

Sulfidation of carbon-supported iron-molybdenum oxide catalysts

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Sulphidation of Carbon-Supported Iron–Molybdenum Oxide Catalysts

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ABSTRACT

Carbon-supported iron-molybdenum sulphide catalysts were characterized by means of Mössbauer spectroscopy at temperatures down to 4.2 K. Thiophene hydrodesulphurization (HDS) activity measurements were performed at 673 K in a flow microreactor operating at atmospheric pressure. The molybdenum content was 9.5 wt.-% whereas the iron content varied from 0.6 to 9.0 wt.-%. Sequential deposition (Molybdenum first) by pore-volume impregnation was employed to prepare oxidic catalyst precursors. The oxidic catalyst precursors were dried at 293 K in an air flow, followed by an additional hydrogen treatment up to 393 K. The type and relative particle sizes of the iron compounds present in the oxidic precursors and in the sulphided and reoxidized catalysts were determined by Mössbauer spectroscopy. It was demonstrated that after sulphidation for 4 h at 623 K, the composition of the sulphide catalyst depends on the iron content. Sulphided Fe-Mo/C catalysts contain a mixed "Fe-Mo-S" phase and "Fe-sulphide". The former is responsible for the observed promoting effect toward thiophene HDS. From the temperature dependence of the resonant absorption areas, it was concluded that the iron atoms in the "Fe-Mo-S" phase are located at the surface of MoS₂ microcrystals. The amount of "Fe-sulphide" present in the catalyst was found to increase with increasing iron content. This "Fe-sulphide" might partly cover the "Fe-Mo-S" phase, thus causing a decrease in the promoting effect.

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INTRODUCTION

Hydrotreating catalysts are widely used in the oil-processing industry. During a process at 573–773 K and 5–20 MPa hydrogen in the presence of a catalyst, carbon-bonded impurities such as sulphur, nitrogen, oxygen and metals (nickel, vanadium) are removed via hydrodesulphurization (HDS), hydrodenitrogenation (HDN) and hydrometallization (HDMe) reactions. Conventional hydrotreating catalysts contain alumina-supported molybdenum sulphide promoted by cobalt or nickel sulphide.

Over the last few years there has been growing interest in the application of carbonaceous substrates as catalyst supports [1–14]. Potential advantages include low costs and easy metal recovery by burning off the carbon support [1,2]. Further, carbon-supported catalysts have been shown to be less sensitive to deactivation due to coke formation [6,8].

Moreover, it is reported that when a relatively inert support, such as carbon, is used instead of a more reactive support such as alumina or silica, the thiophene HDS activity of both promoted and unpromoted MoS_2 catalysts increases [4,5,9,10]. De Beer et al. [3] and Duchet et al. [5] have shown that in addition to molybdenum sulphide, cobalt and nickel sulphide also possess an interestingly high activity for thiophene HDS at atmospheric pressure when a carbon support is used.

Visser et al. [7] and Ledoux et al. [11] reported thiophene HDS activities for first-, second- and third-row transition metal sulphides supported on activated carbon. In accordance with the findings of Pecoraro and Chianelli [15] for unsupported transition metal sulphides, they found that many transition metal sulphides have a considerable thiophene HDS activity. Also for HDN reactions interesting results are obtained with transition metal sulphides supported on activated carbon [13,14].

It is expected that in the future catalyst lifetimes will shorten because of the heavier and more contaminated feedstocks that have to be processed. Therefore, there is a growing need to lower the catalyst costs. In this respect, carbon-supported iron sulphides, either as an active phase or as promoter of MoS_2 , can play a role.

The properties of carbon-supported iron sulphide catalysts have been discussed elsewhere [16–18]. Preparational aspects were found to affect the thiophene HDS activity by causing variations in dispersion of the iron (III) oxide phase and strength of the interaction between the iron (III) oxide particles and the carbon support in the oxidic catalyst precursors. These variations result in differences in the dispersion of the catalytically active iron sulphide phase. It was also established that in the freshly sulphided catalysts always the same iron sulphide phases [“Fe-sulphide” (1) and “Fe-sulphide” (2)] were present, irrespective of the method of preparation and the iron content.

For one carbon-supported Fe–Mo catalyst we have already studied the tran-

sition of the oxidic precursor into the sulphided catalyst and the influence of the sulphidation procedure on the sulphidic phase [19]. It was reported that a mixed Fe–Mo–sulphide phase, the so-called “Fe–Mo–S” phase, is formed on sulphidation and that the promoting effect observed for the thiophene HDS activity is due to this “Fe–Mo–S” phase. In analogy with the “Co–Mo–S” phase in sulphided supported Co–Mo catalysts [20], this “Fe–Mo–S” phase is defined by its isomer shift and quadrupole splitting in the Mössbauer spectrum [21]. However, van der Kraan et al. [22] recently reported that a similar quadrupole splitting as ascribed to the “Co–Mo–S” phase by Topsøe et al. [20] is observed in the Mössbauer spectrum of a sulphided Co/C catalyst. Although, from a fundamental point of view, this special type of cobalt species should not be referred to as “Co–Mo–S” (and in the case of Fe–Mo catalysts as “Fe–Mo–S”), we shall use this notation here.

In this paper, the relationship between the composition of carbon-supported Fe–Mo catalysts and the catalytic properties for thiophene HDS is described. Special attention is paid to the amount of iron atoms present in the “Fe–Mo–S” phase and its relevance for the HDS activity. Also, the thermal stability of the catalysts is discussed. All catalysts were characterized in their oxidic precursor, freshly sulphided and reoxidized forms using in situ Mössbauer spectroscopy. Catalytic activities for thiophene HDS were determined at 673 K and atmospheric pressure.

EXPERIMENTAL

Preparation of oxidic catalyst precursors

Catalyst precursors were prepared by sequential pore-volume impregnation of Norit RX3-extra activated carbon (surface area $1190 \text{ m}^2 \text{ g}^{-1}$; pore volume $1.0 \text{ cm}^3 \text{ g}^{-1}$). Aqueous solutions of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Merck, > 99%) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Baker, > 99%) were used. The iron nitrate solutions were enriched in the Mössbauer isotope ^{57}Fe , using reduced $\alpha\text{-Fe}_2\text{O}_3$ (Intersales, 94.7% ^{57}Fe) dissolved in 2 M HNO_3 and the acidity was adjusted to pH 0.25. In this way, samples with a molybdenum content of 9.5 wt.-% and iron contents of 0.6, 1.8, 2.7, 5.5 and 9.0 wt.-% were prepared.

The molybdenum phase was introduced first via a two-step impregnation followed by intermediate drying in static air according to the following procedure: 1.5 h while increasing the temperature from 293 to 383 K and 16 h at 383 K. After impregnation of the iron phase, the samples were dried in flowing air (flow-rate $100 \text{ cm}^3 \text{ min}^{-1}$) for 16 h at room temperature in order to obtain a well dispersed iron oxide phase (particle size < 4 nm) [23]. It was observed that the catalyst precursors prepared in this way still contain hygroscopic nitrate anions, the presence of which caused a decrease in the thermal stability of the iron phase particles [16,17]. Therefore, these nitrate anions were re-

moved by subjecting the samples to an additional treatment in a hydrogen flow (flow-rate $50 \text{ cm}^3 \text{ min}^{-1}$) [17]. During this treatment the sample was kept at 313, 353 and 393 K for 24 h at each temperature.

The catalyst precursors thus obtained will be denoted as $\text{Fe}(x)\text{Mo}(9.5)/\text{C}$, where x and 9.5 are the variable iron content and the constant molybdenum content in wt.-%, respectively.

Sulphiding procedure and Mössbauer experiments

Mössbauer spectra were recorded at 293, 77 and 4.2 K with a constant-acceleration spectrometer. A ^{57}Co in Rh source, which was kept at room temperature, was used. The spectra were not corrected for the varying distance between source and absorber, hence the curved background is of instrumental origin. Doppler velocities are given relative to the NBS standard sodium nitroprusside (SNP) at 293 K. Magnetic hyperfine fields were calibrated with the 51.5 T field of $\alpha\text{-Fe}_2\text{O}_3$ at room temperature. The spectra were fitted by computer with calculated subspectra consisting of Lorentzian-shaped lines, whereas the curved background was accounted for by a parabola. In order to be able to analyse the very complicated spectra, consisting of relatively very broad resonant absorption lines, first the spectra were measured with good statistical quality. Further, the spectra were fitted with the minimum set of spectral components necessary to obtain reasonable fits between the calculated and the measured spectra. However, one should always realize that it is impossible to present a unique set of fitting parameters, but only a coherent set throughout the systematic study.

Catalyst sulphidation took place in two different stainless-steel Mössbauer in situ reactors. The design of these reactors has been described elsewhere [24,25]. The in situ reactor used for the measurements at room temperature or higher will be denoted as the high-temperature reactor (HTR), and that for measurements down to liquid helium temperatures as the low-temperature reactor (LTR). Different experimental procedures were used in the two reactors. In the HTR, first the effect of exposing the catalyst to a 10 mol-% hydrogen sulphide in hydrogen sulphiding gas mixture at room temperature was investigated. A Mössbauer spectrum was recorded at 293 K while the sample was kept in static hydrogen sulphide-hydrogen at atmospheric pressure. Next the same sample was subjected to various successive sulphidation treatments in a $50 \text{ cm}^3 \text{ min}^{-1}$ flow of hydrogen sulphide-hydrogen. In each treatment the temperature was increased linearly to the desired maximum sulphidation temperature in 1 h, and was then lowered to room temperature in the same gas flow. Mössbauer spectra were recorded at 293 K after each treatment while the sample was kept in the hydrogen sulphide-hydrogen environment at atmospheric pressure. The samples will be denoted $\text{Fe}(x)\text{Mo}(9.5)/\text{C}[z \text{ K}]$, where z is the maximum sulphiding temperature in Kelvin reached during the 1-h sulphiding procedure.

In the LTR the catalyst was heated linearly in a $50 \text{ cm}^3 \text{ min}^{-1}$ flow of hydrogen sulphide–hydrogen to 623 K over a 1-h period, kept at 623 K for 4 h and cooled to room temperature in the same gas flow. Subsequently, the separate absorber holder was in situ sealed vacuum-tight and mounted in a cryostat. These samples will be denoted $\text{Fe}(x)\text{Mo}(9.5)/\text{C}[623 \text{ K}, 4 \text{ h}]$. The sulphided catalysts were reoxidized by opening the LTR absorber holder and exposing them to air at room temperature for at least 1 week.

Sulphiding procedure and catalytic activity measurements

Catalyst sulphiding and thiophene HDS activity testing were successively carried out at atmospheric pressure in a quartz tubular flow reactor (diameter 0.8 cm). The catalyst samples used for the activity test had been previously used for the Mössbauer study. Consequently, the catalyst samples (180–200 mg) had been subjected previously to a sulphidation treatment as described above $\{\text{Fe}(x)\text{Mo}(9.5)/\text{C}[623 \text{ K}, 4 \text{ h}]\}$. The second sulphidation prior to the activity test was carried out in a flow of 10 mol-% hydrogen sulphide in hydrogen (total flow-rate $60 \text{ cm}^3 \text{ min}^{-1}$) for 70 min. In the first 60 min the temperature of the catalyst was increased linearly from room temperature to 623 K, then increased over a 10-min period to 673 K. Next, the reaction gas mixture, consisting of 6.2 mol-% thiophene in hydrogen, was led over the catalyst at a flow-rate of $50 \text{ cm}^3 \text{ min}^{-1}$. The reaction products were analysed by means of an on-line gas chromatograph. Conversions measured after a 2-h run time at 673 K were used to calculate the reaction rate constants (k_{HDS}) assuming a first-order reaction in thiophene.

RESULTS

Mössbauer measurements

Oxidic precursors

In Fig. 1, Mössbauer spectra of the $\text{Fe}(9.0)\text{Mo}(9.5)/\text{C}$ precursor recorded at 293, 77 and 4.2 K are shown. The spectra recorded at 293 and 77 K consist only of a quadrupole doublet. Whereas at 4.2 K a superposition of a quadrupole doublet and a magnetic hyperfine sextuplet is observed. Neither a contribution of the original iron salt, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, which would be a broadened single line, nor a contribution of iron atoms in close contact with nitrate anions is observed. Also, no contributions of iron molybdates such as $\text{Fe}_2(\text{MoO}_4)_3$ or α - or β - FeMoO_4 were measured. This indicates complete decomposition of the iron nitrate and removal of the nitrate anions. The observed temperature behaviour, which is observed for all $\text{Fe}(x)\text{Mo}(9.5)/\text{C}$ oxidic catalyst precursors, is typical of ultrafine iron(III) oxide particles showing superparamagnetism

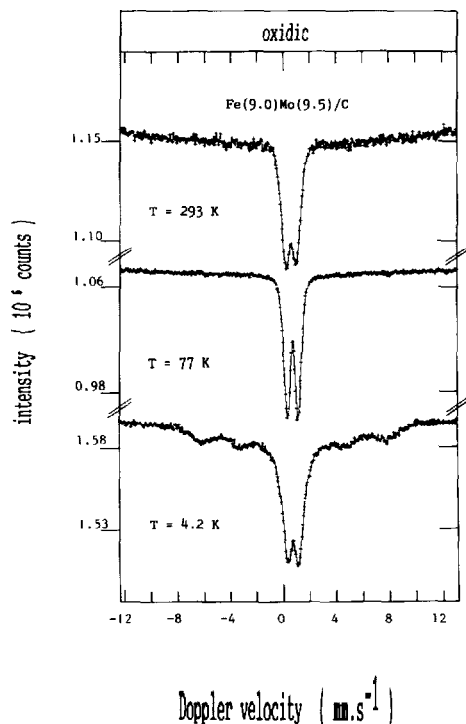


Fig. 1. Mössbauer spectra of the oxidic Fe(9.0)Mo(9.5)/C catalyst precursor recorded at the temperatures indicated.

[26]. The appearance of the magnetic hyperfine sextuplet depends on the mean particle size and also on the temperature.

The spectra of the various oxidic catalyst precursors recorded at 4.2 K are shown in Fig. 2. The spectral contribution of the magnetic hyperfine sextuplet is different for the various samples. As larger particles contribute more than smaller particles to the magnetic hyperfine sextuplet at a certain temperature [26], Fig. 2 in fact shows that the mean particle size increases in the sequence Fe(2.7)Mo(9.5)/C < Fe(1.8)Mo(9.5)/C < Fe(5.5)Mo(9.5)/C < Fe(0.6)Mo(9.5)/C < Fe(9.0)Mo(9.5)/C. This surprising sequence will be discussed below.

From a comparison of the spectra shown in Fig. 2 with those of unsupported α -Fe₂O₃ microcrystals with a known mean particle size [26], it is concluded that the mean particle size of the iron (III) oxide particles is below 4 nm for all catalyst precursors studied. A comparison with data obtained by Jung et al. [27] and Niemantsverdriet et al. [28] indicates that the mean size of the iron (III) oxide particles is below 2 nm for the oxidic catalyst precursors with iron contents up to 5.5 wt.-%.

The quadrupole doublet observed in the spectra of the precursor material consists of broad absorption lines. Therefore, it is reasonable to analyse these

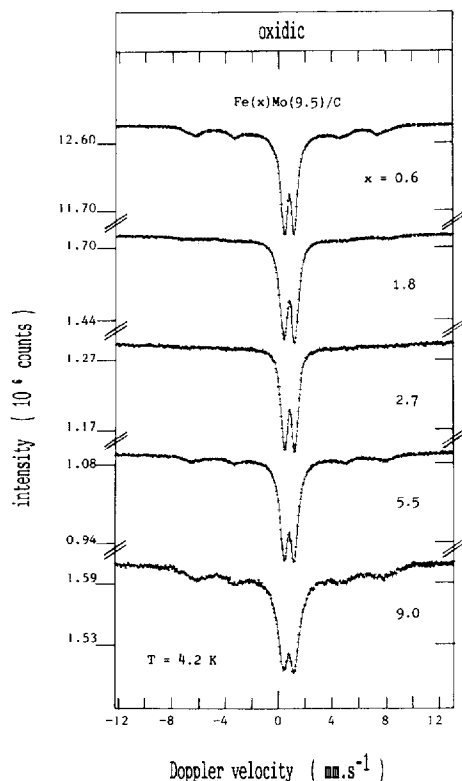


Fig. 2. Mössbauer spectra of the oxidic $\text{Fe}(x)\text{Mo}(9.5)/\text{C}$ catalyst precursors recorded at 4.2 K.

spectra using two doublets. In order to obtain more detailed spectra at 293 K they were recorded on an extended velocity scale. From the analyses it appears that both doublets have an identical isomer shift (IS), but different quadrupole splittings (QS) ($IS_1 = 0.65 \text{ mm}^{-1}\text{s}$, $QS_1 = 0.55 \text{ mm}^{-1}\text{s}$; $IS_2 = 0.66 \text{ mm}^{-1}\text{s}$, $QS_2 = 0.92 \text{ mm}^{-1}\text{s}$). From previous experiments on unsupported small $\alpha\text{-Fe}_2\text{O}_3$ particles (4–7 nm), it is known that such a spectral composition is due to a bulk- and a surface-oxide contribution [26]. The spectral component with the largest QS value can be assigned to the surface-oxide contribution. The same spectral composition is also observed for the oxidic precursors of carbon-supported iron catalysts [17].

Transition of the oxidic precursor into the sulphided catalyst

In addition to characterization of the fully sulphided catalysts in the LTR, we also studied in the HTR how the oxidic precursors are converted into the sulphided catalysts. The preliminary results of such a study on one of the catalyst precursors, $\text{Fe}(1.8)\text{Mo}(9.5)/\text{C}[z \text{ K}]$, has already been presented else-

where [19]. Because it turns out that the general behaviour of the various catalyst precursors is similar, only the results obtained for the catalyst with the highest iron content, Fe(9.0)Mo(9.5)/C [z K], are presented here. In Fig. 3 Mössbauer spectra recorded at 293 K for this catalyst after various successive hydrogen sulphide–hydrogen treatments are shown.

From Fig. 3 it is obvious that the spectrum of the oxidic catalyst precursor has already drastically changed after the catalyst has been exposed to the hydrogen sulphide–hydrogen mixture at room temperature for at least 6 h. As with Fe(1.8)Mo(9.5)/C [293 K] [19], this spectrum has been subdivided into four sub-spectra, one ascribed to pyrite (FeS_2), one to a high-spin Fe^{2+} phase and two components which are not found during the sulphidation of Fe/C catalysts [17]. Therefore, these latter components are ascribed to a mixed

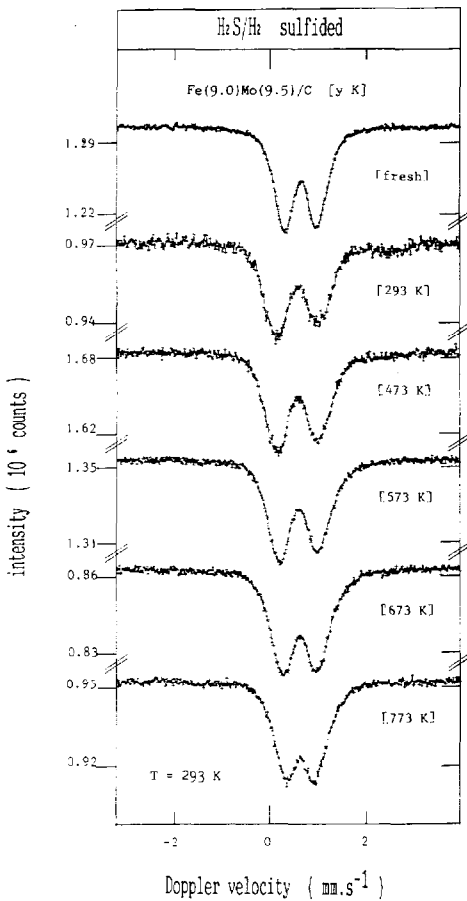


Fig. 3. In situ Mössbauer spectra recorded at room temperature of the Fe(9.0)Mo(9.5)/C catalyst successively sulphided up to the temperatures indicated.

TABLE 1

Isomer shifts (*IS*), electric quadrupole splittings (*QS*) and spectral contributions (*A*) obtained from computer analyses of Mössbauer spectra recorded at 293 K of the Fe(9.0)Mo(9.5)/C catalyst in hydrogen sulphide-hydrogen after various successive sulphidation treatments up to temperatures in Kelvin (*z*) indicated

Experimental uncertainties: *IS*, 0.03 mm s⁻¹; *QS*, 0.05 mm s⁻¹; *A*, 5%

<i>z</i> (K)	High-spin Fe ²⁺			"Fe-sulphide" ^a			"Fe-Mo-S"			<i>IS</i> (mm s ⁻¹)	<i>QS</i> (mm s ⁻¹)	<i>A</i> (%)
	<i>IS</i> (mm s ⁻¹)	<i>QS</i> (mm s ⁻¹)	<i>A</i> (%)	<i>IS</i> (mm s ⁻¹)	<i>QS</i> (mm s ⁻¹)	<i>A</i> (%)	<i>IS</i> (mm s ⁻¹)	<i>QS</i> (mm s ⁻¹)	<i>A</i> (mm s ⁻¹)			
293	1.28	2.36	14	0.57	0.72	65	0.60	1.07	6	0.60	1.33	15
473				0.56	0.65	47	0.59	1.09	47	0.70	1.47	6
573				0.59	0.63	55	0.61	1.02	36	0.69	1.47	9
673				0.62	0.57	66	0.64	0.98	29	0.70	1.45	6
773				0.64	0.53	84	0.65	0.99	14	0.70	1.46	2

^aFrom the appearance of a magnetically split contribution in the spectra recorded at 4.2 K in the catalysts with an iron content of 2.7 wt.-% and higher, it is concluded that the signal referred to as "Fe-sulphide" is due to the presence of superparamagnetic "Fe_{1-x}S"-type particles.

sulphidic Fe-Mo compound which, following Topsøe et al. [21], is denoted "Fe-Mo-S". The numerical results of the computer analyses of the spectra after the various sulphidation treatments are presented in Table 1.

It turns out that by increasing the sulphidation temperature, the spectral contribution of the high-spin Fe²⁺ phase decreases and finally disappears, while the contributions ascribed in ref. 19 to pyrite and the mixed Fe-Mo sulphide phase are still observed. However, the presence of pyrite after the sulphidation treatments at high temperatures is surprising, especially since we know from Mössbauer analysis on both a model system consisting of unsupported 50-nm α -Fe₂O₃ particles [29] and Fe(*x*)/C catalyst [17] that after sulphidation up to 573 K or higher the initially formed FeS₂ is transformed into "Fe_{1-x}S" and "Fe-sulphide" phases respectively.

As with the Fe(*x*)/C catalysts [17], in addition to the spectra recorded at 293 K, in situ Mössbauer measurements at cryogenic temperatures were carried out in order to obtain more detailed information on the composition and/or mean particle size of the various iron phases present in the fully sulphidated catalysts. This was done because it is known that in addition to the isomer shift and the quadrupole splitting, the magnetic hyperfine parameters will also be of help in the identification of possible "Fe_{1-x}S"-type structures [29]. The results of these measurements are presented in the next section.

Fully sulphidated catalysts

To solve the problem raised in the previous section concerning the possible presence of FeS₂ after high-temperatures sulphidation, in situ Mössbauer mea-

measurements at cryogenic temperatures were carried out on the fully sulphided catalysts. In addition, such measurements make it possible to study the temperature dependence of the resonant absorption areas of the various iron phases. This might also lead to a better knowledge of the iron phases, for instance, whether or not the iron atoms are located at the surface of a certain phase.

The spectra recorded at 293 and 77 K only consist of a quadrupole doublet. In Fig. 4, spectra of the sulphided catalysts recorded at 4.2 K are shown. From the preliminary results for the Fe(1.8)Mo(9.5)/C catalyst obtained from only room-temperature measurements [19] it was expected that the spectra at 4.2 K would consist of three doublets, two for the "Fe-Mo-S" phase and one for FeS₂. Roughly, for the Fe(0.6)Mo(9.5)/C [623 K, 4 h] and Fe(1.8)Mo(9.5)/C [623 K, 4 h] catalysts such quadrupole splitted spectra are observed. However, for catalysts with a higher iron content the doublets are superimposed on a much broadened magnetically hyperfine splitted spectrum. The higher the iron content of the catalyst, the larger is the spectral contribution of the latter.

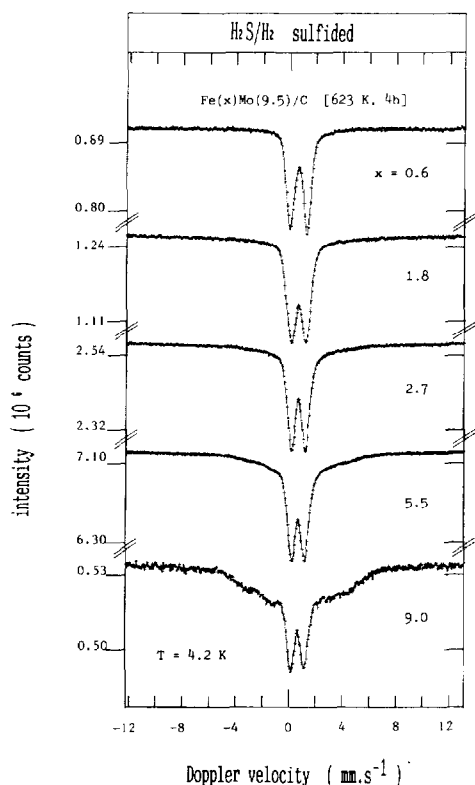


Fig. 4. In situ Mössbauer spectra recorded at 4.2 K of fully sulphided Fe(x)Mo(9.5)/C [623 K, 4 h] catalysts.

The total width of the magnetically split contribution is similar to that of the "Fe-sulphide" phases observed in the 4.2 K spectra of the sulphided Fe(*x*)/C catalysts [17]. The appearance of the magnetically split contributions at 4.2 K indicated undoubtedly that we were not dealing with FeS₂ in the spectra recorded at room temperature of the fully sulphided catalysts Fe(2.7)Mo(9.5)/C [623 K, 4 h], Fe(5.5)Mo(9.5)/C [623 K, 4 h] and Fe(9.0)Mo(9.5)/C [623 K, 4 h]. Probably particles of "Fe_{1-x}S"-like structures, denoted "Fe-sulphide", are formed, which show superparamagnetic behaviour, owing to the small particle sizes. It has been reported previously that the magnetically split spectra of "Fe_{1-x}S" structures can be described by three sextuplets [17,29]. Hence, the computer analyses of the spectra recorded at 4.2 K were carried out using two doublets for the "Fe-Mo-S" contribution, one doublet for the superparamagnetic "Fe-sulphide" contribution and optionally three sextuplets for the magnetically split "Fe-sulphide" contribution. The parameters of the sextuplets were constrained to the values determined from the spectra of the sulphided Fe(*x*)/C catalysts [17].

The results of these analyses are given in Table 2. For the Fe(0.6)Mo(9.5)/C and Fe(1.8)Mo(9.5)/C catalysts only superparamagnetic "Fe-sulphide" and "Fe-Mo-S" were present in the sulphided catalysts. For the catalysts with a

TABLE 2

Mössbauer parameters and spectral contributions: (A) of the sulphided Fe(*x*)Mo(9.5)/C [623 K, 4 h] catalysts at 4.2 K.

Experimental uncertainties: *IS*, 0.05 mm s⁻¹; *QS*, 0.05 mm s⁻¹; *A*, 5%.

<i>x</i> (wt.-%)	"Fe-Mo-S"						"Fe-sulphide" ^a			
	Doublet 1			Doublet 2			Doublet			Sextuplet ^b
	<i>IS</i> (mm s ⁻¹)	<i>QS</i> (mm s ⁻¹)	<i>A</i> (%)	<i>IS</i> (mm s ⁻¹)	<i>QS</i> (mm s ⁻¹)	<i>A</i> (%)	<i>IS</i> (mm s ⁻¹)	<i>QS</i> (mm s ⁻¹)	<i>A</i> (%)	<i>A</i> (%)
0.6	0.66	1.16	49	0.64	1.63	40	0.67	0.62	11	0
1.8	0.68	1.13	50	0.67	1.69	21	0.67	0.62	29	0
2.7	0.67	1.09	27	0.68	1.31	40	0.67	0.67	18	15
5.5	0.63	1.14	24	0.77	1.07	34	0.65	0.70	14	28
9.0	0.67	1.12	11	0.72	1.13	21	0.67	0.67	5	63

^aFrom the appearance of a magnetically split contribution in the spectra recorded at 4.2 K in the catalysts with an iron content of 2.7 wt.-% and higher, it is concluded that the signal referred to as "Fe-sulphide" is due to the presence of superparamagnetic "Fe_{1-x}S"-type particles.

^bThe Mössbauer parameters of the magnetically split "Fe-sulphide" sextuplets were constrained as follows: sextuplet 1, *IS* = 0.89 mm s⁻¹, *QS* = 0.09 mm s⁻¹, *H* = 27.5 T; sextuplet 2, *IS* = 0.81 mm s⁻¹, *QS* = -0.03 mm s⁻¹, *H* = 23.7 T; sextuplet 3, *IS* = 0.82 mm s⁻¹, *QS* = -0.09 mm s⁻¹, *H* = 19.6 T.

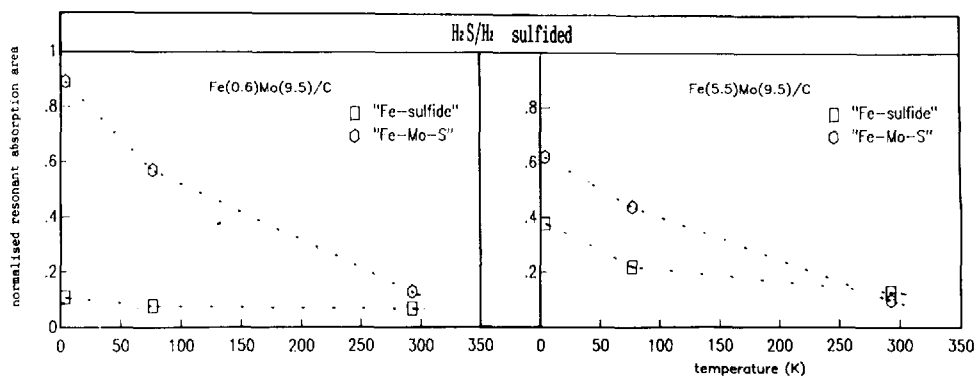


Fig. 5. Influence of the recording temperature on the resonant absorption areas (A) of the "Fe-Mo-S" and "Fe-sulfide" contributions.

higher iron content, a magnetically split "Fe-sulphide" contribution was also observed.

It is shown in Table 2 that the Mössbauer parameters of one of the two doublets attributed to the "Fe-Mo-S" phase (doublet 2) have changed as soon as relatively large "Fe-sulphide" particles (formation of magnetic hyperfine splitting) are observed in the spectra. Hence this iron site ascribed to the "Fe-Mo-S" phase is influenced by the presence of "Fe-sulphide" particles.

As the "Fe-sulphide" particles are superparamagnetic, the spectral contribution of the magnetic hyperfine sextuplet reflects their mean particle size. Therefore, the mean size of these particles increases in the sequence Fe(2.7)Mo(9.5)/C [623 K, 4 h] < Fe(5.5)Mo(9.5)/C [623 K, 4 h] < Fe(9.0)Mo(9.5)/C [623 K, 4 h].

Computer analyses of the 293 and 77 K spectra were carried out using the three spectral contributions found in the 4.2 K spectra. In Fig. 5 the temperature dependence of the resonant absorption areas of the "Fe-Mo-S" and "Fe-sulphide" components present in the Fe(0.6)Mo(9.5)/C [623 K, 4 h] and Fe(5.5)Mo(9.5)/C [623 K, 4 h] catalysts are given. It is observed that, as for the other catalysts, the resonant absorption area of the "Fe-Mo-S" contribution shows the strongest temperature dependence.

Reoxidized catalysts

In Fig. 6, Mössbauer spectra of the reoxidized Fe(9.0)Mo(9.5)/C catalyst at 293, 77 and 4.2 K are shown. In the spectra at 293 and 77 K a superposition of two quadrupole doublets is observed. The spectrum at 4.2 K shows the presence of an additional magnetic hyperfine sextuplet. The quadrupole doublet with the larger splitting is due to a high-spin Fe²⁺ phase. It is noticed that the spectral contribution of this component increases strongly when the temperature is lowered from 293 to 77 K. The other quadrupole doublet is due to the

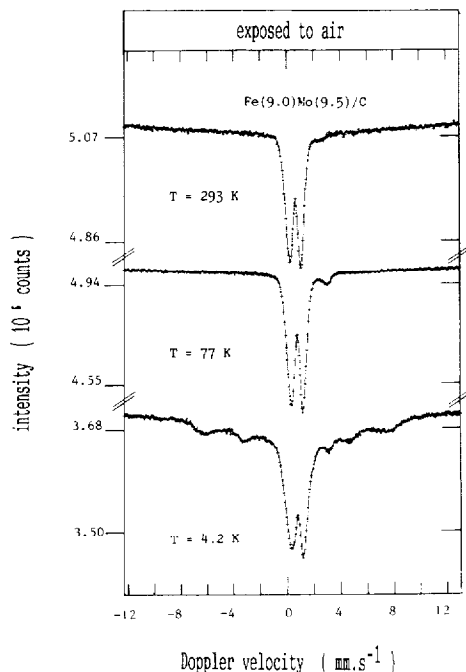


Fig. 6. Mössbauer spectra of the Fe(9.0)Mo(9.5)/C catalyst reoxidized in ambient air at room temperature after sulphidation, recorded at the temperatures indicated.

iron(III) oxide phase. The temperature behaviour observed for the iron(III) oxide contribution is characteristic of ultrafine particles showing superparamagnetism [26].

In Fig. 7, Mössbauer spectra recorded at 4.2 K of all reoxidized catalysts are shown. The central doublet in the spectra of the reoxidized Fe(0.6)Mo(9.5)/C and Fe(1.8)Mo(9.5)/C catalysts is much narrower than that in the spectra of the other reoxidized catalysts. From a comparison with the spectra of the oxidic precursors (Fig. 2), it follows that such a narrow central doublet cannot be due to an iron(III) oxide phase. Hence it is concluded that in the reoxidized Fe(0.6)Mo(9.5)/C and Fe(1.8)Mo(9.5)/C catalysts another iron phase must be present. A magnetically split contribution is clearly observed only in the spectra of the reoxidized Fe(0.6)Mo(9.5)/C and Fe(9.0)Mo(9.5)/C catalysts. However, the magnitude of the magnetic splitting is not the same for both catalysts. With the Fe(9.0)Mo(9.5)/C catalyst the magnetically split contribution turned out to be due to iron(III) oxide. For the Fe(0.6)Mo(9.5)/C catalyst it followed from the isomer shift (ca. 1.5 mm s^{-1}) and the magnetic hyperfine splitting (ca. 530 kOe) that the magnetically split contribution must be due to highly dispersed high-spin Fe^{2+} ions.

Although for the Fe(2.7)Mo(9.5)/C and Fe(5.5)Mo(9.5)/C catalysts no

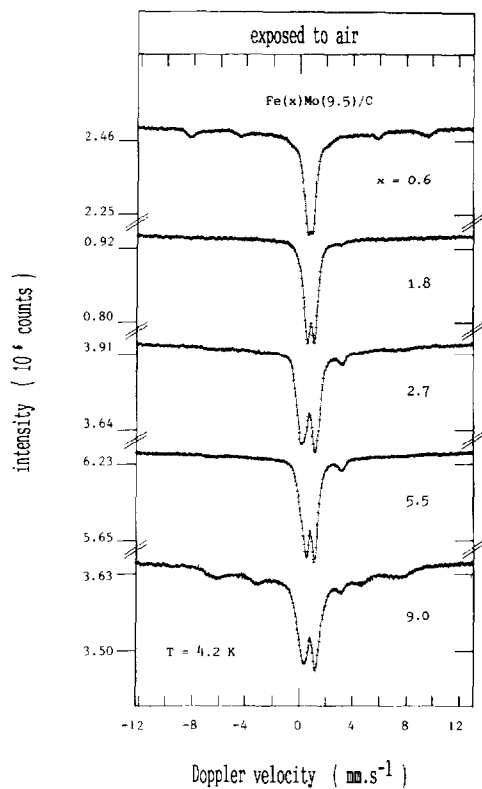


Fig. 7. Mössbauer spectra of the reoxidized Fe(x)Mo(9.5)/C catalysts recorded at 4.2 K.

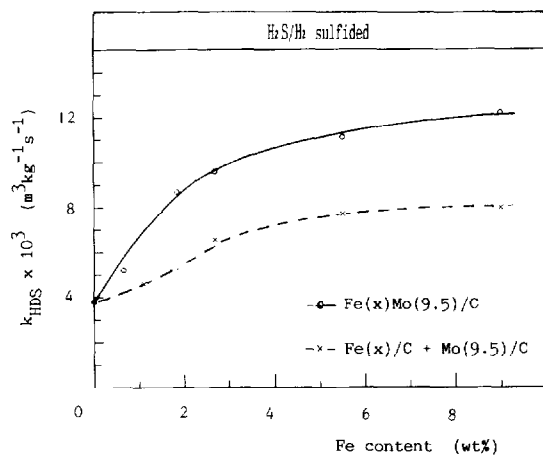


Fig. 8. Thiophene HDS activity measured at 673 K after a 2-h run time as a function of the iron content for (○) Fe(x)Mo(9.5)/C catalysts sulfided at 623 K and (×) the sum of the activities of the corresponding Fe(x)/C and Mo(9.5)/C catalysts [17,19].

influence of the iron content on the mean iron(III) oxide particle size can be detected, it can be concluded from Fig. 7 that the iron(III) oxide particles are clearly the largest in the Fe(9.0)Mo(9.5)/C catalysts.

Catalytic activity measurements

Thiophene HDS activity (k_{HDS}) is plotted as a function of the catalyst composition in Fig. 8. For comparison, the sum of the activities of the Fe(x)/C [17] and Mo(9.5)/C [19] catalysts are also included. The difference between the activities of the Fe–Mo/C and the combined Fe/C and Mo/C catalysts will be called the promoting effect. It is clear that the thiophene HDS activity increases faster than at higher iron contents. There is a significant but moderate promoting effect over the entire iron concentration range.

DISCUSSION

Oxidic catalyst precursors

After impregnation and drying at room temperature, followed by an additional treatment in hydrogen, the iron nitrate used to introduce the iron has been completely transformed into iron(III) oxide while the nitrate anions have been removed. These results are in agreement with those found for Fe(x)/C catalyst precursors [17]. It is striking that the mean iron(III) oxide particle size is smallest in the Fe(2.7)Mo(9.5)/C catalyst precursor. Both a lower and a higher iron content lead to an increase in the mean iron(III) oxide particle size. A similar influence of the iron content on the mean iron(III) oxide particle size is observed for comparably prepared Fe(x)/C catalysts [17]. It was proposed that in these catalysts the iron phase is transported towards the outer pores of the support grains during the additional hydrogen treatment and that this is followed by sintering. For lower iron contents this is more pronounced, probably owing to the lower viscosity of the iron-containing impregnation solution resulting in an inhomogeneous distribution of the iron(III) oxide phase and a longer period during which the particle transport process takes place. A considerable enrichment in iron(III) oxide of the surface located near the outer part of the support grains is observed for Fe(x)/C catalysts which are not subjected to the additional hydrogen treatment according to Groot et al. [30], using XPS and Mössbauer measurements. For the oxidic Fe(x)Mo(9.5)/C catalyst precursors the sequence in the mean iron(III) oxide particle size is assumed to be due to the same mechanism.

It has been found previously that the performance of the Fe(1.8)Mo(9.5)/C catalyst is better when more iron is present in the mixed Fe–Mo sulphide or “Fe–Mo–S”-phase [19]. It is expected that the closer the contact between the iron(III) oxide and molybdenum oxide in the precursor material, the easier

the "Fe-Mo-S" phase will be formed on sulphidation. Hence the question arises whether or not the iron(III) oxide phase is in close contact with the molybdenum oxide phase.

Information about the contact between the oxide phases is obtained by comparing the oxidic Fe(x)/C and Fe(x)Mo(9.5)/C catalyst precursors. It turns out that the Mössbauer parameters of the doublets found for the Fe(x)Mo(9.5)/C catalysts ($IS_1=0.65 \text{ mm s}^{-1}$, $QS_1=0.55 \text{ mm/s}^{-1}$; $IS_2=0.66 \text{ mm s}^{-1}$, $QS_2=0.92 \text{ mm s}^{-1}$) differ from these found for the Fe(x)/C catalysts ($IS_1=0.64 \text{ mm s}^{-1}$, $QS_1=0.63 \text{ mm s}^{-1}$; $IS_2=0.64 \text{ mm s}^{-1}$, $QS_2=1.04 \text{ mm s}^{-1}$). Hence, it turns out that the iron(III) oxide is influenced by the molybdenum oxide phase.

In addition, the mean size of the iron(III) oxide particles is influenced by the molybdenum oxide. Comparing the spectra in Fig. 2 with those recorded at 4.2 K for comparable Fe(x)/C catalysts [17], it followed that in the presence of molybdenum oxide the mean iron(III) oxide particle size is smaller.

Further, following the suggestion of Viegers and Trooster [31] that with small particles the resonant absorption area may be influenced by vibrations of these particles as a whole, the temperature dependence of the resonant absorption areas of the spectra of the oxidic Fe(x)/C and Fe(x)Mo(9.5)/C catalyst precursors were measured. It was observed [32,33] that the temperature dependence of the resonant absorption area was decreased by the presence of a molybdenum oxide phase. This can be interpreted as an increased strength of the interaction between the support and the iron(III) oxide particles. Moreover, it was found that in the presence of a molybdenum oxide phase the vibrations were less influenced by the presence of a layer of hydrated anions [32,33].

The observed contact between the molybdenum oxide phase and the iron(III) oxide phase can be explained as follows. The molybdenum oxide phase is deposited on the activated carbon in an anionic form. Therefore, it interacts more strongly with the positively charged support than the cationic iron oxide phase. Also, if a molybdenum oxide phase is already present when the iron phase is introduced, the positive iron ions will interact with the molybdenum phase and hence the oxidic Fe(x)Mo(9.5)/C catalyst precursors probably contain small iron(III) oxide particles in close contact with a highly dispersed molybdenum oxide phase. This means that the oxidic iron phase is essentially not monoatomically distributed over the molybdenum oxide phase, and that we are not dealing here with the type of bilayer structures described by Delmon [34] for oxidic Co-Mo/Al₂O₃ catalysts.

Sulphided catalysts

Catalyst composition as a function of iron content

Our experiments show that no oxidic iron compounds remain after the sulphidation procedure applied prior to the Mössbauer experiments. This indi-

cates that the Mössbauer spectra represent a sulphidic state of the catalysts comparable to that present during the thiophene HDS activity test.

It has been reported previously that in the Fe(1.8)Mo(9.5)/C catalyst three sulphidic iron phases can be present, viz., "Fe-Mo-S", Fe_{1-x} and FeS₂ [19]. The presence of FeS₂ in this catalyst was surprising as this compound was not found to be formed in a fully sulphided unsupported α -Fe₂O₃ sample (particle size 50 nm) [29]. However, the surprising presence of FeS₂ after sulphidation at high temperature ($T \geq 573$ K) has now been ruled out based on the results obtained with in situ experiments at liquid helium temperature. Therefore, only three doublets are used in the computer analyses of the room-temperature spectra, two ascribed to "Fe-Mo-S" and one to superparamagnetic "Fe-sulphide". The magnetically split hyperfine contribution is observed only in the spectra recorded at 4.2 K for the catalysts with an iron content of 2.7 wt.-% and higher. However, it is unlikely that the Fe(0.6)Mo(9.5)/C [623 K, 4 h] and Fe(1.8)Mo(9.5)/C [623 K, 4 h] catalysts contain a different "Fe-sulphide" phase than the other catalysts and it is therefore assumed that in all catalysts the "Fe-sulphide" is "Fe_{1-x}S".

Remarkably, from computer analyses of the spectra of the sulphided Fe(0.6)Mo(9.5)/C and Fe(1.8)Mo(9.5)/C catalysts recorded at room temperature on an extended velocity scale, it follows that the parameter of the "Fe-sulphide" doublet ($IS = 0.55$ mm s⁻¹, $QS = 0.58$ mm s⁻¹) for these catalysts are almost the same as those of FeS₂ ($IS = 0.58$ mm s⁻¹, $QS = 0.61$ mm s⁻¹).

This contradiction can be explained as follows. In both FeS₂ and "Fe_{1-x}S" the iron atoms are octahedrally coordinated by sulphur atoms. This implies that in these iron sulphides the sulphur atoms in the first coordination shell of the iron atoms are similarly arranged. Hence, for ultrafine iron sulphide particles which consist of only a few iron atoms and show no crystallographic ordering there will be hardly any difference between FeS₂ and "Fe_{1-x}S" with respect to the sulphur coordination of the iron atoms. Therefore, it is only possible to discriminate between ultrafine FeS₂ and "Fe_{1-x}S" particles if the Mössbauer spectra recorded at cryogenic temperatures show magnetic hyperfine splitting. As we observed this type of splitting at liquid helium temperature, it was concluded that no FeS₂ is present in the sulphided Fe(*x*)Mo(9.5)/C [623 K, 4 h] catalysts. This conclusion results in a revision of the proposed composition of the catalysts as reported for the Fe(1.8)Mo(9.5)/C [*z* K] catalyst [19]. It has been established now that only two sulphidic iron phases are present in the sulphided Fe-Mo catalysts, viz., "Fe-Mo-S" and "Fe_{1-x}S".

From our experiments it follows that the contribution of the iron compounds to the spectra of the sulphided catalysts depends on the iron content and on the temperature at which the spectrum is recorded. First, we shall discuss the significance of the latter, and the significance of the former will be discussed later.

It is found that for all catalysts the spectral contribution of the "Fe-Mo-S"

phase depends most strongly on the temperature. Consequently, the "Fe-Mo-S" phase has a lower Debye temperature than the "Fe_{1-x}S" phase. This result either indicates that more iron atoms are located at the surface in the "Fe-Mo-S" phase [35], or that the particles containing the "Fe-Mo-S" molecules are more liable to vibrate as particle [36]. The latter, however, is unlikely as already in the oxidic catalyst precursors the vibrations of the iron (III) oxide particles are restricted by their contact with the molybdenum oxide phase (see previous section). The same behaviour will probably happen in the sulphided catalysts. However, the restriction will be limited to those iron atoms which are in contact with the molybdenum sulphide phase. As the vibrations of the particles which contain the "Fe-Mo-S" molecules will cause a weaker temperature dependence of the spectral contribution of the "Fe-Mo-S" phase, the observed stronger temperature dependence can only be explained whenever the iron atoms in these "Fe-Mo-S" molecules are located at the surface of the catalysts. Because it has been established that MoS₂ microcrystals are present in sulphided Mo/C and Co-Mo/C catalyst [37], it is concluded that in the "Fe-Mo-S" phase the iron atoms are located at the MoS₂ surface. This is in agreement with the "Co-Mo-S" phase present in Co-Mo/Al₂O₃ catalysts [38] where the Co atoms occupy MoS₂ edge sites. The results presented here do not yield a decisive picture about the nature of the two "Fe-Mo-S" sites corresponding to the two different "Fe-Mo-S" doublets. However, investigations are in progress to establish whether or not these doublets represent different locations of iron atoms at the surface of the MoS₂ microcrystals.

The influence of the iron content on the type and relative concentration of the iron phases present in the catalyst can most clearly be seen in the spectra recorded at 4.2 K. An additional advantage of using these spectra is that effects of different Debye temperatures are the smallest at 4.2 K.

It is found that when the iron content increases the spectral contribution of the "Fe-Mo-S" phase decreases, while simultaneously the spectral contribution of the "Fe_{1-x}S" phase increases. The question arises of whether the increase in the spectral contribution of "Fe_{1-x}S" is due to a complete occupation of all the possible "Fe-Mo-S" sites present at the edges of the MoS₂ microcrystallites. This would imply that the amount of "Fe-Mo-S"-type Fe atoms ("Fe-Mo-S" content) would be the same in all the catalysts. The concentration (wt.-%) of iron present as "Fe-Mo-S" can be estimated by multiplying the total iron content of the catalysts by the spectral contribution of the "Fe-Mo-S" phase in the spectra recorded at 4.2 K (see Table 2). In this way, it turns out that on going from Fe(0.6)Mo(9.5)/C to Fe(5.5)Mo(9.5)/C the proportion of "Fe-Mo-S"-type iron gradually increases from 0.5 through 1.3 and 1.8 to 3.2 wt.-% which seems to correspond to saturation of the MoS₂ edge sites, as the Fe(9.0)Mo(9.5)/C catalyst appeared to contain essentially the same amount of "Fe-Mo-S"-type iron, viz., 2.9 wt.-%. Hence, it is concluded that the increase in the spectral contribution of the "Fe_{1-x}S" phase is not due to a complete occupation of "Fe-Mo-S" sites. This is unlike certain Co-Mo/

Al_2O_3 catalysts, for which it has been shown that segregation of Co_9S_8 only starts when the edges of the MoS_2 microcrystals are saturated with Co atoms forming “Co–Mo–S” [39].

Relationship between composition catalyst and thiophene HDS conversion

For Co–Mo catalysts, it is established that the HDS activity is directly related to the amount of “Co–Mo–S” in the catalyst [40,41]. We have shown that a similar relationship exists between the amount of “Fe–Mo–S” and the thiophene HDS activity of a Fe(1.8)Mo(9.5)/C catalyst [19]. Fig. 8 shows that with Fe(x)Mo(9.5)/C catalysts which are subjected to the lower heating rate during the sulphidation procedure (linear temperature increase from 293 to 623 K in 1 h), a promoting effect of iron sulphide on molybdenum sulphide can also be obtained for a wide range of iron contents. However, Topsøe et al. [40] reported that the existence of the “Fe–Mo–S” structure does not necessarily imply a large promotion of the HDS activity. In fact, although “Fe–Mo–S” structures were found in Fe–Mo/ Al_2O_3 catalysts, the HDS activity was not promoted but rather slightly poisoned. From these results, it was proposed that the specific activity of the unpromoted sites will be much larger than that of the “promoted” sites [40].

Based on our present and previous [17,19] findings, it can be concluded that the magnitude of the promoting effect on carbon-supported Fe–Mo sulphide catalysts depends on the preparation and sulphiding conditions. Important parameters in this respect are the method of drying the oxidic catalyst precursors and the heating rate applied during the sulphidation procedure (rather than the maximum sulphidation temperature). In accordance with this, Groot [16], who did not subject the Fe–Mo/C catalysts to an additional drying procedure in a flow of hydrogen (at temperatures up to 393 K) and applied a faster heating rate during sulphidation (from 293 to 673 K instead of 623 K in 1 h), found much smaller promoting effects than those shown in Fig. 8 and, moreover, he observed a maximum at about 4 wt.-% iron and even a negative promoting effect for iron contents higher than 7 wt.-%. It has been established [17,19,23] that under the preparation and sulphidation conditions applied by Groot, the formation of “ Fe_{1-x}S ” is facilitated at the expense of “Fe–Mo–S” formation and that the mean “ Fe_{1-x}S ” particle size is relatively large.

The data presented in Fig. 8 and Table 2 show that to a first approximation the activity of the Fe(x)Mo(9.5)/C catalyst correlates with the amount of iron present in the “Fe–Mo–S” phase. The observation that the effectiveness of the “Fe–Mo–S” phase decreases when its concentration increases suggests, however, that the actual situation is more complex. This is confirmed by the Mössbauer data, showing an increasing formation of less active “ Fe_{1-x}S ” phase which is at least to some extent in contact with the “Fe–Mo–S” phase, as can be inferred from the changes in the Mössbauer parameters of the “Fe–Mo–S” doublet 2 in Table 2. Hence it is very likely that, especially at high iron contents, the “Fe–Mo–S” phase is partly covered by “ Fe_{1-x}S ” particles which are

significantly smaller than the “Fe_{1-x}S” particles in the corresponding Fe(x)/C catalysts. This might explain why the activity of the Fe–Mo/C catalysts levels off and why the slopes of the Fe(x)Mo(9.5)/C catalyst activity curve and the Fe(x)/C+Mo(9.5)/C reference curve become virtually the same at the highest iron contents.

In conclusion, the effect of iron on the thiophene HDS activity of the Fe(x)Mo(9.5)/C catalysts is determined by three factors: (i) the amount of iron present as “Fe–Mo–S”, (ii) the amount and dispersion of iron present as “Fe_{1-x}S” and (iii) the extent to which the “Fe_{1-x}S” phase covers the “Fe–Mo–S” sites. The most important conclusion of the results presented in this study is that the promoting action observed for Fe(x)Mo(9.5)/C catalysts is due to the formation of an “Fe–Mo–S” phase. Hence, during the preparation and sulphidation of Fe–Mo/C catalysts, care should be taken to avoid “Fe_{1-x}S” formation because this could lead to a decrease in “Fe–Mo–S” concentration or to coverage of “Fe–Mo–S” sites by “Fe_{1-x}S”.

Reoxidized catalysts

It was found that the sulphided Fe–Mo/C catalysts do not reoxidize completely to iron (III) oxide at room temperature. This is in contrast to sulphided Fe/C catalysts, which are completely reoxidized to iron (III) oxide under identical conditions [17]. This indicates that in the reoxidized Fe–Mo/C catalysts the high-spin Fe²⁺ phase is in close contact with the molybdenum phase. In the two catalysts with the lowest iron content, viz., Fe(0.6)Mo(9.5)/C and Fe(1.8)Mo(9.5)/C, this contact is so close that no iron (III) oxide is present in the reoxidized catalysts. The parameters of the doublet observed in these catalysts at room temperature ($IS = 0.68 \text{ mm s}^{-1}$, $QS = 0.37 \text{ mm s}^{-1}$) and the very weak temperature dependence of its QS value indicate that the doublet must be ascribed to a high-spin Fe³⁺ phase. It is therefore likely that an Fe₂(MoO₄)₃-like phase is formed in these catalysts, especially as this phase is not observed in reoxidized sulphided Fe(x)/C catalysts. The parameters of the high-spin Fe²⁺ phase, however, do not agree with those reported for α - or β -FeMoO₄ [42]. Hence, it is assumed that in the presence of molybdenum an iron (II) oxide phase is stabilized. The most likely location of the iron (II) oxide ions is at or near the surface of the reoxidized molybdenum sulphide phase. This is in agreement with our observation that the spectral contribution of the high-spin Fe²⁺ phase increases with decreasing temperature. This implies that the Debye temperature of the high-spin Fe²⁺ phase is lower than that of the iron (III) oxide phase, and Somorjai [35] has shown using LEED that in single crystals the Debye temperature for surface atoms is lower than that for bulk atoms.

From the reoxidized catalyst, information about the thermal stability of the catalysts during the sulphidation procedure is obtained by comparing the mean

particle size of the iron(III) oxide phase in the oxidic catalyst precursor (see Fig. 2) and in the reoxidized catalyst (see Fig. 7). This comparison is considered valid because no remaining pure sulphidic contributions are observed in the spectra. The influence of the high-spin Fe^{2+} phase on the spectral contribution of the magnetically split component is assumed to be negligible. This assumption is based on the structure model outlined above, in which the iron(II) phase is located at or near the surface of the molybdenum phase. It is concluded that the mean iron(III) oxide particle size is smaller in the reoxidized catalysts. This implies that either during sulphidation or during reoxidation a re-dispersion of the iron phase has taken place. Comparison of the spectra in Fig. 7 with the spectra recorded at 4.2 K of reoxidized $\text{Fe}(x)/\text{C}$ catalysts [17] indicates that the iron(III) oxide particles are much smaller for the $\text{Fe}(x)\text{Mo}(9.5)/\text{C}$ catalysts. For the $\text{Fe}(x)/\text{C}$ catalysts it has been demonstrated [17] that sintering is less when the interaction strength between the support and the iron(III) oxide particles in the oxidic catalyst precursor is increased. As this interaction strength is larger in the $\text{Fe}(x)\text{Mo}(9.5)/\text{C}$ than in the $\text{Fe}(x)/\text{C}$ catalysts [32,33] the difference in mean particle size is easily understood.

CONCLUSIONS

This study has provided a detailed insight into the structure of carbon-supported Fe–Mo catalysts. The application of in situ Mössbauer spectroscopy at cryogenic temperatures has proved to be essential for the correct description of the catalyst composition. Our results support the view that in promoted molybdenum sulphide catalyst a “Co–Mo–S” type of phase is responsible for the activity.

The main conclusions are the following: an $\text{Fe}(x)\text{Mo}(9.5)/\text{C}$ catalyst is completely sulphided during sulphidation treatment up to 623 K; under typical thiophene HDS conditions the catalyst contains “Fe–sulphide” with an “ Fe_{1-x}S ”-type structure and “Fe–Mo–S”; the “Fe–Mo–S” phase causes the observed promoting effect; in the “Fe–Mo–S” phase the iron atoms are located at the surface of MoS_2 microcrystals; the amount of “Fe–sulphide” in the catalyst increases as the iron content of the catalyst increases, but the “Fe–sulphide” particles are significantly smaller than those present in the corresponding $\text{Fe}(x)/\text{C}$ catalyst; as the iron loading increases, some of the “Fe–Mo–S” sites probably become covered by the “ Fe_{1-x}S ” phase; and owing to the interaction between the molybdenum and iron phases, the sulphided catalysts show high thermal stability.

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