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Citation for published version (APA):

DOI:
10.1016/S0166-9834(00)80211-0

Document status and date:
Published: 01/01/1989

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:

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Sulfidation of Carbon-Supported Iron Oxide Catalysts

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(Received 21 October 1988, revised manuscript received 7 February 1989)

ABSTRACT

The sulfidation of carbon-supported iron oxide catalysts was studied by means of in-situ Mössbauer spectroscopy at temperatures down to 4.2 K. The catalysts were dried in two different ways and then sulfided in a flow of 10% H2S in H2 at temperatures between 293 and 773 K. Thiophene hydrodesulfurization (HDS) activity measurements were performed at 673 K in a flow micro-reactor operating at atmospheric pressure. The iron content varied from 1.1 to 9.0 wt.-% Fe. In the oxidic catalyst precursors, dried in air at 293 K, nitrate anions were still present. These anions could be removed by means of an additional H2 treatment up to 393 K. This treatment also led to an increase in the interaction strength between the iron(III) oxide particles and the carbon support. It is shown that the transition from iron(III) oxide to iron sulfide proceeded through two intermediate phases, viz. an oxidic high-spin Fe²⁺-phase and FeS₂. A correlation between the HDS activity per mole of iron and the mean iron sulfide particle size was observed, with the mean particle size being dependent on the preparational treatments of the oxidic catalyst precursors.

INTRODUCTION

Hydrotreating catalysts are used within the oil-refining industry for the upgrading of fossil fuel fractions. The feedstock is passed together with hydrogen (5-20 MPa at 573-773 K) over the catalyst. Several reactions take place simultaneously, such as removal of carbon-bonded impurities like sulfur, nitrogen, oxygen and metals (Ni and V) via so-called hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO) and hydrodemetalization (HDMe) reactions, hydrogenation of olefinic and aromatic hydrocarbons as well as hydrocracking. The catalyst systems currently applied con-
tain molybdenum sulfide promoted by cobalt or nickel sulfide on an alumina support.

Over the last few years there has been a growing interest in the application of carbonaceous substrates as catalyst supports [1–12]. Potential advantages include low costs and easy metal recovery by burning off the carbon support [1,2]. Carbon-supported catalysts have been shown to be less sensitive to deactivation due to coke formation [6,8]. It is also reported that when a relatively inert support, like carbon, is used instead of a more reactive one, such as alumina or silica, the thiophene HDS activity of both promoted and unpromoted MoS₂ catalysts increases [4,5,9,10]. De Beer et al. [3] and Duchet et al. [5] have shown that besides molybdenum sulfide also cobalt and nickel sulfide possess an interestingly high activity for thiophene HDS at atmospheric pressure when a carbon support is used.

Recently, Vissers et al. [7] and Ledoux et al. [11] reported thiophene HDS activities for first, second and third row transition metal sulfides supported on activated carbon. These authors found that many transition metal sulfides have a considerable thiophene HDS activity, which is in accordance with the results obtained by Pecoraro and Chianelli [13] for unsupported transition metal sulfides. Groot et al. [14] showed that iron sulfide catalysts on an activated carbon support for metal loadings up to 2.0 at nm⁻² support surface area have a higher thiophene HDS activity at atmospheric pressure than carbon-supported molybdenum sulfide catalysts. Furthermore, it has been shown that unsupported iron sulfide particles do have a definite catalytic effect during coal liquefaction [15,16]. So, it is probably advantageous to use an iron sulfide catalyst on a high-surface-area carbon support during coal liquefaction processes. Groot et al. [17] have already reported that an activated carbon-supported iron sulfide catalyst has a promising activity for the conversion of coal extract into lower boiling fractions. This indicates that low cost carbon-supported iron sulfide catalysts could be used in hydrotreating processes using highly contaminated heavy feedstocks, which will cause rapid catalyst deactivation.

In the preparation process for hydrotreating catalysts sulfidation of the oxido catalyst precursor is a crucial step, because it results in the formation of the actual active sulfide phase. So, it is important to know how the sulfidation proceeds and whether the final result (type of sulfide and its dispersion) depends on the sulfiding conditions applied.

Therefore, the sulfidation of activated carbon-supported iron oxide catalysts was investigated using in-situ Mössbauer spectroscopy at 293, 77 and 4.2 K. Also the influence of the procedure for drying of the oxidic precursor on the thermal stability of the catalyst was studied, by comparing the dispersion of the oxidic catalyst precursors and the reoxidized sulfided catalysts. In addition, the relative dispersion of the iron sulfide phase was determined via Mössbauer
spectroscopy and compared to the performance of the Fe/C catalysts for thiophene HDS measured at 673 K and atmospheric pressure.

It is found that preparational aspects play an important role in the activity of the carbon-supported iron sulfide catalysts. The observed differences in the catalytic activity were demonstrated to be due to variations in the dispersion of the active sulfide phase. This dispersion depends on the preparation of the oxidic catalyst precursor material.

EXPERIMENTAL

Preparation of oxidic catalyst precursors

All oxidic catalyst precursors were prepared by pore volume impregnation (incipient wetness) of Norit RX3-extra activated carbon (pore volume 1.0 cm\(^3\) g\(^{-1}\); surface area 1190 m\(^2\) g\(^{-1}\)). The impregnation was carried out using aqueous solutions of Fe(NO\(_3\))\(_3\)·9H\(_2\)O (Baker, 98.7%) enriched in the Mössbauer isotope \(^{57}\)Fe up to 10%. The enrichment was achieved by reducing α-Fe\(_2\)O\(_3\), 94.7% enriched in \(^{57}\)Fe (Intersales), in flowing H\(_2\) at 700 K for 4 h and next dissolving in 2 N HNO\(_3\). This solution was mixed with the impregnation solution and the acidity of this mixture was adjusted to pH = 0.25 by adding 2 N HNO\(_3\) if necessary. In this way samples with an iron loading of 1.1, 1.8, 2.7, 5.5 and 9.0 wt.-% were prepared.

After impregnation, the samples were dried at room temperature, first for 2 h in ambient air and then for 16 h in an air flow of 100 cm\(^3\) min\(^{-1}\). In this way a well dispersed iron oxide phase (particle size < 4 nm) was formed [18]. The dried samples were divided into two portions. One portion was not subjected to any other treatment. The other portion was additionally treated in flowing Hz (50 cm\(^3\) min\(^{-1}\)) for, sequentially, 24 h at 313 K, 24 h at 353 K and 24 h at 393 K.

The oxidic catalyst precursors will be denoted Fe\((x)\)/C\((y)\), in which \(x\) represents the iron content in wt.-% and \(y\) the upper drying temperature in Kelvin.

Sulfiding procedure and Mössbauer experiments

Mössbauer spectra were recorded at 293, 77 and 4.2 K with either a constant acceleration or a constant velocity spectrometer, using a \(^{57}\)Co in Rh source at room temperature. The spectra recorded with a constant acceleration spectrometer were not corrected for the varying distance between source and absorber, hence the curved background in these spectra is of instrumental origin. Doppler velocities are given relative to sodium nitroprusside (SNP) at room temperature. Magnetic hyperfine fields were calibrated with the 51.5 T field of
α-Fe₂O₃ at 293 K. The spectra were fitted by computer with calculated sub-
spectra consisting of Lorentzian-shaped lines, whereas the curved background
was accounted for by a parabola.

Catalyst samples (150-200 mg) were sulfided in stainless steel Mössbauer
in-situ reactors (one for measurements at and above room temperature and
one for measurements down to liquid helium temperature). The design of these
reactors has been described in detail elsewhere [19,20]. The in-situ reactor
used for the measurements at room temperature or higher will be denoted as
the High-Temperature Reactor (HTR), and the one for measurements at cry-
ogenic temperatures as the Low-Temperature Reactor (LTR). Different ex-
perimental procedures were used in the two reactors.

In the HTR at first the influence of the exposure to H₂S/H₂ at room tem-
perature was investigated by replacing the initially present air by a 10 mol-%
H₂S in H₂ gas mixture. A Mössbauer spectrum was recorded at 293 K while
the sample was kept in static H₂S/H₂ at atmospheric pressure. Next, the same
sample was subjected to various successive sulfidation treatments in a 50 cm³
min⁻¹ H₂S/H₂ flow. In each treatment the temperature is linearly increased
to the desired temperature in 1 h, and is then lowered to room temperature in
the same gas flow. Mössbauer spectra were recorded at 293 K after each treat-
ment while the sample was kept in the H₂S/H₂ environment at atmospheric
pressure. The samples will be denoted Fe(x)/C(yK) [zK] in which z is the
maximum sulfiding temperature in Kelvin reached during the 1-h sulfiding
procedure.

In the LTR the temperature was linearly increased to 673 K over a 1-h pe-
riod, kept at 673 K for 4 h in a 50 cm³ min⁻¹ H₂S/H₂ flow and the catalyst was
cooled to room temperature in the same gas flow. Subsequently, the separate
absorber holder is sealed vacuum-tight in situ and mounted in a cryostat. These
samples will be denoted as Fe(x)/C(yK) [673 K, 4 h]. The sulfided catalysts
were reoxidized by opening the LTR absorber holder and exposing them to air
at room temperature for at least one week.

**Sulfiding procedure and catalytic activity measurements**

Catalyst presulfiding and thiophene HDS activity testing were successively
carried out at atmospheric pressure in a quartz tubular flow reactor (diameter
0.8 cm). Catalyst samples (200 mg) were presulfided in a flow of 10 mol-%
H₂S in H₂ (total flow-rate 60 cm³ min⁻¹) for 1 h, while increasing the temper-
ature linearly from 293 to 673 K. Hereafter, the reaction gas mixture, consist-
ing of 6.2 mol-% thiophene in hydrogen, was led through the reactor at a flow-
rate of 50 cm³ min⁻¹. The reaction products were analyzed by means of an on-
line gas chromatograph. Assuming that the HDS reaction is first order in thi-
ophene [21], the quasi turn-over frequency (QTOF; expressed in mol thiophene
converted per mol active metal per second) was calculated from the conversions measured after a 2-h run.

RESULTS

*Mössbauer measurements*

Oxidic precursors

For the oxidic catalyst precursors first we investigated the influence of the drying procedure on the dispersion of the iron (III) oxide phase. In Fig. 1 Mössbauer spectra of the oxidic Fe(5.5)/C(293 K) and Fe(5.5)/C(393 K) precursors recorded at 293, 77 and 4.2 K are given. These spectra are typical for all oxidic precursors with different iron contents.

The spectra measured at 293 and 77 K only consist of an electric quadrupole doublet, while in the spectra at 4.2 K a superposition of a quadrupole doublet and a magnetic hyperfine sextuplet is observed. The observed temperature behaviour for the Fe(x)/C(293 K) and Fe(x)/C(393 K) samples is character-

![Mössbauer spectra](image-url)

Fig. 1. Mössbauer spectra of the oxidic Fe(5.5)/C(293 K) and Fe(5.5)/C(393 K) precursors recorded at temperatures as indicated. The bar diagram indicates the outerlines of the contribution of paramagnetic iron ions. See Experimental for details of sample notation.
istic for ultrafine iron (III) oxide particles showing superparamagnetism [22]. The appearance of the magnetic hyperfine sextuplet depends on the mean particle size as well as on the temperature. As for all samples a spectral contribution of the magnetic hyperfine sextuplet is only observed in the 4.2 K spectra (shown in Fig. 2), its relative magnitude determines the sequence in the mean particle size.

The spectra at 293 and 77 K do not show any presence of the initial iron salt Fe(NO₃)₃·9H₂O, the contribution of which would be a broadened single line due to paramagnetic spin–spin relaxation [23]. However, in the 4.2 K spectra of the Fe(x)/C(293 K) precursors besides the contribution of the iron (III) oxide a contribution due to well separated paramagnetic iron ions, indicated by the full bar-diagram in Fig. 1a, is observed. This last contribution is not found for the Fe(x)/C(393 K) precursors as can be seen in Fig. 1b.

Furthermore, it is obvious from Fig. 2 that the mean size of the iron (III) oxide particles increases during the additional H₂ treatment. Comparison of the 4.2

![Mössbauer spectra](image_url)

Fig. 2. Mössbauer spectra of the oxidic Fe(x)/C(293 K) and Fe(x)/C(393 K) precursors recorded at 4.2 K. See Experimental for details of sample notation.
K spectra in Fig. 2 with those of unsupported ultrafine \( \alpha\)-Fe\(_2\)O\(_3\) particles with a known mean particle size [22,24,25] shows that in all the samples measured the mean iron(III)oxide particle size is estimated to be between 2 and 4 nm. However, it is emphasised that within this particle size range small differences in the mean particle size result in clearly discernible differences in the spectral contribution of the magnetic hyperfine sextuplet to the 4.2 K spectra. The sequence in the mean particle size of the iron(III)oxide particles in the Fe\((x)\)/C(393 K) catalysts is found to be Fe\((2.7)\)/C(393 K) < Fe\((1.8)\)/C(393 K) < Fe\((5.5)\)/C(393 K) < Fe\((9.0)\)/C(393 K). This rather remarkable dependence of the mean particle size on the iron content of the samples will be discussed in more detail later.

In addition, it appears that the observed total resonant absorption areas of the spectra are drastically enlarged by the additional H\(_2\) treatment. This indicates that the bodily vibrations of the iron(III)oxide particles, relative to the support, are less after the additional H\(_2\) treatment [26]. This effect can be interpreted as an increased strength of the bond between support and iron(III)oxide particles [27,28]. For both series of oxidic catalyst precursors it is observed that the strength of the interaction does not depend on the iron content.

The electric quadrupole doublet observed in the spectra of the precursor material consists of rather broad absorption lines. Therefore, it is reasonable to analyze these spectra using two doublets. In order to obtain more detailed spectra at 293 K they were recorded on a more extended velocity scale. From these analyses the ratio of the spectral contributions of doublet 1 and doublet 2 turns out to be 0.55:0.45. It appears that both doublets have an identical isomer shift (IS) but different electric quadrupole splittings (QS) (\(\text{QS}_1 = 0.64\) mm s\(^{-1}\), \(\text{QS}_2 = 0.63\) mm s\(^{-1}\), \(\text{IS}_1 = 0.64\) mm s\(^{-1}\), \(\text{IS}_2 = 0.63\) mm s\(^{-1}\)). From previous experiments with unsupported small \(\alpha\)-Fe\(_2\)O\(_3\) particles (4–7 nm) it is known that such a spectral composition is due to a bulk- and a surface-oxide contribution [22]. The spectral component with the largest QS value can be assigned to the surface-oxide contribution.

**Transition of the oxidic precursor into the active sulfide phase**

Fig. 3 shows spectra of the Fe\((2.7)\)/C(393 K) catalyst recorded at 393 K after various H\(_2\)S/H\(_2\) treatments in the HTR together with that of the oxidic precursor. These experiments illustrate how the oxidic precursor is converted into a sulfidic catalyst. The numerical results of computer analyses of the rather complex spectra are given in Table 1 together with those of the Fe\((1.8)\)/C(393 K) and Fe\((9.0)\)/C(393 K) catalysts. Various stages in the sulfidation process can be observed.

The Mössbauer spectra, hence the compositions of the catalysts, change already when the catalysts are exposed to the sulfidation gas mixture at room temperature. From the spectral analyses it follows that the bulk- and surface-
oxide contributions should behave differently. While the bulk-oxide contribution has completely disappeared, the so-called surface-oxide contribution would only be partly affected by the sulfidation gas mixture. Furthermore, two additional components seem to be discernable in the spectra. One spectral component is due to a high-spin Fe$^{2+}$ phase and one component has Mössbauer parameters which can be ascribed to FeS$_2$ (pyrite; IS = 0.57 mm s$^{-1}$, QS = 0.61 mm s$^{-1}$).

By increasing the sulfidation temperature up to 473 K the contribution of the high-spin Fe$^{2+}$ spectral component decreases, the so-called surface-oxide contribution remains about constant in intensity, and the spectral contribution ascribed to FeS$_2$ increases (see Table 1). After sulfidation up to 573 K or...
TABLE 1

Isomer shifts (IS), electric quadrupole splittings (QS) and spectral contributions (A) obtained from computer analyses of Mössbauer spectra recorded at 293 K in H₂S/H₂ after various successive sulfidation treatments up to temperatures in Kelvin (z) as indicated.

Experimental uncertainties: IS = 0.03 mm s⁻¹; QS = 0.05 mm s⁻¹; A = 5%.

<table>
<thead>
<tr>
<th>z (K)</th>
<th>IS (mm s⁻¹)</th>
<th>QS (mm s⁻¹)</th>
<th>A (%)</th>
<th>IS (mm s⁻¹)</th>
<th>QS (mm s⁻¹)</th>
<th>A (%)</th>
<th>IS (mm s⁻¹)</th>
<th>QS (mm s⁻¹)</th>
<th>A (%)</th>
<th>IS (mm s⁻¹)</th>
<th>QS (mm s⁻¹)</th>
<th>A (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>high-spin Fe²⁺</td>
<td>FeS₂⁺</td>
<td>&quot;Fe-sulfide&quot;(1)ᵇ</td>
<td>&quot;Fe-sulfide&quot;(2)ᵇ</td>
<td></td>
<td></td>
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<td></td>
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<td>293</td>
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<td>26</td>
<td>0.57</td>
<td>0.61</td>
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<td>2.23</td>
<td>8</td>
<td>0.57</td>
<td>0.61</td>
<td>65</td>
<td>0.64</td>
<td>0.98</td>
<td>27</td>
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<tr>
<td>573</td>
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<td></td>
<td>0.58</td>
<td>0.57</td>
<td>72</td>
<td>0.65</td>
<td>0.95</td>
<td>28</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>673</td>
<td></td>
<td></td>
<td></td>
<td>0.65</td>
<td>0.44</td>
<td>67</td>
<td>0.67</td>
<td>0.91</td>
<td>33</td>
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<tr>
<td>773</td>
<td></td>
<td></td>
<td></td>
<td>0.67</td>
<td>0.38</td>
<td>62</td>
<td>0.69</td>
<td>0.85</td>
<td>38</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Fe(1.8)/C(393 K) [z K]

Fe(2.7)/C(393 K) [z K]

Fe(9.0)/C(393 K) [z K]

Values of FeS₂ were constrained to IS = 0.57 mm s⁻¹, QS = 0.61 mm s⁻¹.

The attribution of these spectral components to "Fe-sulfide" follows from in-situ Mössbauer measurements at cryogenic temperatures of the Fe(x)/C(393 K) [673 K, 4 h] catalysts. However, the parameters of "Fe-sulfide"(2) after exposing of the oxidic precursors to the sulfiding gas mixture at room temperature are equal to those assigned to a surface-oxide contribution. On basis of the experimental evidence available it is not possible to decide at which sulfiding temperature this "Fe-sulfide"(2) phase is formed at the expense of the surface-oxide contribution (present in the oxidic precursor).

Higher temperatures, the high-spin Fe²⁺ contribution to the spectra has completely disappeared. On the other hand the parameters of the so-called surface-oxide contribution seem only to be slightly changed indicating that this contribution should still be present. The possible presence of such a surface-oxide component after the high temperature sulfidation treatments is rather surprising. In particular, because we know from sulfidation experiments on a model
system consisting of unsupported 50 nm $\alpha$-Fe$_2$O$_3$ particles [29] that after sulfidation up to 573 K or higher temperatures the particles are fully transformed into iron-sulfides having the Fe$_{1-x}$S-type structure. However, in the present study we are dealing with ultrafine particles which show in their oxidic state superparamagnetic behaviour. Hence, it can not be excluded that also in the sulfidic state the particles show superparamagnetic behaviour. To our knowledge superparamagnetic behaviour in Fe$_{1-x}$S-type structures has not been described in the literature yet. Therefore, 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 sulfided catalysts. For, besides the isomer shift and the quadrupole splitting, the magnetic hyperfine parameters are also well suited for the characterization of possible "Fe$_{1-x}$S" type structures [29]. The results of these measurements are presented in the next section dealing with "Fully sulfided catalysts".

The computer analyses of the Mössbauer spectra do not show unambiguously whether FeS$_2$ is still present after sulfidation up to 573 K. However, for all the Fe(x)/C(393 K) [2K] catalysts presented in Table 1 it is found that sulfidation up to 573 or higher, causes the IS as well as the QS of this spectral component to change. The IS increases and the QS decreases with increasing sulfidation temperatures. As shown in Table 1 the parameters change to such an extent that it can be assumed that the pyrite is converted into another compound denoted as "Fe-sulfide" (1).

Hence, from these experiments it follows that:

1. Already at room temperature the bulk-oxide component is fully transformed by the H$_2$S/H$_2$ gas mixture into FeS$_2$ and a high-spin Fe$^{2+}$ phase.
2. The FeS$_2$ and the high-spin Fe$^{2+}$ phase are intermediate compounds in the sulfidation process.
3. The so-called surface-oxide component would be nearly unaffected by the sulfidation up to 773 K. Only the Mössbauer parameters have changed slightly. However, the formation of an "Fe-sulfide" phase with similar Mössbauer parameters can not be excluded, and will be investigated by in-situ Mössbauer experiments at cryogenic temperatures.
4. Although the Mössbauer parameters of the pyrite contribution are changed after sulfidation up to temperatures higher than 573 K, these values do not match the values of bulk pyrrhotite (Fe$_{1-x}$S; $-0.02 \leq x \leq 0.18$) and troilite (FeS) [29].

**Fully sulfided catalysts**

So, to solve the problem raised in the previous section concerning the possible existence of a surface-oxide contribution in the spectra after the high-temperature sulfidation treatments, in-situ Mössbauer measurements at cryogenic temperatures were carried out on the fully sulfided catalysts. In addi-
tion, such measurements make it possible to determine whether there exists a correlation between the catalytic activity and the composition and/or mean size of the catalytic particles.

In Fig. 4 spectra of the sulfided Fe(1.8)/C(393 K) [673 K, 4 h] catalyst recorded at 77, 4.2 and 2.0 K are given. These spectra are typical for all sulfided Fe(x)/C(293 K) [673 K, 4 h] and Fe(x)/C(393 K) [673 K 4 h] catalysts. As at 293 K, the 77 K spectrum shows only an electric quadrupole doublet. In the spectra recorded at 4.2 and 2.0 K a superposition of several magnetic hyperfine sextuplets and an electric quadrupole doublet is present. The observed magnetic hyperfine splittings indicate that no oxidic compounds are present in the catalysts. Hence, the catalysts are fully sulfided and no surface-oxide phase is present. It is known from experiments on sulfided 50 nm α-Fe₂O₃ particles that magnetically split spectra of Fe₁₋ₓS structures can be described by three hyperfine sextuplets [29]. Therefore, the computer analyses of the spectra at 4.2 and 2.0 K were carried out using three magnetic hyperfine sextuplets and one doublet. The numerical results of these analyses are given in Table 2.

There are two reasons to conclude that the iron sulfide particles show su-

![Graph showing Mössbauer spectra](image)

Fig. 4. In-situ Mössbauer spectra of the Fe(1.8)/C(393 K) [673 K, 4 h] catalyst sulfided in the LTR recorded at temperatures as indicated. See Experimental for details of sulfidation and sample notation.
TABLE 2

Isomer shifts (IS), electric quadrupole splittings (QS), magnetic hyperfine fields (H) and spectral contributions (A) obtained from computer analyses of Mössbauer spectra recorded at cryogenic temperatures as indicated of the Fe(1.8)/C(393 K) [673 K, 4 h] catalyst sulfided in the LTR.

<table>
<thead>
<tr>
<th>T</th>
<th>Sextuplet I</th>
<th>Sextuplet II</th>
<th>Sextuplet III</th>
<th>Doublet</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IS (K)</td>
<td>QS (mm s⁻¹)</td>
<td>H (T) (%)</td>
<td>A (%)</td>
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<tr>
<td>77</td>
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<td>27.5</td>
<td>31</td>
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<td>4.2</td>
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<td>0.07</td>
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<td>35</td>
</tr>
</tbody>
</table>

Experimental uncertainties: IS=0.03 mm s⁻¹; QS=0.05 mm s⁻¹; H=0.5 T; A=5%.

TABLE 3

Mean magnetic hyperfine fields (Hₘₑᵃⁿ) and spectral contributions of the quadrupole doublet (A) obtained from computer analyses of Mössbauer spectra recorded at 4.2 K for the Fe(x)/C (293 K) [673 K, 4 h] and Fe(x)/(393 K) [673 K, 4 h] catalysts sulfided in the LTR.

<table>
<thead>
<tr>
<th>x (wt.-%)</th>
<th>Fe(x)/C (293 K)</th>
<th>Fe(x)/C (393 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sextuplets</td>
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<tr>
<td></td>
<td>H(T) mean</td>
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<tr>
<td>9.0</td>
<td>24.8</td>
<td>10</td>
</tr>
</tbody>
</table>

Experimental uncertainties: Hₘₑᵃⁿ=0.5 T; A=5%.

perparamagnetism, which implies that they are very small. Firstly, magnetic splitting is only observed at temperatures well below the magnetic transition temperature (≈600 K) for bulk Fe₁₋ₓS. And secondly, the values obtained for the magnetic hyperfine fields are well below their saturation values for bulk Fe₁₋ₓS [29] and tend to increase with decreasing recording temperature. The superparamagnetic behaviour enables one to compare the mean size of the iron sulfide particles in the catalysts. Table 3 shows the spectral contribution of the doublet and the mean value of the magnetic hyperfine splitting (Hₘₑᵃⁿ) obtained from computer analyses of the 4.2 K spectra of the sulfided catalysts. From this table it appears that the values of Hₘₑᵃⁿ differ only slightly, so it can be assumed that the type of the iron sulfide is the same for all catalysts. In addition, it can be observed from Table 3 that a decrease in the spectral con-
tribution of the doublet is accompanied by an increase in the value of $H_{\text{mean}}$; both effects indicate an increase in the mean size of the iron sulfide particles.

It follows from Table 3 that the additional $H_2$ treatment influences the mean size of the sulfided particles. For iron contents of 2.7 wt.-% or higher the particles are smaller for the Fe(x)/C(393 K) [673 K, 4 h] than for the Fe(x)/C(293 K) [673 K, 4 h] catalysts. However, for iron contents below 2.7 wt.-% the opposite is observed. So these experiments indicate the following:

1. No oxidic compounds are present in these catalysts. This means that surface-oxide contributions in the spectra after different sulfidation treatments mentioned above have to be ascribed to an iron sulfide phase and are therefore denoted as "Fe-sulfide" (2) in Table 1.

2. The composition of the fully sulfided catalysts is unaffected by the iron content and the additional $H_2$ treatment.

3. The mean particle size in sulfided Fe(x)/C(y K) [673 K, 4 h] catalysts depends on the iron content as well as on the additional $H_2$ treatment of the catalyst.

Fig. 5. Mössbauer spectra of the Fe(5.5)/C(293 K) [673 K, 4 h] and Fe(5.5)/C(393 K) [673 K, 4 h] catalysts reoxidized in ambient air at room temperature after sulfidation in the LTR recorded at temperatures as indicated. See experimental for details of sulfidation, reoxidation and sample notation.
Reoxidized catalysts

The spectra of the Fe(5.5)/C(293 K) [673 K, 4 h] and Fe(5.5)/C(393 K) [673 K, 4 h] catalysts recorded at 293, 77 and 4.2 K after reoxidation (air, 293 K, >7 days) are given in Fig. 5 and are characteristic for all reoxidized catalysts. No remaining sulfidic contributions can be observed. The catalysts are reoxidized completely to iron(III) oxide particles, which show superparamagnetic behaviour. The mean size of these particles is still below 4 nm, as can be concluded from a comparison of the spectra with those of ultrafine α-Fe₂O₃ particles with a known mean particle size [22]. From the spectral contributions of the magnetic sextuplet it turns out that the sequence in mean iron (III) oxide particle size of the reoxidized samples is the same as found for the sulfided catalysts.

![Graph](image_url)

Fig. 6. Thiophene HDS activities per mol iron after 2 h runtime and the spectral contribution of the superparamagnetic doublet to the spectra at 4.2 K as a function of iron content for Fe(x)/C(293 K) and Fe(x)/C(393 K) catalysts. The dotted lines are drawn as a guide to the eye. See Experimental for details of activity measurements and sample notation.
Catalytic activity measurements

Thiophene HDS activities per mol Fe after 2 h runtime as a function of iron content are presented in Fig. 6. For the 4 Fe(\(x\))/C(293 K) catalysts the QTOF value gradually decreases with increasing iron content. For the Fe(\(x\))/C(939 K) catalysts the QTOF value increases when the iron content is increased from 1.1 to 2.7 wt.-% and decreases at higher iron contents.

So, the additional H\(_2\) treatment of the oxidic catalyst precursors results in lower QTOF at values for iron contents up to about 2 wt.-%, while at higher iron contents the opposite occurs.

DISCUSSION

Oxidic catalyst precursors

From the spectra recorded at 4.2 K (see Fig. 2a and 2b) it becomes clear that after drying in air at 293 K of the impregnated samples besides small iron (III) oxide particles (particle size below 4 nm) also paramagnetic iron ions are present. During the additional H\(_2\) treatment up to 393 K the mean iron (III) oxide particle size increased while the spectral contribution of the paramagnetic iron ions has disappeared. However, the particle size remains below 4 nm. From thermal gravimetric analysis (TGA) results reported by Groot [30] it is known that remaining nitrate anions will be removed by the H\(_2\) treatment. So, the occurrence of the paramagnetic iron ions is most probably due to remaining nitrate anions in close contact with iron ions.

In addition to the observed increase in the mean iron (III) oxide particle size, the total resonant absorption area is drastically enlarged (by a factor of 4) after the H\(_2\) treatment [27,28]. This effect has been interpreted as a strengthening of the interaction between the iron (III) oxide particles and the support, in such a way that the bodily vibrations of the iron (III) oxide particles, relative to the support, become less [27,28]. It is also found that the resonant absorption areas are no longer dependent on the atmosphere (e.g. humid air, dry air and vacuum) surrounding the oxidic samples that have been subjected to the H\(_2\) treatment [27,28]. Combining these phenomena with the observed removal of the nitrate anions one can conclude that the presence of the hygroscopic nitrate anions results in a significant weakening of the interaction between the iron (III) oxide particles and the support. This will probably facilitate sintering of the catalytic phase during the sulfidation procedure. So, the additional H\(_2\) treatment may result in a minimization of the mean size of the iron sulfide particles.

For catalysts containing more than 2.7 wt.-% Fe it is observed (see Fig. 2) that the mean iron (III) oxide particle size increases as the iron content increases. However, it is remarkable that for the oxidic catalyst precursors with
an iron content below 2.7 wt.-% the sintering of the iron (III) oxide particles drastically increases (with decreasing iron content) during the additional H$_2$ treatment. This paradoxical effect can be explained as follows. From combined Mössbauer and XPS measurements Groot et al. [14] concluded that for the oxidic Fe(x)/C (393 K) catalyst precursors the distribution of the iron (III) oxide phase over the carbon support surface is influenced by the viscosity of the impregnation solution. At iron contents up to about 5 wt.-%, viscosity of the iron nitrates impregnation solution is rather low and this results in a considerable enrichment in iron (III) oxide of the surface located near the outer part of the support grains. At iron contents of about 5 wt.-% and higher no such inhomogeneous distribution of the iron (III) oxide phase was observed. It is suggested that during the additional H$_2$ treatment water molecules connected with the hygroscopic nitrate anions are transported through the pore system of the oxidic precursors giving rise to an additional particle transport from the inner pores towards the outer pores of the support grains. In the case of an inhomogeneous deposition of the oxidic iron phase, the outer pores of the support grains are already enriched in iron (III) oxide, so sintering will be easier for these precursors.

Transition of the oxidic precursor into the sulfidic catalyst

From our measurements it becomes clear that a well-dispersed iron (III) oxide phase supported on activated carbon transforms rather easily into iron sulfide phases, when exposed to a H$_2$S/H$_2$ gas mixture. The extent to which the oxidic iron phase is sulfided and the type of the iron sulfide phases formed after consecutive 1-h treatments depends on the maximum temperature reached during the exposure to the H$_2$S/H$_2$ gas mixture.

Already at room temperature the iron (III) oxide is partly sulfided to FeS$_3$ (see Table 1). This indicates that the observed H$_2$S uptake at room temperature in temperature programmed sulfiding (TPS) experiments reported by Groot [30], is not only due to physisorption, but that at least part of the H$_2$S uptake is due to a chemical reaction. The analysis of the spectra after sulfidation at room temperature shows that in addition to FeS$_3$ a high-spin Fe$^{2+}$ phase and another spectral component have been found. This last component has very much the same IS and QS values as deduced for the so-called surface-oxide contribution in the spectra of the oxidic precursors (IS$_2$ = 0.63 mm s$^{-1}$, QS$_2$ = 1.04 mm s$^{-1}$). However, as it is rather unlikely that this surface-oxide phase remains nearly unaffected by sulfidation up to 773 K (the IS and QS values are only slightly changed as is shown in Table 1), it is more likely that an “Fe-sulfide” phase is formed which accidentally has about the same Mössbauer parameters. The results of the in-situ measurements of the fully sulfided catalysts at cryogenic temperatures prove that this is indeed the case. This spectral component is denoted as “Fe-sulfide”(2) in Table 1. No oxidic con-
tribution is found in the 4.2 K spectra of the fully sulfided catalysts. However, on basis of the experimental evidence available it is not possible to decide at which sulfidation temperature this “Fe-sulfide”(2) phase is formed at the expense of the surface-oxide contribution. This would have been possible as we should have measured the samples at 4.2 K after each sulfidation step.

During the sulfidation at room temperature we have measured the transmission of the γ-rays as a function of time at a Doppler velocity of the source corresponding to the positive resonant absorption velocity of the high-spin Fe²⁺ phase. It was found that at room temperature the high-spin Fe²⁺ phase is formed to a large extent as soon as the sulfiding gas mixture is present in the reactor. This formation is followed by a decrease in intensity due to transformation of the high-spin Fe²⁺ phase into another compound [31]. So, it turns out that the high-spin Fe²⁺ phase is a transient phase.

The nature of the high-spin Fe²⁺ phase can not be established unambiguously. The deduced values of the isomer shift (IS) and quadrupole splitting (QS) (see Table 1) are close to those reported for the mineral Szomolnokite, FeSO₄ · H₂O (IS = 1.44 mm s⁻¹, QS = 2.69 mm s⁻¹) [32]. The small differences in these parameters can easily be explained by the small particle size. However, the formation of an Fe(II)SO₄ phase, which requires the oxidation of S²⁻ to S⁶⁺, is unlikely to occur under the experimental conditions applied. Moreover, reduction in H₂ of both Fe and Fe–Mo oxide catalysts supported on Al₂O₃, SiO₂ or C also results in the formation of a high-spin Fe²⁺ phase [28,33–35] with similar Mössbauer parameters than those found in the present study. This indicates that the high-spin Fe²⁺ phase in the reduction and sulfidation experiments are of identical nature. The fact that in the sulfidation experiments the high-spin Fe²⁺ phase is observed at lower temperatures than in the reduction experiments is most likely due to the higher reactivity of the H₂S/H₂ gas mixture compared to H₂. Hence, it is concluded that the high-spin Fe²⁺ phase is an oxidic transient phase.

After sulfidation up to a temperature of 573 K or higher the high-spin Fe²⁺ phase has disappeared. Furthermore, the main component in the spectra, ascribed to FeS₂, is transformed into another sulfidic compound. From sulfidation experiments on a model system consisting of 50-nm α-Fe₂O₃ particles [29] it is known that after sulfidation at temperatures up to 523 K or higher only compounds with a Fe₁₋ₓS pyrrhotite–troilite structure are present which means that the FeS₂ initially formed is converted into “Fe₁₋ₓS” compounds. So, it can be assumed that the iron sulfide compound present in the carbon-supported catalysts after the transformation of FeS₂ will have a “Fe₁₋ₓS”-type structure. The magnetic hyperfine fields in the Fe(x)/C(yK) [673 K, 4 h] catalysts observed at 4.2 K support this assumption. Also, the mass decrease of the sulfided catalyst observed after sulfidation at 573 K or higher temperatures [31] is consistent with a conversion of FeS₂ into Fe₁₋ₓS. However, the isomer shifts measured at 293 and 4.2 K do not correspond with the values found for
bulk Fe\(_{1-x}\)S compounds [29]. This may be due to the high dispersion of the catalytic particles. Therefore this spectral component is denoted as “Fe-sulfide” (1) instead of “Fe\(_{1-x}\)S”.

The complete sulfidation to the “Fe-sulfide” compounds, observed when the temperature of the catalyst is linearly increased to 673 K in 1 h in the H\(_2\)S/H\(_2\) flow, is in agreement with results obtained by Groot for thiophene HDS activities of Fe\(_x\)/C (293 K) catalysts [30]. He found that the activity of these catalysts is not improved by extending the sulfidation period at 673 K, which indicates that the catalysts are already completely sulfided after the 1-h sulfidation treatment.

**Fully sulfided catalysts**

From in-situ Mössbauer measurements of sulfided catalysts at 4.2 K it is found that the iron sulfide phases are similar for all Fe\(_x\)/C\(_y\)K catalysts, i.e. “Fe\(_{1-x}\)S”-type structure. This strongly indicates that the observed variations in the QTOF values are not caused by differences in intrinsic activities due to the presence of different iron sulfide phases. But, as can be seen in Fig. 6, the QTOF value is related to the spectral contribution of the superparamagnetic doublet in the spectra at 4.2 K. When the QTOF value decreases also the doublet contribution in the spectrum decreases. This doublet contribution reflects the relative mean particle size of the catalytic iron sulfide phase. Hence, it can be concluded that the variations in the QTOF value are mainly caused by changes in the mean size of the catalytic “Fe-sulfide” particles.

**Reoxidized catalysts**

From measurements at 4.2 K it is found that all catalysts completely reoxidize in air at room temperature within several days. The rate of reoxidation has not been investigated. By comparing the mean size of the iron(III) oxide particles present in the reoxidized catalyst and the precursor, the influence of the sulfidation procedure on the mean particle size can be deduced. It should be noted that such a comparison is only valid if severe sintering or redispersion do not occur during reoxidation. However, this does not seem to happen because the sequence in the mean particle size is the same for the sulfided and reoxidized catalysts. In Fig. 7 the spectral contributions of the superparamagnetic doublet to the spectra of the oxidic precursors and the reoxidized catalysts recorded at 4.2 K are presented. These spectral contributions reflect the relative mean particle size. It is clear that in all catalysts sintering has taken place, and that there are significant differences in the extent of sintering. It is remarkable that for iron contents of 2.7 wt.-% and higher less sintering occurs in the Fe\(_x\)/C (393 K) than in the Fe\(_x\)/C (293 K) catalysts. This indicates that the strengthening of the interaction between the iron(III) oxide particles
Fig. 7. Relative mean iron(III) oxide particle sizes in the oxidic Fe(x)/C(293 K) and Fe(x)/C(393 K) precursors as well as in the Fe(x)/C(293 K) [673 K, 4 h] and Fe(x)/C(393 K) [673 K, 4 h] catalysts reoxidized in ambient air at room temperature after sulfidation in the LTR. Open symbols represent oxidic precursors, closed symbols represent reoxidized catalysts. The dotted lines are drawn as a guide to the eye only. See Experimental for details of sulfidation, reoxidation and sample notation.

and the support due to the additional H_2 treatment results in a higher thermal stability for these catalysts.

CONCLUSIONS

The present study has resulted in a better understanding of the sulfidation of carbon-supported iron sulfide catalysts, and their performance for thiophene hydrodesulfurization. The main conclusions are:

- The iron(III) oxide present in an oxidic Fe(x)/C(yK) catalyst is already partially sulfided as soon as the sample is exposed to a H_2S/H_2 gas mixture at room temperature.
- An oxidic high-spin Fe^{2+} phase and pyrite (FeS_2) are intermediate compounds during the sulfidation process.
- Under typical thiophene HDS conditions (T>573 K, in the presence of H_2S/H_2) the catalysts contain "Fe-sulfide" species of the "Fe_{1-x}S"-type structure.
- The thiophene HDS activity per mol Fe (QTOF) is clearly related to the mean size of the "Fe-sulfide" particles, which can be determined on a relative basis using in-situ Mössbauer spectroscopy at cryogenic temperatures.
For iron contents of 2.7 wt.-% and higher, strengthening of the interaction between the iron (III)oxide particles and the support in the catalyst precursor leads to an increased thermal stability. This brings about a better performance of the sulfided catalysts.

ACKNOWLEDGEMENT

We would like to thank Prof. dr. J.J. van Loef for stimulating discussions and carefully reading the manuscript.

REFERENCES