values

TABLE 1

Mössbauer parameters at 293 K of sulphided Fe_2O_3 (y K) samples

y	Sulphided Fe_2O_3 (y K) samples		
	523 K	573 K	673 K
$\alpha\text{-Fe}_2\text{O}_3$			
IS (mm/s)	0.69	0.71	0.73
QS (mm/s)	0.07	0.09	0.10
H_{eff} (kOe)	515	515	517
A (%)	16	12	7
FeS_2			
IS (mm/s)	0.57		
QS (mm/s)	0.61		
A (%)	3		
Fe_{1-x}S			
IS (mm/s)	0.97	0.98	1.00
QS (mm/s)	-0.06	-0.07	-0.07
H_{eff} (kOe)	301	301	296
A (%)	32	22	25
IS (mm/s)		0.99	1.01
QS (mm/s)		-0.05	-0.06
H_{eff} (kOe)		277	276
A (%)		30	44
IS (mm/s)	0.96	0.98	0.99
QS (mm/s)	-0.04	-0.07	-0.09
H_{eff} (kOe)	259	257	261
A (%)	33	36	24
IS (mm/s)	0.93		
QS (mm/s)	-0.10		
H_{eff} (kOe)	229		
A (%)	16		

Experimental uncertainties: IS = ± 0.02 ; QS = ± 0.05 ; H_{eff} = ± 2 ; A = ± 5 .

obtained after computer deconvolution of the spectra, that the observed doublet could be ascribed to pyrite (FeS_2) (see Tables 1 and 2).

From Figs. 1a and 1b it follows that both an increase in sulphiding temperature or sulphiding time influenced the resonant absorption pattern of the newly formed compounds with magnetic hyperfine splittings, indicating a change in composition and/or crystallographic structures. The observed range of magnetic hyperfine fields corresponded to that of non-stoichiometric Fe_{1-x}S compounds [18–20]. For the samples Fe_2O_3 (473 K), Fe_2O_3 (523 K) and

TABLE 2

Mössbauer parameters at 293 K of sulphided Fe_2O_3 (y K, 4 h) samples

y	Sulphided Fe_2O_3 (y K, 4 h) samples				
	423 K	473 K	523 K	573 K	673 K
$\alpha\text{-Fe}_2\text{O}_3$					
IS (mm/s)	0.69	0.70	0.72		
QS (mm/s)	0.07	0.07	0.1		
H_{eff} (kOe)	516	516	517		
A (%)	13	9	5		
FeS_2					
IS (mm/s)	0.57	0.57			
QS (mm/s)	0.61	0.61			
A (%)	21	2			
Fe_{1-x}S					
IS (mm/s)	0.95	0.97	0.98	0.99	1.00
QS (mm/s)	-0.05	-0.06	-0.07	-0.06	-0.06
H_{eff} (kOe)	300	301	300	296	295
A (%)	29	33	28	36	32
IS (mm/s)			0.99	1.00	1.00
QS (mm/s)			-0.04	-0.05	-0.06
H_{eff} (kOe)			275	275	277
A (%)			35	44	43
IS (mm/s)	0.96	0.95	0.98	0.99	1.00
QS (mm/s)	-0.03	-0.04	-0.08	-0.10	-0.10
H_{eff} (kOe)	255	258	258	259	261
A (%)	21	37	32	20	25
IS (mm/s)	0.95	0.93			
QS (mm/s)	-0.10	-0.09			
H_{eff} (kOe)	225	229			
A (%)	16	19			

Experimental uncertainties: IS = ± 0.02 ; QS = ± 0.05 ; H_{eff} = ± 2 ; A = ± 5 .

Fe_2O_3 (423 K, 4 h), Fe_2O_3 (473 K, 4 h) the spectrum of the sulphidic compound consisted of at least three distinct magnetic hyperfine sextuplets. As a result of increasing the sulphiding time and/or temperature the differences in the observed magnetic hyperfine fields became smaller. Besides the spectral contribution of the doublet in the centre and the sextuplet of the original $\alpha\text{-Fe}_2\text{O}_3$ particles, we used three different magnetic hyperfine sextuplets in the deconvolution procedure. The numerical Mössbauer parameters, (IS, QS and the

Fig. 2. Mössbauer spectrum at 293 K of stoichiometric troilite (FeS) from the meteorite Cape-York, and in-situ Mössbauer spectrum at 293 K of the sulphided Fe₂O₃ (673 K, 4 h) sample. See Experimental for details of the sulphidation procedure and sample notation.

Fig. 3. Room temperature in-situ Mössbauer spectra of the sulphided Fe₂O₃ (523 K, 4 h) sample and of the same sample after replacing the hydrogen sulphide-hydrogen environment by argon at 293 K. See Experimental for details of the sulphidation procedure and sample notation.

Fig. 4. Mössbauer spectra at 293, 77 and 4.2 K of the sulphidized Fe_2O_3 (473 K, 4 h) sample exposed to air for one week at 293 K.

magnetic hyperfine field H_{eff}) as well as the spectral contributions A deduced from the spectra are given in Tables 1 and 2.

Although the observed Fe_{1-x}S magnetic hyperfine fields tended to become less different, the largest field component found in Fe_2O_3 (673 K, 4 h) was still smaller than the magnetic hyperfine field (310 kOe) measured for the stoichiometric compound FeS from the meteorite Cape-York. The room temperature spectra of the latter and the Fe_2O_3 (673 K, 4 h) sample are shown in Fig. 2.

It was necessary to keep the sulphidized samples in the hydrogen sulphide–hydrogen gas mixture during the Mössbauer experiment. This is clearly demonstrated in Fig. 3 and 4. In Fig. 3 we show the in-situ room temperature spectra of the Fe_2O_3 (523 K, 4 h) sample and that of the same sample after removing the hydrogen sulphide–hydrogen environment by flowing argon at 293 K. The small spectral contribution of the $\alpha\text{-Fe}_2\text{O}_3$ particles remained the same. How-

ever, the sulphidic contributions were different, indicating a change in the composition of the sulphided sample by changing the surrounding gas phase from hydrogen sulphide–hydrogen to argon. Fig. 4 shows spectra of the Fe_2O_3 (473 K, 4 h) sample exposed to static air at room temperature for one week, measured at 293, 77 and 4.2 K, respectively. By comparing the room temperature spectrum of the air-exposed sample Fe_2O_3 (473 K, 4 h) with the original spectrum given in Fig. 1b, it follows that the exposure to air caused the appearance of a quadrupole doublet in the centre of the spectrum. This doublet can be ascribed to an iron(III) oxide compound formed through the reoxidation of the sample. At 4.2 K the doublet contribution to the spectrum disappeared while a sextuplet consisting of very broad absorption lines, indicating a broad distribution of magnetic hyperfine fields, appeared. This effect can be explained by superparamagnetic behaviour of either small iron oxide particles [1] or an oxidic surface shell on larger particles [23].

Temperature-programmed sulphiding

The TPS pattern of the well-characterized unsupported, model compound $\alpha\text{-Fe}_2\text{O}_3$ is shown in Fig. 5. For clarity only the hydrogen sulphide partial pressure is given. Before the start of the temperature program hydrogen sulphide uptake was observed at room temperature. The amount of hydrogen sulphide involved corresponded to the amount required to flush argon from the reactor and replace it with the hydrogen sulphide–hydrogen–argon mixture. Therefore this hydrogen sulphide uptake did not indicate sulphiding of the sample at room temperature. Sulphiding started somewhat above room temperature when hydrogen sulphide uptake was observed together with production of water (not shown). It follows from Fig. 5 that sulphiding was complete at about 900 K.

Between 450 K and 750 K, hydrogen consumption was found, with peaks coinciding the “dents” in the hydrogen sulphide consumption peak at 460 K, 600 K and 720 K. This indicated that hydrogen sulphide was produced by re-

Fig. 5. TPS-pattern of unsupported $\alpha\text{-Fe}_2\text{O}_3$ particles.

duction of sulphur or of sulphur-containing species [3,5]. The total hydrogen sulphide consumption corresponded to iron-to-sulphur ratio of 1, and the hydrogen consumption with an iron-to-hydrogen ratio of about 3. These ratios were close to the values found for Fe_2O_3 with a larger particle size [24].

DISCUSSION

From the experimental results shown in Fig. 3 it followed that even at room temperature the iron-to-sulphur ratio of the compounds formed had changed due to the replacement of the hydrogen sulphide–hydrogen environment by argon. Furthermore, it was found (see Fig. 4) that sulphided samples became partly reoxidized after exposure to air at room temperature for a period of one week. Therefore, it was absolutely necessary to keep the sulphided samples in the sulphiding gas mixture during characterization.

Lambert et al. [25] reported that in the iron–sulphur system the composition of the iron sulphides formed depended on the hydrogen sulphide–hydrogen ratio as well as the temperature. Using the results of these authors our results indicated that the hydrogen sulphide:hydrogen ratio at the surface of the particles would increase as a consequence of replacing the hydrogen sulphide–hydrogen gaseous environment by argon gas.

The temperature dependence of the oxidic contributions to the spectra of the sulphided samples after exposure to air (Fig. 4) can be explained by superparamagnetic behaviour of either small iron oxide particles [1] or an oxidic surface shell on large iron sulphide particles [23]. As superparamagnetic behaviour at room temperature was not observed for the sulphided samples, it was most likely that during the sulphidation procedure the size of the particles remained rather large. So, only the outer shell of the sulphided particles became reoxidized by the air exposure. However, in the case of carbon-supported Fe_2O_3 particles with a much smaller mean particle size (<4 nm) we observed superparamagnetic behaviour for the iron sulphide phase formed during treatment in hydrogen sulphide–hydrogen ($\text{Fe}(673\text{ K}, 4\text{ h})/\text{C}$) and this iron sulphide phase could indeed be fully reoxidized by means of exposure to static air at 293 K for one week [26].

From our in-situ Mössbauer as well as TPS analysis it was concluded that the bulk of unsupported $\alpha\text{-Fe}_2\text{O}_3$ particles (diameter ca. 50 nm) was not sulphided at room temperature. However, since the fraction of surface atoms of such particles was only about 5% and, furthermore, the effective Debye temperature of surface atoms is only about half that for bulk atoms [27], sulphidation of the surface iron atoms could not be excluded. In the case of a catalyst consisting of carbon-supported Fe_2O_3 particles with a much smaller mean particle size, we observed sulphidation of the particles to a large extent even at room temperature [26]. Okutani et al. [28] found that an exothermic reaction occurred upon addition of a hydrogen sulphide–hydrogen gas mixture to un-

supported α -Fe₂O₃ at room temperature in a gas-circulating, high-pressure (4–10 MPa) DTA apparatus. Analyzing the crystal structures by ex-situ X-ray diffraction when this particular exothermic reaction was complete, these authors found diffraction lines corresponding to FeS₂ and Fe₃S₄ which had about half the intensity of diffraction lines of the major compound α -Fe₂O₃. As we observed the formation of bulk iron sulphides only at higher temperatures, as shown by the Mössbauer spectra in Figs. 1a and b and the TPS-results given in Fig. 5, the apparent discrepancy between our results and those of Okutani et al. [28] may be due to the vigorous exothermic reaction at high pressure and the resulting local temperature increase observed by these authors.

All our in-situ Mössbauer experiments clearly showed a direct transformation of bulk α -Fe₂O₃ into iron sulphides during the sulphidation process (see Figs. 1a and b). The formation of Fe₃O₄ between 500 and 600 K which was reported by Okutani [28] was not observed in our experiments at atmospheric pressure, so the reaction scheme seems to be less complex than that suggested by these authors.

McGormick et al. [29] proposed a model for the sulphidation of FeO (Wüstite) wafers. They studied the sulphidation of FeO with thermogravimetric techniques and found that during an initial transient stage a layer of FeS was formed on the wafer. It was assumed that this FeS layer was impermeable to oxygen. Therefore, oxygen would be conserved in the sample and there would be virtually no net oxygen transfer to, or from, the gas phase whatever its oxygen potential was. The growth of the FeS layer would proceed by the diffusion of iron from the FeO core to the FeS–gas interface where it reacted with sulphur from the gas phase to form FeS. They stated that the reaction rate was limited by the diffusion of iron through the intermediate Fe₃O₄ layer between FeS and FeO which grew concurrently with the FeS layer and at the expense of the FeO core. When the FeO core was completely converted to Fe₃O₄ the process stopped. Our observations clearly showed that such a model of sulphidation of iron oxides was wrong and only followed from the assumptions made by McCormick et al. [29] that the diffusivity of oxygen and sulfur anions in FeO and Fe₃O₄ were orders of magnitude less than the diffusivity of iron.

It follows from the TPS results shown in Fig. 5 that sulphiding of α -Fe₂O₃ started at a relatively low temperature. The simultaneous consumption of hydrogen sulphide and production of water showed that the reaction proceeded through O–S exchange which means that α -Fe₂O₃ was not first reduced to Fe₃O₄ or FeO. From the TPS results only, it can not be excluded that reduction proceeded via iron (oxy)-sulphides. The “dents” in the hydrogen sulphide consumption peak at 460 K and 600 K coupled with hydrogen consumption peaks may suggest such a reduction behaviour. By combining the Mössbauer and the TPS results it can be shown that these “dents” in the hydrogen sulphide consumption peak and corresponding hydrogen consumption were due to a lowering of the sulphur content of the initially formed iron sulphides.

According to the spectra in Fig. 1a and b, the FeS_2 formed which was associated with the electric quadrupole doublet in the centre of the resonant absorption spectra, was transformed into non-stoichiometric Fe_{1-x}S compounds by prolonged (4 h) sulphiding at 423 K and 473 K. The observed magnetic hyperfine fields for the sulphide compounds in Fe_2O_3 (473 K, 4 h) agreed with those found by Thiel [19] (302 ± 2 , 252 ± 2 , 228 ± 2 kOe) in a sample of synthetic Fe_7S_8 with the 4C-type structure. By increasing the sulphiding temperature to 523, 573 or 673 K, the differences between the observed hyperfine fields gradually became smaller (see Fig. 1b and Tables 1 and 2). This behaviour indicated that we were approaching the composition range with $x < 0.09$ in which the iron vacancies in the non-stoichiometric Fe_{1-x}S compounds were no longer ordered. So, from the measured Mössbauer spectra it follows that the mean sulphur content of the iron-sulphur compounds formed decreases as the sulphidation time and/or the maximum temperature increases. Quantitative analysis of the TPS results showed that, finally, the total hydrogen sulphide consumption corresponded to a iron-to-sulphur ratio of 1 which is in line with the Mössbauer effect results described above. So, it can be concluded that the observed "dents" in the hydrogen sulphide consumption peak were due to the transition of $\text{FeS}_2 \rightarrow \text{Fe}_{1-x}\text{S}$ and the continuous lowering of x with increasing sulphidation time and/or increasing the maximum temperature.

The analyses of the Mössbauer spectra of the sulphided samples were carried out using only three different magnetic hyperfine sextuplets for representation of the sulphur compounds formed. Igaki et al. [18] analyzed their spectra in much more detail and proposed an assignment of the various components of the Mössbauer spectra to iron atoms with different vacancy configurations within the first, second and third neighbouring shells, labelled C, A and B, respectively. When an iron atom had no iron vacancy within these three neighbouring shells, the site was denoted by O. As mentioned before, the observed magnetic hyperfine fields in the sulphided sample Fe_2O_3 (473 K, 4 h) corresponded to those found by Thiel [19] in Fe_7S_8 which has the 4C-type structure. This means, in terms of the nomenclature of Igaki et al. [18], that we are dealing with the sites A_2 (300 kOe), B_4 (258 kOe) and B_2C_1 (228 kOe). The hyperfine field of the O-site corresponds to the hyperfine field for the sample Fe_{1-x}S with $x=0$ in which all iron sites occupy the O-sites. We observed a hyperfine field of 310 kOe at room temperature for a FeS sample from the meteorite Cape-York which has the 2C-type structure. However, for the 1C-type structure Thiel and Van den Berg [20] found a hyperfine field of 290 kOe at room temperature. Since Ono and Ito [30] reported a hyperfine field of 276 kOe for a 1C-type Fe_{1-x}S which, because of its low x value ($x=0.047$), would have a large fraction of occupied O-sites, it seemed reasonable to assign this hyperfine field of the 1C-type structure (290 kOe) to the O-site. Assuming that iron vacancies at the C, A and B positions contributed independently to the hyperfine field, their contribution could be calculated by comparing the values

of the hyperfine fields at the sites A_2 , B_4 , B_2C_1 with those at the O-sites. These contributions, denoted as ΔH_A , ΔH_B and ΔH_C per vacancy, became $\Delta H_A = +5$ kOe, $\Delta H_B = -8$ kOe and $\Delta H_C = -46$ kOe, and they were in reasonable agreement with the different contributions reported by Igaki et al. [18]. These authors used the derived values of ΔH_A , ΔH_B and ΔH_C to calculate the hyperfine fields of the additional iron sites which they used for deconvolution of the measured Mössbauer spectra. We believed that such an analysis of their spectra is not justified by the experimental accuracy, so we analyzed the Mössbauer spectra of the sulphide compounds formed with only three different magnetic hyperfine sextuplets. However, it can be noted from the hyperfine fields given in Tables 1 and 2 that the number of iron vacancies in the $Fe_{1-x}S$ compounds formed decreased as the sulphidation time and/or the maximum temperature increased. The initially observed iron sites A_2 , B_4 and B_2C_1 were changed into the iron sites A_1 , B_2 and B_4 . The spectral contributions of the different sites also indicated that the composition of the $Fe_{1-x}S$ compound formed shifted towards lower values of x .

CONCLUSIONS

It was clearly demonstrated that it was absolutely necessary to keep the samples in the sulphiding gas mixture during characterization. For the model catalyst of unsupported α - Fe_2O_3 particles (diameter ca. 50 nm) no bulk sulphidation took place at room temperature and atmospheric pressure. As the sulphidation temperature increased a direct transformation of bulk α - Fe_2O_3 into iron sulphides was observed without preceding reduction steps to Fe_3O_4 and FeO. The iron-to-sulphur ratio of the iron sulphides formed during the sulphidation process was initially 2 and decreased to 1 with increasing sulphidation time and/or temperature. In-situ Mössbauer spectroscopy and the TPS technique are complementary techniques.

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