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

S. M. A. M. Bouwens, R. Prins,† V. H. J. de Beer, and D. C. Koningsberger*

Laboratory for Inorganic Chemistry and Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands *(Received: July 6, 1988; In Final Form: November 1, 1989)*

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 (γ-Al_2O_3) carrier. Previous laboratory studies[1-4] 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 systems. The exact reasons for this improved activity are unclear.

Vissers et al.[3] studied the differences of carbon- and alumina-supported molybdenum sulfide catalysts by combined dynamic oxygen chemisorption (DOC), X-Ray photoelectron spectroscopy (XPS), and thiophene hydrodesulfurization (HDS) measurements. Their main conclusion was that carbon-supported molybdenum sulfide catalysts (especially at low Mo contents) possessed a higher fraction of catalytically active surface area, as well as a higher HDS activity per active site than the alumina-supported systems. To explain these structural differences, the authors referred to the inert character of the carbon carrier. Furthermore, by using 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, Topsøe 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 oservation that carbon carriers have unique properties is also apparent from the work of Vissers et al.[8] on carbon-supported cobalt sulfide catalysts. In this work the authors reported that the thiophene HDS activities of sulfided Co/C catalysts were about 2–3 times higher than that of sulfided Mo/C. In fact, based on these high activities, it is suggested that in sulfided Co–Mo catalysts the cobalt atoms might very well be the active phase instead of the promoter. Very recently, the influence of the support (alumina and carbon) on the activity of a fully sulfided Co–Mo–S (type II) phase has been investigated.[9] From this work it appeared that, although the Co–Mo–S active phase dispersion in both the alumina- and carbon-supported catalysts is similar, the specific 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 these 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.
† Present address: Technisch-Chemisches Laboratorium, ETH-Zentrum, 8092 Zürich, Switzerland.

(1) de Beer, V. H. J.; Duchet, J. C.; Prins, R. *J. Catal.* **1981**, *72*, 369.
(2) Duchet, J. C.; van Oers, E. M.; de Beer, V. H. J.; Prins, R. *J. Catal.* **1983**, *80*, 386.
(3) Vissers, J. P. R.; Bachelier, J.; ten Doeschate, H. J. M.; Duchet, J. C.; de Beer, V. H. J.; Prins, R. In *Proceedings of the 8th International Congress on Catalysis, Berlin, 1984*; Verlag Chemie: Weinheim, 1984; p II-387.
(4) Topsøe, H. *Bull. Soc. Chim. Belg.* **1984**, *93*, 783.
(5) Vissers, J. P. R.; Scheffer, B.; de Beer, V. H. J.; Moulijn, J. A.; Prins, R. *J. Catal.* **1987**, *105*, 277.
(6) Topsøe, H.; Clausen, B. S. *Catal. Rev.-Sci. Eng.* **1984**, *26*, 395.
(7) Hayden, T. F.; Dumesic, J. A. *J. Catal.* **1987**, *105*, 299.
(8) Vissers, J. P. R.; de Beer, V. H. J.; Prins, R. *J. Chem. Soc., Faraday Trans 1* **1981**, *83*, 2145.
(9) van Veen, J. A. R.; Gerkema, E.; van der Kraan, A. M.; Knoester, A. *J. Chem. Soc., Chem. Commun.* **1987**, 1684.
(10) Clausen, B. S.; Lengeler, B.; Candia, R.; Als-Nielsen, J.; Topsøe, H. *Bull. Soc. Chim. Belg.* **1981**, *90*, 1249.
(11) Bauer, S. H.; Chiu, N.-S.; Johnson, M. F. L. *J. Phys. Chem.* **1986**, *90*, 4888.
(12) Candia, R.; Clausen, B. S.; Bartholdy, J.; Topsøe, N.-Y.; Lengeler, B.; and Topsøe, H. In *Proceedings of the 8th International Congress on Catalysis, Berlin, 1984*; Verlag Chemie: Weinheim, 1984; p II-375.
(13) Boudart, M.; Dalla Betta, R.; Foyer, K.; Loffler, D. G. *EXAFS and Near Edge Structure III*; Springer Proceedings in Physics 2; Hodgson, K. O., Hedman, B., Penner-Hahn, J. E., Eds.; Springer Verlag: Berlin, 1984; p 181.
(14) Parham, T. G.; Merrill, R. P. *J. Catal.* **1984**, *85*, 295.
(15) Bommannavar, A. S.; Montano, P. A. *Appl. Surf. Sci.* **1984**, *19*, 250.
(16) Kochubei, D. I.; Kozlov, M. A.; Zamaraev, K. I.; Burmistov, V. A.; Startsev, A. N.; Yermakov, Yu. I. *Appl. Catal.* **1985**, *14*, 1.
(17) Chiu, N.-S.; Bauer, S. H.; Johnson, M. F. L. *J. Catal.* **1986**, *98*, 32.
(18) Sankar, G.; Vasudevan, S.; Rao, C. N. R. *J. Phys. Chem.* **1987**, *91*, 2011.

0022-3654/90/2094-3711$02.50/0

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.[19,20] The first preliminary results of our EXAFS study on sulfided Mo/C and Co–Mo/C catalysts have already been published.[21] 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 $m^2 \cdot g^{-1}$; pore volume, 1.03 $cm^3 \cdot g^{-1}$). The catalysts were prepared by pore volume impregnation using aqueous solutions of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ (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 oxidic precusor catalyst was determined by means of atomic absorption spectroscopy using a Perkin-Elmer 3030 AAS spectrometer and was found to be Mo (7.0%)/C and Co (2.7%)–Mo (6.0%)/C (Co/Mo ratio is 0.7 atom/atom). The catalytic activity of the sulfided catalysts was determined by a thiophene HDS measurement at 673 K and atmospheric pressure. The thiophene HDS reaction rate constant k_{HDS} (approximated as a first-order reaction) was found to be 2.6×10^{-3} $m^3 \cdot kg^{-1} \cdot s^{-1}$ for Mo (7.0)/C and 25.7 $\times 10^{-3}$ $m^3 \cdot kg^{-1} \cdot s^{-1}$ for Co (2.7)–Mo (6.0)/C. For details on the activity test we refer to Vissers et al.[3]

The dried catalysts were pressed into self-supporting wafers and mounted in an EXAFS cell enabling in situ sulfiding. The thickness of the wafers was chosen to give an absorbance (μx) of about 2.5, assuring an optimum signal-to-noise ratio. The wafers were prepared by using a special carbon binder. The presence of the carbon binder did not significantly change the catalytic system since it was found to have no effect on the thiophene HDS properties of the catalysts. The sulfidation of the samples was carried out in a flow of 10% H_2S in H_2 (flow rate 60 $cm^3 \cdot min^{-1}$, atmospheric pressure) for 45 min, while increasing the temperature linearly from 293 to 673 K, followed by an extended sulfiding at 673 K for 2 h. After sulfiding, the samples were cooled to 293 K under flowing He within 30 min and the cell was evacuated and flushed again with He (two or three times) in order to remove all H_2S gas. The EXAFS spectra at the molybdenum K-edge were subsequently recorded with the sample at liquid nitrogen temperature and under He atmosphere.

The measurements were carried out at EXAFS station 9.2 at the Synchrotron Radiation Source (SRS) in Daresbury (United Kingdom). The storage ring was operated at 1.8–2.0 GeV, and the ring current was in the range of 100–250 mA.

Phase shifts and backscattering amplitudes from reference compounds were used to calculate the EXAFS contributions. For the Mo–S and Mo–Mo EXAFS signals MoS_2 (Janssen Pharmaceutica, minimum 99%) was used. For possible Mo–C or Mo–O contributions, $Mo(CO)_6$ and $Na_2MoO_4 \cdot 2H_2O$ (both Merck p.a.) were used, respectively. The purity of the reference compounds was checked by X-ray diffraction. Supporting wafers of the reference compounds with an absorbance of 1.5 were prepared by mixing them with an appropriate amount of Al_2O_3. EXAFS spectra of these compounds were also recorded at liquid nitrogen temperature under He atmosphere.

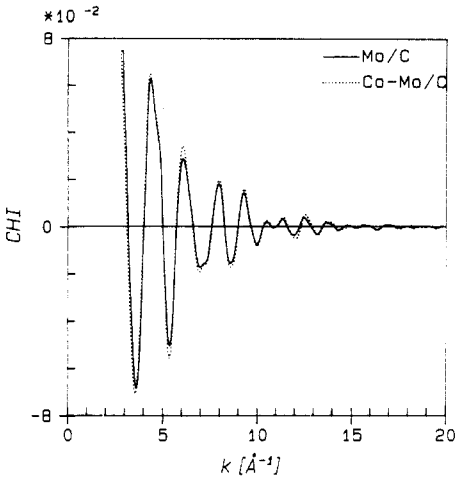

Figure 1. EXAFS spectra of Mo/C (solid line) and Co–Mo/C (dotted line).

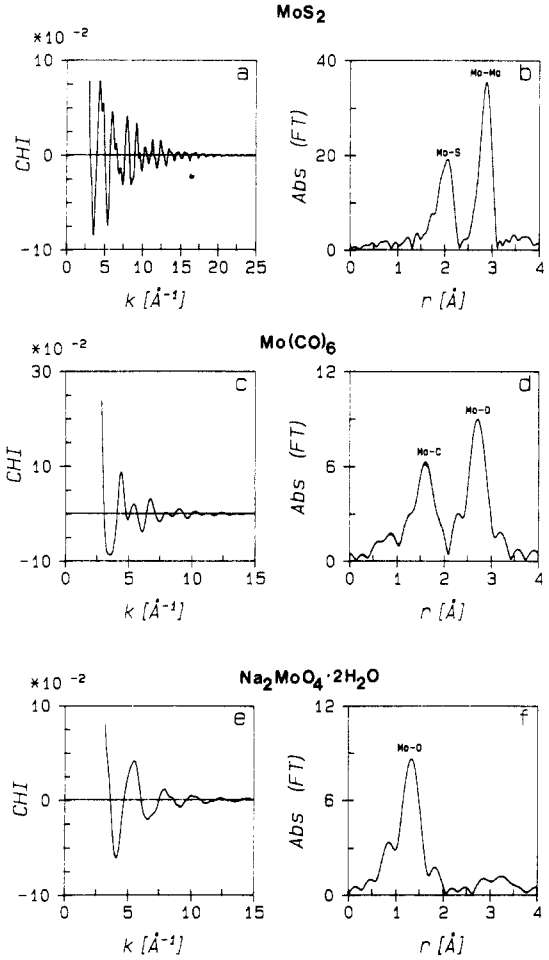

Figure 2. EXAFS spectra and Fourier transforms of the reference compounds: (a, b) MoS_2, (c, d) $Mo(CO)_6$, and (e, f) $Na_2MoO_4 \cdot 2H_2O$.

Results

The EXAFS oscillations in k space were obtained from the X-ray absorption spectra by substracting a victoreen curve, followed by a cubic spline background removal.[22] 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

(19) van Zon, J. B. A. D.; Koningsberger, D. C.; van't Blik, H. F. J.; Sayers, D. E. *J. Chem. Phys.* **1985**, *82*, 5742.
(20) Duivenvoorden, F. B. M.; Koningsberger, D. C.; Uh, Y. S.; Gates, B. C. *J. Am. Chem. Soc.* **1986**, *108*, 6254.
(21) Bouwens, S. M. A. M.; Koningsberger, D. C.; de Beer, V. H. J.; Prins, R. *Bull. Soc. Chim. Belg.* **1987**, *96*, 951.
(22) Cook, J. W.; Sayers, D. E. *J. Appl. Phys.* **1981**, *52*, 5024.
(23) Dickinson, R. G.; Pauling, L. *J. Am. Chem. Soc.* **1923**, *45*, 1466.
(24) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 3rd ed.; Wiley: New York, 1972; p 684.
(25) Matsumoto, K.; Kobayashi, A.; Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1009.

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

compound	type of coordn	R,[a] Å	N[b]	Fourier transform[c] k range, Å^{-1}	Fourier transform[c] r range, Å	ref
MoS_2	Mo–S	2.41	6	3.16–24.48	0.88–2.40	23
	Mo–Mo	3.16	6	3.16–24.48	2.40–3.22	23
$Mo(CO)_6$	Mo–C	2.06	6	3.07–13.36	0.00–2.10	24
$Na_2MoO_4{\cdot}2H_2O$	Mo–O	1.77	4	3.64–12.84	0.00–2.08	25

[a] Coordination distance. [b] Coordination number. [c] The weighting factor of the Fourier transform is in all cases 3.

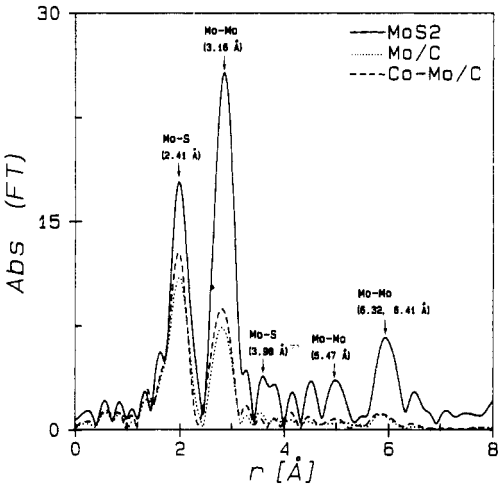

Figure 3. Magnitude of the k^3-weighted Fourier transforms (Δk = 3.2–16.0 Å^{-1}) of the MoS_2 reference compound (solid line), the Mo/C catalyst (dotted line), and the Co–Mo/C catalyst (dashed line).

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 (k^3, Δk = 3.2–16.0 Å^{-1}) of the catalysts together with the MoS_2 reference compound. As is obvious from this figure, the spectra of the Mo/C and Co–Mo/C catalysts exhibit identical features as the MoS_2 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 MoS_2 compound. This demonstrates that the sulfide structure in the catalysts is a MoS_2-like structure. The magnitude of the Mo–S shell in the catalysts is smaller than that of MoS_2, while the Mo–Mo shell is much smaller. Furthermore, the higher shells in the catalysts are much weaker than those of MoS_2. 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 r range: 1.0–3.2 Å (after Fourier transformation: (k^3, 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 MoS_2 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

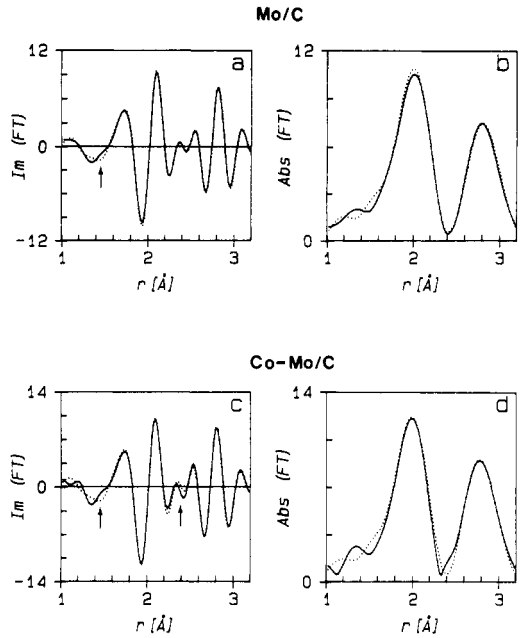

Figure 4. Imaginary and absolute Fourier transforms (k^3, Δk = 4.0–15.0 Å^{-1}) of the experimental (isolated) EXAFS (solid line) and the calculated Mo–S and Mo–Mo shells (dotted line) of the Mo/C catalyst (a, b) and the Co–Mo/C catalyst (c, d). The arrows indicate the deviations between the calculated EXAFS and the experimental EXAFS spectra.

TABLE II: Structural Parameters for the Mo–S and Mo–Mo Coordinations

catalyst	shell	N	R, Å	$10^3\Delta\sigma^2$,[a] Å^2	ΔE_0,[b] eV
Mo/C	Mo–S	5.2 ± 0.5	2.41 ± 0.01	1.7 ± 0.4	1.9 ± 1
	Mo–Mo	2.7 ± 0.3	3.15 ± 0.01	1.7 ± 0.4	1.7 ± 1
Co–Mo/C	Mo–S	5.5 ± 0.5	2.40 ± 0.01	1.4 ± 0.4	4.3 ± 2
	Mo–Mo	3.2 ± 0.3	3.13 ± 0.01	1.7 ± 0.4	4.5 ± 2

[a] Debye–Waller factor. [b] Inner-potential correction.

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 k-weighting factor of 1 (to emphasize the low Z scatterers) as well as a k-weighting factor of 3 (to emphasize the high Z scatterers). The resulting parameters N, R, $\Delta\sigma^2$, and ΔE_0 of the Mo-S and Mo-Mo shells were subsequently optimized by comparing the Fourier transformations (k^1- and k^3-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 k^1 and k^3 fit in k space and k^1- and k^3-weighted Fourier transforms, respectively, a unique set of parameters is obtained for the Mo–S and Mo–Mo shells to be analyzed.[27] In Figure 4 the k^3-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. Concerning the deviation at about 2.4 Å (only in the promoted catalyst) one might think of an interaction of Mo with a Co

(26) van't Blik, H. F. J.; van Zon, J. B. A. D.; Huizinga, T.; Vis, J. C.; Koningsberger, D. C.; Prins, R. *J. Am. Chem. Soc.* **1985**, *107*, 3139.

(27) Kampers, F. W. H. Ph.D. Thesis, University of Technology, Eindhoven 1988.

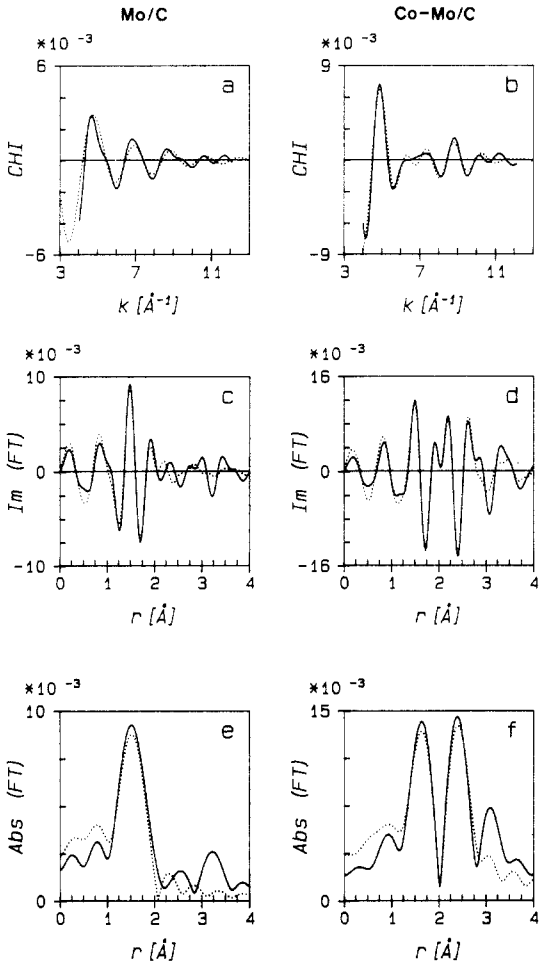

Figure 5. Difference EXAFS spectra of Mo/C and Co–Mo/C in k space (a, b) and in r space (k^1, Δk = 4.3–10.4 Å^{-1}) (imaginary part, c and d; and absolute part, e and f), represented by solid curves. The dotted curves represent the calculated Mo–C shell (in Mo/C) and the calculated Mo–C and Mo–Co shells (in Co–Mo/C).

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 (Δr = 1.0–3.2 Å; after Fourier transformation, k^3, Δk = 4.0–12.2 Å^{-1}). This shorter k range was chosen because of the smaller accuracy range of the $Mo(CO)_6$ 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

(28) Teo, B. K.; Lee, P. A. *J. Am. Chem. Soc.* **1979**, *101*, 2815.
(29) Lengeler, B. *J. Phys. C8*, **1986**, *47*, 75.

TABLE III: Structural Parameters for the Mo–C and Mo–Co Coordinations

catalyst	shell	N	R, Å	$10^3\Delta\sigma^2$, Å^2	ΔE_0, eV
Mo/C	Mo–C	0.4 ± 0.1	2.05 ± 0.03	−3 ± 1.5	−2.4 ± 1
Co–Mo/C	Mo–C	0.6 ± 0.2	2.12 ± 0.05	−2 ± 1	−17 ± 5
	Mo–Co	0.3 ± 0.2[a]	2.8 ± 0.1	−0.5 ± 0.2[b]	−12 ± 4

[a] The coordination number was estimated by taking into account an atomic overlap factor (S_0^2) of 0.69 (value for Fe backscatterer[50]) and a mean free path of 6 Å^{-1} of the photoelectron. [b] Absolute Debye–Waller factor.

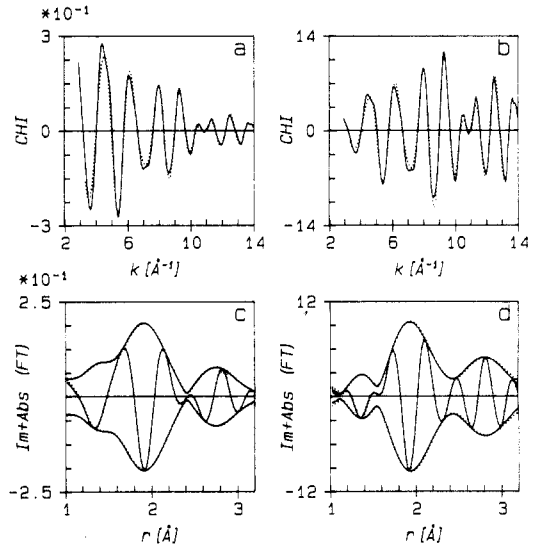

Figure 6. Comparison of the experimental (primary) EXAFS data (solid line) and the sum of the calculated Mo–S, Mo–Mo, Mo–C, and Mo–Co shells (dotted line) in the Mo/C catalyst: (a) $k^1\chi$; (b) $k^3\chi$, and Fourier transforms (imaginary and absolute part; Δk = 4.0–12.2 Å^{-1}); (c) k^1; (d) k^3.

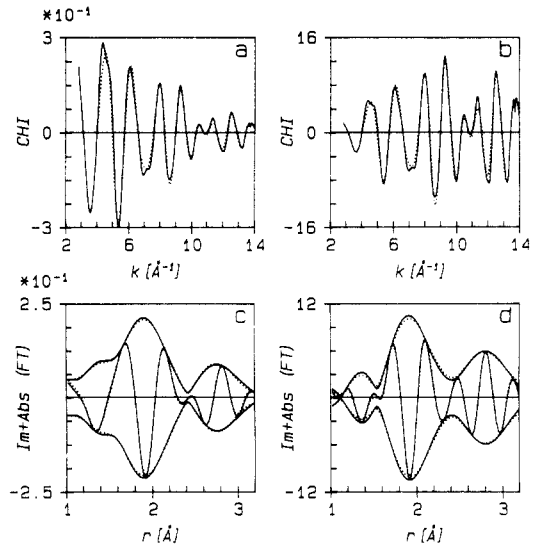

Figure 7. Comparison of the experimental (primary EXAFS data (solid line) and the sum of the calculated Mo–S, Mo–Mo, Mo–C, and Mo–Co shells (dotted lines) of the Co–Mo/C catalyst: (a) $k^1\chi$; (b) $k^3\chi$, and Fourier transforms (imaginary and absolute part; Δk = 4.0–12.2 Å^{-1}); (c) k^1; (d) k^3.

show that the calculated EXAFS reproduces the difference EXAFS quite well. The structural parameters (N, R, $\Delta\sigma^2$, and ΔE_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

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[30]), we also tried to fit the difference EXAFS spectrum (at the low r value) with a Mo–O coordination, derived from the $Na_2MoO_4.2H_2O$ 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 (E_0) is much higher compared to the calculated Mo–C 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 MoS_2, indicating the presence of MoS_2-like particles. Moreover, this outcome signifies that the supported MoS_2 particles do not show any anharmonic behavior, since this should lead to shorter distances.[31] 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 MoS_2 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 MoS_2 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 Co–Mo/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 preparation of Co–Mo/C is weakly acid. During this impregnation stage, the initially present molybdenum species will again dissolve and, due to the acidic nature of the solution, the heptamolybdate–monomolybdate equilibrium may shift to the heptamolybdate side,[32] leading to larger molybdenum species as the oxidic as well as in the sulfided catalyst.

The local ordered structure as determined by EXAFS can provide information about the actual MoS_2 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 disordered highly folded MoS_2 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 MoS_2 slabs was discovered and investigated by Chianelli et al.[33] and Liang et al.[34]

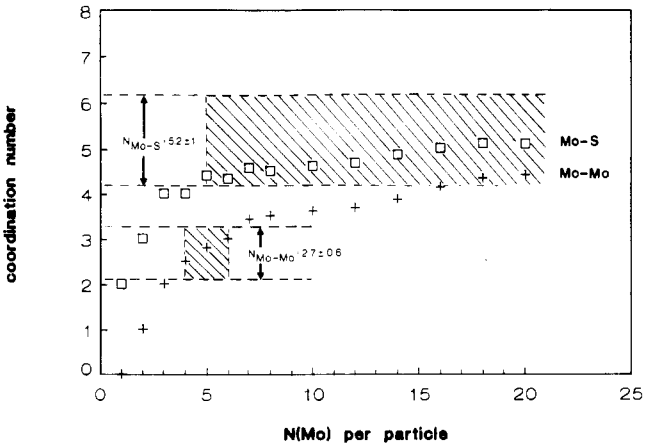

Figure 8. Theoretical Mo–S and Mo–Co coordination numbers ((□) N_{Mo-S}; (+) N_{Mo-Mo}) as a function of the total number of Mo atoms per particle. The Mo–S coordination numbers are calculated on the basis of a S-over-Mo atomic ratio of 2 and a stacked configuration of the sulfur atoms (see text for further comment). The shaded bands show the experimental values of the sulfided Mo/C catalyst (N_{Mo-S} = 5.2 ± 1 and N_{Mo-Mo} = 2.7 ± 0.6, respectively).

However, several arguments exist which favor the presence of small crystallites of MoS_2 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 MoS_2 crystallites, rather than in terms of large MoS_2 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 0.3. If it is assumed that the Co atoms present in a "Co–Mo–S" phase are decorating the MoS_2 crystallite edges,[4] this Mo–Co interaction in analogy with the Mo–C interaction points to the presence of small MoS_2 crystallites.

The third argument is based upon the work of van Veen et al.[9,35] 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 striae with lengths of about 25–50 Å.[35] 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 MoS_2 particle size as observed by TEM. The latter results might be explained by the fact that, after presulfiding at 673 K, the MoS_2 particles consist of a conglomeration of small MoS_2 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

(30) van Driel, J. In *Activated carbon... a fascinating material*; Capelle, A., de Vooys, F., Eds.; Norit N. V.; Amersfoort, The Netherlands, 1983; p 40.

(31) Crozier, E. D.; Rehr, J. J.; Ingalls, R. In *X-ray Absorption*, Koningsberger, D. C., Prins, R., Eds.; Wiley: New York, 1988; Chapter 9, p 373.

(32) Tsigdinos, G. A.; Chen, H. Y.; Streusand, B. J. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 619.

(33) Chianelli, R. R.; Prestridge, E. B.; Pecoraro, T. A.; De Neufville, J. P. *Science* **1979**, *203*, 1105.

(34) Liang, K. S.; Chianelli, R. R.; Chien, F. Z.; Moss, S. C. *J. Non-cryst. Solids* **1986**, *79*, 251.

(35) van Veen, J. A. R.; private communication.

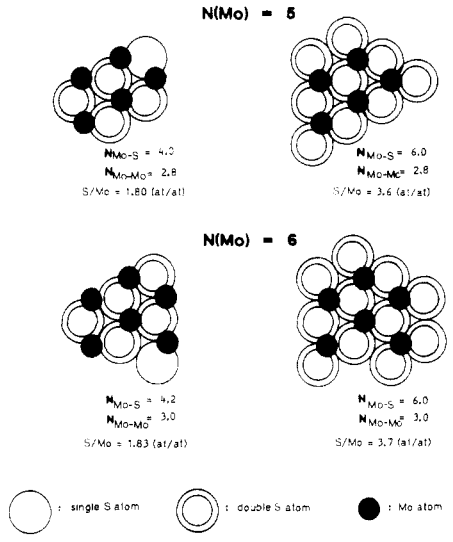

Figure 9. Models representing the average local ordered structure in a MoS_2 single slab of the sulfided Mo/C catalyst (containing 5 or 6 Mo atoms, respectively) as a function of the minimum and maximum values of the calculated Mo–S coordination number, viz., 4.2 and 6.0, respectively.

Mo/C and 5.5 for Co–Mo/C). These values are close to that in pure MoS_2 ($N_{Mo-S} = 6$), suggesting that the Mo atoms are to a large extent surrounded by sulfur atoms. To investigate the possible arrangement of the sulfur atoms in the MoS_2 particles, a model study has been carried out in which a molybdenum sulfide structure unit consisting of two sulfur atoms per molybdenum atom was built up by increasing the number of molybdenum atoms per particle. In this model, every additional molybdenum atom is accompanied by two sulfur atoms, such that the first is placed in the lower sulfur layer and the second one, stacked on the former, in the upper sulfur layer. The corresponding Mo–S coordination numbers as a function of the number of molybdenum atoms per particle can then be compared with the value obtained from the data analysis. The results of this procedure are shown in Figure 8, in which the experimental Mo–S coordination number of the Mo/C catlalyst, with an inaccuracy of 20% ($N_{Mo-S} = 5.1 \pm 1$), is also depicted. From this figure it is obvious that, on the basis of a Mo–S coordination number of 5.2, the MoS_2 stoichiometry (according to this model) is restricted to particles containing five or more Mo atoms.

Since the range of the allowed Mo–S coordination numbers is rather broad (because of the 20% inaccuracy), it is of interest to investigate the actual S to Mo stoichiometry as a function of the minimum and maximum values of the experimental Mo–S coordination numbers, viz., 4.2 and 6.2, respectively. In Figure 9 some models are depicted representing the average local ordered structure of the sulfided Mo/C catalyst (containing 5 or 6 Mo atoms, respectively) as a function of the experimental Mo–S coordination numbers. Since a value of 6.2 is unrealistic, a maximum value of 6.0 has been taken. It is apparent from Figure 9 that the actual S to Mo stoichiometry may range from 1.8 to 3.7. Although this lower limit agrees very well with literature data on sulfided Mo/C catalysts,[5] the presence of S to Mo atomic ratios higher than 2 cannot be excluded.

It should be noted that the above model is restricted to a specific morphology, in which the sulfur atoms are present in a stacked configuration. However, other types of morphology are also possible, like the arrangement of sulfur atoms preferentially in one of the two sulfur layers, or the presence of chainlike MoS_2 particles. With respect to the latter possibilities, the experimental Mo–S coordination number of 5.2 ± 1 would preferably point to S to Mo stoichiometries higher than 2.

Summarizing our results on the atomic sulfur arrangement, we may conclude that the sulfur stoichiometry in a single slab is difficult to establish due to the broad range in the experimental Mo–S coordination number, as well as its dependence on particle morphology.

A further structural question which EXAFS might answer is if we are dealing with single layer or multilayer MoS_2 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 backscatterers in the two adjacent MoS_2 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 $Mo(8.1)/Al_2O_3$ 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.,[36] a sulfided Mo/Al_2O_3 catalyst containing up to about 8 wt % Mo consists of a one slab thick MoS_2 layer (monolayered catalyst), our findings would indicate that the MoS_2 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,[37] 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 this phenomenon for a sulfided Mo/Al_2O_3 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 MoS_2,[12,13] similar to what we find for the carbon-supported catalysts. This suggests that the crystallite structure of the MoS_2-like particles in both catalyst systems is similar. Candia et al.[12] reported a N_{Mo-Mo} value of 3.1 for both a Mo $(8.6)/Al_2O_3$ and a Co–Mo/Al_2O_3 (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/Al_2O_3 (Co/Co + Mo = 0.33 atom/atom) catalyst, mentioned a N_{Mo-Mo} value of 4.0, which is clearly larger than our value. These literature data indicate that sulfided (Co–)Mo/Al_2O_3 catalysts might have about the same or slightly larger local ordered structure of the MoS_2 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 rather large, 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

(36) Zmierczak, W.; Quader, Q.; Massoth, F. E. *J. Catal.* **1987**, *106*, 65.
(37) Teo, B.-K., *J. Am. Chem. Soc.* **1981**, *103*, 3990.

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 phase-support interaction is likely to occur at the edges of the graphite structure which contain carbon atoms having free electron pairs. The carbon–carbon bond length in graphite is 1.42 Å,[38] and, hence, the atomic radius of carbon can be estimated to be 0.71 Å. In crystalline MoS_2 the atomic radius of the sulfur atoms was calculated to be 1.58 Å.[39] Assuming a close contact between molybdenum and sulfur, the atomic 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.

Approaching from the other end, the atomic radius of the carbon atoms in the Mo–C interface is 2.1–0.83 = 1.27 Å. This value is relatively close to that of the sulfur atom (1.58 Å) which, moreover, supports the idea of a carbon atom taking the place of a sulfur vacancy. Also it is important to realize that the Mo–C coordination distance of 2.1 Å corresponds closely to that in molybdenum carbide, Mo_2C: R_{Mo-C} = 2.00–2.22 Å.[40] This observation is interesting, since transition-metal carbides are reported to have unique physical properties such as metallike thermal and electronic conductivities[41] and a good initial HDS activity.[42]

Our findings shed a new light on the so-called inertness of a carbon carrier. On the other hand, they agree with the work of Hayden et al.[7] who concluded from HRTEM measurements that some kind of interaction might exist between the MoS_2 phase and a graphite carbon support. Furthermore, the fact that the local ordered structure of the MoS_2 slabs in Mo/C and Co–Mo/C is similar or even smaller compared to that of the 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 the fit, 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 cannot be explained in terms of dispersion differences, since the local ordered structure of the MoS_2 slabs, as deduced from the EXAFS results, is not much different. Our results are corroborated by TEM measurements on sulfided carbon- and alumina-supported Co–Mo catalysts with nearly the same amounts of Co and Mo: in both catalysts similar-sized particles appeared to be present.[9] This suggests that the HDS activity differences should primarily be explained in terms of an electronic effect. The Mo–C interaction possibly leads to more electron donation to the Mo atoms (e.g., by the free electron pairs of the carbon edge atoms), compared to the Mo–O–Al linkages in sulfided Mo/Al_2O_3 catalysts.

Mo–Co Coordination. For the expected Mo–Co coordination, theoretically determined phase shifts and backscattering amplitudes according to Teo and Lee[28] were used which in general yield reasonable accurate coordination distances. The coordination distance is calculated to be 2.8 ± 0.1 Å. The coordination numbers are less accurate (±50%). The coordination number is probably smaller than 1, in accordance with its small spectral contribution.

Our study is the first to provide in situ information on the exact location of the Co promoter. In the literature, several EXAFS studies at the Co K-edge of sulfided $Co–Mo/Al_2O_3$ catalysts have been reported but only a few reports gave indications of Co neighbors next to the Mo ions. Chiu and Bauer,[11] who studied sulfided $Co–Mo/Al_2O_3$ catlysts 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[15] reported a Ni–Mo coordination distance of 2.95 Å in a sulfided $Ni–Mo/Al_2O_3$ catalyst; however, their study was not in situ. Clausen et al.[10] and Topsøe et al.,[43] who studied a sulfided $Co–Mo/Al_2O_3$ 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.[43] No indications of Co–Mo backscattering were found, possibly because of the low signal-to-noise ratio of their EXAFS data. Sankar et al.[18] 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 $Co(MoS_4)_2^{3-}$ organometallic complexes, prepared and studied by Muller et al.[44] In such complexes the Mo–Co distance is typical 2.75 Å.

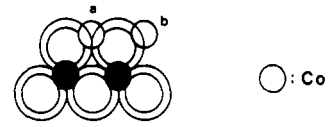

Figure 10. Possible locations of the Co promoter atom in contact with the MoS_2 crystallite edges. The extra sulfur atoms surrounding the Co promoter atom are not included. For symbols see Figure 9.

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[45] and Farragher and Cossee.[46] Let alone the other structural requirements that have to be fulfilled, the Mo–Co distance of 2–8 Å fits with a structure in which the Co atom is positioned 1.27 Å above a Mo-containing trigonal prison. 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.[46]

According to the model of Ratnasamy and Sivasanker[47] and Topsøe,[4] 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 surrounded Mo atoms at a Mo–Co 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 2.8 ± 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.[43] and Sanker et al.,[18] 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[48] revealed that approximately two Co atoms are in contact with one Mo atom. Hence, this one-to-two coordination of Co-

(38) *CRC Handbook of Chemistry and Physics*, 59th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1978–1979; p F-215.
(39) Bell, R. E.; Herbert, R. E. *J. Am. Chem. Soc.* **1957**, *79*, 3351.
(40) Christensen, A. N. *J. Am. Chem. Soc.* **1979**, *101*, 2815.
(41) Kojima, I.; Miyazaki, E. *J. Catal.* **1984**, *89*, 168.
(42) Lee, J. S.; Boudart, M. *Appl. Catal.* **1985**, *19*, 207.
(43) Topsøe, H.; Müller, A.; Clausen, B. S.; Topsøe, N.-Y.; Pedersen, E.; Bögge, H.; Lengeler, B.; Niemann, W. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 2157.
(44) Müller, A.; Jostes, R.; Hellman, W.; Romer, C.; Bögge, H.; Schimanski, U. *Z. Anorg. Allg. Chem.* **1986**, *533*, 125.
(45) Voorhoeve, R. J. H.; Stuiver, J. C. M. *J. Catal.* **1971**, *23*, 243.
(46) Farragher, A. L.; Cossee, P. *Proceedings of the 5th International Congress on Catalysis, Palm Beach, 1972*; North Holland: Amsterdam, 1973; p 1301.
(47) Ratnasamy, P.; Sivasanker, S. *Catal. Rev.-Sci. Eng.* **1980**, *22*, 401.
(48) Bouwens, S. M. A. M.; van Veen, J. A. R.; Koningsberger, D. C.; de Beer, V. H. J.; Prins, R., to be published.

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, as we have recently reported.[49] 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_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–C 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.

Acknowledgment. We acknowledge the technical assistance of the SRS staff and the design of the H_2S resistant in situ EXAFS cell by Dr. F. W. H. Kampers. The information included in this paper is partly derived from a contract (EN3V-0009/NL) concluded with the European Economic Community. This study was supported by the Netherlands Organization for Scientific Research (NWO).

Registry No. Co, 7440-48-4; MoS_2, 1317-33-5; C, 7440-44-0.

(49) Bouwens, S. M. A. M.; Koningsberger, D. C.; de Beer, V. H. J.; Prins, R. *Catal. Lett.* **1988**, *1*, 55.

(50) Stern, E. A. In *X-Ray Absorption, Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES*; Koningsberger, D. C., and Prins, R., Eds.; Wiley: New York, 1988; p 40.

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

C. A. Fyfe,*,† H. Gies,*,‡ G. T. Kokotailo,† B. Marler,‡ and D. E. Cox§

Department of Chemistry, UBC Vancouver, Vancouver, British Columbia, Canada, Mineralogisches Institut der CAU, 23 Kiel, FRG, and Brookhaven National Laboratory, Upton, New York 11973 *(Received: July 13, 1989; In Final Form: November 15, 1989)*

The crystal structure of the synthetic zeolite silica–ZSM-12, 56 SiO_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 $C2/c$ with a_0 = 24.863 Å, b_0 = 5.012 Å, c_0 = 24.328 Å, and β = 107.7°. The zeolite host structure is built from corner-linked SiO_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[1] and as molecular sieves[2] and more recently as potential host structures for quantum-size particles, quantum dots, etc.[3] 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.[4] LaPierre et al. proposed the host framework topology from electron and X-ray powder diffraction data combined with model building.[5] 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[6] and dealuminated by steaming the sample at elevated temperatures.[7] 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′-trimethylenedipiperidine as template.

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

† UBC Vancouver.
‡ Mineralogisches Institut der CAU.
§ Brookhaven National Laboratory.

(1) Hölderrich, W.; Hesse, M.; Näumann, F. *Angew. Chem.* **1988**, *100*, 232.

(2) Barrer, R. M. *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*; Academic Press: London, 1978.

(3) Ozin, G. A.; Kuperman, A.; Stein, A. *Angew. Chem.* **1989**, *100*, 373.

(4) Rosinski, E. J.; Rubin, M. K. US Patent 3832449, 1974.

(5) LaPierre, R. B.; Rohrman, A. C.; Schlenker, J. L.; Wood, J. D.; Rubin, M. K.; Rohrbaugh, W. J. *Zeolites* **1985**, *5*, 346.

(6) Fyfe, C. A.; Strobl, H.; Kokotailo, G. T.; Pasztor, C. T.; Barlow, G. E.; Bradley, S. *Zeolites* **1988**, *8*, 132.

(7) Fyfe, C. A.; Gobbi, G. C.; Kennedy, G. J. *J. Phys. Chem.* **1984**, *88*, 3248.

0022-3654/90/2094-3718$02.50/0