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Sulfidation of alumina-supported iron and iron-molybdenum oxide catalysts

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Abstract

The transition of alumina-supported iron and iron-molybdenum catalysts from the oxidic precursor to the sulfided catalysts was systematically studied by means of in-situ Mössbauer spectroscopy at room temperature. This enabled the adjudgement of various sulfidic phases in the sulfided catalysts. The alumina support material prevents complete sulfidation of the iron phase. Some of the iron diffuses into the support material at temperatures of 573 K and higher. The relative amount of iron diffused into the alumina was reduced at higher iron content and in the presence of molybdenum. Together with the formation of elemental sulfur and a lower intrinsic activity, the incomplete sulfidation accounts for the poor HDS activity of alumina-supported iron and iron-molybdenum sulfide catalysts.

Keywords: iron, iron-molybdenum, sulphidation, catalyst characterization (Mössbauer spectroscopy), hydrodesulfurization.

INTRODUCTION

Transition metal sulfide catalysts are of great interest, as they are widely used in the oil-processing industry for the removal of, environmental pollutive, hetero-atoms like sulfur and nitrogen from crude oil fractions. Catalysts con-

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sisting of molybdenum or tungsten sulfide promoted by cobalt or nickel sulfide supported on porous alumina are most commonly applied. However, in the case of coal hydroliquefaction and heavy oil conversion also iron sulfide based catalysts are considered to be useful since they can be produced at relatively low costs. The bulk of the available evidence indicates that pyrrhotite \((Fe_{1-x}S)\) is the active iron phase present in these catalysts under reaction conditions \([1-5]\). Iron sulfide catalysts prepared on a high surface area carbon support are studied by Groot et al. \([6]\). Due to a relatively weak interaction with the carbon surface, the oxidative catalyst precursor species can be readily and quantitatively converted into the active sulfide form.

Groot et al. \([7]\) also compared thiophene HDS activities of carbon-, silica- and alumina-supported iron sulfide catalysts. They found that carbon-supported catalysts are much more active than those supported on alumina. Similar observations are made for the iron–molybdenum catalyst \([8]\).

Recently we have been able to produce detailed information on the sulfiding process of oxidative carbon-supported Fe and Fe–Mo catalysts via an in-situ Mössbauer study of stepwise sulfided samples \([9-11]\). In an attempt to understand the relatively very low thiophene HDS activity of alumina-supported Fe(–Mo) sulfide catalysts, it was decided to study the sulfidation of these catalysts using the same multi step approach. The results will be compared with those of in-situ Mössbauer studies on samples sulfided in one step \([12-14]\).

**Experimental**

**Preparation of oxidative catalyst precursors**

The oxidative catalyst precursors were prepared by pore volume impregnation (incipient wetness) of Ketjen 001-1.5E γ-Al₂O₃ (surface area 271 m²g⁻¹; pore volume 0.7 cm³g⁻¹). Aqueous solutions of \((NH₄)₆Mo₇O₂₄·4H₂O\) (Merck, >99%) and \(Fe(NO₃)₃·9H₂O\) (Baker, >99%) were used. The iron nitrate solutions were enriched in the Mössbauer isotope \(^{57}\)Fe, using reduced \(α-Fe₂O₃\) (Intersales, 94.7% \(^{57}\)Fe) dissolved in \(2 \text{ M HNO₃}\) and the acidity of the impregnation solution was adjusted to \(pH = 0.25\).

Samples containing both molybdenum and iron were prepared by a two-step impregnation procedure, in which the molybdenum phase was introduced first. After impregnation with ammonium heptamolybdate the samples were dried under ambient conditions for 1 h at 293 K, subsequently at 383 K for 16 h and additionally calcined at 773 K for 4 h. Iron nitrate impregnation was followed by drying in flowing air (flow-rate 100 cm³min⁻¹) for 16 h at room temperature in order to obtain a well-dispersed iron oxide phase. It was observed that carbon-supported catalyst precursors prepared in this way still contain hygroscopic nitrate anions whose presence caused a decrease in thermal stability of the iron phase particles \([9,15]\). Therefore, the samples were subjected to an
additional treatment in flowing hydrogen (flow-rate 50 cm$^3$ min$^{-1}$) in order to remove the amonic nitrate species [9]. During this treatment the sample was kept at 313, 353 and 393 K for 24 h at each temperature. It is important to note that the drying procedure was never followed by a calcination step. From reduction experiments in hydrogen it is known that iron (III) oxide in the dried catalysts is not reduced at these relatively low temperatures [16]. In addition, Arnoldy [17] has shown by temperature-programmed reduction that reduction of MoO$_3$ supported on SiO$_2$, Al$_2$O$_3$ and C also occurs at temperatures well above 393 K. The samples are denoted Fe$(x)/Al_2O_3$ and Fe$(x)$Mo$(0.6)/Al_2O_3$, where $x$ ($x = 0.15, 0.50, 0.80$) and 0.6 are the variable iron and the constant molybdenum loading expressed in atoms per nm$^2$ support surface area which correspond with 0.4, 1.3, 2.1 wt.-% iron and 5 wt.-% molybdenum respectively.

Sulfiding procedure and Mössbauer experiments

Mössbauer spectra were recorded with a constant velocity spectrometer using a $^{57}$Co in rhodium source at room temperature. Doppler velocities are given relative to sodium nitroprusside. The spectra were fitted by computer with calculated subspectra consisting of Lorentzian shaped lines.

As the sulfidation of the alumina-supported iron and iron–molybdenum oxide catalysts might be influenced by the dispersion of the oxidic catalyst precursor phase, the relative dispersion of the iron phase is determined by Mössbauer spectroscopy. Samples of the oxidic catalyst precursors are measured at 293, 77 and 4.2 K.

Catalyst samples (200–300 mg) were sulfided in-situ using a stainless steel Mössbauer reactor, the design of which is described in detail elsewhere [18]. First the effect of exposing the catalyst to the 10 mol% H$_2$S in hydrogen sulfiding gas mixture at room temperature was investigated by replacing the initially present air by a 50 cm$^3$ min$^{-1}$ flow of the sulfiding gas mixture during a period of about 2 h. A Mössbauer spectrum was recorded while the sample was kept in static H$_2$S/H$_2$ at atmospheric pressure. Next, the same sample was subjected to various successive sulfidation treatments in a 50 cm$^3$ min$^{-1}$ H$_2$S/H$_2$ flow. In each treatment the temperature of the sample was linearly increased to the desired maximum sulfiding temperature in 1 h, and was then within 0.75 h decreased 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 H$_2$S/H$_2$ environment at atmospheric pressure. The samples will be denoted as Fe$(x)/Al_2O_3[z]$ and Fe$(x)$Mo$(0.6)/Al_2O_3[z]$ in which $z$ is the maximum sulfiding temperature in Kelvin reached during the 1-h sulfiding procedure.
RESULTS

Oxidic catalyst precursors

As the sulfidation of the alumina-supported iron and iron–molybdenum oxide catalysts might be influenced by the dispersion of the oxidic catalyst precursor phase, the relative dispersion of the iron phase is determined by Mössbauer spectroscopy. Spectra of the Fe(0.15)/Al₂O₃, Fe(0.5)/Al₂O₃, Fe(0.15)Mo(0.6)/Al₂O₃, and Fe(0.8)Mo(0.6)/Al₂O₃ precursors are recorded at 293, 77 and 4.2 K. The spectra recorded at 293 and 77 K consist of a quadrupole doublet. A contribution of the original salt Fe(NO₃)₃·9H₂O, which would be a broadened single line [19], is absent in the spectra of all catalyst precursors and in those of the Fe–Mo catalyst precursors also no contributions of iron molybdates like Fe₃(FeO₄)₂ (Iₛ = 0.67 mm/s, Qₛ = 0 mm/s [20]), α-FeMo₄ (Iₛ = 0.86 mm/s, Qₛ = 1.52 mm/s [21]), β-FeMo₄ (Iₛ = 0.9 mm/s, Qₛ = 2.6 mm/s, Iₛ₂ = 1.0 mm/s, Qₛ₂ = 0.9 mm/s [21]) and FeMoO₄-II (Iₛ = 1.12 mm/s, Qₛ = 1.52 mm/s [21]) are found to be present. At 4.2 K for three of the precursor samples (Fe(0.15)/Al₂O₃, Fe(0.15)Mo(0.6)/Al₂O₃ and Fe(0.8)Mo(0.6)/Al₂O₃) a superposition of an electric quadrupole doublet and magnetic hyperfine splittings is observed. For the precursor sample Fe(0.5)/Al₂O₃ at 4.2 K only a magnetic hyperfine sextuplet is measured (see Fig. 1) which is in the region of iron (III) oxide, and its temperature behaviour is characteristic for ultrafine iron (III) oxide particles showing superparamagnetism [22]. However, in the spectra at 4.2 K of the other samples besides the iron (III) oxide magnetic contribution (indicated by the full bar-diagram in Fig. 1) a much larger magnetic hyperfine splitting is observed which must be due to well-separated paramagnetic iron ions as found in the case of Fe(x)/C catalyst precursors which were only dried at room temperature [9].

Fig. 1 shows that the iron (III) oxide dispersion in Fe(0.15)/Al₂O₃, Fe(0.15)Mo(0.6)/Al₂O₃ and Fe(0.8)Mo(0.6)/Al₂O₃ is about equal and substantially higher than in Fe(0.5)/Al₂O₃. This points to a stabilizing effect of the monolayer type oxidic molybdenum phase on the dispersion of the iron (III) oxide phase since in contrast to Fe(x)/Al₂O₃ no dispersion loss is observed when the iron loading of Fe(x)Mo(0.6)/Al₂O₃ was increased from 0.15 to 0.5 at nm. In case of the low iron loading the dispersion of the iron (III) oxide species is already so large that an influence of the presence of the molybdenum phase on the dispersion can hardly be observed. From a comparison of the spectra shown in Fig. 1 with those of unsupported α-Fe₂O₃ microcrystals with a known mean particle size [22] it is concluded that the mean particle size of the iron (III) oxide particles is below 4 nm for all catalyst precursors studied.
Fig. 1. Mössbauer spectra of the oxidic Fe(0.15)/Al₂O₃, Fe(0.5)/Al₂O₃, Fe(0.15)Mo(0.6)/Al₂O₃, and Fe(0.8)Mo(0.6)/Al₂O₃ catalyst precursors recorded at 4.2 K. The full-bar diagrams indicate the magnetic hyperfine splittings of the iron(III) oxide particles.

**Sulfidation of iron–molybdenum catalysts**

In Fig. 2 the spectra of the Fe(0.15)Mo(0.6)/Al₂O₃ and Fe(0.8)Mo(0.6)/Al₂O₃ catalysts recorded at room temperature after various successive sulfidation treatments are shown. The spectra of the corresponding oxidic catalyst precursors are also included in this figure. These experiments illustrate how the sulfiding proceeds.

Like in case of carbon-supported catalysts [9-11] the doublet observed in the spectra of the precursors consists of rather broad absorption lines and is therefore analyzed by using two doublets. For the Fe(0.15)Mo(0.6)/Al₂O₃ sample the analysis results are: IS₁ = 0.61 mm/s, QS₁ = 0.66 mm/s, A₁ = 30% and IS₂ = 0.62 mm/s, QS₂ = 1.03 mm/s, A₂ = 70%. For the Fe(0.8)Mo(0.6)/Al₂O₃ sample nearly the same values are found: IS₁ = 0.63 mm/s, QS₁ = 0.64 mm/s, A₁ = 39% and IS₂ = 0.62 mm/s, QS₂ = 1.07 mm/s, A₂ = 61%. The Mössbauer parameters of these doublets indicate that the iron is present as iron(III) oxide. These doublets have an identical isomer shift (IS) but different quadrupole splittings (QS). From previous experiments on unsupported small α-Fe₂O₃ 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 is assigned to the surface-oxide contribution.

Analysis of the spectra in Fig. 2 recorded after the different sulfidation treatments is rather difficult. However, remarkable changes in spectral shape as well as total resonant absorption areas occur after the different sulfidation
Fig. 2. In-situ Mössbauer spectra recorded at room temperature of the Fe(0.15)Mo(0.6)/Al₂O₃ and Fe(0.8)Mo(0.6)/Al₂O₃ catalysts successively sulfided up to temperatures indicated.

treatments. (One can make these changes in spectral shape visible by drawing a vertical line at zero velocity in Fig. 2.) Sulfidation up to 473 K, causes a shift of spectral components to lower Doppler velocities, while after sulfidation at higher temperatures spectral components move back to their original positions. Furthermore, at increasing sulfidation temperature, an increase in the spectral contribution of high-spin Fe²⁺-phase(s) is observed. The drastic changes in the total resonant absorption areas of the spectra after the different sulfidation treatments are shown by the normalized values which are summarized in Table 1. It turns out that the strong decrease of the total resonant absorption area is accompanied by the above mentioned shift of spectral components to lower Doppler velocities.

Room temperature exposure of the catalyst precursors to the sulfidation gas mixture causes slight changes in the shape of the spectra. In both samples a small contribution of a high-spin Fe²⁺-phase, is observed. Such a spectral component is also observed during the sulfidation of carbon-supported Fe [9] and
TABLE 1

Normalized total resonant absorption areas of the room-temperature spectra of alumina-supported iron and iron-molybdenum catalysts fresh and after successive sulfidation treatments up to temperatures indicated by \( z(K) \)

<table>
<thead>
<tr>
<th>( z(K) )</th>
<th>( \text{Fe}(0.15)\text{Mo}(0.6) )</th>
<th>( \text{Fe}(0.8)\text{Mo}(0.6) )</th>
<th>( \text{Fe}(0.5) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>fresh</td>
<td>11.4</td>
<td>14.3</td>
<td>15.0</td>
</tr>
<tr>
<td>293</td>
<td>12.3</td>
<td>5.1</td>
<td>7.6</td>
</tr>
<tr>
<td>373</td>
<td>6.9</td>
<td>6.5</td>
<td>7.7</td>
</tr>
<tr>
<td>473</td>
<td>6.7</td>
<td>6.0</td>
<td>10.2</td>
</tr>
<tr>
<td>573</td>
<td>12.0</td>
<td>12.0</td>
<td>12.7</td>
</tr>
<tr>
<td>673</td>
<td>14.6</td>
<td>15.5</td>
<td></td>
</tr>
<tr>
<td>773</td>
<td>16.7</td>
<td>14.6</td>
<td>17.0</td>
</tr>
</tbody>
</table>

Fe–Mo \([10,11]\) catalysts and during reduction in hydrogen of both iron and iron–molybdenum oxide catalysts supported on \( \text{Al}_2\text{O}_3, \text{SiO}_2 \) and \( \text{C} \) \([16,23–25]\) and is assumed to be an oxidic phase \([9]\). It appears from Fig. 2 that only for the \( \text{Fe}(0.8)\text{Mo}(0.6)/\text{Al}_2\text{O}_3 \) sample a shift of the mean spectrum to lower Doppler velocities occurs and from Table 1 it follows that also only for this sample a drastic decrease in the total resonant absorption area of the spectrum is measured. In Table 2 the data of the computer analyses of the spectra are presented and it is shown that for the \( \text{Fe}(0.15)\text{Mo}(0.6)/\text{Al}_2\text{O}_3 \) sample only the high-spin \( \text{Fe}^{2+} \) contribution is increased at the expense of the surface-oxide contribution. For the \( \text{Fe}(0.8)\text{Mo}(0.6)/\text{Al}_2\text{O}_3 \) sample, in addition to the high-spin \( \text{Fe}^{2+} \) contribution it was necessary to analyze the spectrum by three doublets instead of the original bulk- and surface-oxide doublets.

After the sulfidation treatment at 373 K the drastic decrease in the total resonant absorption area of the spectrum is also observed for the \( \text{Fe}(0.15)\text{Mo}(0.6)/\text{Al}_2\text{O}_3 \) sample (Table 1), and its spectrum has now also to be analyzed by three doublets in addition to the small high-spin \( \text{Fe}^{2+} \) contribution (Table 2).

It turns out that after sulfidation at 573 K or higher the total resonant absorption areas of the spectra are almost completely restored to the original values observed for the fresh oxidic precursor samples. Furthermore, a second high-spin \( \text{Fe}^{2+} \) component is measured in the spectra of the catalysts. This \( \text{Fe}^{2+} \) component is not found during the sulfidation of carbon-supported catalysts \([9–11]\). However, when the oxidic \( \text{Fe}(x)\text{Mo}(0.6)/\text{Al}_2\text{O}_3 \) catalysts are subjected to reduction treatments in hydrogen, a high-spin \( \text{Fe}^{2+} \)-phase with similar Mössbauer parameters (\( IS = 1.3 \text{ mm s}^{-1}, QS = 1.75 \text{ mm s}^{-1} \)) is formed \([16]\). This high-spin \( \text{Fe}^{2+} \)-phase seems not to reoxidize to iron (III) oxide when the catalysts are exposed to air after the various successive hydrogen treatments up to 773 K. So, the iron atoms in this phase are strongly influenced by
<table>
<thead>
<tr>
<th>Sulfidic iron species</th>
<th>&quot;Fe$_{1-x}$S&quot;</th>
<th>&quot;Fe-Mo-S&quot;</th>
<th>High-spin Fe$^{2+}$</th>
<th>&quot;Iron (II) aluminate&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>z (K)</td>
<td>IS (mm/s)</td>
<td>QS (mm/s)</td>
<td>A (%)</td>
<td>IS (mm/s)</td>
</tr>
<tr>
<td>293</td>
<td>0.57</td>
<td>0.64</td>
<td>34</td>
<td>0.66</td>
</tr>
<tr>
<td>373</td>
<td>0.56</td>
<td>0.63</td>
<td>33</td>
<td>0.63</td>
</tr>
<tr>
<td>473</td>
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<td>0.68</td>
<td>37</td>
<td>0.51</td>
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<tr>
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<td>0.57</td>
</tr>
<tr>
<td>673</td>
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<td>0.63</td>
<td>35</td>
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</tr>
<tr>
<td>773</td>
<td>0.63</td>
<td>0.62</td>
<td>37</td>
<td>0.66</td>
</tr>
<tr>
<td>293</td>
<td>0.82</td>
<td>0.66</td>
<td>30a</td>
<td>0.61</td>
</tr>
<tr>
<td>373</td>
<td>0.53</td>
<td>0.61</td>
<td>25</td>
<td>0.63</td>
</tr>
<tr>
<td>473</td>
<td>0.50</td>
<td>0.66</td>
<td>26</td>
<td>0.53</td>
</tr>
<tr>
<td>573</td>
<td>0.59</td>
<td>0.62</td>
<td>16</td>
<td>0.60</td>
</tr>
<tr>
<td>673</td>
<td>0.60</td>
<td>0.55</td>
<td>8</td>
<td>0.63</td>
</tr>
<tr>
<td>773</td>
<td>0.67</td>
<td>0.87</td>
<td>24</td>
<td>0.67</td>
</tr>
</tbody>
</table>

*As no change in the normalized total resonant absorption area is observed (see Table 1) we believe that these spectral contributions are still due to bulk- and surface-oxide.
the alumina support. Therefore, these high-spin Fe$^{2+}$-species are assumed to indicate the presence of an iron (II) aluminate type phase.

As stated before, besides the "iron (II) aluminate" spectral contribution, three additional contributions were necessary to analyze the spectra, measured after the different sulfidation steps. The parameters of two of these contributions (see Table 2) agree rather well with those of the bulk- and surface-oxide contributions in the oxidic precursor material. It is however rather unlikely that a more severe sulfidation treatment would cause a reformation of the original oxidic phases. Particularly as it is known from hydrogen reduction experiments that the iron (III) oxide spectral contributions have nearly disappeared after a 1-h treatment at 573 K in hydrogen [16]. Such a similarity between the room-temperature Mössbauer parameters of Fe–Mo/Al$_2$O$_3$ catalysts in the oxidic precursor state and the sulfided state has also been observed by Clausen [13]. This author deduced from the temperature dependence of the quadrupole splitting that in the sulfided sample the Fe$^{3+}$ component is present in the low-spin state in stead of the high-spin state and assumed that the H$_2$/H$_2$S treatment has sulfided the sample. Hence, it is assumed that the three subspectra represent sulfidic iron phases. By comparison of the parameters of these subspectra with those of sulfided carbon-supported iron [9] and iron–molybdenum [10,11] catalysts, these subspectra can be ascribed to "Fe$_{1-x}$S" and a mixed iron–molybdenum–sulfide phase, the so-called "Fe–Mo–S" phase. By means of γ-ray transmission experiments it is determined that during sulfidation up to 673 or 773 K the mass of the catalyst increases considerably (up to 10 wt.%). Because the same mass increase is also observed for the blank support it is concluded that considerable amounts of elemental sulfur are formed during these sulfidation treatments. (Sulfidation of the support material can be excluded at these temperatures [26].)

From Fig. 2 it is concluded that no large differences between the spectra of the two Fe($x$)Mo(0.6)/Al$_2$O$_3$ catalysts can be observed. In Table 2 results of the computer analyses of the spectra of the Fe(0.15)Mo(0.6)/Al$_2$O$_3$ catalyst after different sulfidation treatments up to 773 K are included. It is remarkable that the spectral contribution of the so-called "Fe–Mo–S" phase is only slightly dependent on the iron loading and is not exclusively formed neither at the lowest nor the highest iron loading.

**Iron catalysts**

In order to enable a comparison between the sulfidation behaviour of Fe–Mo/Al$_2$O$_3$ and Fe/Al$_2$O$_3$ catalysts, an Fe(0.5)/Al$_2$O$_3$ catalyst is subjected to the same series of sulfidation treatments as used for the Fe($x$)Mo(0.6)/Al$_2$O$_3$ catalysts. The spectra of the Fe(0.5)/Al$_2$O$_3$ catalyst recorded after the various successive sulfidation treatments are given in Fig. 3. It turns out that the transition of the precursor material into the sulfidic catalyst proceeds more or less
in the same way as found for the iron–molybdenum catalysts. As is shown in Table 1, also for the Fe(0.5)/Al₂O₃ catalyst a drastic decrease in the total resonant absorption area of the spectrum is found after exposing the catalyst precursor to the sulfidation gas mixture at room temperature, while also the resonant absorption area becomes almost completely restored after sulfidation at 573 K or higher temperatures. However, there are also differences and the main one becomes already clear from a visual inspection of the spectra (see Figs. 2 and 3). Upon sulfidation up to 473 K of the Fe(0.5)/Al₂O₃ catalyst a shift of the spectral components to lower Doppler velocities is much less than observed for the iron–molybdenum catalysts. The results of the computer analyses of the complex spectra are also given in Table 2.

Also for this precursor the observed spectrum consists of rather broad absorption lines. Therefore, the spectrum is analyzed by using two doublets and the analysis results are: $I_{S1}=0.61$ mm/s, $Q_{S1}=0.59$ mm/s, $A_1=50\%$ and
IS₂ = 0.61 mm/s, QS₂ = 0.98 mm/s, A₂ = 50%. Also in this case, such a spectral composition is ascribed to a bulk- and a surface-oxide contribution (largest QS-value) [22].

After exposure of the precursor material to the H₂S/H₂ gas mixture at room temperature a small contribution of an oxidic high-spin Fe⁵⁺-phase is observed besides three other spectral components. This is in line with the results obtained for the Fe(0.8)Mo(0.6)/Al₂O₃ catalyst. In addition, after sulfidation up to temperatures of 573 K or higher about the same spectral components are found in the Fe(0.5)/Al₂O₃ as in the Fe(0.8)Mo(0.6)/Al₂O₃ catalyst, which is rather remarkable. Only the deduced QS-values turned out to be slightly different. This indicates that in the Fe(0.5)/Al₂O₃ sample iron atoms are present which are similarly coordinated by sulfur atoms as the iron atoms in the so-called “Fe–Mo–S”-phase. From Table 2 it follows that the spectral contribution of the “iron(II) aluminate” increases and that of the “Fe₁₋ₓS” decreases significantly when the maximum sulfidation temperature is increased to 773 K. This indicates that “Fe₁₋ₓS” is converted into “iron(II) aluminate”, due to diffusion of iron atoms into the alumina lattice.

As is shown in Fig. 4 the iron loading clearly influences the composition of the sulfidic catalyst. The results of the computer analysis of the spectrum of the Fe(0.15)/Al₂O₃ catalyst after the sulfidation treatment up to 773 K are also presented in Table 2. It is striking that in the catalyst with the lowest iron loading the spectral contribution of the “iron(II) aluminate” is much larger and the contribution of the sulfidic iron species much lower than in the other sample. It is shown before, via measurements at 4.2 K of the oxidic precursor material, that the dispersion of the iron is higher in the Fe(0.15)/Al₂O₃ than in the Fe(0.5)/Al₂O₃ sample. Consequently, relatively more iron atoms will be in close contact with the alumina support in the sulfided catalyst.

![In-situ Mössbauer spectra](image-url)
DISCUSSION

Comparison of alumina-supported Fe and Fe-Mo catalysts

For the oxidic precursors of the alumina-supported iron and iron–molybdenum sulfide catalysts, the spectral doublets with rather broad absorption lines of the iron(III) oxide species are ascribed to a bulk- and a surface-oxide contribution [22]. Vaishnava et al. [14] have also analyzed their spectra of calcined oxidic Fe-Mo/Al_2O_3 catalyst with two different quadrupole doublets. These authors ascribed the spectral component with a comparably large QS-value (0.95–1.01 mm/s) to an iron aluminate phase in the alumina support, which phase should remain unaffected during sulfidation. However, in the literature, iron aluminate is reported to have a QS-value of about 0.45–0.60 mm/s [27,28]. Hence, such an assignment seems to be incorrect. In the 4.2 K spectra of Fe(0.15)/Al_2O_3, Fe(0.15)Mo(0.6)/Al_2O_3 and Fe(0.8)Mo(0.6)/Al_2O_3, we observed a contribution of paramagnetic iron ions. But, we believed that these iron ions are monoatomically dispersed on the support and will not be observed in the room temperature spectra, due to their low effective Debye temperature. Therefore, only a spectral composition consisting of a bulk- and a surface-oxide contribution has been taken into account. Such a two-component spectral composition has also been observed for the oxidic precursors of carbon-supported iron [9] and iron–molybdenum [11] catalysts. As for the alumina-supported oxidic precursors as well as for the carbon-supported ones similar isomer shifts and quadrupole splittings are deduced for both spectral components, the appearance of an iron aluminate phase in the alumina support is rather unlikely. Furthermore, for the precursor sample Fe(0.5)/Al_2O_3 at 4.2 K only a magnetic hyperfine sextuplet is measured (see Fig. 1) in the region of iron(III) oxide.

From the experimental results as shown in the Figs. 2 and 3 it follows that an assignment of the various spectral components in the catalysts after a sulfidation treatment up to 773 K would have been impossible without the information from the spectra recorded after sulfidation treatments at lower temperatures. The occurrence of the shift to lower Doppler velocities of those components in the spectra of the Fe(x)Mo(0.6)/Al_2O_3 catalysts sulfided up to 473 K which are ascribed to sulfidic iron species in Table 2 and the drastic decrease of the total resonant absorption areas of the spectra, turned out to be essential for the assignment. In addition, the assignment of spectral components to sulfidic iron species as given in Table 2 is supported by results of H_2-reduction experiments [18]. Hence, only the high-spin Fe^{2+} (iron(II) aluminate) phase, is not sulfided during our sulfidation treatments. This result has been verified by a temperature-programmed reduction experiment on a Fe/Al_2O_3 catalyst sulfided in H_2S/H_2 up to 673 K and it is also in accordance with the results of temperature-programmed sulfidation experiments on Fe/Al_2O_3.
catalysts [29]. As a consequence of this interpretation, in the Fe–Mo catalysts the surface-oxide contribution of the precursor material would have about the same Mössbauer parameters (IS and QS) as the first doublet ascribed to the so-called “Fe–Mo–S” in Table 2. Furthermore, it appeared that the second doublet ascribed to the so-called “Fe–Mo–S” phase in Table 2 also occurs in the alumina-supported iron catalysts in the absence of molybdenum.

At least this last result is remarkable, but asks for more decisive experimental evidence in the near future. It should be mentioned however, that we have already found in a sulfidation study of carbon-supported iron catalysts, that after a sulfidation treatment up to 773 K a spectral component is present with the same Mössbauer parameters as the surface-oxide contribution in the spectrum of the oxodic precursor [9]. It seemed unlikely that the surface-oxide phase should remain nearly unaffected by such a treatment in H₂S/H₂, while already at room temperature iron sulfides are formed in these catalysts [9]. Furthermore, recently Van der Kraan et al. [30,31] have reported a similar quadrupole splitting as ascribed to the “Co–Mo–S” phase by Topsøe et al. [32] in the Mössbauer spectra of sulfided Co/C catalysts.

From the difference in the spectral contribution of the high-spin Fe²⁺-phases observed in the sulfided Fe and Fe–Mo catalysts with about the same iron loading it is concluded that the molybdenum hampers the formation of the “iron(II) aluminate”. Moreover, by increasing the iron loading of the catalysts the spectral contribution of the “iron (II) aluminate” decreases. So, the relative amount of iron atoms that can be converted into a sulfidic phase increases with increasing iron loading. This effect might explain why alumina-supported iron catalysts appear to have a surface loading threshold for HDS activity [7]. However, it seems rather unlikely that the very low thiophene HDS activities for the alumina-supported catalysts is exclusively due to the formation of inactive “iron(II) aluminate”, as there are still sulfidic phases formed to a large extent in the catalysts.

Comparison of alumina- and carbon-supported catalysts

In the present study it is shown how the transformation of the precursor material to the sulfided catalyst proceeds for alumina-supported catalysts. From the comparison of the results with those obtained for carbon-supported catalysts [9–11], it follows that the most prominent difference is the fact that in the alumina-supported catalysts the iron is not completely sulfided after the final sulfidation treatment up to 773 K as is demonstrated in Fig. 5 for the iron and iron–molybdenum catalysts with an iron loading of 0.15 at/nm². For the carbon-supported iron and iron–molybdenum catalysts it was established that the activity increases as the amount of “Fe₁₋₂S” and/or “Fe–Mo–S” in the catalyst increases [9–11]. Hence, the lower degree of sulfidation in the alu-
In-situ Mössbauer spectra recorded at room temperature of the Fe(0.15)/C, Fe(0.15)Mo(0.6)/C, Fe(0.15)/Al₂O₃ and Fe(0.15)Mo(0.6)/Al₂O₃ catalysts after final sulfidation treatment up to 773 K.

Fig. 5. In-situ Mössbauer spectra recorded at room temperature of the Fe(0.15)/C, Fe(0.15)Mo(0.6)/C, Fe(0.15)/Al₂O₃ and Fe(0.15)Mo(0.6)/Al₂O₃ catalysts after final sulfidation treatment up to 773 K.

mmina-supported catalysts brings about a lower activity. However, the degree of sulfidation of the carbon- and alumina-supported iron catalysts differs not that much that it could completely account for a difference in activity between the two catalysts as large as observed by Groot et al. [7]. So, it is assumed that besides the degree of sulfidation other mechanisms lower the activity of the alumina-supported catalyst. The most plausible ones are a lower intrinsic activity and/or covering of the potentially active phase. Van Veen et al. [33] showed a much higher intrinsic activity for carbon-supported Co–Mo catalysts than for silica- and alumina-supported Co–Mo catalysts. Hence, a lower intrinsic activity plays a role. However, as stated before, large amounts of elemental sulfur are formed on the alumina-supported catalysts during the sulfidation treatments up to 673 and 773 K. The elemental sulfur could cover the potentially active phase thus causing a decrease in activity of the catalyst.

So, the lower activity of alumina-supported catalysts compared to carbon-supported ones, might be explained as follows. Less iron is converted into the actual sulfidic state, but a lower intrinsic activity and/or a covering of the potentially active phase play the most important role.

CONCLUSIONS

Via a systematic study of the transition of the oxidic precursor material to the sulfided catalysts, useful information about the sulfidation process of alumina-supported Fe and Fe–Mo catalysts could be obtained. It is found that a fraction of the iron ions diffuses into the alumina support under typical thiophene HDS conditions \( T \geq 573 \) K in \( \text{H}_2\text{S}/\text{H}_2 \), giving rise to the formation of an “iron (II) aluminate”. The presence of molybdenum hampers the formation
of this "iron(II) aluminate". Furthermore the relative amount of formed "iron (II) aluminate" decreases with increasing iron loading.

Together with the formation of considerable amounts of elemental sulfur and a lower intrinsic activity of the sulfidic phase(s), the incomplete sulfidation accounts for the poor HDS activity of the alumina-supported catalysts.

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