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Extended X-ray Absorption Fine Structure Determination of the Structure of Cobalt in Carbon-Supported Co and Co-Mo Sulfide Hydrodesulfurization Catalysts

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The structure of the cobalt present in carbon-supported Co and Co-Mo sulfide catalysts was studied by means of X-ray absorption spectroscopy at the Co K-edge and by X-ray photoelectron spectroscopy (XPS). Thiophene hydrodesulfurization activities were used to measure the catalytic properties of these catalysts. By comparison of the EXAFS and XANES spectra of the catalysts with those of Co_9S_8 and CoS_2 model compounds, it was concluded that all Co atoms in a catalyst prepared with nitrilotriacetic acid as complexing agent were in the "Co-Mo-S" state, while the Co atoms in a conventionally prepared catalyst were partly present in a Co_9S_8 -like structure and partly in a "Co-Mo-S" structure. The Co atoms in the "Co-Mo-S" state have a distorted 5- to 6-fold sulfur coordination, and on the average, every Co atom is in contact with two Mo atoms at a distance of 2.80 Å. On the basis of these data, the most likely position for the Co atoms is in front of the square sulfur faces of the MoS_6 trigonal prisms along the edges of the MoS_2 crystallites with two additional sulfur atoms or H_2S molecules attached. The Co atoms in the sulfided Co/C catalyst have Co-S and Co-Co coordinations as in Co_9S_8 , although the sulfur coordination number is higher.

Introduction

Cobalt- or nickel-promoted molybdenum sulfide catalysts supported on alumina are extensively used in the hydrotreatment of petroleum feedstocks. The increasing need for efficient removal of sulfur, nitrogen, and metal contaminants has led to a continuous drive to clarify the structure and the related catalytic activity of these complex catalyst systems. Especially the role and the chemical state of the promoter cobalt and nickel atoms in the sulfided catalysts is a subject of great interest, and numerous studies have been devoted to it.^{1,2} The introduction of in situ Mössbauer emission spectroscopy (MES) provided for the first time direct information regarding the nature of the cobalt phases present in a working Co-Mo hydrodesulfurization (HDS) catalyst. With the use of MES, Topsøe et al.³ and Wivel et al.⁴ showed that most of the cobalt atoms are situated at MoS_2 crystallite edges in a so-called "Co-Mo-S" structure and that this structure governs almost completely the HDS activity. However, the precise local structure of the cobalt promoter atoms is still unknown. Also, the high specific activity of the "Co-Mo-S" structure is not understood. In this respect, it has not been established whether the cobalt atoms are the active sites or whether the neighboring molybdenum atoms also play a direct role in the catalytic activity.⁵⁻⁷

Detailed information on the chemical state of the cobalt atoms was obtained by Ledoux et al. with the use of ^{59}Co NMR.⁸ They argued that the promotion effect of cobalt was correlated with the concentration of cobalt sites having a distorted tetrahedral symmetry and that these sites were stabilized by so-called "rapid octahedral" cobalt atoms acting as a glue between the tetrahedral cobalt sites and the MoS_2 phase. Although the "rapid octahedral" cobalt atoms could not be related to the HDS activity,⁸ Ledoux later proposed that they could be the origin of very active sites.⁹ It was suggested that, as in the theory of Harris and Chianelli,¹⁰ an electron transfer can take place from the "rapid octahedral" cobalt to the molybdenum atom, resulting in a strong activation of the three sulfur atoms sandwiched between them.

A different model was postulated by Duchet et al.⁶ and by Vissers et al.,⁷ who observed a high thiophene HDS 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 this model it is assumed that the structure of the active cobalt sulfide sites in a

Co/C catalyst is similar to that in a Co-Mo/C catalyst. In order to test the latter assumption, we applied the EXAFS (extended X-ray absorption fine structure) and the XANES (X-ray absorption near edge structure) techniques at the Co K-edge to a sulfided Co/C and a Co-Mo/C catalyst. The first preliminary results of this study¹¹ revealed that the structure of the cobalt sulfide phase in both catalyst systems is indeed comparable: i.e., in both systems the cobalt atoms have a high sulfur coordination. These results therefore substantiated the assumption of Duchet et al.⁶ and Vissers et al.⁷ Very recently, our conclusions were further confirmed by MES investigations on a sulfided Co/C and a Co-Mo/C catalyst having a very low cobalt content,¹² in which it was found that the Mössbauer spectra of these catalysts are essentially equal. This implies that the formation of a cobalt species like the one present in the so-called "Co-Mo-S" state¹³ does not necessarily require the presence of molybdenum sulfide.

In their study of sulfided Co-Mo/ Al_2O_3 catalysts Candia et al. distinguished between two types of "Co-Mo-S" species, type I and type II.¹³ According to these authors the intrinsic activity (per Co atom present as "Co-Mo-S") is much higher for type II than for type I "Co-Mo-S". Type I "Co-Mo-S" is supposed to have an interaction with the alumina support, while type II is almost free of interactions with the alumina support. In the case of carbon as support, Topsøe⁵ observed that the "Co-Mo-S" structures are only weakly bound to the support surface and, hence, concluded that the type II "Co-Mo-S" is the one which resembles the carbon-supported "Co-Mo-S" structures most.

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In the present study, therefore, a detailed data analysis is presented of the EXAFS data of a sulfided Co/C and two Co-Mo/C catalysts, prepared in different ways. One Co-Mo/C catalyst was prepared in the conventional way (two-step impregnation method, Mo phase introduced first); the other one was prepared in a special way to ensure a maximum amount of the "Co-Mo-S" type II structure.¹⁴ The X-ray absorption spectra of the catalyst samples are compared with those of pure Co₉S₈ and CoS₂ model compounds. A comparison will also be made between the structural characteristics and the thiophene HDS activity of these catalysts.

Experimental Section

Catalyst Preparation. The carbon support was a Norit activated carbon (RX3 extra) having a surface area of 1190 m²·g⁻¹ and a pore volume of 1.0 cm³·g⁻¹. A Co/C catalyst (4.1 wt % Co) was prepared by pore volume impregnation with an aqueous solution of Co(NO₃)₂·6H₂O (Merck p.a.), followed by drying in air at 383 K (16 h). A series of Co-Mo/C catalysts with Co loading between 0 and 5.5 wt % and Mo loading of 7.5 wt % were prepared via a two-step pore volume impregnation procedure in which the molybdenum phase was introduced first using an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O (Merck p.a.), followed by drying in air at 383 K (16 h). Next, the cobalt phase was introduced as described above for the Co/C catalyst. Due to the additional presence of Co, the final Mo content was slightly lower than 7.5%. Precursor catalyst compositions were determined by means of atomic absorption spectroscopy using a Perkin-Elmer 3030 AAS spectrometer.

The carbon-supported "Co-Mo-S" precursor catalyst was prepared by pore volume impregnation using an aqueous solution containing the required amounts of 1.5 wt % Co and 7.7 wt % Mo (Co/Mo = 0.32 mol/mol) and nitrilotriacetic acid (NTA) (NTA/Mo = 1.2 mol/mol).¹⁴ In this way a maximum amount of the "Co-Mo-S" structure is ensured. MES analysis showed that this preparation method results in a promoted catalyst in which, after sulfidation, cobalt is exclusively present in the form of "Co-Mo-S". Furthermore, this "Co-Mo-S" is most probably a "Co-Mo-S" type II structure, which has a minor interaction with the support.^{12,14} In the following, this catalyst will be denoted as Co-Mo-S/C, to differentiate it from the other promoted catalysts, which will simply be denoted as Co-Mo/C.

Catalytic Activity Measurements. Catalyst samples (0.2 g) were sulfided in a flow of 10% H₂S in H₂ (flow rate 60 cm³·min⁻¹ at atmospheric pressure) for 1 h while increasing the temperature linearly from 293 to 673 K, followed by an extended sulfiding at 673 K for 2 h. In case of the Co-Mo-S/C catalyst, the temperature was increased with only 2 K·min⁻¹ from 293 to 673 K and kept constant at 673 K for 1 h, in order to obtain a maximum amount of the Co-Mo-S structure. After sulfidation, the reaction mixture consisting of 6.2 mol % thiophene in hydrogen was introduced at a flow rate of 50 cm³·min⁻¹. The temperature and pressure were 673 K and 1 atm, respectively. The reaction products were analyzed by on-line gas chromatography. The thiophene conversion measured after 2-h run time was taken to calculate the first-order reaction constant for HDS (*k*_{HDS}).

EXAFS Measurements. EXAFS spectra were recorded of the following freshly sulfided catalysts: Co(4.1)/C, Co-Mo/C (Co/Mo = 0.73), and Co-Mo-S/C. The oxidic precursor samples were pressed into self-supporting wafers, the thickness *x* of which was chosen to give an absorbance (*μx*) of about 2.5, assuring an optimum signal-to-noise ratio. Since activated carbon is difficult to press, a special carbon binder had to be used for the catalyst samples. The presence of this 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.¹⁵

The sulfidation was carried out in a 10% H₂S in H₂ flow at a flow rate of 60 cm³·min⁻¹ under atmospheric pressure. The temperature was increased linearly from 293 to 673 K (8 K·min⁻¹ for Co/C and Co-Mo/C and 2 K·min⁻¹ for Co-Mo-S/C) and kept constant at 673 K for 2 h (Co/C, Co-Mo/C) or 1 h (Co-Mo-S/C). After sulfiding, the samples were cooled to room temperature under flowing helium. Prior to cooling down, only the Co-Mo-S/C catalyst was flushed with helium at 673 K for 15 min. The cell was evacuated at room temperature in order to remove all H₂S gas; next it was flushed again with helium. The EXAFS spectra of the cobalt K-edge were recorded in a static helium atmosphere with the sample at liquid nitrogen temperature. Co₉S₈ was used as a model compound. Its preparation has been described in ref 11, and its purity was checked by X-ray diffraction.

Phase shifts and backscattering amplitudes from reference compounds were used to analyze the EXAFS contributions. For the Co-S EXAFS signals the Co²⁺-S⁻ coordination in CoS₂ was used, for the Co-Co contributions the Ni²⁺-Ni²⁺ coordination in NiO (Merck p.a.) was chosen, and for the Co-Mo contributions in the promoted catalysts we took the Ni²⁺-Mo⁶⁺ coordination in ((C₆H₅)₄P)₂Ni(MoS₄)₂, obtained from Dr. F. W. Baumann, University of Bielefeld, West Germany. The use of a Ni absorber and backscatterer instead of Co is justified since it has been shown^{16,17} that the phases and backscattering amplitudes of neighboring elements such as Co and Ni hardly differ. The preparation of the reference compound CoS₂ has been described in ref 18, and its purity was checked by X-ray diffraction. Supporting wafers of the model and reference compounds were prepared by mixing each compound with the appropriate amount of boron nitride such that the step size *μx* ~ 1. EXAFS spectra of these compounds were also recorded at liquid nitrogen temperature while keeping the samples in a helium atmosphere.

The EXAFS data were collected on EXAFS station 9.2 of the wiggler line of the Synchrotron Radiation Source at Daresbury, UK (2 GeV, 100–250 mA), using a flat Si (220) double-crystal monochromator. The monochromator was detuned to 50% intensity in order to eliminate the presence of higher harmonics in the X-ray beam. The EXAFS spectrum of the CoS₂ model compound was recorded at the EXAFS station of beam line X-11 A of the NSLS at Brookhaven (ring energy 2.5 GeV, ring currents 50–100 mA). This EXAFS beam line is equipped with a Si(111) monochromator, which was detuned to 50% of the primary intensity. Of each sample typically two scans were recorded, which were averaged in the data analysis procedure.

X-ray Photoelectron Spectroscopy (XPS). XPS spectra of the sulfided catalysts were recorded on an AEI ES 200 spectrometer equipped with an Al anode (1486.6 eV) and a spherical analyzer operating at a pass energy of 60 eV. In order to avoid contact of the sulfided catalysts with air, a special sulfiding reactor was used¹⁹ which allowed transfer of the samples to a N₂-flushed glovebox attached to the XPS apparatus without exposure to air. After sulfidation, under exactly the same conditions as described above, the catalyst samples were flushed with purified He for 30 min at 673 K and subsequently cooled to room temperature. The samples were mounted on the specimen holder by means of double-sided adhesive tape. Spectra were recorded at 293 K in steps of 0.1 eV; the pressure was lower than 1.3 × 10⁻⁶ Pa.

The C 1s peak (284.6 eV) was used as an internal standard for binding energy calibration. Curves were integrated by using a linear baseline. The Mo(3d) to C(1s) photoelectron intensity ratios were used to measure the degree of dispersion of the molybdenum sulfide phase on the support. Theoretical intensity ratios were calculated according to the quantitative XPS model described by Kuipers,²⁰ electron mean free paths according to Seah,²¹ and

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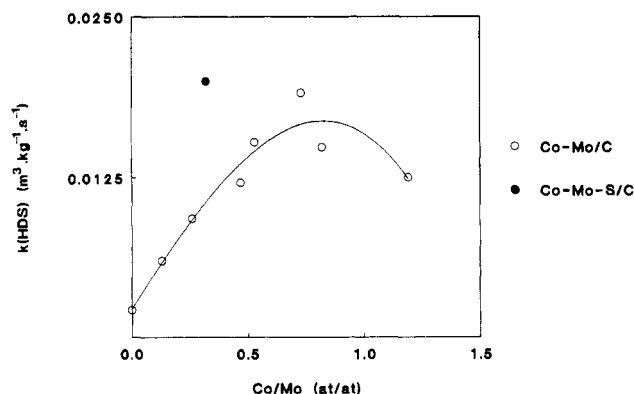


Figure 1. Thiophene HDS reaction rate constants, k_{HDS} , of the sulfided Co-Mo/C and Co-Mo-S/C catalysts as a function of the Co/Mo atomic ratio.

TABLE I: XPS Results of the Sulfided Co-Mo/C and Co-Mo-S/C Catalysts

	Co-Mo/C	Co-Mo-S/C
XPS binding energies, eV		
Co 2p _{3/2}	779.4	778.6
S 2p	162.4	162.5
$\Delta E(\text{Co } 2p_{3/2} - \text{S } 2p)$	617.0	616.1
Mo 3d _{5/2}	229.3	229.1
quantitative results		
$I_{\text{Mo}}/I_{\text{C}}^a$	0.08	0.11
MoS ₂ particle thickness, nm	0.7	0.5
$I_{\text{Co}}/I_{\text{C}}^b$	0.14	0.14
$S/(\text{Co} + \text{Mo}),^c \text{ mol} \cdot \text{mol}^{-1}$	1.4	2.1

^a Experimental Mo 3d to C 1s intensity ratio. ^b Experimental Co 2p to C 1s intensity ratio. ^c The total sulfur amount was corrected for the sulfur uptake of the carbon support itself ($I_{\text{S}}/I_{\text{C}} = 0.003$).

electron cross sections according to Scofield.²² The sulfur to molybdenum and cobalt stoichiometries were calculated according to Penn,²³ using the electron cross sections determined by Scofield²² and assuming the detector efficiency to depend on the reciprocal value of the electron kinetic energy.²⁴

Results

Catalytic Properties. The thiophene HDS reaction rate constants (k_{HDS}) of the promoted catalysts are represented in Figure 1 as a function of their Co/Mo atomic ratios. Since the Co-Mo-S/C catalyst (7.7 wt % Mo) contains about the same Mo content as the Co-Mo/C catalysts (7.5 wt % Mo), a direct comparison can be made. From Figure 1 it is apparent that the HDS activity of the Co-Mo-S/C catalyst is almost twice that of the conventionally prepared Co-Mo/C catalyst at Co/Mo = 0.3 atom/atom, which, fortuitously or not, is about the same factor as between the thiophene HDS activities of the Al₂O₃-supported "Co-Mo-S" type I and II structures reported by Candia et al.¹³ The maximum in HDS activity of the Co-Mo/C catalysts is situated at a Co/Mo atomic ratio of about 0.7. At higher Co contents the HDS activity decreases fast, resembling that of the Co(4.1)/C catalyst which is 0.011 m³·kg⁻¹·s⁻¹. The most active Co-Mo/C catalyst (Co/Mo = 0.73) was investigated with EXAFS and XPS.

XPS Results. XPS spectra were recorded of the sulfided Co-Mo/C (Co/Mo = 0.73) and the Co-Mo-S/C catalyst. The results are presented in Table I. As can be seen in Table I, the Co 2p_{3/2} XPS peak binding energies (BE's) are not the same in both catalysts. This is more clearly seen in the BE difference between the Co 2p_{3/2} and the S 2p peak (ΔE): ΔE is 617.0 eV for Co-Mo/C and 616.1 eV for Co-Mo-S/C. According to Alstrup et al.,²⁵ this XPS energy difference ΔE can be used to distinguish whether Co is present in a "Co-Mo-S" structure or

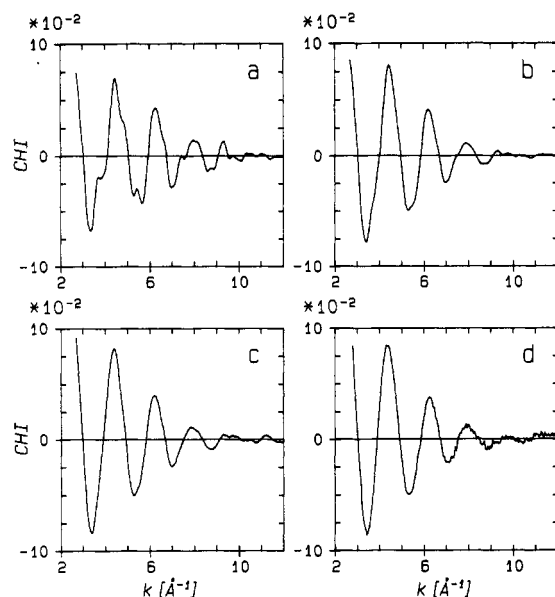


Figure 2. Raw EXAFS data of the Co₉S₈ model compound and the sulfided catalysts: (a) Co₉S₈, (b) Co/C, (c) Co-Mo/C, and (d) Co-Mo-S/C.

as Co₉S₈. In the case of Co₉S₈ a ΔE value of 616.2 eV was reported, whereas for "Co-Mo-S" this value was 617.0 eV.²⁵ Applying the latter findings to our results, the Co-Mo-S/C catalyst should actually consist of Co in the form of Co₉S₈. This is rather unlikely since MES clearly showed that only the "Co-Mo-S" structure is present in this catalyst.¹⁴ We therefore have to conclude that XPS peak binding energies do not allow to make an unequivocal distinction between Co₉S₈ and "Co-Mo-S". One might speculate whether the different carrier used by Alstrup et al. is the reason why their ΔE values are not applicable to our catalysts. We have at present no answer to this question.

As regards the Mo 3d_{5/2} BE's, both samples show nearly the same value, 229.2 eV, as reported by Vissers et al. for sulfided Mo/C catalysts and bulk MoS₂.²⁶ The quantitative XPS results also reveal some differences between the two promoted catalysts. The thickness of the MoS₂ particles in the Co-Mo-S/C catalyst (0.5 nm) seems slightly smaller than that in the Co-Mo/C catalyst (0.7 nm) but is actually within the accuracy of the measurements. The total sulfur content, expressed in the ratio S/(Co + Mo), is not the same in the two samples. The Co-Mo-S/C catalyst contains the highest sulfur percentage, as was to be expected on the basis of its lower Co/Mo ratio. But the observed S/(Co + Mo) ratios of respectively 1.4 and 2.1 for the Co-Mo/C (Co/Mo = 0.73) and Co-Mo-S/C (Co/Mo = 0.32) catalysts are different from the ratios of respectively 1.58 and 1.76, calculated on the basis of a CoS + MoS₂ stoichiometry. Why this is the case is not clear. The experimental S/(Co + Mo) ratio for Co-Mo/C is lower than the calculated one, which might point to a relatively high amount of cobalt sulfide at the outside of the catalyst support grains. Such a maldistribution has been observed before in Co/C catalysts.⁷ The Co-Mo/C catalyst, with its relatively high Co loading, might contain separate cobalt sulfide (as substantiated by the EXAFS results, see below), which is preferentially present at the outer part of the support grains. Why the S/(Co + Mo) ratio for the Co-Mo-S/C catalyst is higher than expected is not clear. MES analysis had shown that this catalyst exclusively contains the "Co-Mo-S" structure, so that a S/(Co + Mo) = 2.1 ratio can only be explained if the cobalt atoms are present in a CoS₂ type stoichiometry. Surprisingly, the XPS results show that the Co/C intensity ratio is the same for both samples. Since it

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TABLE II: Crystallographic Data and Fourier Transform Ranges for the Reference Compounds and the Co₉S₈ Model Compound

compound	crystallographic data				Fourier transformation		
	coordination	$R, \text{\AA}$	N^b	ref	n^c	k range, \AA^{-1}	r range, \AA
CoS ₂	Co-S	2.315	6	29	2	2.7–11.8	0.6–2.7
NiO	Ni-Ni	2.966	12	30	3	2.4–14.5	2.0–3.2
((C ₆ H ₅) ₄ P) ₂ Ni(MoS ₄) ₂	Ni-S	2.228	2	31			
		2.230	2				
	Ni-Mo	2.798	2		2	2.9–12.4	<i>d</i>
	Co ₉ S ₈	Co(t)-S ^e	2.127	1	32		
		2.227	3				
		Co(o)-S	2.359	6			
		Co(t)-Co(t)	2.505	3			
	Co(t)-Co(t)	3.474	3				
		3.543	3				

^aCoordination distance. ^bCoordination number. ^cWeight factor in the Fourier transformation. ^dNo direct inverse transformation has been applied on these data. See text for further comment. ^e(t) and (o) denote a tetrahedral and an octahedral cobalt atom, respectively. The ratio of tetrahedral to octahedral Co atoms is 8 to 1.

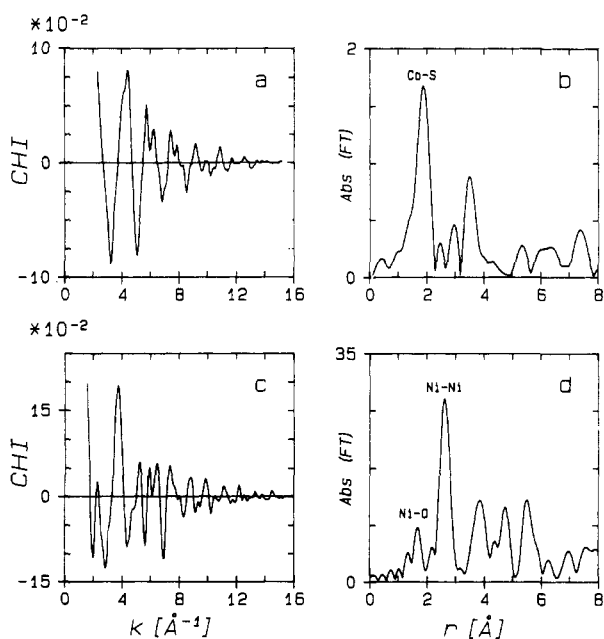


Figure 3. Raw EXAFS data and Fourier transforms of the reference compounds: (a, b) CoS₂ and (c, d) NiO.

is especially the Co/C ratio for the Co-Mo-S/C catalyst which is abnormally high, this result might indicate that during preparation of the Co-Mo-S/C catalyst Mo-Co-NTA complexes are preferentially deposited at the outside of the carbon support grains. Additional investigations are clearly needed.

EXAFS Spectral Characteristics. The EXAFS functions ($\chi(k)$) were obtained from the X-ray absorption spectra by standard procedures. Cubic spline routines²⁷ were used to remove the background. Normalization was performed by division of the edge height.²⁸ In Figure 2 the original EXAFS functions of the three catalysts together with that of the Co₉S₈ model compound are shown. The spectra of the reference compounds were processed in the same way as the catalyst samples, resulting in the EXAFS functions as displayed in the Figures 3a,c and 4a. Since the Co K-edge EXAFS spectra contained a Ni impurity (probably present in the beryllium windows of the EXAFS cell), the EXAFS data could only be used up to $k = 12 \text{ \AA}^{-1}$.

To obtain phase shifts and backscattering amplitudes, the EXAFS spectra of the reference compounds were Fourier-

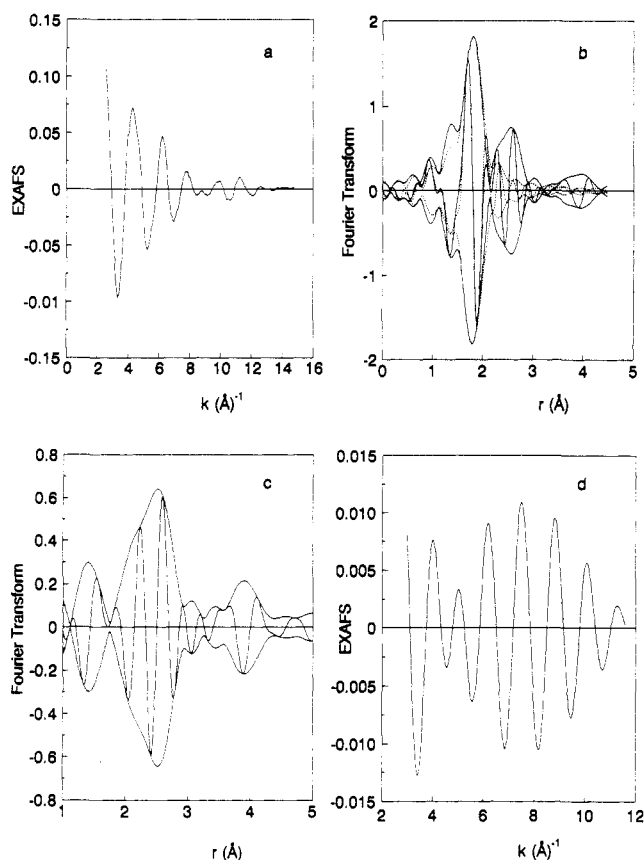


Figure 4. Raw EXAFS data (a) and Fourier transforms (b) of the ((C₆H₅)₄P)₂Ni(MoS₄)₂ reference compound. Dotted line in (b) corresponds to the best fit Ni-S contribution (see text). (c) Fourier transform (k^2 , $\Delta k = 2.9\text{--}12.4 \text{ \AA}^{-1}$) of difference EXAFS obtained by subtracting the best fit Ni-S EXAFS from the experimental data. (d) Isolated Ni-Mo reference data obtained by inverse Fourier transformation of (c) with $\Delta r = 1.8\text{--}3.3 \text{ \AA}$.

transformed over the largest possible range in k space. To avoid cutoff effects, k_{min} and k_{max} were chosen in nodes of the EXAFS function. In Figures 3b,d and 4b the Fourier transforms of the reference compounds are shown. An inverse transformation over a limited range in r space produced the EXAFS functions for the phase shift and backscattering amplitude of the desired absorber-scatterer pair. Table II presents the crystallographic data and the Fourier transform ranges of the reference compounds. For the ((C₆H₅)₄P)₂Ni(MoS₄)₂ compound no direct inverse transformation on the Ni-Mo peak could be applied since this peak was overlapped by the nearby Ni-S contribution; see Figure 4b. Hence, a different procedure was followed. The Ni-S first-shell contribution to the experimental data was calculated by using the phase shift and backscattering amplitude of the Co-S

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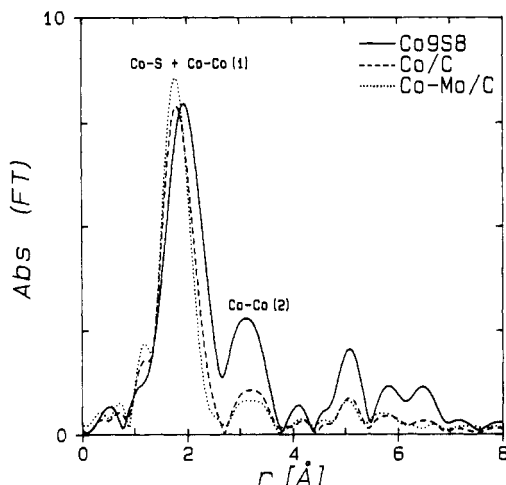


Figure 5. Absolute Fourier transforms (k^3 -weighted, $\Delta k = 3.0$ – 10.9 \AA^{-1}) of the Co_9S_8 model compound and the sulfided Co/C, Co-Mo/C, and Co-Mo-S/C catalysts.

absorber-scatterer pair from the CoS_2 reference compound with the crystallographic values $N = 4$ (coordination number) and $R = 2.22 \text{ \AA}$ (coordination distance) as input parameters. The two other coordination parameters $\Delta\sigma^2$ (difference between the Debye-Waller factors of the coordination to be analyzed and the corresponding coordination in the reference compound) and ΔE_0 (difference between the inner potentials of sample and reference compound) were adjusted until the peak of the calculated Ni-S contribution in the k^1 -weighted as well as in the k^3 -weighted Fourier transform superimposes with the corresponding peak of both the absolute and the imaginary part of the Fourier transform of the experimental data³³ (see also Figure 4b). This calculated Ni-S EXAFS was subtracted from the experimental data, and the difference spectrum was used to obtain the Ni-Mo phase shift and backscattering amplitude. The Fourier transform of the difference spectrum (see Figure 4c) showed one single peak which, after inverse transformation over the r range 1.8 – 3.3 \AA , yielded the Ni-Mo EXAFS (see Figure 4d) and the corresponding phase shift and backscattering amplitude.

The Co_9S_8 model compound is of particular interest in this study since it is the thermodynamical most stable cobalt sulfide compound under our reaction conditions. Co_9S_8 contains in its unit cell eight cobalt atoms in a distorted tetrahedron of sulfur atoms and one cobalt atom in a regular octahedron of sulfur atoms. The crystallographic data of Co_9S_8 are also collected in Table II. The absolute part of the Fourier transform (FT) spectrum of Co_9S_8 together with that of the Co/C and Co-Mo/C catalyst samples is shown in Figure 5. The three separate Co-S coordinations in Co_9S_8 (see Table II) will be denoted in the Fourier transform spectrum as one overall Co-S coordination. Likewise, the two separate Co-Co coordinations at about 3.5 \AA will be denoted as one overall Co-Co(2) coordination (indexed (2) to differentiate it from the first Co-Co coordination at 2.505 \AA). Regarding the known crystallographic distances, the first peak in the spectrum of Co_9S_8 has to be attributed to combined Co-S and Co-Co(1) coordinations and the second peak only to the Co-Co(2) coordination. (N.B. Fourier transforms of EXAFS data give peaks which are displaced to lower r values due to the phase shift function.) With regard to the spectra of Co/C and Co-Mo/C, it can be seen that their first peak is slightly shifted to lower r values. In general, however, it appears that the Co/C as well as the Co-Mo/C catalyst exhibits identical features as the Co_9S_8 compound. Furthermore, both catalyst spectra exhibit a small peak at about 5 \AA , indicating a relatively long range order in the cobalt sulfide particles.

Conclusive and more important information can be obtained from the imaginary part of the Fourier transform. In Figure 6

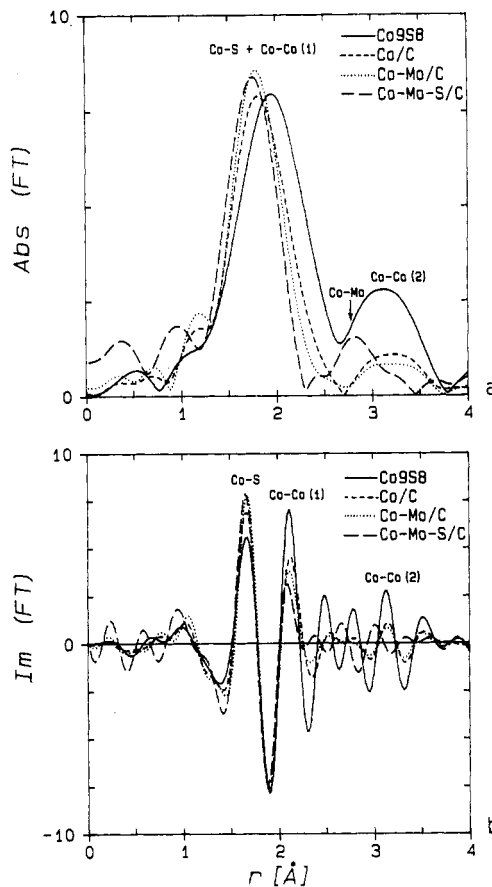


Figure 6. Fourier transform (k^3 , $k = 3.0$ – 10.9 \AA^{-1}) of the Co_9S_8 model compound and the sulfided Co/C, Co-Mo/C, and Co-Mo-S/C catalysts, showing in detail the first and second peaks: (a) absolute FT, (b) imaginary FT.

both the absolute (Figure 6a) and the imaginary part (Figure 6b) of the data characterizing Co_9S_8 , Co/C, Co-Mo/C, and Co-Mo-S/C are plotted over a smaller range of r values. The imaginary part of the Fourier transform (Figure 6b) shows the separate Co-S and Co-Co(1) coordinations which cannot be discerned in the absolute part of the FT (Figure 6a). It appears that the Co-S peak amplitude increases in the order $\text{Co}_9\text{S}_8 < \text{Co/C} < \text{Co-Mo/C} \leq \text{Co-Mo-S/C}$, while the Co-Co(1) peak amplitude decreases in the same order. It is striking in Figure 6b that the peak positions of the imaginary parts of the FT's of the Co-S and the Co-Co(1) coordinations are nearly equal in the Co_9S_8 , Co/C, and Co-Mo/C samples. Since these two contributions together compose the first peak in the absolute part of the FT, the observed shift of the latter peak to lower r values for the catalyst samples, therefore, can be fully explained by the increase in the Co-S peak amplitudes and the simultaneous decrease in the Co-Co(1) peak amplitudes. Hence, these results stress the importance of studying both the imaginary part and the absolute part of the Fourier transform. From Figure 6 it is furthermore clear that the Co-Co(2) coordination is not present in the Co-Mo-S/C catalyst, in contrast to the Co/C and the Co-Mo/C samples. On the other hand, the Co-Mo-S/C catalyst shows an additional peak at about 2.8 \AA which is not present in the other three samples and, consequently, might be ascribed to additional Mo backscatters.

EXAFS Data Analysis. The data analysis was carried out in two stages. The first stage comprised of isolating the first peak (Co-S and Co-Co(1)) in the FT (k^3 -weighted, the range was taken from about 3 to 11 \AA^{-1} , depending on the nodes of the EXAFS function). The inverse Fourier transformation was taken over the r range between 0 and about 2.7 \AA , depending on the nodes in the Fourier transforms (imaginary as well as absolute part). The Co-S and Co-Co(1) contributions in the resulting EXAFS functions were subsequently fitted by using the Co-S and Ni-Ni

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TABLE III: Structural Parameters of the Co-S, Co-Co(1), Co-Co(2), and Co-Mo Coordinations^a

sample	Co-S				Co-Co(1)				Co-Co(2)				Co-Mo			
	<i>N</i>	<i>R</i> , Å	$10^4\Delta\sigma^2$, Å ²	ΔE_0 , eV	<i>N</i>	<i>R</i> , Å	$10^4\Delta\sigma^2$, Å ²	ΔE_0 , eV	<i>N</i>	<i>R</i> , Å	$10^4\Delta\sigma^2$, Å ²	ΔE_0 , eV	<i>N</i>	<i>R</i> , Å	$10^4\Delta\sigma^2$, Å ²	ΔE_0 , eV
Co ₉ S ₈	4.8	2.21	48	3.0	2.7	2.51	17	-7.4	2.7	3.54	-6	-7.8				
Co/C	5.4	2.22	31	1.0	1.6	2.55	15	-6.5	1.2	3.55	-5	-7.0				
Co-Mo/C	6.2	2.22	36	3.0	1.2	2.53	26	-6.0	0.9	3.52	5	-6.0	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
Co-Mo-S/C	6.2	2.21	25	2.3									1.7	2.80	81	-6.5

^a Accuracies: *N*, ±20%; *R*, ±1%; $\Delta\sigma^2$, ±20%; ΔE_0 , ±10%. ^b Due to the overlap with the Co-Co shells, the Co-Mo contribution for the Co-Mo/C catalyst could not be observed. The coordination numbers have been corrected for the photoelectron mean free path (λ) dependency,³⁵ assuming that $\lambda = 5 \text{ \AA}$ for a Co atom.

EXAFS functions derived from the reference compounds. In the second stage, an inverse Fourier transformation was taken over the *r* range between 0 and about 3.7 Å. This resulted in an isolated EXAFS function containing the first (Co-S and Co-Co(1)) and the second peak (Co-Co(2)). The calculated Co-S + Co-Co(1) contributions were subtracted from the resulting EXAFS function, and the difference spectrum, which only contained the Co-Co(2) coordination, was fitted with the Ni-Ni reference EXAFS function. In the case of the Co-Mo-S/C catalyst, the difference spectrum, which only contained the expected Co-Mo coordination, was fitted by using the Ni-Mo reference EXAFS function. To determine reliably the parameters characterizing the high-*Z* (Co and Mo) and low-*Z* (S) contributions multiple-shell fitting in *k* and *r* space was done with application of both *k*¹ and *k*³ weighting. The use of both *k*¹ and *k*³ weighting is a prerequisite since the *k* dependence of the backscattering amplitude of low-*Z* elements (like S) is different from high-*Z* elements (like Co and Mo). The backscattering amplitude of the low-*Z* elements becomes very small at *k* ≥ 7 Å⁻¹, certainly in comparison with the amplitude of high-*Z* scatterers, which is still significant at higher *k* values.¹⁶ Application of only *k*³ weighting leads to an underestimation of the contribution of low-*Z* elements. Moreover, optimizing *k*¹ and *k*³ fits both in *k* and *r* space results in a better decoupling of *N* (coordination number) and $\Delta\sigma^2$ (Debye-Waller factor) as well as *R* (coordination distance) and ΔE_0 (inner potential correction) and therefore leads a more reliable set of parameters.³⁴

In some cases the EXAFS coordination numbers *N_E* obtained in the data analysis had to be corrected for the difference in distance between the absorber-backscattering pair of the reference shell and the shell to be analyzed. This is due to the factor $\exp(-2R/\lambda)$ in the EXAFS formula with λ the photoelectron mean free path.³⁵ The real coordination number *N* therefore is $N = N_E \exp\{2(R - R_{ref})/\lambda\}$. λ was taken to be equal to 5 Å, which is a reasonable approximation above *k* = 3 Å⁻¹.

The final results of the multiple-shell fitting procedures are shown in Figure 7. (The results are only shown with *k*³ weighting; the data with *k*¹ weighting are omitted for sake of superfluity.) The agreement between the primary EXAFS and the fits both in *k* and *r* space is entirely satisfactory. The structural parameters obtained with these EXAFS data analysis procedures are presented in Table III. This table shows a decrease of the Co-Co(1) and Co-Co(2) coordinations in the order of Co₉S₈, Co/C, and Co-Mo/C and a complete absence for Co-Mo-S/C; in the latter sample a Co-Mo coordination could be analyzed. This is further illustrated in detail in Figure 8a, where the curves represent EXAFS data obtained after subtraction of the Co-S contribution (calculated for each sample with the coordination parameters as given in Table III) from the isolated EXAFS functions. Therefore, the two peaks in the Fourier transform are due to the Co-Co(1) and the Co-Co(2) coordinations. Details for the Co-Mo coordination in the Co-Mo-S sample are given in Figure 8, b (in *k* space) and c (in *r* space). The solid line in these figures represents the difference data between the isolated EXAFS and the Co-S contribution calculated with the coordination parameters given in Table III. The analyzed Co-Mo contribution is given in Figure

8b,c with dotted lines. No clear indication of a Co-Mo coordination could be observed in the Co-Mo/C catalyst, possibly because it is strongly overlapped by the Co-Co(2) peak, as well as the Co-S plus Co-Co(1) peak.

It is now possible to estimate the statistical significance of the Co-Mo contribution in the Co-Mo-S/C sample. The noise amplitude in the raw EXAFS data of this sample (see Figure 2d) can be determined to be 5×10^{-3} at *k* = 11 Å⁻¹. The signal amplitude of the Co-Mo EXAFS presented in Figure 8b amounts to 10⁻² at *k* = 6 Å⁻¹, leading to a S/N = 2 which is above the detection limit.

Discussion

To answer the question about the role of Co in Co-Mo catalysts, we must first discuss the structure of the catalytic phases present on the support. To that end we will discuss our EXAFS results shell by shell in the order as presented in Table III, starting with the Co-S shell and ending with the Co-Mo shell. The catalysts will be compared among themselves and with the Co₉S₈ model compound. Having analyzed the EXAFS and XPS data, we will use the resulting information to construct a geometric model of the location of the Co promoter atoms at the edges of the MoS₂ crystallites. All the structural results will finally be used to explain the catalytic activities of the Co-promoted carbon-supported MoS₂ catalysts.

Co-S Coordination. The three nearest Co-S coordinations in the Co₉S₈ model compound were fitted by using one overall Co-S coordination, and the results should be compared with the average Co-S coordination distance and coordination number obtained from the crystallographic data (Table II). The theoretical average Co-S coordination number is $N = 8/9 \times 4 + 1/9 \times 6 = 4.22$, while the theoretical average Co-S distance as determined by EXAFS is $R = [8/9 \times (2.127 + 3 \times 2.227) + 1/9 \times 6 \times 2.359]/4.22 = 2.228 \text{ \AA}$. Comparing these data with the EXAFS results *N* = 4.8 and *R* = 2.21 Å (Table III), the agreement is good. Hence, the use of one overall Co-S coordination is justified.

The EXAFS data analysis revealed that the Co-S coordination number increases in the order Co₉S₈ < Co/C < Co-Mo/C ≈ Co-Mo-S/C. Apparently, the cobalt atoms in the freshly sulfided catalysts have a higher sulfur coordination than those in Co₉S₈. Taking into account a 20% absolute inaccuracy of the coordination number, the Co-S coordination numbers of 6.2 and 6.3 of the sulfided Co-Mo/C and Co-Mo-S/C catalysts, respectively, point to a 5-, 6-, or 7-fold sulfur surrounding of the cobalt atoms. A seven coordination of first-row transition metal ions has only been observed in very special cases, however. For instance, Lewis and Fay published the structure of monochlorotitanium tris(*N,N*-dimethyldithiocarbamate), in which the titanium atom is surrounded by a chlorine atom at 2.31 Å and six sulfur atoms at an average distance of 2.51 Å.³⁶ As to be expected for such a high coordination, these M-S distances are much larger than our Co-S distance of 2.22 Å. The coordination numbers observed for the Co-Mo/C and Co-Mo-S/C catalysts thus point to a 6-fold (may be 5-fold) sulfur coordination by the Co atoms. It is remarkable that the Co-S coordination number of the sulfided Co/C catalyst is higher than that of Co₉S₈. For, if small Co₉S₈ crystallites with a relatively large surface area were present in this catalyst, one

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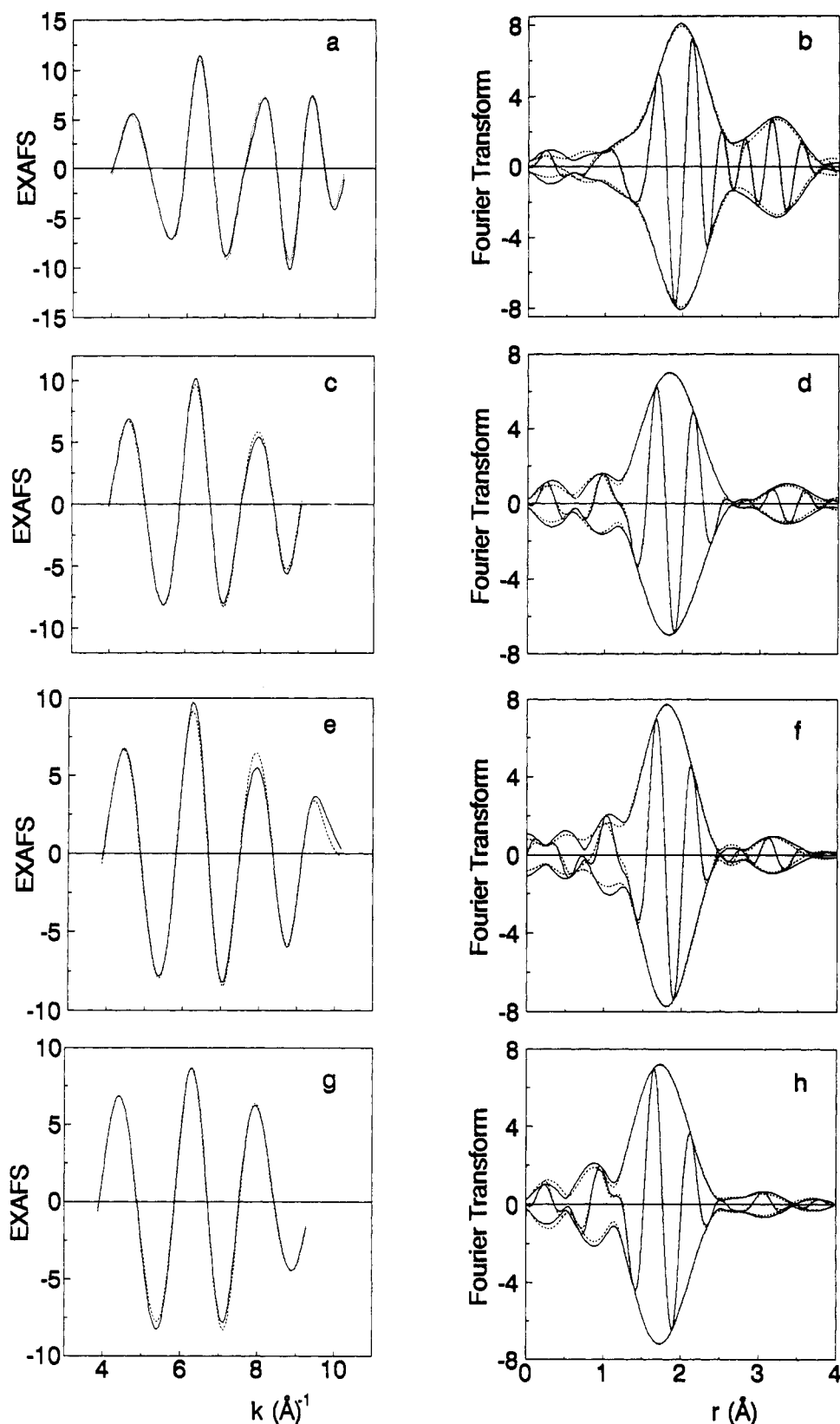


Figure 7. k^3 -weighted fits in k and r space. Solid lines represent isolated EXAFS functions, while the sum of the calculated Co-S, Co-Co(1), Co-Co(2), and Co-Mo shells is given by dotted lines. The Fourier transform ranges in k space are shown in brackets. (a, b) Co_9S_8 (4.0–10.2 \AA^{-1}), (c, d) Co/C (4.0–9.1 \AA^{-1}), (e, f) Co-Mo/C (3.9–10.2 \AA^{-1}), and (g, h) Co-Mo-S/C (3.9–9.3 \AA^{-1}).

would expect a lower average coordination number than in bulk Co_9S_8 . This is illustrated by our EXAFS study of a sulfided Mo/C catalyst, in which we obtained a Mo-S coordination number clearly below 6, the value for bulk MoS_2 .^{37,38} XPS measurements

on sulfided Co/C catalysts by Vissers et al.⁷ showed atomic S-to-Co ratios of 1.3 to 1.5, much higher than the theoretical value of 0.89 for Co_9S_8 . Having only XPS data available, these authors explained this excess of sulfur as resulting from the deposition

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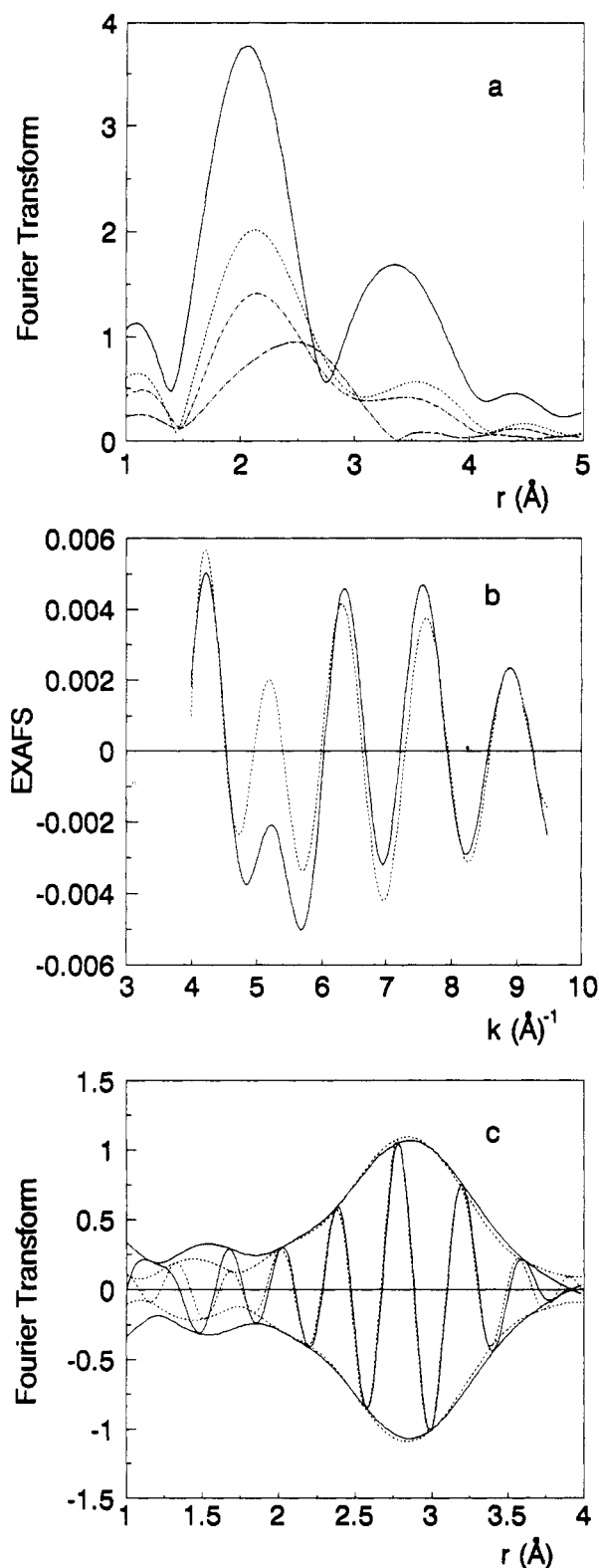


Figure 8. (a) Magnitude of Fourier transform (k^3 , $\Delta k = 4.3\text{--}9 \text{ \AA}^{-1}$) of EXAFS difference data, obtained after subtracting the best fit Co-S contribution from the isolated EXAFS functions of Co_9S_8 (—), Co/C (---), Co-Mo/C (---), and Co-Mo-S (---). (b) Difference EXAFS data ($k^3\chi(k)$) for the Co-Mo-S/C sample obtained after subtracting the best fit Co-S from the isolated EXAFS data (solid line) and best fit Co-Mo contribution (dotted line) and (c) the corresponding Fourier transforms (k^3 , $\Delta k = 4\text{--}9.2 \text{ \AA}^{-1}$, Ni-Mo phase corrected).

of sulfur in the micropores of the carbon support, but it is certainly possible that all sulfur is associated with the cobalt atoms. It might well be that the Co atoms at the surface of the Co_9S_8 crystallites have adsorbed H_2S to fill the vacancies. In this way the XPS results would be in line with the EXAFS findings.

TABLE IV: Crystallographic Co-S and Co-Co Distances in Cobalt Sulfides

compound	distances, \AA			Co-Co	ref
	Co-S ^a				
	t	o	sqp		
Co_9S_8	2.13	2.36		2.50	32
	2.23			3.47	
$\beta\text{-CoS}^b$		2.33		3.54	40
				2.55	
$\gamma\text{-NiS}^c$			2.26	3.38	41
			2.38	2.53	
Co_3S_4 , Co_2S_3	2.19	2.40		3.15	42, 43
CoS_2		2.32		3.90	29
				3.91	

^aCo in tetrahedral (t), octahedral (o), or square-pyramidal (sqp) site. ^bWith NiAs structure. ^cWith NiS millerite structure. The corresponding distances for $\gamma\text{-CoS}$ should be close to those of NiS millerite.

TABLE V: Structural Parameters for Co-Mo-S/C

	Co-S				Co-Mo			
	N	R, \AA	$10^4\Delta\sigma^2$, \AA^2	ΔE_0 , eV	N	R, \AA	$10^4\Delta\sigma^2$, \AA^2	ΔE_0 , eV
model A	6.2	2.21	48	3	1.7	2.80	81	-7
model B	4.4	2.18	28	0	2.0	2.87	90	-14
	2.2	2.24	-8	3				

Concerning the Co-S coordination distance in the samples studied, it is noteworthy that this distance remained the same ($2.22 \pm 0.01 \text{ \AA}$), regardless of the Co-S coordination number. Almost the same value (2.23 \AA) has been measured for a sulfided Co-Mo/ Al_2O_3 catalyst by Topsøe et al.³⁹ For the Co-Mo/C and Co-Mo-S/C catalysts, in which the Co atoms seem to be coordinated by six sulfur atoms, the Co-S distance of 2.22 \AA is even more remarkable since 6-fold octahedrally coordinated Co in cobalt sulfides has significantly longer Co-S distances. For instance, 2.33 \AA in CoS, 2.32 \AA in CoS_2 , 2.40 \AA in Co_3S_4 and Co_2S_3 , and 2.36 \AA in Co_9S_8 (Table IV). In fact, a Co-S distance of 2.22 \AA is typical for a 4- or 5-fold Co-S coordination. Thus, the tetrahedral Co atoms in Co_9S_8 have Co-S distances of 2.13 and 2.23 \AA and square-planar Co coordination complexes have Co-S distances of $2.15\text{--}2.17 \text{ \AA}$,⁴⁴ while for 5-fold sulfur coordinated square-pyramidal Co complexes four short Co-S distances in the range of $2.14\text{--}2.21 \text{ \AA}$ and one long Co-S distance of about 2.4 \AA have been measured.⁴⁵ Evidently, there is a conflict between the Co-S coordination distances and coordination numbers of the Co-Mo-S/C and Co-Mo/C catalysts. Since the reliability of distances measured by EXAFS is much higher than that of coordination numbers, and also since the reliability of the measured distances is good enough to be able to distinguish between 4- and 5-fold S coordination on the one hand and 6-fold S coordination on the other hand, we feel that the only way to resolve this discrepancy is to assume that the cobalt atoms have a distorted 6-fold coordination. Probably there are four short Co-S distances like in a square-planar or square-pyramidal coordination, and two additional sulfur atoms at somewhat longer distance. To check this suggestion, we reanalyzed the EXAFS spectrum under the assumption that there are two kinds of Co-S distances. The results of this analysis are presented under Model B in Table V. For comparison, the results of the analysis with equal Co-S distances are also presented in Table V under model A. The reanalysis

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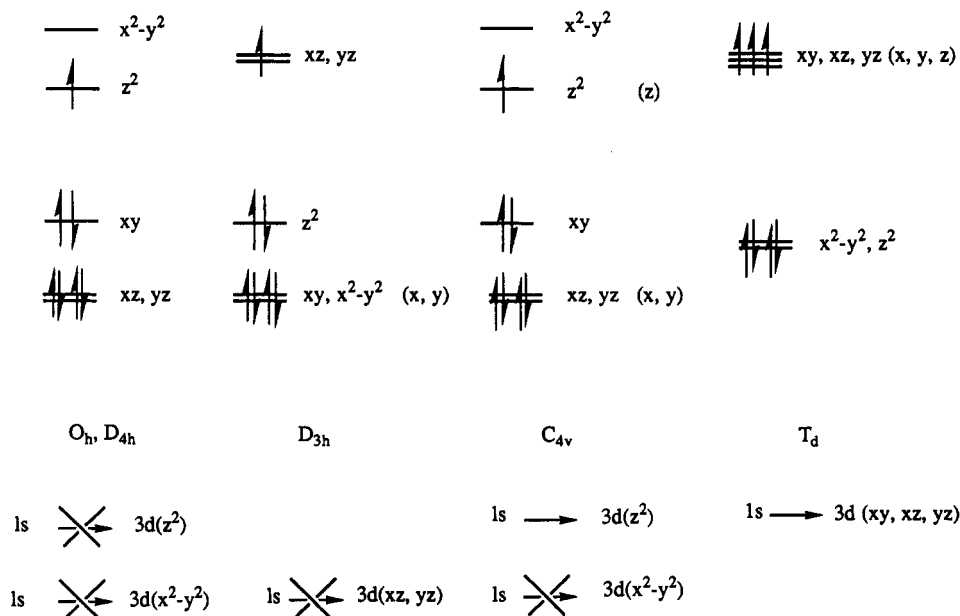


Figure 9. Molecular orbital diagram and 3d electron filling for Co^{2+} in an octahedral (O_h), square-planar (D_{4h}), trigonal-prismatic (D_{3h}), square-pyramidal (C_{4v}), and tetrahedral (T_d) site. The notation (x, y) and (z) indicates that an electronically allowed $1s \rightarrow 3d$ transition to the corresponding molecular orbital is allowed.

showed that the EXAFS spectrum of the Co-Mo-S/C catalyst could very well be fitted with about four sulfur neighbors at 2.18 Å, two sulfur neighbors at 2.24 Å, and two molybdenum neighbors at 2.87 Å. The improvement of the fit by adding an additional shell of neighbors in comparison to model A was, however, not significant enough to be able to state unequivocally that model B is to be preferred over model A.

It is instructive to compare the EXAFS results on the sulfur surrounding with the preedge $1s \rightarrow 3d$ transition present in the XANES spectra.¹¹ As indicated in Figure 9, group theory predicts that no $1s \rightarrow 3d$ transition is allowed for sites containing a center of symmetry (octahedral and square-planar sites, O_h and D_{4h}). For trigonal-prismatic sites such a transition is only possible to the xy and $x^2 - y^2$ orbitals, meaning that transition-metal ions (like Co and Ni) with four or more d electrons in D_{3h} sites will have a low preedge intensity. For square-pyramidally coordinated transition-metal ions $1s \rightarrow 3d$ transitions are possible not only to the xz and yz orbitals but also to the z^2 orbital. As a consequence, a transition-metal ion in a C_{4v} site with seven or fewer d electrons might have a considerable preedge intensity, whereas an ion with eight or more d electrons will have a very small preedge intensity. For a transition-metal ion that is tetrahedrally coordinated, the $1s \rightarrow 3d$ transition is always allowed unless the d orbitals are completely filled. In the XANES spectra of Co/C, Co-Mo/C, Co-Mo-S/C, Co_9S_8 , and CoS_2 a weak preedge absorption peak is present.¹¹ This peak is most intense in Co_9S_8 , in which 8/9 of the Co ions are in tetrahedral positions, whereas it is very low for CoS_2 , in which all Co ions are in octahedral positions. The sulfided Co/C catalyst shows a similar intensity as Co_9S_8 , Co-Mo/C has a slightly lower intensity, but the Co-Mo-S/C catalyst had a comparably low intensity as CoS_2 . The low $1s \rightarrow 3d$ peak intensity of the Co-Mo-S catalyst thus indicates that its cobalt sites have a center of symmetry or that the cobalt sites are in trigonal-prismatic sites. Since the Co-S coordination numbers are all clearly above 4, the presence of square-planar sites can be excluded. The observation that the $1s \rightarrow 3d$ transition of the Co-Mo-S/C catalyst is comparable in intensity to that of CoS_2 even suggests a pure octahedral or trigonal-prismatic coordination in the Co-Mo-S/C catalyst.

Co-Co Coordination. The first Co-Co coordination (Co-Co(1)) in bulk Co_9S_8 could be fitted with $R = 2.50$ Å, a value which agrees very well with the crystallographic data (Tables II and IV). The Co-Co(1) coordination number of 2.7 is close to the theoretical value of $3 \times 8/9 = 2.67$. In the Co/C and Co-Mo/C catalysts a Co-Co(1) coordination is present with an in-

teratomic distance of 2.55 and 2.53 Å, respectively, slightly longer than in bulk Co_9S_8 (2.505 Å). The shortest Co-Co distance in bulk β -CoS, which has the NiAs structure with Co in octahedral holes, is 2.55 Å,⁴⁰ while that in γ -CoS⁴⁰ should be close to that in NiS millerite, which is 2.53 Å.⁴¹ These values correspond closely to our findings and might suggest that a CoS-like structure is present in the catalysts. However, the observed Co-S distances (Table III) are too short for CoS (cf. Table IV), while also the Co-Co(2) distances do not fit (vide infra). Other cobalt sulfide structures can be excluded too, since their shortest Co-Co coordination distance is much longer than 2.55 Å (cf. Table IV). The EXAFS spectrum of the Co-Mo-S/C catalyst could be fitted without any Co-Co contribution.

The Co-Co(2) coordination in Co_9S_8 ($R = 3.54$ Å) appeared to have a coordination number of 2.1, which is much smaller than the theoretical value of $6 \times 8/9 = 5.33$. The explanation for this is not clear, but it might be that higher shells interfere with the Co-Co(2) shell, since not fewer than seven different coordination shells are situated between 4 and 4.5 Å. The occurrence of interference effects is also suggested by the absolute FT spectrum of Co_9S_8 between 4 and 5 Å (Figure 5): a small peak is present at about 4 Å, flanked by a much larger peak at about 5 Å. Since the number of coordinations in both regions is approximately the same, the $1/R^2$ dependency in the EXAFS amplitude equation^{28,33} would predict that the peak at 4 Å is larger than that at 5 Å. It is clear that the higher shells in the Co_9S_8 compound are difficult to analyze due to the complexity of the crystal structure.

A Co-Co(2) contribution was present in the Co/C and Co-Mo/C catalysts but not in the Co-Mo-S/C sample. The Co-Co(2) coordination distances of 3.55 Å for Co/C and 3.52 Å for Co-Mo/C are characteristic for Co_9S_8 and not for other types of cobalt sulfides. Thus, in bulk β -CoS the second Co-Co distance is 3.38 Å⁴⁰ and in millerite (NiS) which should be close to γ -CoS it is 3.15 Å,⁴¹ while in Co_3S_4 it is 3.90 Å⁴² and in Co_2S_3 3.92 Å⁴³ (cf. Table IV). Furthermore, the spectral features of the higher shells in the Co/C and Co-Mo/C catalysts resemble those of bulk Co_9S_8 (see Figure 5). Hence, both the Co-Co(1) and Co-Co(2) findings suggest that a Co_9S_8 type phase is present in the Co/C and Co-Mo/C catalysts.

Co-Mo Coordination. The EXAFS data analysis of the Co-Mo-S/C catalyst revealed the presence of a Co-Mo contribution. The Co-Mo coordination distance was found to be 2.80 Å (model A) or 2.87 Å (model B) (cf. Table V), which is in agreement with our EXAFS study of a Co-Mo/C catalyst at the Mo K-edge,^{37,38} in which we reported a Mo-Co distance of 2.8 ± 0.1 Å. The

calculated Co–Mo coordination number of 2.3 (Table III) suggests that in the Co–Mo–S/C catalyst every cobalt atom is in contact with two molybdenum atoms. No clear indication of a Co–Mo coordination could be observed in the Co–Mo/C (Co/Mo = 0.73) catalyst. This might be due to the fact that for this catalyst the Co–Mo coordination number $N(\text{Co–Mo})$ is lower than in the Co–Mo–S/C catalyst. Namely, since EXAFS is a bulk technique and measures every atom of the element under study, the relation $N(\text{Co–Mo}) = N(\text{Mo–Co}) \cdot N(\text{Mo}) / N(\text{Co})$ must hold if all Co atoms are present in the Co–Mo–S structure. ($N(\text{Mo})$ and $N(\text{Co})$ are the total number of Mo and Co atoms in the sample, respectively.) With $N(\text{Mo–Co}) = 0.3^{38}$ and $N(\text{Co})/N(\text{Mo}) = 0.73$, one obtains $N(\text{Co–Mo}) = 0.4$. Since it is obvious from the observed Co–Co(1) and Co–Co(2) distances that the Co–Mo/C sample contains a substantial amount of a Co_9S_8 -like cobalt sulfide phase, the real $N(\text{Co–Mo})$ will be even smaller than 0.4. Such a small Co–Mo coordination number originating from the Co–Mo–S structure will be difficult to analyze in the midst of the Co–Co contributions of the cobalt sulfide phase.

Structure of the “Co–Mo–S” State. From the Mo K-edge EXAFS spectrum of a sulfided Co(2.7)–Mo(6.0)/C catalyst it was concluded that the Mo phase has a MoS_2 structure.^{37,38} Furthermore, in our EXAFS study of alumina-supported “Co–Mo–S” type I and type II structures, we concluded that the Mo sulfide particles in the type II “Co–Mo–S” structure consisted of fully sulfided Mo atoms.⁴⁶ Hence, it can be assumed that in the Co–Mo–S/C catalyst the Mo sulfide phase is also present in the form of fully sulfided MoS_2 particles. According to the Co K-edge EXAFS the Co atoms must be located at the surface of these fully sulfided MoS_2 particles in such a way that every Co atom is surrounded by four S atoms at 2.2 Å and by two other S atoms, probably at a somewhat larger distance (Table V). Furthermore, there are about two Mo atoms at 2.80 Å. We shall show that these data cannot be reconciled with a position of the Co atom in between subsequent MoS_2 sandwich layers, as proposed by Farragher and Cossee.⁴⁷ Nor can our data be explained by the models of Ledoux et al.^{8,9,48} and Harris and Chianelli.¹⁰ They can, however, be explained by a model in which the Co atoms are attached to the square S_4 faces along the MoS_2 edges.

Some time ago Farragher and Cossee suggested that the Ni atoms in Ni– WS_2 are situated at the edges of the WS_2 crystallites in octahedral holes between the top layer of one WS_2 sandwich layer and the bottom sulfur layer of the next WS_2 sandwich layer.⁴⁷ In analogy, the same edge-intercalated octahedral position should be occupied by the Co atoms in Co– MoS_2 . But the Co atoms cannot occupy such positions, because our short EXAFS Co–S coordination distances exclude the possibility of Co being in octahedral holes. Furthermore, the minimum Co–Mo distance in a MoS_2 lattice would be $c/4 = 3.08$ Å, which is much larger than the observed value of 2.80 Å. Also, the Co atom would have to be directly above a Mo atom (along the c axis) in contrast to the position proposed.⁴⁷

In their review on the structural chemistry of Co–Mo/ Al_2O_3 catalysts, Ratnasamy and Sivasanker suggested that the Co atoms are not intercalated between MoS_2 sandwich layers but are situated along the MoS_2 edges in the plane of the Mo atoms.⁴⁹ The IR study of NO adsorption on Co–Mo/ Al_2O_3 catalysts by Topsøe and Topsøe proved that the Co atoms are indeed located at the MoS_2 edges in the plane of the Mo atoms.⁵⁰ Ledoux et al.^{8,48} proposed that half of these Co atoms are in octahedral sulfur coordination and attached to the MoS_2 edge via two Mo atoms. The other half of the Co atoms are in tetrahedral sites which are bridged to the octahedral Co sites. This structure would yield

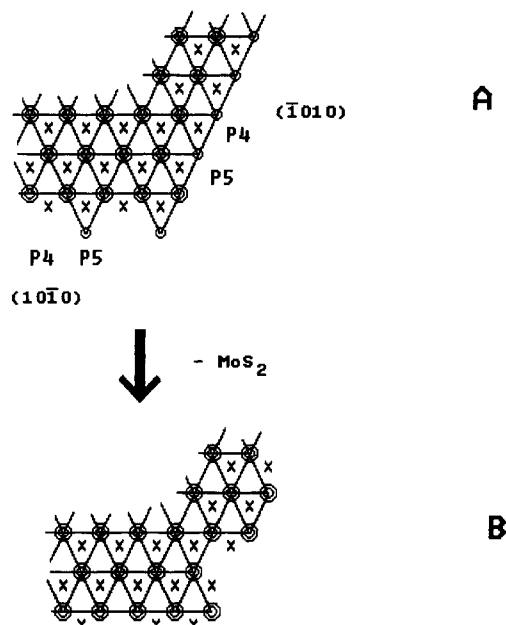


Figure 10. Top view of the $(10\bar{1}0)$ and $(\bar{1}010)$ edges of a single slab of MoS_2 . (A) Most stable edges and (B) reconstructed edges after removal of one MoS_2 unit: \times , Mo (or Co at the edge); \circ , single S atom; \odot , two S atoms on top of each other; $P(n)$ stands for a Mo(Co) site with n sulfur ligands.

an average Co–Mo as well as Co–Co coordination number of one and an average Co–S coordination number of five. These coordination numbers (and also the coordination distances) do not agree with our results. In addition, it should be remarked that the proposal of Ledoux et al.⁴⁸ is based on the wrong idea that the ideal, nonreconstructed edge surface of MoS_2 contains triangular groups of S atoms which can form the basis for an octahedral Co site.

Another model for the Co–Mo site was used by Harris and Chianelli in molecular orbital calculations of the promoter effect.¹⁰ Also this model, in which it is assumed that the Co as well as the Mo atom is octahedrally surrounded by six sulfur atoms and that the two octahedra share a face of three sulfur atoms, can be rejected.

Our EXAFS results are in full agreement with a model in which the Co atoms are located at the MoS_2 edges in the plane of the Mo atoms. The $(10\bar{1}0)$ and $(\bar{1}010)$ edges are the most dominant edges in pure MoS_2 crystals.⁵¹ When no reconstruction takes place, several different Mo sites exist on these edges, the most stable of which are indicated in Figure 10A. If it is assumed that the Co atoms replace the edge Mo atoms, the Co atoms will occupy P4 or P5 sites⁵¹ with a 4-fold or a 5-fold sulfur coordination, respectively. Because of the lower sulfur-to-metal stoichiometry for cobalt sulfide than for MoS_2 , the coordination number of Co may even be lower. On the other hand, additional adsorption of H_2S may increase it again. In three of the four positions indicated in Figure 10A part of the local structure around Co consists of a square of S atoms to which the Co atom is attached. In the P5 sites there is an additional S atom which completes a square-pyramidal coordination. A slight reconstruction of the “most stable” MoS_2 edges gives an edge surface in which all Mo (and thus Co) surface atoms have the same square-pyramidal structure (Figure 10B). The observed Co–S distances of 2.21–2.22 Å are in perfect agreement^{44,45} with such a square coordination. To attain these distances, which are shorter than the Mo–S distance of 2.41 Å, a small contraction of the S_4 square along its edges and a slight inward displacement of the Co atoms from the ideal Mo positions are necessary. Such a displacement also brings the Co–Mo distance in better agreement with the experimental value (2.80 Å, instead of the Mo–Mo distance of 3.16 Å). It is conceivable that the coordination of the Co atoms is essentially

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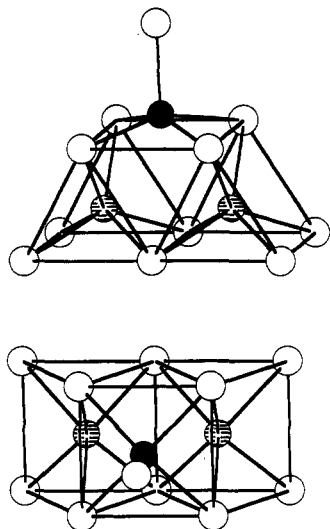


Figure 11. Top and side view of a square-pyramidal "Co-Mo-S" structure.

that of five sulfur atoms in a square-pyramidal structure (Figure 11). Adsorption of H_2S might add a sixth sulfur atom which could, together with the fifth sulfur atom, be positioned in front of the S_4 plane in the fifth and sixth position of a trigonal prism. If the Co atom in this trigonal prism is slightly off center toward the S_4 plane, there will be four short and two long Co-S distances. Why Co is six-coordinated by sulfur in Co-Mo-S on carbon while it is five-coordinated in Co-Mo-S on Al_2O_3 and SiO_2 ⁴⁶ is not clear. If indeed the high S coordination is due to H_2S adsorption, it may have to do with the narrower pores of the carbon support, which could hinder the desorption of H_2S during flushing with helium. This question will be a subject of further study.

Although the square-pyramidal CoS_5 unit may seem strange for cobalt sulfides, γ -CoS has been reported to have the millerite structure.⁴⁰ In millerite (NiS) each Ni atom is 5-fold coordinated by sulfur atoms in a square-pyramidal way.⁴¹ It is remarkable that not only Co in Co-Mo-S but also Ni in Ni-Mo-S adopts such a square-pyramidal coordination, as shown by our EXAFS investigation of the Ni coordination in sulfided Ni-Mo catalysts.⁵²

A question which has been left unanswered is if also in the Co-Mo/C catalyst Co atoms are present at the edges of the MoS_2 crystallites, as in the Co-Mo-S/C catalyst. The observation of Co-Co(1), Co-Co(2), and higher EXAFS coordinations (Figure 5) as well as a low S/(Co + Mo) XPS ratio demonstrates that at least part of the Co in the Co-Mo/C catalyst is present in the form of a Co_9S_8 -like phase. No Co-Mo coordination was observed, and therefore one might be tempted to conclude that no Co-Mo-S structure is present. However, if part of the Co is present as Co_9S_8 and the other part as Co-Mo-S, it is difficult to detect the weak Co-Mo contribution, also because of the short k range of the data ($\Delta k = 6.3 \text{ \AA}^{-1}$). For the Brillouin theorem ($N = 2\Delta k\Delta R/\pi$) only allows a three-shell EXAFS analysis, instead of a four-shell analysis (Co-S, Co-Co(1), Co-Co(2), and Co-Mo, $N = 4 \times 4 = 16$) to be made in the $R = 1\text{-}4\text{-\AA}$ range. Our EXAFS data therefore do not prove, but also do not disprove, the existence of a Co-Mo-S structure in the Co-Mo/C catalyst. In a study of a series of equivalent Ni-Mo/C catalysts with varying Ni/Mo ratio and with a larger k range, it proved possible to detect both Ni_3S_2 and Ni-Mo-S structures in catalysts with Ni/Mo > 0.5.⁵³ This suggests that also in the Co-Mo/C catalyst (Co/Mo = 0.73) a Co-Mo-S structure may be present. Support for this suggestion comes from the observation of a Mo-Co contribution in the Mo EXAFS spectrum of Co-Mo/C³⁸ and from the observation that the Mössbauer spectrum of a Co-Mo/C catalyst with Co/Mo = 0.54 can be fully assigned to Co in the Co-Mo-S structure.⁵⁴

At the end of this discussion of the EXAFS data in terms of models for the local Co structure, it is appropriate to reiterate on the one hand that EXAFS is a bulk technique, which can only give average coordination parameters, and on the other hand that the ability to fit a structural model to the EXAFS data is a necessary but not sufficient condition for the uniqueness of the model. Even if one can fit a model very well with the EXAFS data, one is never completely sure that there is no other model which is in accordance with the data. But this unidirectionality is of course not unique to EXAFS.

Catalytic Properties. The final question to be addressed is whether one can understand the thiophene HDS activities of the Co and Co-Mo sulfide catalysts from their structures. The EXAFS results indicate that the Co atoms in Co-Mo-S/C have a distorted 6-fold S coordination, with four short and two long Co-S distances. One (or both) of the long Co-S distances might belong to a H_2S molecule adsorbed on the Co. In accordance with this suggestion, in Al_2O_3 - and SiO_2 -supported Co-Mo-S catalysts the sixth Co-S coordination was not observed.⁴⁶ All this suggests that the Co sites in freshly sulfided and (lightly) purged carbon-supported catalysts have a square-pyramidal CoS_5 or square-planar CoS_4 basic structure. If the sixth and fifth ligands are indeed H_2S molecules, they can desorb at the elevated temperature of the catalytic reaction and make place for a thiophene molecule. A five-coordinated catalytically active site can still adsorb a thiophene molecule via σ bonding, while a four-coordinated site can adsorb the thiophene molecule via σ bonding as well as via π bonding. If one furthermore realizes that some of the remaining ligands are actually SH ligands (because of charge neutrality, when replacing a Mo^{4+} by a Co^{2+} cation), one has all the ingredients needed for hydrodesulfurization:¹ the adsorbate, the protons, and the electrons, which come from the MoS_2 lattice and are transmitted by the Co atom.

Apparently a Co atom attached to a square of sulfur atoms, with or without an additional fifth S atom, is needed for the hydrodesulfurization. In the unpromoted MoS_2 many of the Mo edge atoms assume similar positions, and it thus looks as if the function of the MoS_2 is to induce the Co atoms to assume the same or similar positions as the edge Mo atoms do. Of course, the Co atoms will only do so and stay in these positions if these positions are not too unfavorable. In this respect it is worthwhile to repeat that among the Co and Ni sulfides there is one structure, the millerite structure, in which the Co and Ni atoms are exactly in such square-pyramidal sites, CoS_5 and NiS_5 .

More or less implicit in the foregoing discussion has been that the catalytically active site in Co-Mo-S/C is a Co site and not a Mo or a mixed Mo-Co site. Support for this assumption comes from our Mo K-edge EXAFS results,⁴⁶ which demonstrated that the Mo-S coordination number in the same Co-Mo-S/C catalyst is 6.0. Obviously, in this cautiously prepared¹⁴ catalyst all Mo atoms are fully surrounded by sulfur atoms, as confirmed by the high S to Co + Mo stoichiometry observed with XPS (Table I). Also, the IR study of the adsorption of NO on Co-Mo catalysts by Topsøe and Topsøe indicated that the edge Mo atoms in Co-Mo-S catalysts are covered.⁵⁰ But if the Mo atoms are fully surrounded, they have no room left for the thiophene to adsorb and they cannot be directly responsible for the catalysis. We conclude that either the Co atoms by themselves, or modified by electronic interactions with the Mo atoms, are responsible for the HDS catalytic properties.

The idea that the cobalt in sulfided Co-Mo catalysts is the actual catalyst rather than the promoter originates from the observations that sulfided Co/C catalysts have a very high activity for the HDS of thiophene⁶ and that the estimated turn over frequency of the cobalt in sulfided Co-Mo/C catalysts is about equal to that of cobalt in sulfided Co/C.⁷ From our EXAFS data it is not obvious whether the structure of the cobalt atoms in Co/C is equal to that in Co-Mo-S/C, as one might expect if Co/C is a good model system for Co in Co-Mo-S/C. As discussed in the

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foregoing, the Co-S and Co-Co coordinations point to the presence of Co_9S_8 in Co/C. The Co-S coordination number of 5.4 is too large for Co_9S_8 , however, since there are eight Co atoms with a tetrahedral sulfur coordination and one with an octahedral coordination in Co_9S_8 . One possibility is that the Co_9S_8 surface contains relatively more octahedral sites, but the octahedral-to-tetrahedral surface site ratio should be substantially higher than one to explain the observed (overall) Co-S coordination number of 5.4. Other possible explanations are adsorption of H_2S on the surface of the Co_9S_8 particles and the occurrence of millerite type of sites at the surface. The latter type of sites would explain the catalytic similarity between Co/C and Co-Mo-S/C. At present, however, the reason for the high Co-S coordination number of Co/C remains unexplained, and consequently also the structure of the surface of the cobalt sulfide phase in this catalyst remains unknown.

Burch and Collins have suggested that the differences in the HDS properties of nickel sulfide on Al_2O_3 , SiO_2 , or carbon are due to a different morphology, because of a different interaction of the metal sulfide with the support.⁵⁵ If that is true, the structure of cobalt sulfide might also depend upon the preparation conditions, and this would explain why Mössbauer studies indicated that the cobalt sulfide structure changed when increasing the sulfidation temperature.⁵⁴ After low-temperature sulfidation of Co/C a Co signal was observed equal to that of Co in Co-Mo-S, while after high-temperature sulfidation a different signal was observed. This suggests that the structure of Co in Co/C sulfided at low temperature is equal to that in Co-Mo-S/C. Probably a cobalt sulfide like γ -CoS had been formed, while during high-temperature sulfidation Co_9S_8 was formed.

Conclusions

Detailed information on the structure of the cobalt in carbon-supported Co and Co-Mo sulfide catalysts has been obtained by comparing the EXAFS and XANES Co K-edge spectra of the catalysts with those of Co_9S_8 and CoS_2 model compounds. For

a freshly sulfided carbon-supported Co-Mo sulfide catalyst, consisting of Co exclusively in the form of "Co-Mo-S", the Co atoms are found to be present in a distorted 6-fold sulfur coordination. There are four short Co-S distances of 2.18 Å, which is significantly shorter than in bulk octahedrally coordinated Co sulfides, but in accordance with four- or five-coordinated Co. Furthermore, there are two Co-S distances of 2.24 Å, and every Co atom is in contact with two Mo atoms at a distance of 2.87 Å. On the basis of this information, the most likely position for the Co atoms is slightly above the square faces of the MoS_6 trigonal prisms along the edges of the MoS_2 crystallites, with two additional sulfur atoms or H_2S molecules in apical positions. The sixth and probably also the fifth ligand of these Co sites can be removed at elevated temperature, to make room for thiophene and start the hydrodesulfurization reaction. The structure of Co with one ligand removed is square pyramidal, and this is the structure of Co in the metastable γ -CoS with the NiS millerite structure. Apparently, the function of MoS_2 is to stabilize the Co atoms in this square-pyramidal structure.

The sulfided Co/C catalyst appeared to contain Co_9S_8 particles, although the high Co-S coordination number indicated that these particles must have a higher fraction of 6-fold sulfur-coordinated Co atoms than bulk Co_9S_8 . It is not clear whether this high fraction of 6-fold sulfur coordination was due to different surface sites or to adsorbed H_2S . In view of the sensitivity of the Co structure in sulfided Co/C catalysts,⁵⁴ it seems worthwhile to study this structure as a function of sulfidation and of final evacuation and flushing conditions. Such EXAFS investigations are now in progress.

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Raman Study of a New Solid Phase in Cyclopentene: Evidence of Planar Ring Configuration

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The Raman spectra of solid monohydrogenated cyclopentenes C_5D_7 -3H and C_5D_7 -4H and of solid perdeuterated cyclopentene C_5D_8 have been analyzed between 130 and 80 K and reveal a new ordered solid phase. In this new phase, very distinct lattice and internal mode spectra suggest that the cyclopentene ring takes a planar configuration.

I. Introduction

Most investigations devoted to cyclopentene are related to its nonrigid nature. In the gas phase, numerous studies using IR and Raman,¹⁻¹³ electron diffraction,¹⁴ and microwave¹⁵⁻¹⁷ spectroscopies have established that the equilibrium conformation of cyclopentene is bent with an angle of about 22 to 26°, the molecule puckering between two conformations separated by a barrier of 232 cm^{-1} .

In condensed states, the intermolecular repulsive forces together with denser packing considerations could lead to the flattening of the ring. However, IR and Raman,^{8,10,11,13,18} neutron scat-

tering,¹⁸ thermodynamic,¹⁹ and NMR²⁰⁻²⁴ results conclude that a bent equilibrium conformation also exists in the liquid state.

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