

## Chapter 29

# Structure of Cobalt Sulfide Phase in Carbon-Supported Co and Co-Mo Sulfide Catalysts

Studies by Extended X-ray Absorption Fine Structure (EXAFS)  
and X-ray Absorption Near Edge Structure (XANES)

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An X-Ray absorption spectroscopy study has been carried out on a carbon-supported Co and Co-Mo sulfide catalyst, the latter consisting of a fully sulfided Co-Mo-S (type II) phase. Detailed information on the structure of the cobalt sulfide phase is obtained by comparing the EXAFS and XANES spectra of the catalysts with those of  $\text{Co}_9\text{S}_8$  and  $\text{CoS}_2$  reference compounds. It is shown that the cobalt atoms in the Co-Mo-S phase have an octahedral-like sulfur coordination while the cobalt atoms in the sulfided Co/C catalyst have a larger fraction of octahedral cobalt than  $\text{Co}_9\text{S}_8$ . On the basis of these results, the high HDS activity of a sulfided Co/C catalyst can be understood since it appears that the structure of the cobalt sulfide phase in Co/C is in agreement with that in Co-Mo/C. In the Co-Mo-S phase, approximately one cobalt atom is in contact with one molybdenum atom at a distance of 2.85 Å.

The EXAFS (Extended X-Ray Absorption Fine Structure) technique is nowadays a valuable tool in the characterization of catalysts. The strength of EXAFS is that it can provide structural information on highly dispersed systems that are difficult to study with other conventional techniques. With respect to hydrotreating catalysts (e.g., sulfided Co-Mo/ $\text{Al}_2\text{O}_3$  or Ni-Mo/ $\text{Al}_2\text{O}_3$ ) EXAFS has been able to provide direct information regarding the local structure of the phases present in a working catalyst (1-3). Although the study of hydrotreating catalysts in general has received much attention during the last decade, several important questions regarding the structural characteristics are still unanswered. One of these concerns the role of the promoter Co and Ni ions in sulfided Co(Ni)-Mo catalysts.

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Topsøe and coworkers showed that the cobalt atoms are situated at  $\text{MoS}_2$  crystallite edges in a so-called "Co-Mo-S" structure, which structure governs almost completely the hydrodesulfurization (HDS) activity (4,5). Nevertheless, the exact structure of this phase or more precisely the location of the cobalt promoter is still unknown. Furthermore, the high specific activity of the Co-Mo-S structure is not understood. Recently, Ledoux et al. (6) showed with the use of  $^{59}\text{Co}$  NMR that the promotion effect of cobalt was correlated with the concentration of cobalt sites having a distorted tetrahedral symmetry. These cobalt sites were stabilized by so-called "rapid octahedral" cobalt atoms acting as a glue between the tetrahedral cobalt sites and the  $\text{MoS}_2$  phase. Although the "rapid octahedral" cobalt atoms could not be related to the HDS activity, Ledoux et al. lately proposed that they could be the origin of very active sites (7). Their explanation, based upon the theory of Harris and Chianelli (8), was that an electron transfer takes place between the "rapid octahedral" cobalt to the molybdenum ion resulting in a strong activation of the three sulfur ions sandwiched between them.

A different model was postulated by Duchet et al. (9) and by Vissers et al. (10) who observed a high activity for pure cobalt sulfide supported on activated carbon and hence explained the activity of a sulfided Co-Mo/C catalyst completely by the very high activity of the cobalt sites. In their theory the authors implicitly assumed that a cobalt site in sulfided Co/C has the same activity as a cobalt site in sulfided Co-Mo/C. However, this does not have to be the case since the structure of cobalt sulfide in Co/C can be very different from that in Co-Mo/C. In order to elucidate the structure of the cobalt sulfide phase in a sulfided Co/C and a Co-Mo/C catalyst we applied in this study the EXAFS and XANES (X-Ray Absorption Near Edge Structure) techniques at the Co K-edge.

### Experimental

The carbon support used was a Norit activated carbon (RX3 extra) having a surface area of  $1190 \text{ m}^2 \cdot \text{g}^{-1}$  and a pore volume of  $1.0 \text{ cm}^3 \cdot \text{g}^{-1}$ . The Co/C catalyst (4.1 wt% Co) was prepared by pore volume impregnation with an aqueous solution of cobalt nitrate (Merck p.a.) followed by drying in air at 383 K (16 h). The promoted catalyst (1.5 wt% Co, 7.7 wt% Mo) was prepared in a special way to ensure a maximum amount of the Co-Mo-S phase (11). Mössbauer spectroscopy of this promoted catalyst clearly showed that only the Co-Mo-S phase was present after sulfiding (11) and furthermore that this Co-Mo-S is probably a Co-Mo-S type II phase, meaning a minor influence of active phase-support interaction (11,12). The catalytic activity of the sulfided catalysts was determined by a thiophene HDS measurement at 673 K and atmospheric pressure, as described elsewhere (10). The thiophene HDS reaction rate constant  $k_{\text{HDS}}$  per mol Co present (approximated as a first order reaction) was found to be  $17 \cdot 10^{-3} \text{ s}^{-1}$  for Co/C and  $61 \cdot 10^{-3} \text{ s}^{-1}$  for Co-Mo/C.

The X-Ray absorption measurements were carried out on freshly in situ sulfided catalysts at liquid nitrogen temperature at the SRS in Daresbury (EXAFS station 9.2). The sulfidation was carried out in a



10% H<sub>2</sub>S in H<sub>2</sub> flow, flow rate 60 ml.min<sup>-1</sup> under atmospheric pressure, the temperature was increased linearly from 293 to 673 K (8.5 K.min<sup>-1</sup> for Co/C, 2 K.min<sup>-1</sup> for Co-Mo/C) and kept constant at 673 K for 2 h (Co/C) or 1 h (Co-Mo/C). The preparation of the model compounds Co<sub>9</sub>S<sub>8</sub> and CoS<sub>2</sub> has been described in (13) and (14), respectively. The purity of these compounds was checked by X-Ray diffraction. Phase shifts and backscattering amplitudes from reference compounds were used to calculate the EXAFS contributions. For the Co-S EXAFS signals CoS<sub>2</sub> was used, for the Co-Co contributions the Ni-Ni coordination in NiO (Merck p.a.) was chosen, and for the Co-Mo contribution in the Co-Mo/C catalyst we took ((C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>P)<sub>2</sub>Ni(MoS<sub>4</sub>)<sub>2</sub> as a model compound. The use of a Ni absorber and backscatterer instead of Co is justified since calculations of Teo and Lee (15) showed that phases and backscattering amplitudes of nearest and next-nearest neighbours in the periodic table hardly differ.

### Results

In Figure 1 (a,b) the Fourier-Transformed (FT) EXAFS spectra of the Co/C and the Co-Mo/C catalyst together with the Co<sub>9</sub>S<sub>8</sub> reference compound are plotted. The absolute FT spectrum of Co<sub>9</sub>S<sub>8</sub> (Fig. 1 (a)) exhibits two peaks. The first peak is attributed to combined Co-S and Co-Co coordinations, the second one only to a Co-Co coordination (denoted Co-Co(2), to differentiate it from the Co-Co(1) coordination in the first peak). In bulk Co<sub>9</sub>S<sub>8</sub> 8/9 of the cobalt atoms are tetrahedrally coordinated and 1/9 are octahedrally coordinated by sulfurs. The Co-S coordination distances are in the range 2.13-2.39 Å. The Co-Co coordination distance of Co-Co(1) is 2.50 Å, for Co-Co(2) the distance is 3.51 Å. From Figure 1 (a) it is apparent that in the catalyst spectra the first peak is shifted to lower r-values compared to that in Co<sub>9</sub>S<sub>8</sub>. This shift is larger for Co-Mo/C than for Co/C. It is furthermore clear that a Co-Co(2) coordination is also present in the Co/C catalyst, but not in the promoted catalyst. On the other hand, the latter catalyst shows an additional peak which is not present in Co<sub>9</sub>S<sub>8</sub> and Co/C and, consequently, might be ascribed to Mo backscatterers.

The imaginary FT spectra in Figure 1 (b) show the separate Co-S and Co-Co(1) coordinations which cannot be discerned in the absolute FT spectra. It appears that the Co-S peak amplitude increases in the order Co<sub>9</sub>S<sub>8</sub> Co/C Co-Mo/C, whereas the Co-Co(1) peak amplitude decreases in the same order. Data analysis was carried out by isolating the first and second peak in the absolute FT spectra and fitting the resulting EXAFS functions using Co-S and Co-Co EXAFS contributions. For a detailed description of the data analysis procedure we refer to (16). The structural parameters (N, R and  $\Delta\sigma^2$ ) obtained in this way are collected in Table I.

Supplementary information on the cobalt coordination can be derived from the XANES region. The near-edge structure of the samples is shown in Figure 2. The spectra all show a weak absorption peak near threshold which has been identified as a 1s → 3d transition (17,18). This transition has been observed to be more intense in te-



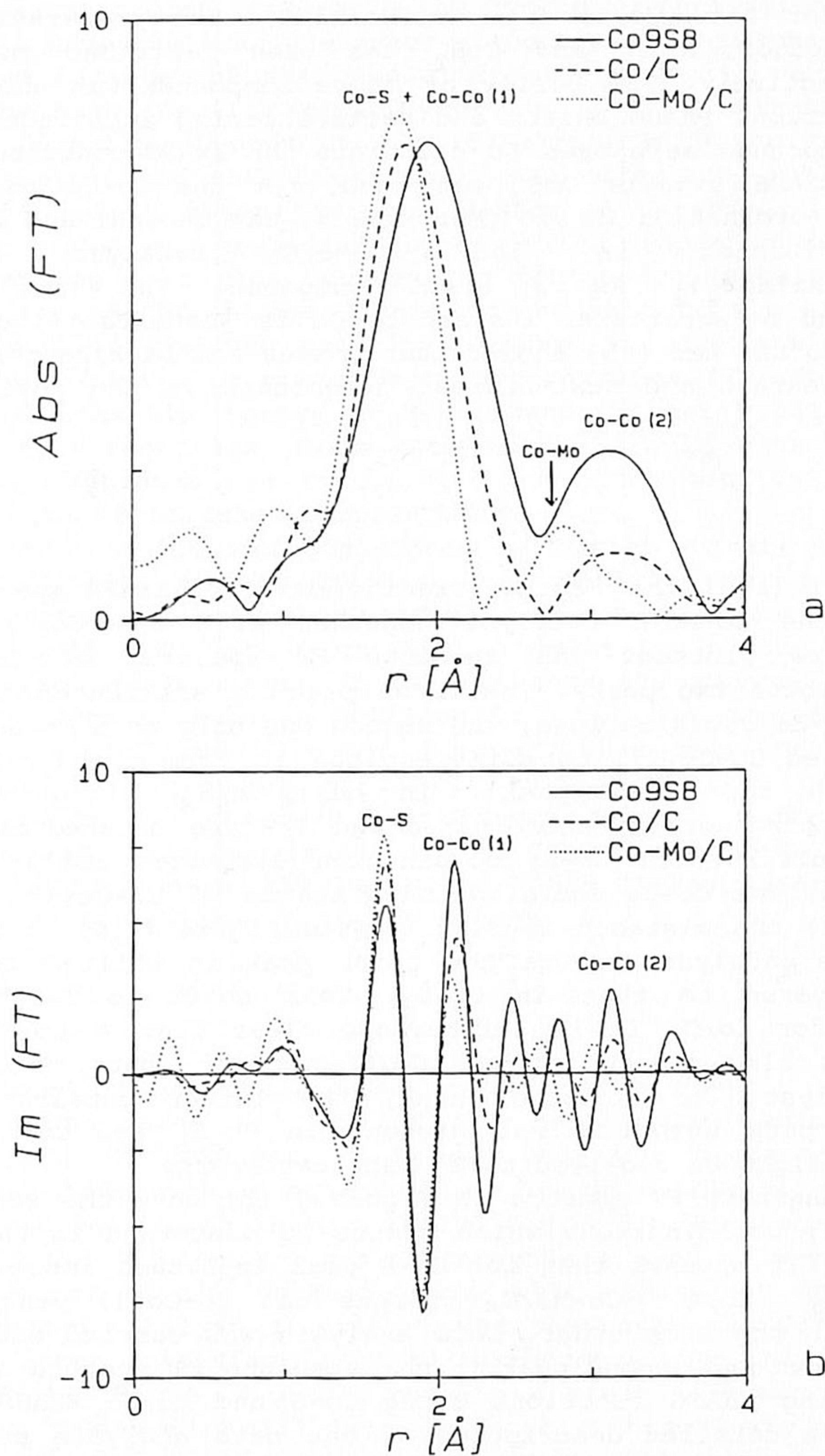


Figure 1: Imaginary  $k^3$ -weighted Fourier-Transforms ( $\Delta k=3.0 - 10.9 \text{ \AA}^{-1}$ ) of the EXAFS data of Co<sub>9</sub>S<sub>8</sub>, Co/C and Co-Mo/C: (a) absolute part, (b) imaginary part.



Table I. Structural parameters for the Co-S, Co-Co(1), Co-Co(2) and Co-Mo coordinations

	Co-S			Co-Co(1)			Co-Co(2)			Co-Mo		
	N <sup>a</sup>	R(Å) <sup>b</sup>	$\Delta\sigma^2(\text{Å}^2)^c$	N	R(Å)	$\Delta\sigma^2(\text{Å}^2)$	N	R(Å)	$\Delta\sigma^2(\text{Å}^2)$	N	R(Å)	$\Delta\sigma^2(\text{Å}^2)$
Co <sub>9</sub> S <sub>8</sub>	4.3	2.22	0.0038	2.4	2.51	0.0015	2.8	3.54	-0.0011			
Co/C	5.2	2.22	0.0029	1.6	2.55	0.0017	1.5	3.54	0.0018			
Co-Mo/C	6.7	2.21	0.0045	0.6	2.55	0.0076				0.8	2.85	0.0050

<sup>a</sup>Coordination number<sup>b</sup>Coordination distance<sup>c</sup>Debye-Waller factor



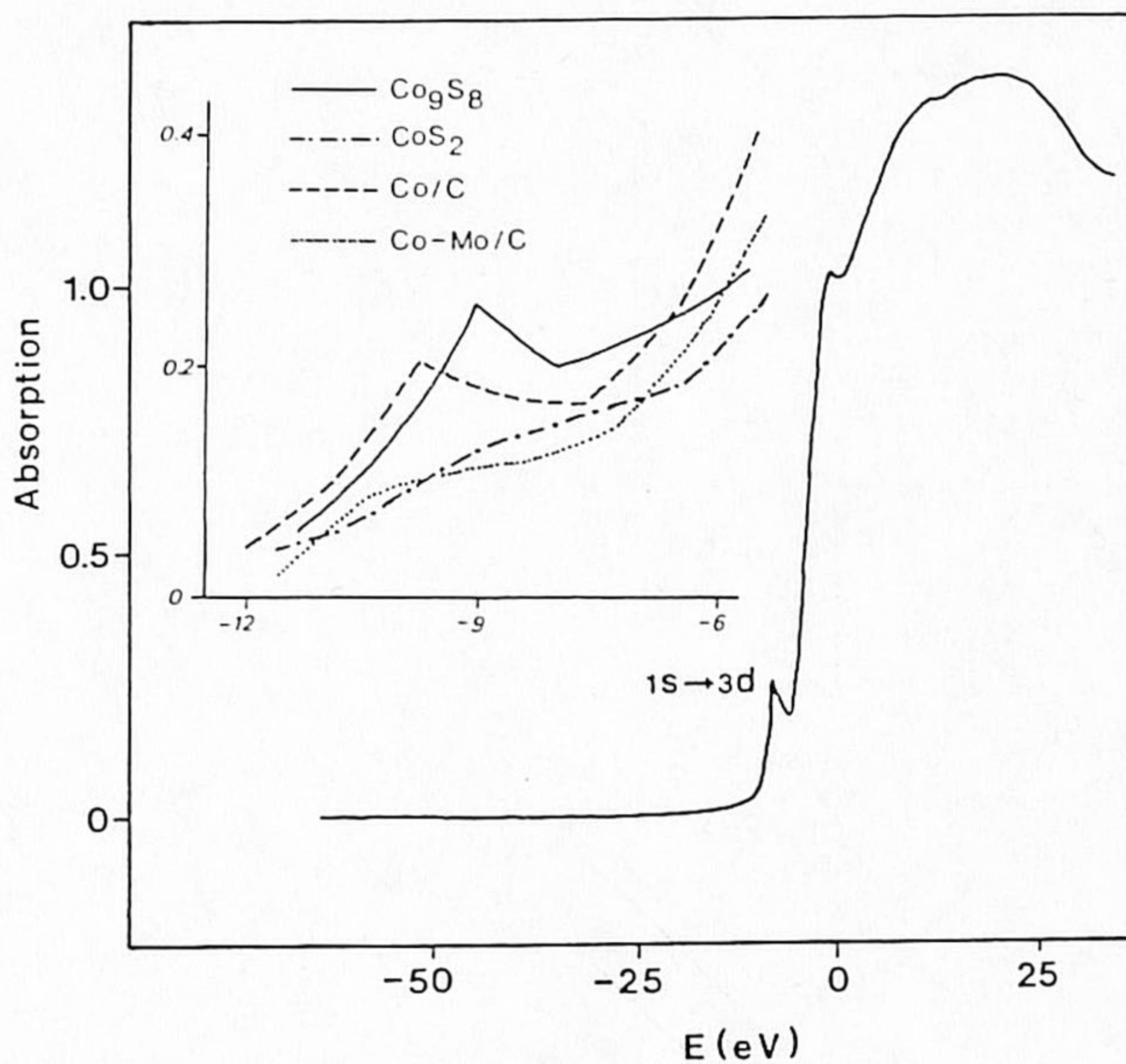


Figure 2: XANES spectrum of  $\text{Co}_9\text{S}_8$ . The expanded inset shows the  $1s \rightarrow 3d$  transition of  $\text{Co}_9\text{S}_8$ ,  $\text{CoS}_2$ ,  $\text{Co/C}$  and  $\text{Co-Mo/C}$ .



trahedral than in octahedral coordination of the absorbing atom (17), hence, it can be used as a measure of the coordination of the cobalt atoms. In Figure 2 the XANES spectra of both catalysts are compared with that of  $\text{Co}_9\text{S}_8$ , consisting of 89% tetrahedral and 11% octahedral cobalt, and with  $\text{CoS}_2$ , consisting of 100% octahedral cobalt. It is clear in this Figure that the  $1s \rightarrow 3d$  transition is most intense for  $\text{Co}_9\text{S}_8$  whereas in  $\text{CoS}_2$  its intensity is very small. The sulfided Co/C catalyst shows a somewhat smaller intensity than that of  $\text{Co}_9\text{S}_8$  while the Co-Mo/C catalyst shows a very small intensity, comparable to the  $\text{CoS}_2$  compound.

### Discussion

The data analysis reveals that the Co-S coordination number increases in the order  $\text{Co}_9\text{S}_8 < \text{Co/C} < \text{Co-Mo/C}$ . This means that the cobalt atoms in the catalysts have a higher sulfur coordination than those in  $\text{Co}_9\text{S}_8$  and furthermore, that this phenomenon is more pronounced when cobalt is present in a Co-Mo-S structure. The EXAFS results are substantiated by the XANES spectra. The  $1s \rightarrow 3d$  transition of the Co/C catalyst suggests a somewhat higher percentage of octahedral cobalt as present in  $\text{Co}_9\text{S}_8$  whereas for the Co-Mo/C catalyst it indicates an octahedral-like sulfur coordination.

Our results stress the importance of studying the imaginary FT spectra in combination with the absolute ones. By doing so, the observed shift of the first peak in the absolute FT spectra to lower  $r$ -values in the order  $\text{Co}_9\text{S}_8 > \text{Co/C} > \text{Co-Mo/C}$  can be fully explained by the increase in the corresponding Co-S peak amplitude and the simultaneous decrease in the Co-Co(1) peak amplitude. In fact, the Co-S coordination distance in the three samples is similar (2.22 Å). From these observations it might be clear that conclusions based only upon absolute FT spectra can turn out to be erroneous.

The EXAFS parameters for the Co/C catalyst show a Co-Co(1) coordination distance of 2.55 Å, which is slightly larger than that in  $\text{Co}_9\text{S}_8$  (2.51 Å). On the other hand, the Co-Co(2) coordination distances of both samples are equal. These results suggest that the cobalt sulfide phase in the sulfided Co/C catalysts essentially has a  $\text{Co}_9\text{S}_8$ -like structure, the only difference being its higher sulfur coordination. In case of the Co-Mo/C catalyst, the presence of a small Co-Co(1) contribution is evident. From the large Debye-Waller factor it can be inferred that this coordination has a high degree of disorder. Surprisingly, however, its coordination distance (2.55 Å) corresponds exactly to that in Co/C. The expected Co-Mo peak could be fitted well using the Ni-Mo EXAFS functions from the  $((\text{C}_6\text{H}_5)_4\text{P})_2\text{Ni}(\text{MoS}_4)_2$  reference compound, which confirms the presence of molybdenum neighbouring atoms. The Co-Mo coordination distance is calculated to be 2.85 Å, which is in good agreement with our EXAFS study of a sulfided Co-Mo/C catalyst at the Mo K-edge (19), in which we reported a Mo-Co coordination distance of 2.8 Å. The calculated Co-Mo coordination number of 0.8 (Table I) suggests that in the Co-Mo-S (II) structure approximately one cobalt atom is in contact with one molybdenum atom.

According to our EXAFS and XANES results, the structure of the cobalt phase in sulfided Co/C is in agreement with that in the



Co-Mo/C catalyst: in both catalysts a high sulfur coordination of the cobalt atoms is present. This is an interesting observation with regard to the activity per cobalt atom in both catalyst systems. Vissers et al. (10) stated that the intrinsic activity of a cobalt site in sulfided Co/C can be close to that in sulfided Co-Mo/C. Hence, our results of the structural resemblance between sulfided Co/C and Co-Mo/C, support the theory of Vissers et al. (10) that the cobalt phase in sulfided Co-Mo catalysts can be the actual active phase. Moreover, on the basis of these results the high HDS activity of a sulfided Co/C catalyst can be understood.

Our findings also coincide with the proposal of Ledoux et al. (7) that the "rapid octahedral" cobalt atoms might be the origin of very active sites, since we observe an octahedral-like coordination in the promoted catalyst. However, the earlier proposal of Ledoux et al. of tetrahedral cobalt sites being responsible for the high HDS activity of cobalt-molybdenum sulfide catalysts (6) must be rejected. Finally, our observation that the cobalt sulfide phase in the Co/C catalyst contains a higher sulfur coordination than that in  $\text{Co}_9\text{S}_8$ , which is expected from thermodynamical considerations, might point to a modification of the active cobalt sites through the carbon carrier. Support for the latter idea can be found in the work of Burch and Collins (20) who discussed a possible interaction between the nickel sulfide phase and an alumina, silica and carbon carrier. These authors proposed that a metal sulfide-support interaction may alter the morphology or composition of the nickel sulfide phase.

### Conclusions

Detailed information on the structure of the supported cobalt sulfide phase could be obtained by studying the imaginary Fourier Transformed EXAFS spectra as well as the cobalt  $1s \rightarrow 3d$  transition in the XANES spectra. It is shown that the cobalt atoms in the Co-Mo-S (II) phase have an octahedral-like sulfur coordination while the sulfided Co/C catalyst has a larger fraction of octahedral cobalt than  $\text{Co}_9\text{S}_8$ . On the basis of these results, the high HDS activity of a sulfided Co/C catalyst can be understood since it appears that the structure of the cobalt sulfide phase in Co/C is in agreement with that in Co-Mo/C. In the Co-Mo-S (II) phase approximately one cobalt atom is in contact with one molybdenum atom at a distance of 2.85 Å.

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