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AN EXAFS STUDY ON CARBON-SUPPORTED MO AND Co-Mo SULFIDE
HYDRODESULFURIZATION CATALYSTS

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ABSTRACT

The structure and dispersion of the active phase present in sulfided Mo/C and Co-Mo/C catalysts are studied by means of Mo K-edge EXAFS. EXAFS measurements were carried out at liquid N₂ temperature on freshly sulfided catalysts in situ. Due to a high signal-to-noise ratio of the experimental data, detailed information about the structural parameters of the active phase can be obtained. The Mo/C and Co-Mo/C catalysts consist of very small MoS₂-like particles, which contain on average 5 to 6 Mo ions (Mo/C), and 7 to 8 Mo ions (Co-Mo/C). There are indications for the presence of a Mo-C interaction in Mo/C and Co-Mo/C. The Mo-C coordination distance is estimated to be 1.9 ± 0.1 Å. There are also indications for the presence of a Mo-Co interaction. The Mo-Co coordination distance was estimated to be 2.8 ± 0.1 Å.

INTRODUCTION

Commercial hydrotreating catalysts usually consist of alumina-supported molybdenum sulfide, promoted with Co or Ni ions. Use of carbon instead of alumina as the carrier material results in improved catalytic activity for hydrodesulfurization (HDS), as demonstrated in the work of Duchet et al. (1), on carbon-supported Mo, W, Co, Ni, Co-Mo and Ni-W catalysts. In later work, Vissers et al. explained the higher activity of Mo/C compared to Mo/Al₂O₃ by differences in the structure of the sulfide phases present, and in the interaction between these phases and the support (2). In this respect, the inert character of the carbon carrier has often been used as an explanation for the higher HDS-activities, because of the expected weaker interaction of the sulfides with the carrier. However, the exact causes for the improvement in HDS activity have not been found at present.

In the case of promoted catalysts, the role of the promoter Co and Ni ions is a subject of great interest. It has been demonstrated that the catalytic activity is related to the Co(Ni) ions, which are situated at MoS₂ crystallite edges (3-5) in typical structures called "Co-Mo-S" phases.

By using Mössbauer emission spectroscopy (MES), Topsøe and coworkers clearly demonstrated that the HDS activity is closely related to the presence of this distinct Co-Mo-S phase (4). It is, however, not understood why the sites associated with these promoter atoms and neighbouring Mo atoms should be much more active than Mo-edge sites alone (4-6). Whether the catalysis is solely determined by the promoter edge atoms as was suggested in the work of Vissers et al. in a study on carbon-supported Co- and Co-Mo catalysts (7), is a subject of present study.

In that study it was suggested that Co sulfide acts as a catalyst instead of as a promoter. In that case the MoS₂ phase should merely be regarded as the

carrier material for the Co sulfide.

One of the main reasons for the confusion about the role of the Co promoter is the fact that the local structure of the Co-Mo-S phase is still unknown. In order to shed more light on the structure and dispersion of the carbon-supported sulfide phases, we have studied Extended X-Ray Absorption Fine Structure (EXAFS) Mo K-spectra to determine the dispersion of the molybdenum sulfide particles in both the unpromoted Mo/C and the Co-promoted catalyst. Since the EXAFS technique provides direct information on the local structure of the Mo atoms, we have also looked for information about the interface between the Mo sulfide particles and the surface of the support. Furthermore, we studied the local structure of Mo in the promoted Co-Mo/C catalyst, in order to gain information about the Co-Mo-S phase. EXAFS studies have already been carried out on several alumina- and silica-supported hydrotreating catalysts (8-15), However, to our knowledge, EXAFS has not been used to study carbon-supported hydrotreating catalysts.

EXPERIMENTAL

Catalysts preparation

The catalysts were prepared by pore volume impregnation of a Norit activated carbon (RX3 extra, surface area $1190 \text{ m}^2 \cdot \text{g}^{-1}$, pore volume $1.03 \text{ cm}^3 \cdot \text{g}^{-1}$) with aqueous solutions of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Merck p.a.) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck p.a.) respectively.

In the case of the promoted Co-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 further heat treatment or calcination was applied.

The metal content (wt%) of the oxidic precursor catalysts 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). The catalytic activity was checked by a thiophene HDS measurement at atmospheric pressure.

EXAFS measurements

The experiments 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 or 2.0 GeV, the ring current was in the range of 100-300 mA.

The oxidic samples were pressed into self supporting wafers.

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 impregnating the catalysts with an aqueous solution of a carbon binder (5 wt%), and pressing the wet catalyst samples in a stainless steel die. They were subsequently dried in static air at 383 K for 16 h. The presence of the carbon binder did not significantly change the thiophene HDS properties of the catalysts. The wafers were mounted in an EXAFS cell enabling in situ sulfiding and measurements in different gas atmospheres. The samples were sulfided in a flow of 10 vol % H_2S in H_2 (flow rate $60 \text{ cm}^3 \cdot \text{min}^{-1}$; atmospheric pressure) for 45 min, while increasing the temperature linearly from 293 K to 673 K, followed by an extended sulfiding at 673 K for 2 h.

After sulfiding, the samples were cooled to room temperature under flowing He for 30 min. At room temperature the cell was evacuated and flushed again with He (two or three times). The EXAFS spectra of the molybdenum K-edge were subsequently recorded with the sample at liquid nitrogen temperature and under He atmosphere.

The phase shift and backscattering amplitude from MoS_2 (Janssen Pharmaceutica, min. 99%) as reference compound were used to calculate Mo-S and Mo-Mo EXAFS contributions. The purity of the MoS_2 compound was checked by X-Ray diffraction. For MoS_2 a supporting wafer with an absorbance of 2.5 was prepared by mixing MoS_2 with an appropriate amount of Al_2O_3 .

EXAFS spectra of MoS_2 were also recorded at liquid nitrogen temperature under a He atmosphere.

RESULTS

The EXAFS functions ($X(k)$) were obtained from the X-Ray absorption spectra by subtracting a Victoreen curve, followed by a cubic spline background removal (16). Normalisation was performed by division of the edge height. In Figure 1, the resulting EXAFS functions of the Mo/C and the Co-Mo/C catalysts are represented. As can be judged from Figure 1, the signal-to-noise ratio is very good: about 240 to 1. Figure 2 shows the magnitude of the k^3 -weighed Fourier transform from $k_{\min} = 4.0$ to $k_{\max} = 16.0 \text{ \AA}^{-1}$ of the catalysts and the MoS_2 reference compound. The integration limits are chosen in nodes of the EXAFS function to avoid cut-off effects. A k^3 -weighed Fourier transform was chosen to emphasize the high k -value part of the EXAFS-spectrum, thereby strongly enhancing the Mo-Mo contribution.

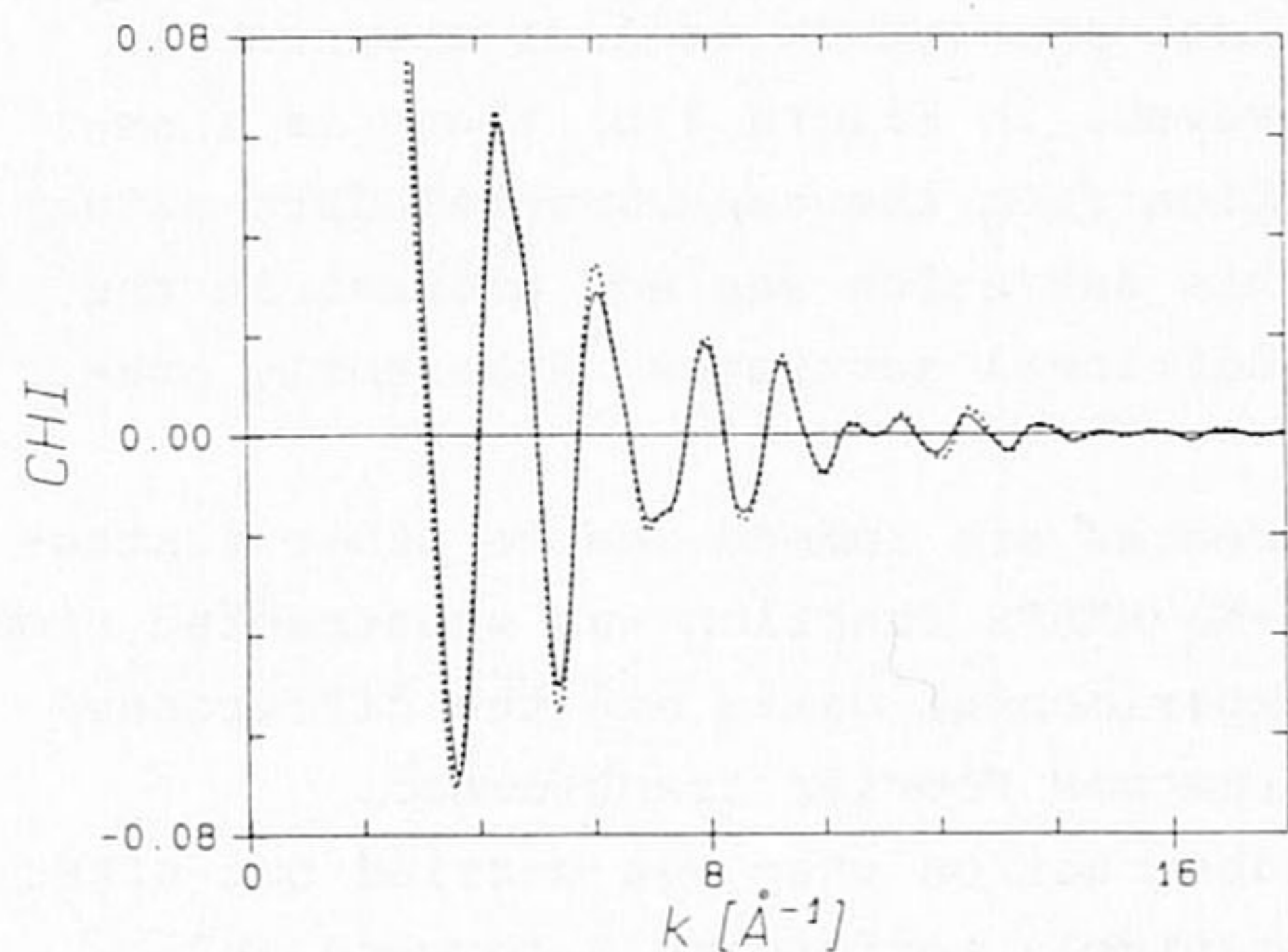


FIG. 1. EXAFS spectra of Mo/C (solid line) and Co-Mo/C (dotted line).

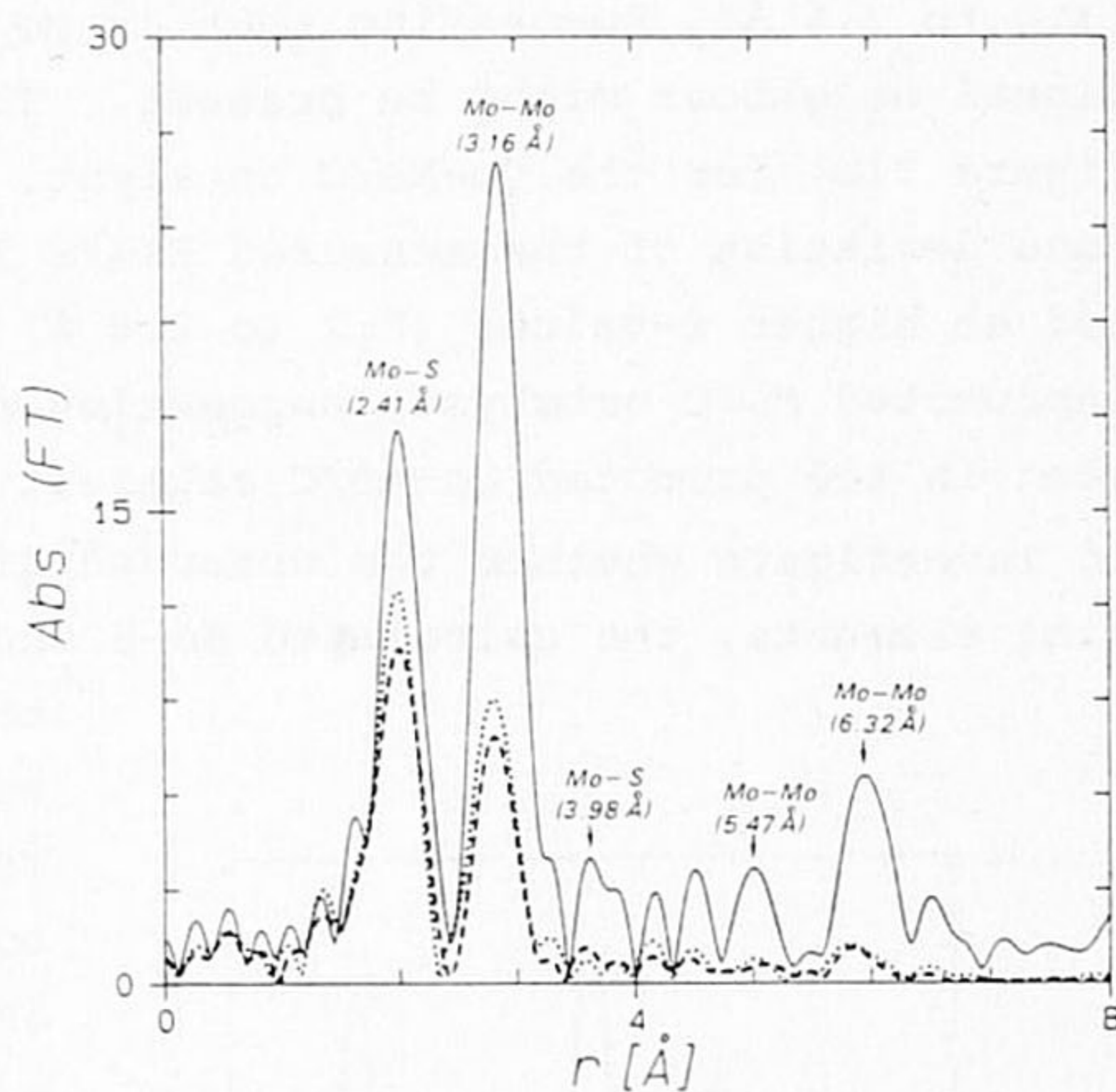


FIG. 2. Magnitude of the k^3 -weighed Fourier transforms ($\Delta k = 4.0$ - 16.0 \AA^{-1}) of the MoS_2 reference compound (solid line), the Mo/C catalyst (dashed line), and the Co-Mo/C catalyst (dotted line).

As can be seen in Figure 2, the spectra of the Mo/C and Co-Mo/C catalysts exhibit identical features as the MoS_2 compound, viz. a peak at 2.0 \AA (corresponding to the first Mo-S shell at a distance of 2.41 \AA) and a peak at 2.8 \AA (corresponding to the first Mo-Mo shell at a distance of 3.16 \AA).

The magnitude of the first Mo-S shell in the catalysts is smaller than that of MoS_2 while the first Mo-Mo shell is still smaller. This shows that small particles are present. There is also a difference between the catalysts themselves, the Co-Mo/C catalyst exhibits slightly larger Mo-S and Mo-Mo peak amplitudes than Mo/C. Finally, the absence of higher shells in the catalysts compared to MoS_2 confirms the existence of small particles.

The Mo-S and Mo-Mo first-shell contributions of the catalyst samples were isolated by consecutively performing a forward and an inverse Fourier transformation on the raw EXAFS data.

The back-Fourier-transformed signal ($\Delta r = 1.0$ to 3.2 \AA , in this range the Mo-S and Mo-Mo shells are located) was subsequently fitted (2-shell fit), using the phase and amplitude functions of the absorber-scatterer pair Mo-S (first shell) and Mo-Mo (first shell) of the MoS_2 reference compound. The crystallographic data for the MoS_2 compound were taken from the literature (17). The parameters $N, R, \Delta\sigma^2$ and E_0 of both the Mo-S and the Mo-Mo shell were chosen in such a way as to give the best agreement in r -space between the k^1 -weighed Fourier transform of the experimental data and the calculated (Mo-S)+(Mo-Mo) EXAFS function (see Figure 3(a) and 3(b)). For a detailed description of the data analysis procedure, we refer to (18-20). The structural parameters obtained in this manner are presented in Table 1. The full data analysis will be presented elsewhere (21).

As can be seen in Figure 3(a), the fit is nearly optimal except at low r -values (1.0 to 1.6 \AA), suggesting that in Mo/C besides sulfur and molybdenum an additional neighbour might be present. This last phenomenon is also apparent in Figure 3(b) for the Co-Mo/C catalyst. However, in Figure 3(b) there is a second deviation of the measured EXAFS function from the experimental data situated at higher r -values (2.2 to 2.6 \AA). This deviation was not present in the unpromoted Mo/C catalyst, suggesting an additional scatterer inherently present in the promoted Co-Mo/C catalyst.

To investigate whether the observed differences are indeed due to other scattering elements, the calculated Mo-S and Mo-Mo EXAFS function was subtracted from the experimental data, and the difference spectrum was Fourier transformed.

The subtraction step was carried out after consecutively performing a forward (k^1 , $\Delta k = 4.0-12.2 \text{ \AA}^{-1}$) and an inverse ($\Delta r = 1.0-3.2 \text{ \AA}$) transformation of the experimental data, as well as of the calculated Mo-S and Mo-Mo EXAFS function. The magnitude of the difference spectrum after Fourier transformation (k^1 , $\Delta k = 4.5-10.4 \text{ \AA}^{-1}$) is shown for the Mo/C and Co-Mo/C samples in Figure 4(a) and 4(b) respectively.

As is obvious from Figure 4(a), there is a peak (denoted : x) at 1.4 \AA in the magnitude of the Fourier Transformation. The spectrum of the promoted catalyst presented in Figure 4(b), shows 2 peaks (denoted : x and y) at r -values of 1.4 and 2.2 \AA respectively.

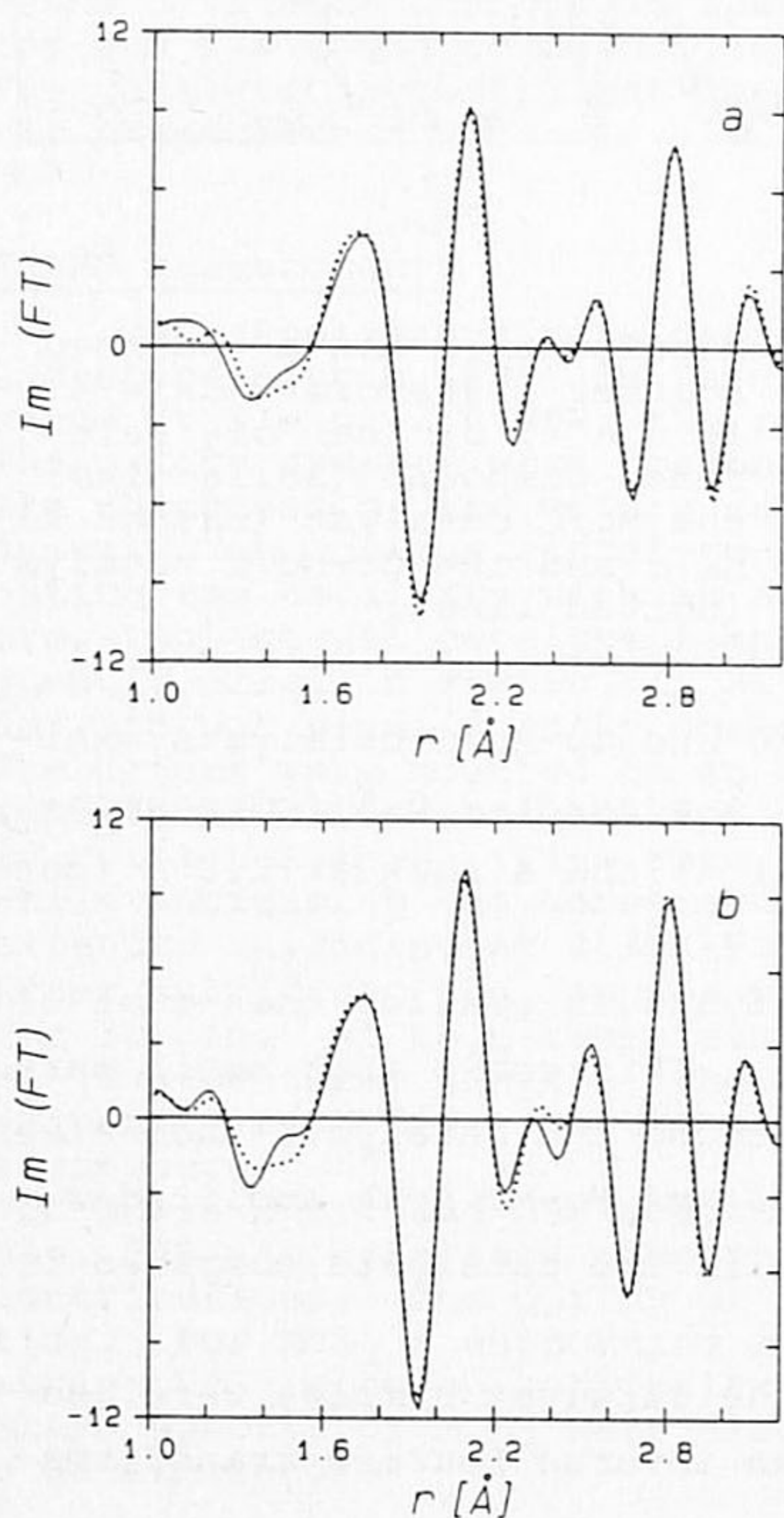


FIG. 3. Imaginary k^1 -weighed Fourier transform ($\Delta k = 4.0-12.2 \text{ \AA}^{-1}$) of :
 a. the Mo/C catalyst (solid line) and the calculated Mo-S and Mo-Mo shells (dotted line).
 b. the Co-Mo/C catalyst (solid line) and the calculated Mo-S and Mo-Mo shells (dotted line).

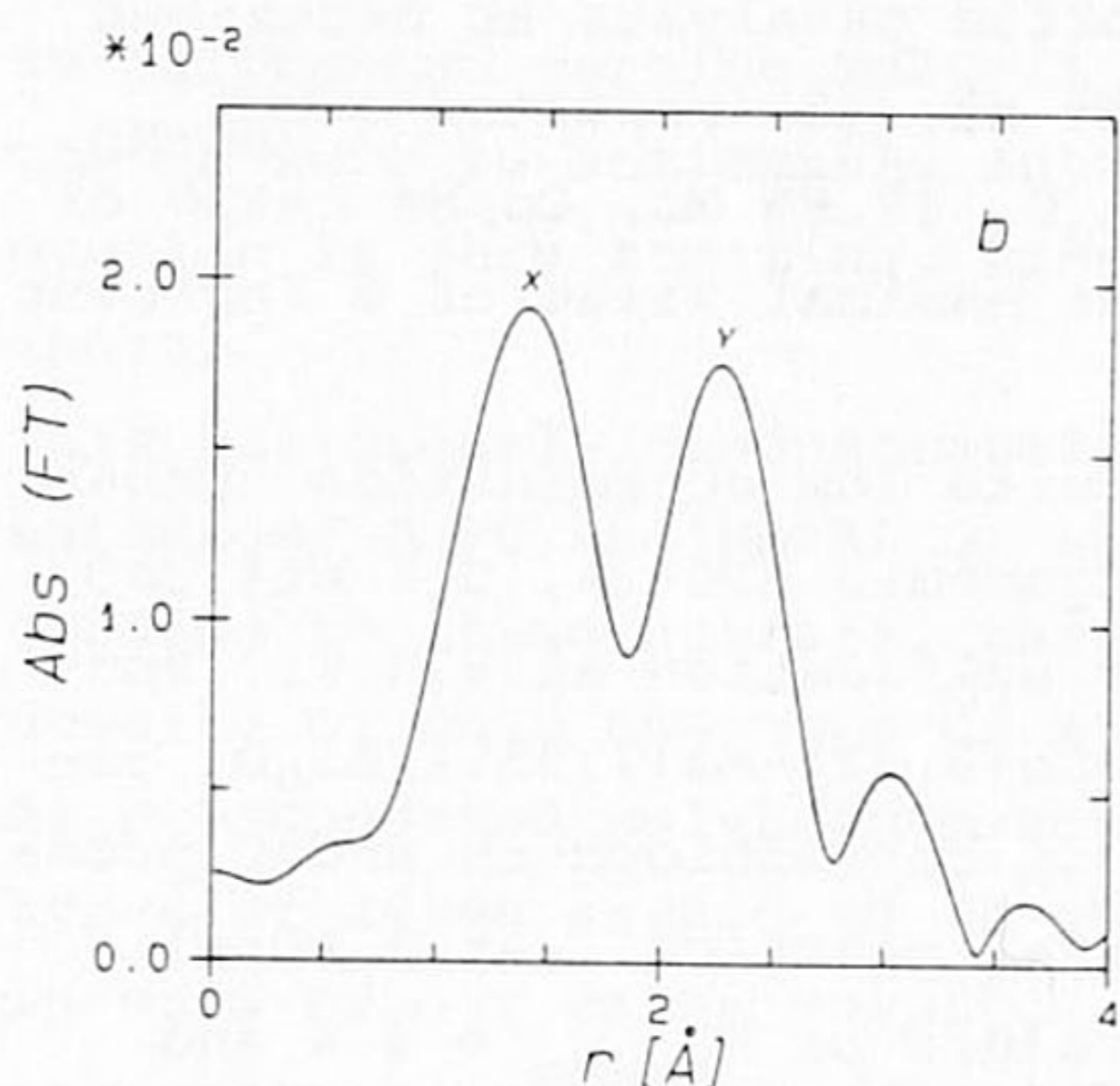
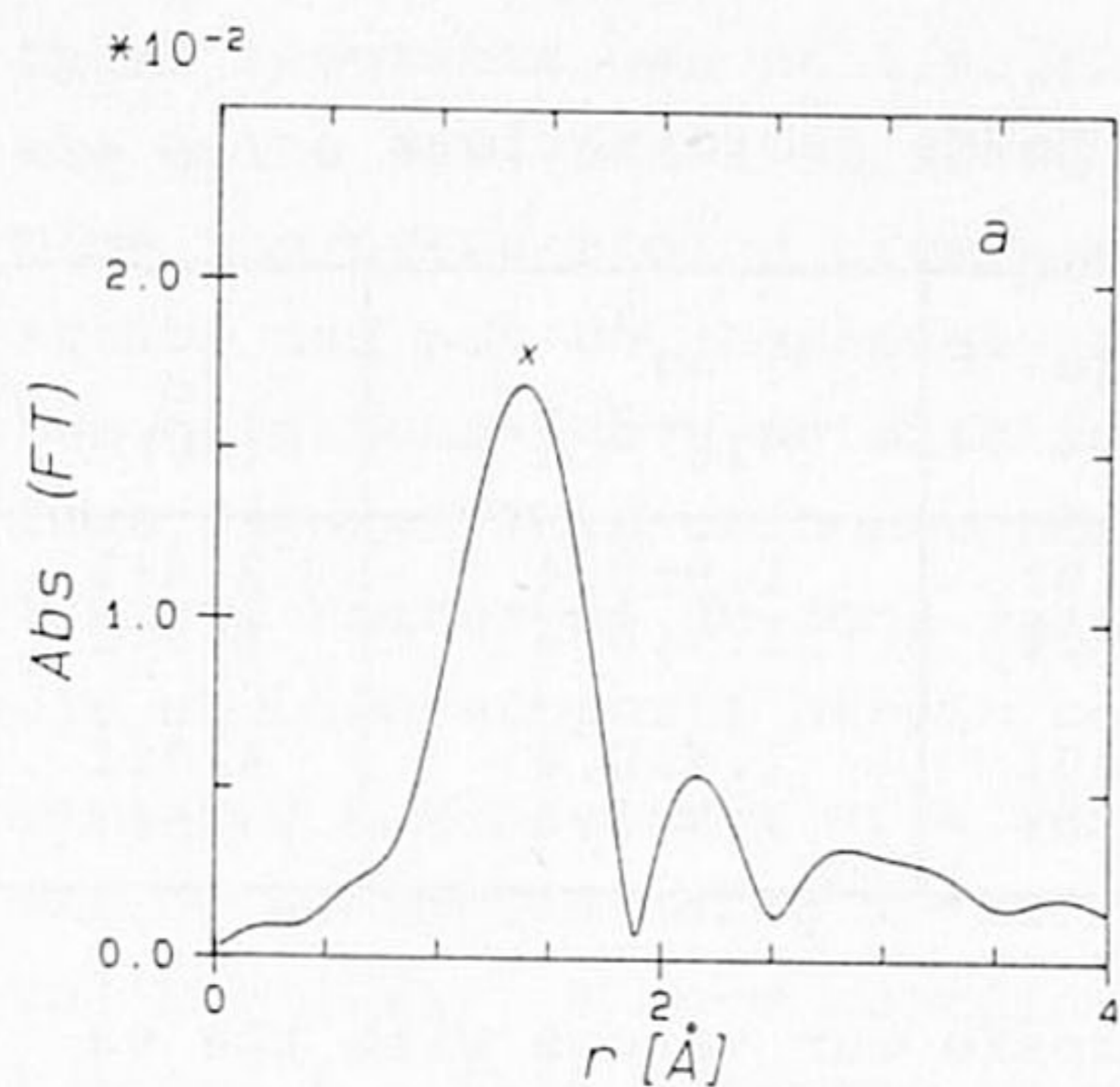


FIG. 4. Magnitude of the k^1 -weighed Fourier transforms ($\Delta k = 4.5-10.4 \text{ \AA}^{-1}$) of the difference spectra (original EXAFS spectra minus the calculated Mo-S and Mo-Mo EXAFS functions) of :
 a. Mo/C
 b. Co-Mo/C

Thus, it appears that in both catalysts an additional EXAFS contribution is present. In the promoted catalyst a second additional EXAFS contribution is present having a larger coordination distance.

DISCUSSION

As can be seen in Figure 3(a) and 3(b), the first Mo-S and Mo-Mo shell of the experimental data could be nearly optimally fitted by using the first Mo-S and Mo-Mo shells of the MoS_2 reference compound. From this data analysis the coordination distances of Mo-S and Mo-Mo in the catalyst samples were (within the limits of accuracy) found to be equal to the corresponding distances in pure MoS_2 , indicating the presence of MoS_2 -like particles. EXAFS measurements on sulfided alumina-supported Mo and Co-Mo catalysts showed similar Mo-S and Mo-Mo distances (8, 9), indicating that the crystallite structure of the MoS_2 -like particles in both carbon- and alumina-supported systems is similar.

On the basis of the calculated coordination numbers for the first Mo-Mo and Mo-S shell (cf. Table 1), an estimation can be made about the particle sizes of the MoS_2 crystallites in our catalysts. Since the coordination numbers have an uncertainty of 10% or even less, a detailed determination is possible. In the case of the Mo/C catalyst, the MoS_2 particles contain on average 5 to 6 Mo ions. In the promoted Co-Mo/C catalyst the MoS_2 particles are slightly larger. An average of 7 to 8 Mo ions can be deduced (note that the Mo-Mo coordination number of Co-Mo/C is 3.2 versus a value of 2.7 for Mo/C). As regards the Mo-S coordination number, a value of 5.2 for both catalysts has been found. This value is quite high ($N_{\text{Mo-S}} = 6$ for pure MoS_2), suggesting that the Mo ions in the MoS_2 -like particles are to a large extent sur-

TABLE 1
Structural parameters for the Mo-S and Mo-Mo coordinations

catalyst	shell	coordination number, N	Distance (Å)	$\Delta\sigma^2$ ($\times 10^{-3} \text{ \AA}^2$)	E_o (eV)
Mo/C	Mo-S	5.2±0.5	2.41±0.01	1.9±0.4	2.4±1
	Mo-Mo	2.7±0.3	3.15±0.01	1.7±0.4	1.3±1
Co-Mo/C	Mo-S	5.2±0.5	2.40±0.01	1.4±0.4	4.3±1
	Mo-Mo	3.2±0.3	3.13±0.01	1.7±0.4	4.5±1

rounded by sulfur ions. It is interesting to compare our values with the values obtained for the corresponding alumina-supported catalysts as described in the literature (8-11). For instance, Candia et al. (8) reported a $N_{\text{Mo-Mo}}$ value of 3.1 for both Mo(8.6%)/Al₂O₃ and Co-Mo/Al₂O₃ (8.6% Mo, Co/Mo ratio of 0.30). Their values of $N_{\text{Mo-S}}$, however, exceed the maximal value of 6 (present in bulk MoS₂), which seems unlikely.

Parham and Merrill (10) on the other hand, found quite low coordination numbers for a commercial Co-Mo/Al₂O₃ catalyst (American Cyanamid HDS-2A, 3.2 wt% CoO, 15.4 wt% MoO₃): $N_{\text{Mo-S}} = 2.7$, $N_{\text{Mo-Mo}} = 1.7$, after sulfidation at 673 K. Boudart et al. (9) reported EXAFS measurements on a Co(2.3%)-Mo(7.55%)/Al₂O₃ catalyst, measured during the hydrodesulfurization of benzothiophene under pressures and temperatures similar to those in industrial practice. At a total pressure of 7.3 MPa and a temperature of 523 K, values of $N_{\text{Mo-Mo}} = 4.4$ and $N_{\text{Mo-S}} = 6.3$ were calculated, whereas at a pressure of 0.1 MPa and at room temperature the values were: $N_{\text{Mo-Mo}} = 3.8$, $N_{\text{Mo-S}} = 6.0$. It should be noted that in many previous EXAFS publications on HDS catalysts, the uncertainty in determining coordination numbers is either not mentioned, or it is fairly high (20% or more). In the present EXAFS study, the very high signal-to-noise ratio of the raw data allows an accurate calculation of the MoS₂ particle sizes.

Summarizing, we can conclude from our EXAFS data that carbon-supported Mo and Co-Mo catalysts contain very disperse MoS₂-like particles, however, it is not yet clear whether these carbon-supported catalysts have a better dispersion than the corresponding alumina-supported catalysts.

As can be seen in Figure 3(a) and 3(b), a 2-shell fit using only Mo-S and Mo-Mo contributions resulted in the r-range 1.0-1.6 Å in small differences with the experimental data. Since the signal-to-noise ratio is very high, it is unlikely that these differences are caused by noise contributions. Furthermore, since it is impossible to fit the experimental data between 1.0 and 1.6 Å using only S and Mo neighbours, these differences appear to be significant.

The difference spectrum after Fourier transformation, presented in Figure 4(a) and 4(b), showed a clear peak (denoted x) for both the Mo/C and Co-Mo/C samples. Since this peak cannot be ascribed to a S or Mo neighbour, it seems likely that another element is present.

Assuming that the active phase only consists of S and Mo ions, the additional neighbour could be attributed to the interface between the Mo sulfide particles and the carbon carrier surface layer.

Although activated carbon consists, besides of carbon, also of oxygen-containing functional groups and metal impurities, it seems unlikely that some of

these reactants can be discerned by EXAFS since their relative concentrations are quite low, and also since some of the oxygen groups will be decomposed during the presulfiding treatment. Even though the possibility of a Mo-O interaction can not be completely excluded, we believe that peak x is due to a carbon neighbour (Mo-C interaction), probably present in the carbon carrier surface layer. This carbon contribution is rather small, probably because only a limited number of Mo-ions (namely those at the interface of the sulfide particle and the support) are in contact with carbon.

Assuming the presence of a carbon neighbour, the actual average Mo-C distance can be estimated using a theoretically determined phase shift according to Teo and Lee (22). A Mo-C coordination distance is calculated in this way to be 1.9 ± 0.1 Å. This distance is quite short, even slightly shorter than that in molybdenum carbide Mo_2C , $R_{\text{Mo-C}} = 2.00-2.22$ Å (23), suggesting that part of the Mo ions is intimately interacting with the carbon support. This last deduction is very striking, since a carbon carrier is expected to be rather inert.

This was clearly demonstrated in the work by Vissers et al. (24) who studied a series of Mo/C and Mo/ Al_2O_3 catalysts using dynamic oxygen chemisorption. According to these authors, the molybdenum sulfide phase in Mo/C possessed a high density of only one type of site with a high turn-over frequency, whereas the Al_2O_3 -supported molybdenum sulfide phase had a lower site density and different types of sites seemed to be present at low and high molybdenum concentration. In view of our EXAFS results, it might be reasonable to assume that the Mo-C interaction in (Co-)Mo/C catalysts is much weaker than the Mo-O-Al linkages, which are generally accepted as being responsible for the strong interaction in sulfided Mo/ Al_2O_3 catalysts (25, 26). On the other hand, an interaction between the Mo sulfide phase and the carbon support might not be that unlikely regarding the presence of very disperse MoS_2 -like particles in Mo/C and Co-Mo/C. A full analysis of the Mo-C distance and coordination numbers must await the analysis of a Mo-C reference compound.

For the promoted Co-Mo/C catalyst, a 2-shell fit using only Mo-S and Mo-Mo contributions also resulted in a deviation compared to the experimental data in the r-range 2.2-2.6 Å. Because this deviation is not present in the unpromoted Mo/C catalyst, it is a significant feature.

Since the only difference in chemical composition between a Mo/C and a Co-Mo/C catalyst is the cobalt phase, it seems obvious to ascribe peak y to a cobalt neighbour (Mo-Co interaction).

It is clear that the cobalt contribution is very small, probably because only a small number of Mo-ions are in contact with cobalt ions (just like the Mo-C interaction).

Assuming the presence of a cobalt neighbour, the actual average Mo-Co distance can be estimated using a theoretically determined phase shift according to Teo and Lee (22). A Mo-Co coordination distance can be calculated in this way to be 2.8 ± 0.1 Å. However, for a full data analysis a Mo-Co reference compound should be used.

On the basis of this Mo-Co coordination distance alone, it is not yet possible to derive structural parameters on the Co-Mo-S phase, as it is not known whether

all the Co neighbouring ions are indeed present in a Co-Mo-S phase, or rather in a Co_9S_8 phase adjacent to the MoS_2 crystallites. Considering that the atomic Co/Mo ratio is fairly high (0.7), one could expect that at least part of the Co phase is present as Co_9S_8 . In this respect, EXAFS measurements at the Co K-edge of the Co-Mo/C and the Co/C catalyst should provide us with additional information to further elucidate the structure of the Co-Mo-S phase.

CONCLUSIONS

Regarding the structure and dispersion of sulfided Mo/C and Co-Mo/C catalysts as determined by EXAFS, the following conclusions can be drawn :

1. The sulfided Mo/C and Co-Mo/C catalysts consist of very small MoS_2 -like particles, which contain on average 5 to 6 Mo ions (Mo/C) and 7 to 8 Mo ions (Co-Mo/C) respectively. The promoted Co-Mo/C catalyst has slightly larger sulfide particles than the unpromoted Mo/C catalyst. A high sulfur coordination number for both catalysts has been found.
2. There are indications for the presence of carbon neighbours next to molybdenum. The coordination distance Mo-C is estimated to be 1.9 ± 0.1 Å. This short distance could imply an intimate interaction between the active phase and the carbon support.
3. There are indications for the presence of cobalt neighbours next to molybdenum, the corresponding Mo-Co distance was estimated to be 2.8 ± 0.1 Å.

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