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Structure of the Molybdenum Sulfide Phase in Carbon-Supported Mo and Co–Mo Sulfide Catalysts As Studied by Extended X-ray Absorption Fine Structure Spectroscopy

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The structure and dispersion of the active phase present in carbon-supported Mo and Co–Mo sulfide catalysts were studied by means of Mo K-edge EXAFS. In situ EXAFS measurements were carried out at liquid N\(_2\) temperature on freshly sulfided (at 673 K) catalysts. Due to the high signal-to-noise ratio of the experimental data, detailed information about the structural parameters of the active phase could be obtained. The catalysts probably consist of small MoS\(_2\)-like particles with an average local ordered structure of 5–6 Mo atoms (Mo/C) and 7–8 Mo atoms (Co–Mo/C). Comparison with literature data shows that the MoS\(_2\) dispersion in these carbon-supported catalysts is probably as good as in their alumina-supported counterparts. A detailed EXAFS data analysis shows the presence of carbon neighbors next to the Mo atoms in both catalysts with a Mo–C coordination distance of 2.1 ± 0.1 Å. This short distance could imply an intimate interaction between the active phase and the carbon support, which may explain the high active-phase dispersion. From the value of 2.1 Å it can be inferred that the Mo–C coordination is restricted to the exposed Mo atoms and that a support carbon atom takes the place of a sulfur vacancy. The high-quality EXAFS spectra show evidence for the existence of cobalt neighbors next to the Mo atoms in the Co–Mo/C catalyst, with a Mo–Co coordination distance of 2.8 ± 0.1 Å.

Introduction

Commercial hydrotreating catalysts usually consist of molybdenum sulfide promoted with cobalt or nickel sulfide as the active phase, supported on an alumina (\(\gamma\)-Al\(_2\)O\(_3\)) carrier. Previous laboratory studies\(^*\) have shown that the application of carbon as a support for sulfide hydrotreating catalysts results in improved catalyst activity compared to the commercial alumina-supported phase, supported on an alumina (\(\gamma\)-Al\(_2\)O\(_3\)) carrier. Previous XPS, Vissers et al.\(^5\) showed that sulfided Mo/C catalysts (with Mo loadings above 3 wt %) consisted of tiny three-dimensional MoS\(_2\) particles. On the other hand, Topsoe et al.\(^6\) claimed that MoS\(_2\) supported on an industrial alumina support can be present as very large patches of a wrinkled, one slab thick, MoS\(_2\) layer. These findings point to a different molybdenum sulfide morphology on each carrier, viz., a single slab monolayer strongly interacting with the support in case of alumina, and small three-dimensional particles almost free of interaction with the support in case of carbon. However, in a recent HRTEM model study of molybdenum sulfide supported on graphite, Hayden et al.\(^7\) observed that a MoS\(_2\) rag phase was formed and concluded that a strong sulfide–support interaction was present.

The observation that carbon carriers have unique properties is also apparent from the work of Vissers et al.\(^3\) on carbon-supported cobalt sulfide catalysts. In this work the authors reported that the thiophene HDS activity is higher when carbon is used as a support. In view of the intriguing properties of carbon-supported HDS catalysts, we decided to study their structure with the use of in situ EXAFS (extended X-ray absorption fine structure) spectroscopy. Several EXAFS studies on alumina- and silica-supported HDS catalysts have been reported in the literature,\(^10–18\) However, to our knowledge, carbon-supported catalysts have not yet been studied with EXAFS. In our EXAFS study of the Mo K-edge in a sulfided Mo/C and a Co–Mo/C catalyst we wanted to focus our attention to the following items:

(i) What is the structure of the molybdenum sulfide phase in the unpromoted Mo/C as well as in the Co-promoted Mo/C catalyst?

(ii) Does an interaction take place between the molybdenum sulfide phase and the carbon support?

(iii) Are there indications for the presence of Co atoms next to the Mo atoms?

It is shown in this article that as a result of a very high signal-to-noise ratio of the EXAFS data, detailed information on the structure of the sulfide phase could be obtained. Moreover, to whom correspondence should be addressed.

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indications have been found of an interaction between the Mo atoms and the carbon support as well as indications of a Mo–Co interaction in the promoted catalyst. In the EXAFS data analysis, analytical procedures (the use of the imaginary part of the Fourier transform and the difference file technique) have been applied, which are able to reliably separate the smaller EXAFS signals from the dominant contributions (Mo–S and Mo–Mo) present in the EXAFS spectrum. These analysis procedures have proven to be successful for the analysis of the structure of the metal–support interface in metal-supported catalysts. The first preliminary results of our EXAFS study on sulfided Mo/C and Co–Mo/C catalysts have already been published. In the present article, a complete data analysis will be presented as well as a thorough interpretation of its outcome.

Experimental Section

The carbon support used was a Norit activated carbon (Norit RX3 extra; surface area, 1190 m²g⁻¹; pore volume, 1.03 cm³g⁻¹). The catalysts were prepared by pore volume impregnation using aqueous solutions of (NH₄)ₓMoO₄·4H₂O and Co(NO₃)₂·6H₂O (both Merck p.a.). In case of the promoted Mo/C catalyst, the Mo phase was introduced first. After each impregnation step the samples were dried in static air at 383 K for 16 h. No calcination was applied. The metal content (weight percent) of the oxic precursor catalyst was determined by means of atomic absorption spectroscopy using a Perkin-Elmer 3030 AAS spectrometer and a graphite furnace. The metal content (weight percent) of the oxidic precursor catalyst was determined by means of atomic absorption spectroscopy using a Perkin-Elmer 3030 AAS spectrometer and a graphite furnace. The metal content (weight percent) of the oxidic precursor catalyst was determined by means of atomic absorption spectroscopy using a Perkin-Elmer 3030 AAS spectrometer and a graphite furnace.

The EXAFS oscillations in k space were obtained from the X-ray absorption spectra by subtracting a victoreen curve, followed by a cubic spline background removal. Normalization was performed by division by the height of the edge. In Figure 1 the resulting EXAFS functions of the Mo/C and the Co–Mo/C

![Figure 1. EXAFS spectra of Mo/C (solid line) and Co–Mo/C (dotted line).](image1)

![Figure 2. EXAFS spectra and Fourier transforms of the reference compounds: (a, b) MoS₂, (c, d) Mo(CO)₆, and (e, f) Na₂MoO₄·2H₂O.](image2)
EXAFS of Sulfided Mo/C and Co-Mo/C

**TABLE I: Crystallographic Data and Fourier Transform Ranges of the Reference Compounds**

<table>
<thead>
<tr>
<th>compound</th>
<th>type of coord</th>
<th>R value Å</th>
<th>k range, Å⁻¹</th>
<th>r range, Å</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS₂</td>
<td>Mo-S</td>
<td>2.41</td>
<td>3.16-24.48</td>
<td>0.88-2.40</td>
<td>23</td>
</tr>
<tr>
<td>Mo-Mo</td>
<td>3.16</td>
<td>2.40-3.22</td>
<td>23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo(CO)₃</td>
<td>Mo-C</td>
<td>2.06</td>
<td>3.07-13.36</td>
<td>0.00-2.10</td>
<td>24</td>
</tr>
<tr>
<td>Na₂MoO₂H₂O</td>
<td>Mo-O</td>
<td>1.77</td>
<td>3.64-12.84</td>
<td>0.00-2.08</td>
<td>25</td>
</tr>
</tbody>
</table>

*Coordination distance. †Coordination number. ‡The weighting factor of the Fourier transform is in all cases 3.

Figure 3. Magnitude of the k³-weighted Fourier transforms (Δk = 3.2-16.0 Å⁻¹) of the MoS₂ reference compound (solid line), the Mo/C catalyst (dotted line), and the Co-Mo/C catalyst (dashed line).

catalysts are shown. As can be seen in this figure, the signal-to-noise ratio is very high: about 240 to 1. Furthermore, it appears that small but significant differences between these EXAFS functions seem to be present. The spectra of the reference compounds were processed in the same way as the catalyst samples. To obtain the phase shifts and backscattering amplitudes, the EXAFS spectra of the reference compounds were Fourier transformed over the largest possible range in k space (Table I). In Figure 2 these EXAFS functions as well as their Fourier transformations are shown.

Figure 3 shows the magnitude of the Fourier transforms (k¹, Δk = 3.2-16.0 Å⁻¹) of the catalysts together with the MoS₂ reference compound. As is obvious from this figure, the spectra of the Mo/C and Co-Mo/C catalysts exhibit identical features as the MoS₂ compound: the first and second peaks of the catalyst spectra are positioned at the same distance as the Mo-S and Mo-Mo peaks of the MoS₂ compound. This demonstrates that the sulfide structure in the catalysts is a MoS₂-like structure. The magnitude of the Mo-S shell in the catalysts is smaller than that of MoS₂, while the Mo-Mo shell is much smaller. Furthermore, the higher shells in the catalysts are much weaker than those of MoS₂. From these spectral characteristics it is clear that the molybdenum sulfide particles of the catalysts are quite small. There is also a difference between the catalysts themselves: the Co-Mo/C catalyst exhibits slightly larger peak amplitudes than the Mo/C catalyst.

The data analysis of the Mo-S and Mo-Mo peaks has been carried out by inverse Fourier transformation of the range 1.0-3.2 Å (after Fourier transformation: k¹, Δk = 3.2-16.0 Å⁻¹), followed by a two-shell fitting procedure on the isolated EXAFS function. In this fitting procedure the phase and amplitude functions of the absorber-backscatterer pair Mo-S and Mo-Mo of MoS₂ were used. For a detailed description of the data analysis procedure we refer to refs 19 and 26. No differences were observed between the Fourier transforms of the isolated EXAFS.

Concerning the deviation at about 2.4 Å (only in the promoted catalyst) one might think of an interaction of Mo with a Co function and the raw data, taken over a k range of 4-15 Å⁻¹. Thus, this k range is free of cutoff effects and can be used for the analysis of the isolated EXAFS function. The isolated EXAFS was fitted with a k²-weighting factor of 1 (to emphasize the low Z scatterers) as well as a k³-weighting factor of 3 (to emphasize the high Z scatterers). The resulting parameters N, R, ΔR², and ΔE₀ of the Mo-S and Mo-Mo shells were subsequently optimized by comparing the Fourier transformations (k¹ and k³-weighted) of the EXAFS function calculated with these parameters and the experimental (i.e., the isolated) EXAFS. By checking both the agreement in k space and in r space using a k¹ and k³ fit in k space and k¹- and k³-weighted Fourier transforms, respectively, a unique set of parameters is obtained for the Mo-S and Mo-Mo shells to be analyzed. In Figure 4 the k³-weighted Fourier transforms of the experimental (isolated) EXAFS and the calculated best-fit Mo-S and Mo-Mo EXAFS contributions are shown. The structural parameters obtained in this way are presented in Table II.

As can be seen in Figure 4, the agreement is nearly optimal except at low r values (about r = 1.5 Å) and at a higher r value (about 2.4 Å), the latter only in the promoted catalyst. Since it was impossible to get a good agreement in those two regions by using only S and Mo backscatterers, it is possible that other neighboring atoms are present. In view of the fact that both catalysts exhibit differences at the same r value about r = 1.5 Å, one might think of an interaction of the Mo atoms and the carbon support. This would imply for instance a Mo-C coordination.

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Curves represent the calculated M0-C shell (in Mo/C) and the calculated and absolute part, e and (a, b) and in space, respectively. The subtraction step is applied because of the smaller accuracy range of the promoter atom, since this deviation is not present in the unpromoted catalyst.

In order to investigate both possibilities, the calculated Mo-S and Mo-Mo EXAFS signals were subtracted from the experimental data and it was tried to fit the resulting difference spectra with Mo-C and Mo-C + Mo-Co EXAFS contributions, respectively. The subtraction step is applied on the isolated experimental data and the calculated (Mo-S) + (Mo-Mo) spectrum, isolated in the same way ($\Delta r = 1.0-3.2$ Å) after Fourier transformation ($k^2$, $\Delta k = 4.0-12.2$ Å$^{-1}$). This shorter $k$ range was chosen because of the smaller accuracy range of the Mo(CO)$_3$ reference compound used for fitting the expected Mo-C coordination. The difference EXAFS spectrum (in $k$ space) is shown in Figure 5, a and b. The envelope of the spectrum of Mo/C shows a monotonically decreasing amplitude, indicative of a low Z scatterer. The promoted catalyst, on the other hand, shows an interference effect at $k = 7$ Å$^{-1}$ and a maximum in the backscattering amplitude at $k = 9$ Å$^{-1}$, indicative of an additional high Z scatterer. For the expected Mo-Co coordination in the Co-Mo/C catalyst, theoretically determined phase shifts and backscattering amplitudes according to Teo and Lee$^{28}$ were used. For the latter purpose the absorber-backscatterer pair Mo-Fe was used, which is permitted.$^{28,29}$ The fitting procedure was similar as described above for Mo-S and Mo-Mo shells. Figure 5 shows a comparison between the calculated and the experimental (difference) EXAFS functions in $k$ space as well as in $r$ space, for the Mo/C and the Co-Mo/C catalyst sample. These figures show that the calculated EXAFS reproduces the difference EXAFS quite well. The structural parameters ($N$, $R$, $\Delta r^2$, and $\Delta E_0$) of the calculated Mo-C and Mo-Co shells are collected in Table III.

In order to check the reliability of the calculated EXAFS shells, a comparison was made of the experimental primary EXAFS data and the calculated EXAFS functions: Mo-S + Mo-Mo + Mo-C and (for the promoted catalyst) + Mo-C. The results are shown in Figure 6 (Mo/C) and Figure 7 (Co-Mo/C) in both $k$ space.

### Table III: Structural Parameters for the Mo-C and Mo-Co Coordinations

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Shell</th>
<th>$N$</th>
<th>$R$, Å</th>
<th>$10^2 \Delta r^2$, Å$^2$</th>
<th>$\Delta E_0$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo/C</td>
<td>Mo-C</td>
<td>0.4 ± 0.1</td>
<td>2.05 ± 0.02</td>
<td>-3 ± 1.5</td>
<td>-2.4 ± 1</td>
</tr>
<tr>
<td>Co-Mo/C</td>
<td>Mo-C</td>
<td>0.6 ± 0.2</td>
<td>2.12 ± 0.05</td>
<td>-2 ± 1</td>
<td>-17 ± 5</td>
</tr>
<tr>
<td>Mo/Co</td>
<td>0.3 ± 0.2</td>
<td>2.8 ± 0.1</td>
<td>-0.5 ± 0.2</td>
<td>-12 ± 4</td>
<td></td>
</tr>
</tbody>
</table>

* The coordination number was estimated by taking into account an atomic overlap factor ($S_{ij}^2$) of 0.69 (value for Fe backscatterer$^{30}$) and a mean free path of 6 Å$^{-1}$ of the photoelectron. *Absolute Debye-Waller factor.

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EXAFS of Sulfided Mo/C and Co–Mo/C

and r space (imaginary and absolute Fourier transforms). From these figures it is obvious that the sum of the calculated EXAFS contributions agrees very well with the experimental data.

Since it is possible that an interaction of the Mo atoms and the carbon support might involve surface oxygen groups (activated carbon is known to contain a relatively high percentage of oxygen functional surface groups), we also tried to fit the difference EXAFS spectrum (at the low r value) with a Mo-O coordination, derived from the Na2MoO4·2H2O reference compound. Although it was indeed possible to fit this difference feature with an oxygen scatterer in both Mo/C and Co–Mo/C, the quality of the fit is less good than when a carbon scatterer is used. Also the inner-potential correction (E0) is much higher compared to the calculated Mo–O contribution, which makes a carbon scatterer more probable than an oxygen scatterer. In addition, it should be mentioned that a Mo–O interaction is not very likely, merely because oxygen surface groups can be expected to become easily sulfided during the presulfiding treatment.

The statistical significance of the contributions showing up in the difference spectra (see Figure 5) can be judged as follows. The average noise amplitude present in the raw data (Figure 1) can be determined for 18 < k < 20 Å⁻¹ and amounts approximately 0.3 × 10⁻³. Determining the EXAFS amplitude at k = 5 Å⁻¹ results in a S/N ratio for the main contribution (S and Mo) around 270 (Figure 1), while the S/N ratios in the difference file of Co/C (Figure 5a) and CoMo/C (Figure 5b) are still 10 and 24, respectively. The Fourier transforms of both difference files confirm the presence of one (Figure 5e) and two (Figure 5f) significant contributions, respectively.

Discussion

Structure of the Molybdenum Sulfide Phase. The coordination distances of the Mo–S and Mo–Mo shells are (within the limits of accuracy) equal to the corresponding distances in pure MoS₂, indicating the presence of MoS₂-like particles. Moreover, this outcome signifies that the supported MoS₂ particles do not show any anharmonic behavior, since this should lead to shorter distances. Hence, the experimental coordination numbers for the catalyst particles are reliable and do not have to be corrected for anharmonicity.

From the experimental Mo–Mo coordination numbers (N_{Mo-Mo} = 2.7 for Mo/C and 3.2 for Co–Mo/C), information can be obtained about the local ordering of Mo atoms in a MoS₂ single slab. Taking into account an inaccuracy of 20% in the coordination number, it can be inferred that in a single slab of the Mo/C catalyst, the local ordered structure consists of 4–6 Mo atoms.

This is shown in Figure 8, in which the theoretical Mo–Mo coordination numbers of a MoS₂ slab structure are calculated as a function of the number of Mo atoms. These values of 4–6 Mo atoms indicate an average local ordered structure of 10–13 Å. In the case of the sulfided Mo/C–Co/C catalyst, the experimental Mo–Mo coordination number points to a local ordered structure of 7–8 Mo atoms, corresponding to an average dimension of about 12–15 Å. The explanation for the slightly larger local ordered structure in the promoted catalyst might be related to the fact that the aqueous impregnation solution of cobalt nitrate used for the promotion contains approximately 0.3 Mo–S coordination, which makes a carbon scatterer more probable than an oxygen scatterer.

The local ordered structure as determined by EXAFS can provide information about the actual MoS₂ particle size. Although the small size of the local ordering (10–15 Å) suggests the presence of small particles, this does not have to be the case. For instance, if the sulfided catalysts consist of disorderly highly folded MoS₂ slabs, the local ordered structure in these slabs is small, but the overall slab size can be quite large. The existence of highly folded unsupported MoS₂ slabs was discovered and investigated by Chianelli et al. and Liang et al. However, several arguments exist which favor the presence of small crystallites of MoS₂ in our catalysts, instead of large highly folded slabs. The first argument is the detection with EXAFS of a Mo–C interaction in both catalysts with a coordination number of about 0.5. This indicates that a relatively large fraction of the Mo atoms have carbon neighboring atoms. If it is assumed that only the edge Mo atoms can have an interaction with carbon atoms, this Mo–C interaction can only be explained in terms of small MoS₂ crystallites, rather than in terms of large MoS₂ slabs. The second argument is the detection with EXAFS of a Mo–Co interaction in the promoted catalyst (Co–Mo/C) with a coordination number of about 3. If it is assumed that the Co atoms present in a “Co–Mo–S” phase are decorating the MoS₂ crystallite edges, this Mo–Co interaction in analogy with the Mo–C interaction points to the presence of small MoS₂ crystallites.

The third argument is based upon the work of van Veen et al. who used transmission electron microscopy (TEM) to study the structure of sulfided catalysts. TEM measurements of carbon- and alumina-supported Co–Mo catalysts which were presulfided at 623 K revealed the presence of “fuzzy spots” with dimensions of 7–15 Å. These values correspond closely to our EXAFS results for the local ordered structure. After presulfiding at 673 K (similar to what we have employed) TEM revealed the presence of stripes with lengths of about 25–50 Å. In this respect it is very striking that the properties of these catalysts (thiophene HDS activity, NO chemisorption capacity and Mössbauer spectroscopy) did not change when increasing the presulfiding temperature from 623 to 673 K, despite the increase in MoS₂ particle size as observed by TEM. The latter results might be explained by the fact that, after presulfiding at 673 K, the MoS₂ particles consist of a conglomeration of small MoS₂ entities (7–15 Å large). Our EXAFS results fit in with this explanation. Summarizing, although it is in principle impossible to discriminate between large highly folded Mo–Mo EXAFS contribution, we think that in our case several additional arguments point to the latter situation.

Information on the arrangement of the sulfur atoms can be obtained from the Mo–S coordination number (N_{Mo-S} = 5.2 for...
A further structural question which EXAFS might answer is if we are dealing with single layer or multilayer MoS2 slabs. Information on this might be obtained from the third Mo–Mo shell, which consists of a Mo–Mo coordination at 6.32 Å (directly aligned with the 3.16 Å first Mo–Mo shell) and a second Mo–Mo coordination at 6.41 Å, the latter from Mo backscattering in the adjacent MoS2 slabs. Since the 6.32 Å Mo–Mo coordination is directly associated with the 3.16 Å Mo–Mo shell, the contribution of the multilayer 6.41 Å Mo–Mo coordination can be estimated by comparing the intensity of the first (3.16 Å) Mo–Mo shell with that of the third Mo–Mo shell. A comparison has been made between the Mo/C catalyst and a sulfided Mo(8.1)Al2O3 catalyst on which a similar sulfidation and EXAFS measuring procedure has been applied. Essentially the same intensity ratio of the first and the third Mo–Mo shell was found to be present in both catalyst systems. Since, as was shown by Zmierczak et al.,26 a sulfided Mo/Al2O3 catalyst containing up to about 8 wt % Mo consists of a single thickest MoS2 layer (monolayered catalyst), our findings would indicate that the MoS2 phase dispersion in the sulfided Mo/C catalyst is also monolayer-like. However, this interpretation should be taken with caution, since the 6.32 Å Mo–Mo shell is subject to the focusing effect,14,37 as a result of which its backscattering amplitude will be much higher than usual. It is possible, therefore, that the amplitude contribution of the multilayer 6.41 Å Mo–Mo shell should be neglected with respect to the strong 6.32 Å Mo–Mo shell. In fact, theoretical calculations of Teo,27 using an oxygen scatterer in a linear focusing pathway, revealed an amplitude enhancement with a factor of 9. In that case the peak at about 6 Å cannot be used to measure layer stacking but only to measure lateral size. Further investigations of the phenomenon for a sulfided Mo/Al2O3 catalyst containing a high Mo loading (about 8 wt % Mo) would be of interest.

Our results, in general, can now be compared to literature data. EXAFS measurements on alumina-supported Mo and Co–Mo sulfide catalysts showed Mo–S and Mo–Mo coordination distances almost equal to those in pure MoS2.12,13 Similar to what we find for the carbon-supported catalysts, this suggests that the crystalline structure of the MoS2-like particles in both catalyst systems is similar. Candida et al.1 reported a NMo-Mo value of 3.1 for both a Mo(8.6)/Al2O3 and a Co–Mo/Al2O3 (8.6 wt % Mo, Co/Mo = 0.3 atom/atom) catalyst, which is slightly larger than our value of 2.7 for Mo(7.0%)/C. Sankar et al.18, who studied a sulfided Co–Mo/Al2O3 (Co/Mo = 0.33 atom/atom) catalyst, mentioned a NMo-Mo value of 4.0, which is clearly larger than our value. These literature data indicate that sulfided (Co–)Mo/Al2O3 catalysts might have about the same or slightly larger local ordered structure of the MoS2 slabs than the carbon-supported systems.

Molybdenum Sulfide–Support Interaction. Fitting of the experimental data in the r range 1.0–3.2 Å with S and Mo backscattering elements only resulted in small differences which were impossible to fit with either S or Mo neighbors. Since the signal-to-noise ratio is very high, it is unlikely that these differences are caused by noise contributions. Therefore, the presence of other elements has to be taken into account. The good quality fit of the difference spectrum obtained by using the well-defined Mo(CO)6 reference compound indeed indicates the presence of another element, namely carbon. The fact that the EXAFS spectrum of the Co–Mo/C catalyst exhibits a second slight deviation which is clearly not present in the unpromoted catalyst strongly points to the presence of a Co backscatterer.

As can be seen in Table III, the Mo–C coordination distance is calculated to be 2.05 Å for Mo/C and 2.12 Å for Co–Mo/C. The inner-potential correction of this coordination in the case of the promoted catalyst is larger, possibly because of a spectral overlap between the Mo–C and the Mo–Co EXAFS contributions which complicates the fitting procedure. The Mo–C coordination numbers are both below 1 as is to be expected from their very small spectral contributions. If we use an average Mo–C coordination distance of 2.1 Å, a model can be proposed for the

interface between the MoS\(_2\) particles and the carbon support. The Mo–C interaction is probably restricted to the exposed Mo atoms, because in this conformation a carbon atom of the support layer can take the place of a sulfur vacancy. Furthermore, since the structure of the active carbon substrate is graphitelike, the active interface between the MoS\(_2\) particles and the carbon support. The graphite structure which contains carbon atoms having free electron pairs. The carbon atom would imply a Mo-C interatomic distance of 0.71 Å. In crystalline MoS\(_2\), the atomic radius of the sulfur atoms was calculated to be 1.58 Å. Assuming a close contact between molybdenum and sulfur, the sulfur radius of the Mo atoms will then be 2.41–1.58 = 0.83 Å. A close contact between the Mo and a carbon atom would imply a Mo-C interatomic distance of 0.71 + 0.83 = 1.54 Å, which is quite small compared to the calculated value of 2.1 Å. On the other hand, a carbon atom with a free electron pair might have an atomic radius larger than 0.71 Å.

Applying the concepts above, a Mo–C coordination is more likely. It may also be clear that the high HDS activity of carbon-supported molybdenum sulfide catalysts compared to their alumina-supported counterparts suggests that the active-phase-support interaction for the carbon-supported catalysts is not weaker than that of the alumina-supported systems. In this respect, it should be noted that oxygen instead of carbon as neighboring element in the Mo/C and Co–Mo/C catalysts cannot be excluded. This would mean that the active-phase-support interaction might be exerted through Mo–O–C linkages. On the other hand, judged from the quality of XAFS, a Mo–C coordination is more likely.

The coordination number is probably smaller than 1, in accordance with its small spectral contribution. Our study is the first to provide evidence for the Mo promoter in the literature, several XAFS studies at the Co K-edge of sulfided Co–Mo/Al\(_2\)O\(_3\) catalysts have been reported but only a few reports gave indications of Co neighbors next to the Mo ions. Chiu and Bauer, who studied sulfided Co–Mo/Al\(_2\)O\(_3\) catalysts with different Co/Mo atomic ratios, observed a persistent small peak at about 2.9 Å and suggested that this peak might be ascribed to Co–Mo scattering. Bommannavar and Montano reported a Ni–Mo coordination distance of 2.95 Å in a sulfided Ni–Mo/Al\(_2\)O\(_3\) catalyst; however, their study was not in situ. Clausen et al. and Topsøe et al. who studied a sulfided Co–Mo/Al\(_2\)O\(_3\) catalyst containing about 90% of Co ions present in the Co–Mo–S phase, observed one strong Co–S backscatterer peak at a coordination distance of 2.23 Å. No indications of Co–Mo backscattering were found, possibly because of the low signal-to-noise ratio of their XAFS data. Sankar et al. mentioned for the same kind of catalyst a Co–S coordination distance of 2.33 Å. Finally, it is interesting to note that the Mo–Co coordination distance of 2.8 Å corresponds quite well to that in known Co(MoS\(_2\))\(_3\), organometallic complexes, prepared and studied by Muller et al. In such complexes the Mo–Co distance is typical 2.75 Å.

Although, as outlined above, it is not clear whether the MoS\(_2\) phase present in the sulfided Co–Mo/C catalysts is essentially composed of single slabs or multilayer units, it is still interesting to compare the Mo EXAFS results with the MoS\(_2\) crystal edge structures proposed by Voorhoeve and Stuiver and Farragher and Cossee. Let alone the other structural requirements that have to be fulfilled, the Mo–Co distance of 2–3 Å fits with a structure in which the Co atom is positioned 1.27 Å above a Mo-containing trigonal prism. However, a Mo–Co distance of 2.8 Å is too short to fit the structural model proposed by Farragher and Cossee in which Co is positioned above an empty trigonal prism next to a Mo-containing prism.

According to the model of Ratnasamy and Sivasanker and Topsøe, the Co atoms are all situated at MoS\(_2\) crystallite edges and in the same plane as the Mo atoms. Using the latter model, two possible locations of Co, coordinated with fully sulfur surrounding Mo atoms at a Co–Mo distance of 2.8 Å, can be considered, as is shown in Figure 10. In position a one Co atom is coordinated with two Mo atoms at equal distances to the four neighboring sulfur atoms. The Co–S coordination distance in this position can be calculated to be in the range 2.27–2.32 Å, taking into account the inaccuracy of 0.8 ± 0.1 Å of the Mo–Co coordination distance. This calculated Co–S distance is in good agreement with the literature data of Topsøe et al. and Sankar et al. 2.23 and 2.33 Å, respectively. In position b one Co atom is in contact with one Mo atom. In this position, the Co–S coordination distance is difficult to calculate since there is one degree of freedom more than in position a. On the other hand, it can be expected that the Co–S distance in both positions will not differ much. EXAFS measurements at the Co K-edge of a fully sulfided Co–Mo/C catalyst containing only a Co–Mo–S type of phase revealed that approximately two Co atoms are in contact with one Mo atom. Hence, this one-to-two coordination of Co–Mo

![Figure 10](image_url) Figure 10. Possible locations of the Co promoter atom in contact with the MoS\(_2\) crystallite edges. The extra sulfur atoms surrounding the Co promoter atom are not included. For symbols see Figure 9.
to-Mo points to position a instead of b.

It should be noticed that the local surrounding of the Co atoms, as is shown in Figure 10, is incomplete, since the Co atom is expected to be coordinated to more than 2 (or 4, respectively) sulfur atoms. In fact, the Co atom in the sulfided Co-Mo/C catalyst appears to be coordinated by at least five sulfur atoms, extra sulfur atoms surrounding the Co promoter atom are not sulfur atoms. In fact, the Co atom in the sulfided Co-Mo/C expected to be coordinated to more than 2 (or 4, respectively) as is shown in Figure 10, in this respect, is restricted to the local surrounding of the Mo atom, in which the extra sulfur atoms surrounding the Co promoter atom are not included.

Conclusions

Detailed information regarding the structure of the sulfide particles in carbon-supported Mo and Co-Mo sulfide catalysts have been obtained.

1. The catalysts probably consist of very small MoS\textsubscript{2} particles which contain on average 5–6 Mo ions (Mo/C) and 7–8 Mo ions (Co–Mo/C), respectively. Comparison with literature data shows that the average local ordered structure in these carbon-supported catalysts is very much the same as their alumina-supported counterparts.

2. A detailed EXAFS data analysis shows the presence of carbon neighbors next to the Mo atoms at a distance of 2.1 ± 0.1 Å. This short distance could imply an intimate interaction between the active phase and the carbon support, which may be the cause of the high dispersion of the active phase. From the value of 2.1 Å it can be inferred that the Mo–Co coordination is restricted to the exposed Mo atoms and that a support carbon atom takes the place of a sulfur vacancy.

3. The EXAFS spectra show evidence for the existence of cobalt neighbors next to the Mo atoms at a distance of 2.8 ± 0.1 Å.

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Crystal Structure of Silica–ZSM-12 by the Combined Use of High-Resolution Solid-State MAS NMR Spectroscopy and Synchrotron X-ray Powder Diffraction

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The crystal structure of the synthetic zeolite silica–ZSM-12, 56 SiO\textsubscript{2}, has been solved by the combined use of high-resolution solid-state MAS NMR spectroscopy and high-resolution synchrotron X-ray powder diffraction. ZSM-12 crystallizes in the monoclinic space group C\textsubscript{2v}/c with a\textsubscript{0} = 24.863 Å, b\textsubscript{0} = 5.012 Å, c\textsubscript{0} = 24.328 Å, and β = 107.7°. The zeolite host structure is built from corner-linked SiO\textsubscript{4} tetrahedra to give a three-dimensional 4-connected net. The pores of the structure are one-dimensional channels that do not intersect, with 12-membered ring pore openings of approximately 5.6 × 7.7 Å. The structure of ZSM-12 is frequently twinned with (100) as the twin plane, which indicates a new zeolite structure type.

Introduction

High-silica zeolites have attracted much attention due to their unique properties in catalysis\textsuperscript{1} and as molecular sieves\textsuperscript{2} and more recently as potential host structures for quantum-size particles, etc. Since it is the crystal structure, or more precisely the topology of the silica host framework, that determines the properties of these systems, it is therefore essential to have precise information available on both the local and long-range order of zeolite structures.

ZSM-12 is a high-silica zeolite first synthesized by Rosinski and Rubin.\textsuperscript{4} LaPierre et al. proposed the host framework topology from electron and X-ray powder diffraction data combined with model building.\textsuperscript{3} We report here on the first crystal structure refinement of silica–ZSM-12, where the structural investigations have been carried out by use of a combination of two different techniques, high-resolution solid-state NMR and synchrotron X-ray powder diffraction. These are sensitive to short- and long-range order, respectively, and are therefore complementary in nature for the characterization of solid-state structures. Only with a combination of the two techniques was it possible to arrive at a complete description of the structure that involves a subtle pseudosymmetry problem not recognized in previous structural studies.

Experimental Section

Synthesis. Highly crystalline ZSM-12 was obtained by hydrothermal synthesis\textsuperscript{5} and dealuminated by steaming the sample at elevated temperatures.\textsuperscript{6} The same material was used for both the NMR and XRD investigations. Single crystals of silica–ZSM-12 were synthesized in sealed silica tubes at 200 °C from 1 M aqueous solutions of silicic acid in the presence of 4,4′-trimethylene dipiperidine as template.

NMR Experiments. 29Si NMR spectra were recorded with a Bruker MSL-400 spectrometer at 79.6 MHz (proton frequency

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