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A Combined X-Ray Photoelectron and Mössbauer Emission Spectroscopy Study of the State of Cobalt in Sulfided, Supported, and Unsupported Co–Mo Catalysts

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Alumina-supported and unsupported Co–Mo catalysts, as well as Co metal, Co_9S_8, and $CoMo_2S_4$ samples, have been studied using X-ray photoelectron spectroscopy (XPS) and Mössbauer emission spectroscopy (MES). The main aim of the study was to examine the feasibility of using XPS to characterize the different Co-containing phases which may be present in sulfided Co–Mo catalysts. The Co phase distributions in the catalyst samples studied by XPS were determined by means of MES. The different cobalt phases observed in the catalysts were Co–Mo–S and Co_9S_8, and for the supported catalysts cobalt in the alumina lattice was also observed. Although Co metal, Co_9S_8, Co–Mo–S, and $CoMo_2S_4$ are structurally and chemically different and give rise to very different MES spectra, the Co 2p spectra of these compounds are similar. It is shown, however, that by a combination of accurate determinations of binding energy differences and comparisons of peak shapes it is possible to distinguish the different Co phases in the catalysts by XPS. The Co 2p binding energies of Co_9S_8 are about 0.5 eV smaller than those of Co–Mo–S, and also the Co 2p peak shapes are different. Using XPS, Co_9S_8 can only be distinguished from Co metal by a detailed comparison of the Co 2p peak shapes. The close similarity between the Co 2p spectra of Co–Mo–S and $CoMo_2S_4$ suggests that the electronic state of Co in Co–Mo–S is similar to that in $CoMo_2S_4$. However, the MES results show that the two phases are structurally different.

INTRODUCTION

The increasing need for efficient removal of sulfur from various petroleum and coal feedstocks has made hydrodesulfurization (HDS) catalysts one of the most important groups of catalysts industrially. These catalysts generally consist of molybdenum supported on high-surface-area γ- or η-alumina with promoters such as cobalt or nickel added to improve the catalyst activity. In view of their industrial importance great efforts have been devoted to understanding the form in which the molybdenum and the promoter atoms are present at the surface of the alumina in the active catalysts and their role in the reaction. The research efforts have recently yielded a better understanding of this complicated catalyst system. There still exist, however, different views, especially with respect to the nature of the phases present at the catalyst surface (see, e.g., *1–8*). The difficulties in studying this catalyst system are related to the active phases being X-ray amorphous, thereby excluding the use of conventional X-ray diffraction in structural determinations. Consequently, structural information has been obtained mainly by the use of various spectroscopic techniques. X-ray photoelectron spectroscopy (XPS) belongs to the newer of these techniques and due to its high surface sensitivity numerous applications to HDS catalysts have appeared (see, e.g., *9–29*). Many of these studies have aimed at obtaining information about the chemical state of the cobalt promoter atoms in the sulfided, active state of $Co-Mo/Al_2O_3$ catalysts, but

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so far the results appear somewhat conflicting.

Friedman *et al.* (*12*) found XPS peaks from two Co phases in the sulfided catalyst, which they interpreted as due to reduced and sulfided Co and to $CoAl_2O_4$. Patterson *et al.* (*20*) observed that the cobalt atoms sulfided only slightly. Brinen and Armstrong (*24*) and Okamoto *et al.* (*23*) concluded from XPS studies that metallic cobalt is formed upon sulfiding alumina-supported Co–Mo HDS catalysts. The validity of this suggestion was questioned on thermodynamic grounds by Massoth (*30*). Metallic cobalt was also suggested by Declerck-Grimee *et al.* (*25*), but only in the absence of molybdenum. In the presence of molybdenum these authors reported two cobalt species, namely, cobalt in the alumina and cobalt as Co_9S_8. In a recent study, Okamoto *et al.* (*31*) have also presented arguments for the presence of these two forms of cobalt. The difficulty in reaching definite conclusions concerning the state of cobalt may in part be related to the fact that the binding energies (BEs) of the Co $2p_{3/2}$ peak and the spin-orbit splitting of the Co 2p level of cobalt sulfides, relative to metallic cobalt, have not yet been firmly established. Very different values have been claimed in the literature. Recently, several authors (*27–29*) have suggested that the differences in Co 2p BEs and spin-orbit splitting between cobalt metal and Co_9S_8 may be very small. Dufresne *et al.* (*28*) suggest that the BE difference is 0.4 eV which was considered to be too small to enable a clear distinction between the two cobalt phases.

Recent Mössbauer emission spectroscopy (MES) studies (*7, 8, 32–34*) have shown that the dominating Co phase in many sulfided Co–Mo/Al_2O_3 catalysts is a Co–Mo–S phase. The MES results also show that depending on the preparation parameters some of the cobalt atoms may be located in the alumina or be present as a separate Co_9S_8 phase. It is, however, observed that the promoting role of cobalt is associated with the cobalt present as Co–Mo–S (*33, 34*).

The presence of a Co–Mo–S phase appears to be in conflict with the interpretations given in the previously published XPS studies. In order to test if it is possible to distinguish the Co–Mo–S phase from the other Co phases by XPS we report in the present paper XPS studies of different sulfided Co–Mo catalysts for which the phase composition is determined by MES. Studies of unsupported catalysts prepared by the homogeneous sulfide precipitation (HSP) method are also included since this method allows one to prepare samples in which all the cobalt atoms are present in the Co–Mo–S phase (*8*). For comparisons, and to settle the discrepancies in the XPS assignments of the other Co phases, data for cobalt metal (single-crystal), sulfided Co single-crystal, MoS_2, Co_9S_8, and $CoMo_2S_4$ are also reported.

EXPERIMENTAL

Sample preparations. The reference samples, Co crystal, Co_9S_8, MoS_2, Co Mo_2S_4, are briefly characterized in Table 1 whereas the catalysts are described in Table 2.

The Co single crystal (1 × 6^{ϕ} mm) was mechanically polished and cleaned in the spectrometer by many argon ion sputtering and annealing cycles. The crystal was later sulfided in a flow of 2% H_2S in H_2 at 675 K for 24 h.

The Co metal sample used for the MES experiments was prepared by reduction of Co_3O_4 in H_2 at 675 K for 16 h.

Co_9S_8 was prepared from $Co(NO_3)_2 \cdot 6H_2O$ by sulfiding in a mixture of 2%

TABLE 1

Reference Samples

Co	Single crystal with $(10\bar{1}1)$ surface; studied before and after sulfiding
Co_9S_8	Well-crystallized powders with particle size > 500 Å
MoS_2	
$CoMo_2S_4$	

TABLE 2

Catalyst Samples

		Co/Mo atomic ratio
Co/MoS$_2$ (0.063)	Unsupported catalysts prepared by the HSP method	0.063
Co/MoS$_2$ (0.50)		0.50
Co–Mo/Al$_2$O$_3$ (0.27)	Alumina-supported catalysts prepared by sequential impregnation of η-Al$_2$O$_3$ by Mo and Co	0.27
Co–Mo/Al$_2$O$_3$ (0.53)		0.53

H_2S in H_2 at 775 K for 6 h. $CoMo_2S_4$ was prepared as described earlier (*8*). Well-crystallized MoS_2 powder (BET surface area = 1.79 m^2 g^{-1}) was obtained from Riedel-de Haën, A.G. The phase purity of the Co_9S_8, $CoMo_2S_4$, and MoS_2 samples was confirmed by X-ray powder diffraction.

The unsupported catalysts were prepared according to the homogeneous sulfide precipitation (HSP) method (*8, 35*). In short, this method consists of adding simultaneously, under vigorous stirring, solutions of ammonium heptamolybdate and cobalt nitrate to a solution of ammonium sulfide. The solutions were kept at 350 K. After evaporation to dryness at 350 K the resulting product was treated in H_2S/H_2 (2% H_2S) at 675 K for 4 h.

The alumina-supported catalysts were prepared as described previously (*33*) by first impregnating η-Al_2O_3 extrudates (250 m^2/g) with ammonium heptamolybdate. This was followed by drying and by calcining in air at 775 K for 2 h. The Mo/Al_2O_3 (8.6% Mo) catalysts were then impregnated with cobalt nitrate followed by drying and by calcining in air at 775 K for 2 h.

X-ray photoelectron spectroscopy (XPS). The XPS spectra were recorded using a VG Scientific surface spectrometer with facilities for XPS, UPS, AES, and SIMS. The XPS part of the spectrometer is essentially identical to the standard Vacuum Generators VG ESCA 3 spectrometer. A stainless-steel glove box system with a turbo molecular pump was fitted to the preparation chamber. Various sample treatments can take place in the glove box in either vacuum or in pure argon. Furthermore, reactors containing catalysts can be transferred from the outside into the glove box system. Thus, catalysts can be studied after different treatments without exposure to air.

A gold sample was used for the calibration of the spectrometer and all the BEs refer to a BE of the Au 4f$_{7/2}$ peak of 84.0 eV. The spectra were obtained with Al$K\alpha$ radiation. The slit width was 4 mm, and the pass energy 50 eV for all the spectra.

All the samples (except the Co single crystal) were prepared as powders and were sulfided in a flow of 2% H_2S in H_2 at 675 K for 24 h. After sulfiding, the powders were transferred without contact with air to a nitrogen-filled glove bag in which the powders were pressed into wafers (1 × 8$^{\phi}$ mm). The wafers were then placed in a reactor and given another sulfiding treatment at 675 K for 4 h in the H_2S/H_2 mixture. After cooling to room temperature the reactor was flushed for 16 h with purified nitrogen. Without any contact with air the sample wafers were then brought into the electron spectrometer through the stainless-steel high-vacuum glove box.

It was found necessary to presulfide the catalysts in powder form since if the samples were sulfided only after pressing the powders into wafers, a strong pressure rise in the analyzing chamber was observed when the samples were subsequently irradiated with X rays. Spectra taken with a mass spectrometer fitted to the surface spectrometer showed that water vapor was the main component of the released gas. The pressure rise was avoided when the samples were presulfided in powder form.

The importance of avoiding contact with air or oxygen was demonstrated in preliminary XPS studies, where fewer precautions were taken to avoid exposure to air during the transfer of the samples to the spectrometer or where the above presulfiding procedure was not used. These spectra showed clear evidence of the presence of sulfate and oxidized species of Co and Mo.

Mössbauer emission spectroscopy (*MES*). The MES experiments were performed using a constant-acceleration spectrometer with a moving single-line absorber of $K_4Fe(CN)_6 \cdot 3H_2O$ enriched in ^{57}Fe. Zero velocity is defined as the centroid of a spectrum obtained at room temperature with a source of ^{57}Co in metallic iron. Positive velocity corresponds to the absorber moving away from the source.

All the samples used in the MES experiments were prepared in parallel with those described above by adding to the Co nitrate radioactive carrier-free ^{57}Co (from the Radiochemical Centre, Amersham, England). A source strength of about 1 mCi (36 MBq) was used. The conditions under which the MES spectra were recorded *in situ* have already been described in detail (*8*).

RESULTS

MES

Figure 1 shows the MES spectra of Co metal, Co_9S_8, and $CoMo_2S_4$ obtained at room temperature. Co metal gives rise to a hyperfine split 6-line spectrum (H = 322 kOe), Co_9S_8 gives rise to a broad unresolved single-line spectrum, and $CoMo_2S_4$ shows the presence of a quadrupole split doublet. A detailed discussion of the spectra of Co_9S_8 and $CoMo_2S_4$ is given in Ref. (*8*). For the present purpose we will simply note that by MES the above three compounds can easily be distinguished.

Figure 2 shows room-temperature spectra of the unsupported HSP catalysts (Co/MoS_2 (0.063) and Co/MoS_2 (0.50)) and of the supported catalysts (Co–Mo/Al_2O_3 (0.27) and Co–Mo/Al_2O_3 (0.53)). From the MES spectra the relative amounts of Co–Mo–S, Co:Al_2O_3, and Co_9S_8 were determined by computer analysis as described previously (*8*, *33*) and the results are shown in Table 3 (the results for the two supported catalysts have been reported previously (*33*)). It is seen that the Co/MoS_2 (0.063) catalyst contains cobalt only in the Co–Mo–S phase whereas most of the cobalt in the Co/MoS_2 (0.50) catalyst is present in the form of Co_9S_8.

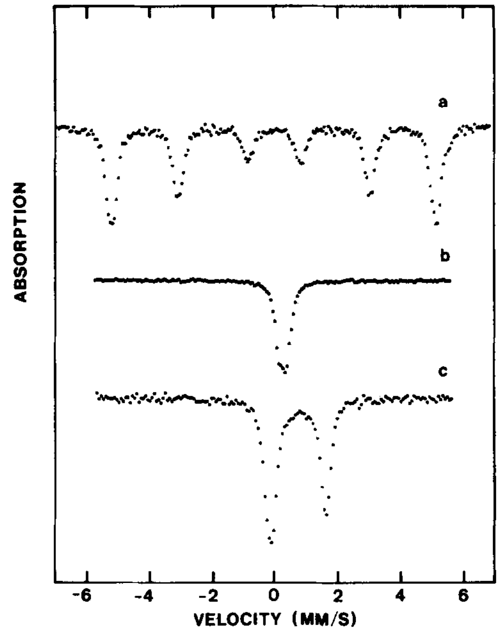

FIG. 1. Room-temperature Mössbauer spectra of reference samples. (a) Co metal; (b) Co_9S_8; (c) $CoMo_2S_4$.

XPS

Binding energies. The XPS binding energies (BEs) measured for the Co $2p_{3/2}$, S 2p, Mo $3d_{5/2}$, and C 1s peaks for all the samples are given in Table 4. The BEs obtained for

TABLE 3

Relative Concentrations of Cobalt in Different Phases Determined by MES

Catalysts	Co:Al_2O_3 (%)	Co_9S_8 (%)	Co–Mo–S (%)
Co/MoS_2 (0.063)	—	0(+7)	100(−7)
Co/MoS_2 (0.50)	—	77(±10)	23(±10)
Co–Mo/Al_2O_2 (0.27)[a]	9(±7)	0(+4)	91(±7)
Co–Mo/Al_2O_3 (0.53)[a]	12(±7)	6(±5)	82(±7)

[a] These results are taken from Ref. (*33*).

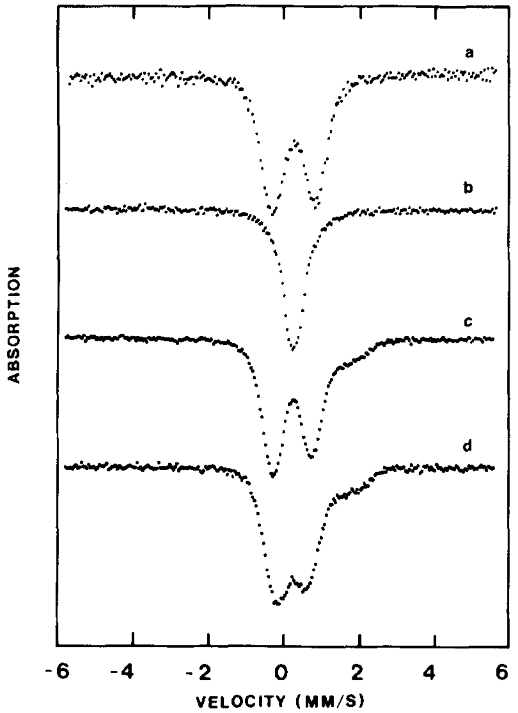

FIG. 2. Room-temperature *in situ* Mössbauer spectra of sulfided, unsupported, and alumina-supported catalysts. (a) Co/MoS_2 (0.063); (b) Co/MoS_2 (0.50); (c) Co–Mo/Al_2O_3 (0.27); (d) Co–Mo/Al_2O_3 (0.53).

Co 2p peaks of the clean Co metal (778.5 and 793.6 eV) are in excellent agreement with the recent accurate determination by Lebugle *et al.* (*36*).

When the Co crystal was sulfided, the Co 2p BE values did not change within the accuracy of the measurements (±0.1 eV). The S 2p BE of the sulfided crystal varied between 162.6 and 162.8 eV and the C 1s BE between 283.8 and 284.2 eV depending upon sputtering and annealing treatments. X-Ray diffraction showed that the Co crystal was sulfided to Co_9S_8 and optical microscopic examination indicated that the sulfide layer extended to a depth of several hundred micrometers.

The BE values obtained for the Co_9S_8 powder sample were quite close to the values obtained for the sulfided Co crystal (see Table 4).

Slightly higher Co 2p BE values were obtained for $CoMo_2S_4$ than for Co metal and for Co_9S_8. The Co $2p_{3/2}$ BEs of the two unsupported catalysts are seen to be slightly higher than that of Co_9S_8 while the supported catalysts have significantly higher Co 2p BEs. The fact that the other peaks of the supported catalysts also have correspondingly higher BEs than the other samples (as seen in Table 4 for S 2p and Mo $3d_{5/2}$) indicates that the supported catalysts become charged due to the electron emission during X-ray irradiation. It has often been suggested that to overcome the charging problem the sample can be mixed with

TABLE 4

XPS Binding Energies (eV)[a,b]

Sample	E(Co) Co $2p_{3/2}$	E(S) S 2p	E(Mo) Mo $3d_{5/2}$	ΔE_1 E(Co)–E(S)	ΔE_2 E(Mo)–E(S)	C 1s
Co crystal	778.5	—	—	—	—	283.4
Co crystal, sulfided	778.5	162.6–162.8	—	615.7–615.9	—	283.8–284.2
Co_9S_8	778.4	162.1	—	616.2	—	284.6
MoS_2	—	161.9	228.8	—	66.9	284.2
$CoMo_2S_4$	778.9	161.9	228.7	617.0	66.8	284.5
Co/MoS_2 (0.063)	779.0	162.0	228.9	617.0	66.9	284.3
Co/MoS_2 (0.50)	778.6	162.2	228.9	616.4	66.7	285.0
Co–Mo/Al_2O_3 (0.27)	780.6	163.6	230.4	617.0	66.8	285.4
Co–Mo/Al_2O_3 (0.53)	780.0	163.0	229.9	617.0	66.9	285.0

[a] Not corrected for charging.

[b] Reference level Au $4f_{7/2}$ = 84.0 eV.

powder of a material with known BEs. However, the equilibrium charge on the crystallites of each material may well be different, and the method has been shown to be unreliable in many cases (*37, 38*). The use of adventitious carbon as calibrant has also often been recommended. It is our experience, however, that on samples in ultra high vacuum carbon states with a C 1s BE different from that of "pump oil" hydrocarbon often dominate. It is therefore preferable to use energy differences between electrons from the same phase for comparisons between different samples. In Table 4 are shown the two BE differences ΔE_1 and ΔE_2 obtained by subtracting the BE of the S 2p peak from the BE of the Co $2p_{3/2}$ peak and from the BE of the Mo $3d_{5/2}$ peak, respectively. It is seen that the ΔE_1s fall into two groups: one group, which includes $CoMo_2S_4$, Co/MoS_2 (0.063), $Co–Mo/Al_2O_3$ (0.27), and $Co–Mo/Al_2O_3$ (0.53), has ΔE_1 = 617.0 eV. The other group, which includes Co_9S_8 and Co/MoS_2 (0.50), has ΔE_1 values of about 616.3 eV. It is seen from Tables 3 and 4 that the catalyst samples with ΔE_1 = 617.0 eV are those where Co is present mainly in the Co–Mo–S phase as observed by MES. In Co/MoS_2 (0.50), which has nearly the same ΔE_1 as Co_9S_8, MES shows that Co is present mainly as Co_9S_8.

By subtracting 1.7 and 1.1 eV from all the BEs of $Co–Mo/Al_2O_3$ (0.27) and $Co–Mo/Al_2O_3$ (0.53), respectively, Co 2p, S 2p, and Mo 3d BEs identical to those of $CoMo_2S_4$ are obtained. This also indicates that the peak shifts of the supported catalysts are due to charging. The results in Table 4 for the unsupported catalysts indicate that the charging of these samples is small. The C 1s BEs of the reference samples and the unsupported catalysts range from 283.4 to 285.0 eV, i.e., they vary more than any of the other BEs.

Peak shapes. The Co 2p spectra of the reference samples are shown in Fig. 3 and those of the catalyst samples in Fig. 4. The Co 2p spectra in Fig. 3 show small but significant differences between the peak shapes of Co metal, Co_9S_8, and $CoMo_2S_4$. These differences may help the interpretation of the Co 2p spectra of the catalysts. Figure 5 shows more detailed Co $2p_{3/2}$ spectra (corrected for X-ray satellites) and parameters characterizing the widths and asymmetries of the Co $2p_{3/2}$ peaks are given in Table 5.

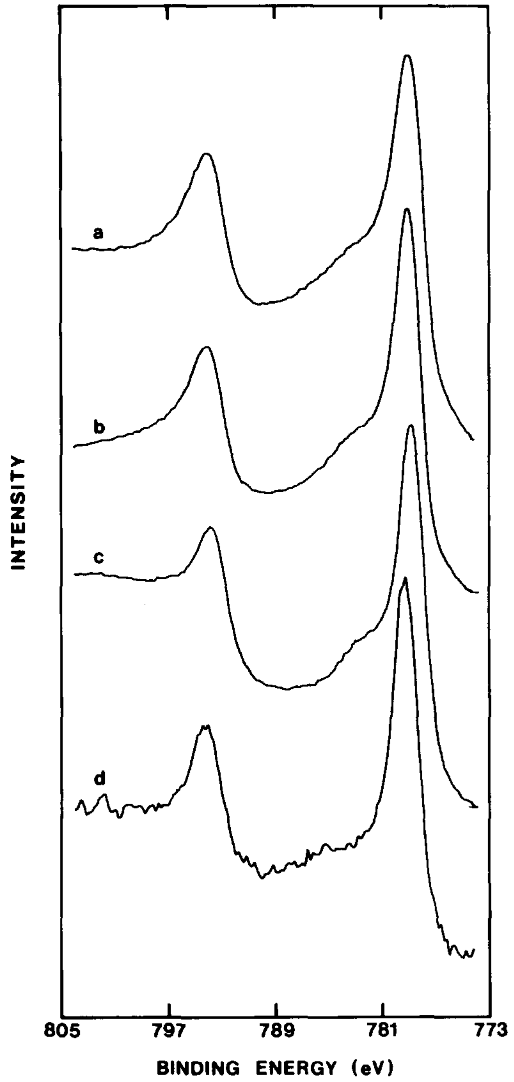

FIG. 3. XPS Co 2p spectra of reference samples. (a) clean Co single crystal; (b) sulfided Co single crystal; (c) Co_9S_8; (d) $CoMo_2S_4$.

Many metals, including cobalt, have asymmetric core electron peaks (*39*). This asymmetry is explained by the theory of

Doniach and Šunjić (*40*) to be due to excitations of electron-hole pairs at the Fermi level subsequent to the formation of the core hole. The width and asymmetry of the Co 2p peaks of the metal are therefore related to the joint density of states for electron-hole pair excitations.

Apart from the asymmetry a significant intensity is present in the tail at the high BE side of the Co $2p_{3/2}$ peak of the Co metal. In the corresponding Ni $2p_{3/2}$ spectrum there is a distinct satellite in the tail, which is explained by a mechanism where an electron state is pulled down below the Fermi level due to the formation of a core hole (*41*). The 2p main peaks correspond to the subsequent filling of this extra hole during the excitation process whereby the photoelectron acquires extra kinetic energy (corresponding to a lower BE) while the satellite corresponds to a final state with an unfilled hole (*41*). In the 2p spectra of cobalt and iron the intensities of the corresponding satellites are known to be much smaller than in the Ni 2p spectrum (*41*). The broad peak seen in the tail of the Co $2p_{3/2}$ metal peak in Fig. 3 is not due to this satellite but to the $K\alpha_3$ and $K\alpha_4$ X-ray satellites inherent in the nonmonochromatized radiation used in the present work. After these X-ray satellites have been subtracted from the spectrum (using the satellite data given in Ref. (*42*)) no satellite structure can be seen (Fig. 5a).

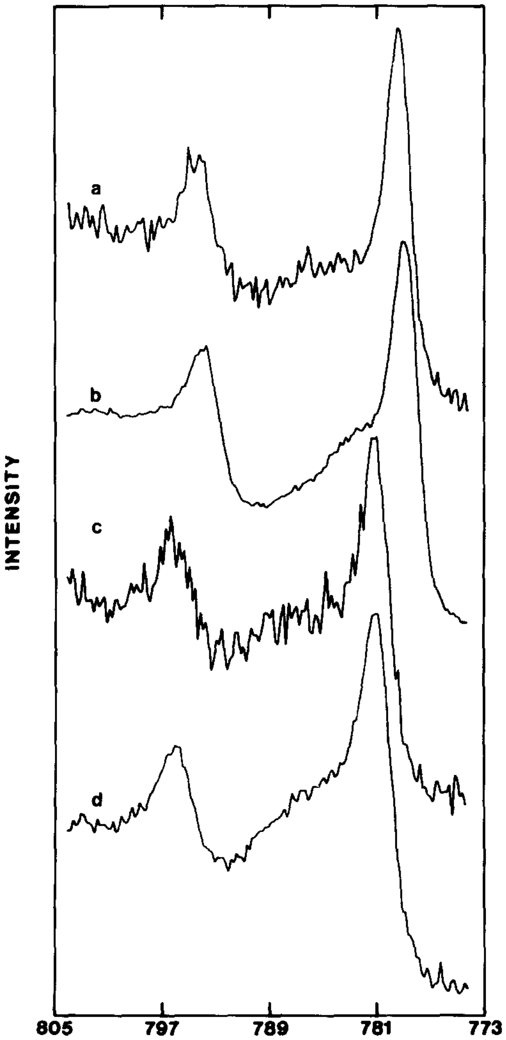

FIG. 4. XPS Co 2p spectra of sulfided, unsupported, and alumina-supported catalysts. (a) Co/MoS_2 (0.063); (b) Co/MoS_2 (0.50); (c) Co–Mo/Al_2O_3 (0.27); (d) Co–Mo/Al_2O_3 (0.50).

TABLE 5

Width and Asymmetry of the Co $2p_{3/2}$ Peaks

Sample	"FWHM" 2w (eV)[a]	Asymmetry parameter u/w[a]
Co crystal	2.7	2.7
Co crystal, sulfided	2.2	2.0
Co_9S_8	2.2	2.0
$CoMo_2S_4$	2.2	1.4
Co/MoS_2 (0.063)	2.2	1.6
Co/MoS_2 (0.50)	2.4	2.4
Co–Mo/Al_2O_3 (0.27)	2.6	3.1
Co–Mo/Al_2O_3 (0.53)	2.7	3.8

[a] u and w are defined in Fig. 5a.

The Co 2p spectrum of Co_9S_8 is similar to that of Co metal, but the asymmetry is somewhat smaller (Table 5) and a weak and broad satellite structure is seen (Figs. 5b and c) at about 4 eV higher BE than the $2p_{3/2}$ main peak.

The Co 2p spectrum of $CoMo_2S_4$ can be clearly distinguished from the corresponding spectra of Co_9S_8 and Co metal. The asymmetry of the $2p_{3/2}$ peak is very small (Table 5). The intensity in the tail is much smaller than in the spectra of Co_9S_8 and Co metal, and no satellite is seen (Fig. 5d).

A comparison of the Co 2p spectra of the unsupported catalysts with those of the reference samples shows (Table 5 and Fig. 5) that the Co 2p spectrum of Co/MoS_2 (0.063) (Fig. 5e) is very similar to that of $CoMo_2S_4$, while the Co 2p spectrum of Co/MoS_2 (0.50) (Fig. 5f) resembles that of Co_9S_8 both with respect to asymmetry and tail. The shapes of the Co 2p peaks of the supported catalysts (Figs. 5g and h) are somewhat different from those of the reference samples and unsupported catalysts. The Co $2p_{3/2}$ peak is broader than those of Co_9S_8 and $CoMo_2S_4$, and the relative intensity of the tail of the Co $2p_{3/2}$ peak is higher for the supported catalysts than for the reference samples. This may partly be due to the fact that in these catalysts some of the Co atoms are present in the alumina lattice.

The shapes of the S 2p and the Mo 3d peaks did not change significantly from sample to sample and cannot easily be used to distinguish between them. The widths of the S 2p peaks range from 2.5 to 2.7 eV where the lower value applies to MoS_2, $CoMo_2S_4$, and Co/MoS_2 (0.063) and the higher one to Co_9S_8, Co/MoS_2 (0.50), and the supported catalysts.

DISCUSSION

The main purpose of the present work is to establish a firm base for the interpretation of XPS Co spectra of sulfided Co–Mo catalysts (i) through a careful study of the XPS Co 2p spectra of clean Co metal, Co_9S_8 and $CoMo_2S_4$, and (ii) through comparisons of these results with XPS measurements on catalysts which have been characterized by means of MES with respect to the Co-containing phases present.

MES

It is seen from Figs. 1 and 2 that by the use of MES it is possible to distinguish clearly between Co_9S_8, $CoMo_2S_4$, and Co metal, and that these Co-containing phases all give MES spectra which are different from that obtained for the Co–Mo–S phase. In accordance with previous results for unsupported HSP catalysts (*8*, *35*) the present results show that the catalyst with low Co/Mo atomic ratio (Co/MoS_2 (0.063)) has all the Co atoms present in the Co–Mo–S phase while the one with the higher Co/Mo ratio (Co/MoS_2 (0.50)) contains Co mainly as Co_9S_8.

In the two supported catalysts studied here (Co/Mo = 0.27 and 0.53) Co is mainly present as Co–Mo–S. For both catalysts a small fraction of Co is present in the alumina, and for the high Co loading catalyst Co_9S_8 can also be detected (Table 3).

XPS

Co metal, Co_9S_8, $CoMo_2S_4$. The present results show that XPS BEs cannot be used to distinguish between Co metal and Co_9S_8, but the distinction can be made by comparing the Co 2p peak shapes.

Brinen and Armstrong (*24*) concluded from an XPS study of sulfided Co–Mo catalysts that Co was present in a metallic or zero-valent state. This conclusion was based on the lack of change in Co $2p_{3/2}$ BE and in spin-orbit splitting in the Co 2p spectrum as compared with Co metal and on the absence of the shake-up satellite structure which has been observed for a number of Co^{2+} compounds, e.g., CoF_2, $CoCl_2$, Co Br_2, CoO, and CoS (*43–46*). The conclusion was further supported by the observation that the S/Mo intensity ratio did not increase when the cobalt concentration was increased. The present results for Co_9S_8 as well as XPS results reported for CoS_2 (*47*) show, however, that pronounced shake-up satellite structures are not necessarily present in the Co 2p spectra of cobalt sulfides.

Townsend *et al.* (*48*) and Knop *et al.* (*49*) concluded from susceptibility and thermoelectric power measurements that Co_9S_8 is a broad-band metal with substantial electron delocalization. The metallic character

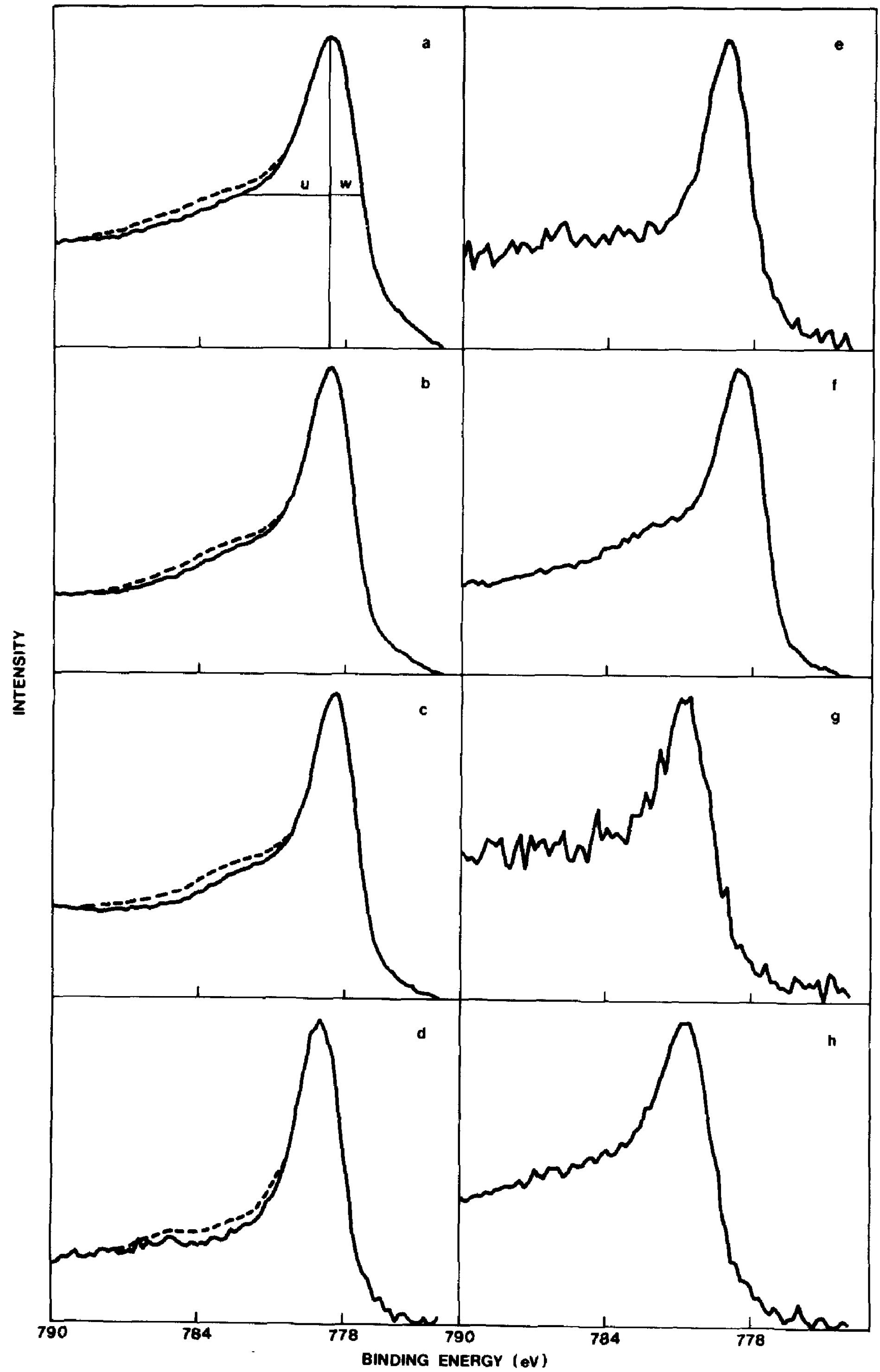

FIG. 5. XPS Co $2p_{3/2}$ spectra after subtraction of X-ray satellites. (a) Clean Co single crystal; (b) sulfided Co single crystal; (c) Co_9S_8; (d) $CoMo_2S_4$; (e) Co/MoS_2 (0.063); (f) Co/MoS_2 (0.50); (g) Co-Mo/Al_2O_3 (0.27); (h) Co-Mo/Al_2O_3 (0.53). In (a)–(d) the contribution from Co $2p_{1/2}$ before subtraction is indicated by a broken line.

of Co_9S_8 makes the similarity between the Co 2p spectra of Co_9S_8 and Co metal as well as the small differences in the BEs understandable. The asymmetry and the weak satellite structure in the Co 2p spectrum of Co_9S_8 can probably be explained in the same way as for the transition metals, i.e., as due to the excitation of electron-hole pairs at the Fermi level and to the presence of a hole in the final state, respectively.

Chevrel *et al.* (*50*) studied the magnetic and electrical properties of $CoMo_2S_4$. They concluded that it is antiferromagnetic at low temperatures with a Neél point of 195 K and paramagnetic at high temperatures. The magnetic moment corresponds to one unpaired electron and is compatible with one localized electron on Co^{2+} in an e_g level of the low-spin state d^7 (*51*). As the presence of empty *d*-levels is considered to be a necessary condition for shake-up satellites (*43*), the existence of a shake-up satellite cannot be excluded. The intensity of the satellite appears to be too small to make it visible (Fig. 5d). This is in accordance with the results of Borod'ko *et al.* (*44*) who have shown that the intensity ratio of the satellite to the main peak plus satellite is roughly proportional to the magnitude of the magnetic moment for a large number of paramagnetic Co(II) compounds. From electrical measurements (*50*) it was concluded that $CoMo_2S_4$ is a semiconductor but that the small Mo–Mo distances within the Mo chains point to metallic bonds between the Mo atoms. This is in accordance with the negligible charging observed.

Co–Mo catalysts. Comparisons of the MES and the XPS spectra for both the supported and unsupported catalysts show that it is possible by means of the XPS energy difference ΔE_1 to detect whether Co_9S_8 or Co–Mo–S is the dominating Co-containing phase. For the unsupported catalysts, this distinction can also be made on the basis of the shapes of the Co 2p peaks. The differences between the shape of the Co 2p spectra of the supported catalysts and those of the unsupported catalysts and reference samples may be mainly due to the presence of Co in the alumina in the supported catalysts.

The use of ΔE_1 for discriminating between Co–Mo–S and Co_9S_8 does not imply that the S 2p peak can be used as a reference peak for the absolute determination of the BEs. However, the observations that the shape and the width of the S 2p peak changed very little from sample to sample and that the differences between the S 2p BEs of the reference samples were small in comparison with the changes in the C 1s BEs indicate that the S 2p peak is superior to the C 1s peak as an internal reference peak in the present conditions.

The close similarity between the Co 2p spectra of $CoMo_2S_4$ and of the unsupported catalyst Co/MoS_2 (0.063) for which the Co–Mo–S phase dominates suggests that the electronic surroundings of the Co atom in the Co–Mo–S phase are very similar to those in $CoMo_2S_4$. It is therefore probable that Co is present as Co^{2+} in a low spin state in the Co–Mo–S phase. It is interesting that XPS may give information about the electronic structure of Co in the Co–Mo–S phase since such information is not available from MES due to "after-effects" (*8*). However, the MES results show that structurally Co–Mo–S and $CoMo_2S_4$ are very different.

Comparisons with Published XPS Data

From the present results it is apparent that one reason for the Co–Mo–S phase not being reported in previous XPS studies of sulfided Co–Mo catalysts is the fact that this phase has a Co 2p XPS spectrum which is quite similar to those of Co metal and Co_9S_8. Co metal is not observed in the MES spectra of any of the sulfided Co–Mo catalysts and the assignment of the XPS spectra to this phase (see, e.g., Ref. (*24*)) is undoubtedly due to the close similarity of the XPS spectrum of Co metal with those of the Co compounds present in the sulfided catalysts. The present results also show that the assignment of absolute BEs may be complicated by sample charging, which is seen to be especially important for the supported catalysts.

It is interesting to compare the Co 2p spectra in Fig. 8 in the work of Brinen and Armstrong (BA) (*24*) with Fig. 4 in the present work. The Co 2p spectrum reported by BA for a sulfided, carbon-supported catalyst (6/30 Co–Mo/DARCO) has a narrow, symmetrical Co $2p_{3/2}$ peak and a low intensity tail without structure and is thus very similar to the Co 2p spectrum of Co/MoS_2 (0.063) shown in Fig. 4. It is therefore probable that BA's sulfided, carbon-supported catalyst contained Co mainly in the form of Co–Mo–S. The Co–Mo–S phase has in fact also been observed in carbon-supported Co–Mo catalysts (*32*). BA also studied alumina-supported catalysts and obtained Co 2p spectra similar to those of the supported catalysts in Figs. 4c and d. However, no conclusion as to the presence of the Co–Mo–S phase in BA's catalysts can be arrived at because accurate BE values are not given in their paper (*24*).

Declerck-Grimee *et al.* (*25*) have studied a number of sulfided Co–Mo/Al_2O_3 catalysts by XPS. They find two overlapping Co 2p spectra with Co $2p_{3/2}$ BE equal to 778.3 and 781.2 eV, respectively. The difference between the former, dominating peak, and the S 2p BE is 617.0 eV and that between the Mo $3d_{5/2}$ BE and S 2p BE reported in Ref. (*25*) is 66.9 eV, i.e., exactly the same values as found in the present work for Co/MoS_2 (0.063) and Co–Mo/Al_2O_3 (0.53) in which Co–Mo–S is the dominating Co-containing phase. We therefore suggest that Co–Mo–S may have been present in the catalysts reported in Ref. (*25*). The authors report only one set of BE values indicating that these were the same for all the samples. On the basis of the present results, however, we suggest that careful measurements would show that the low BE Co $2p_{3/2}$ peak is displaced slightly toward lower BE values when the Co/Mo ratio is increased. Indeed, this suggestion finds some support in the BE values reported by Gajardo *et al.* (*21*), where the same XPS study is briefly discussed. One set of Mo $3d_{5/2}$ and Co $2p_{3/2}$ BE values is given for a sulfided Co–Mo/Al_2O_3 catalyst with a relatively high Co content in the alumina as judged from the strong "Co-in-alumina" peak in the Co $2p_{3/2}$ spectrum. The energy difference between the Mo $3d_{5/2}$ BE and the low Co $2p_{3/2}$ BE is equal to the value (549.7 eV) found in the present work for Co/MoS_2 (0.50) in which Co is present mainly as Co_9S_8.

Recently, Breysse *et al.* (*29*) made a combined MES and XPS study of a sulfided, graphite-supported Co–Mo catalyst (with Co/Mo = 0.27). They concluded from the MES spectrum that the only Co-containing phase present in the sulfided catalyst was Co_9S_8. The BEs measured by Breysse *et al.* appear to be in good agreement with the values obtained in the present work for Co_9S_8.

CONCLUSION

The present XPS results confirm the recent suggestions of other authors (*27–29*) that the differences in the BE of the Co $2p_{3/2}$ peak and in the spin-orbit splitting of the Co 2p peaks are too small to distinguish between Co_9S_8 and metallic Co. These differences are even smaller than suggested previously (*27–29*).

It is shown, however, that the width and asymmetry of the main Co $2p_{3/2}$ peak and the ratio between the intensity of the main peak and its tail are significantly different for Co_9S_8 and cobalt metal and can thus be used to distinguish between them.

While Co_9S_8 may dominate in some sulfided Co–Mo catalysts, no evidence has been found for the presence of cobalt metal in such catalysts. Another important result of the present work is that the presence of the Co–Mo–S phase in sulfided catalysts may be revealed by XPS. For example the Co–Mo–S phase can be distinguished from Co_9S_8 by a Co 2p BE difference of about 0.5 eV. For alumina-supported catalysts charging makes the measurements of the BEs with the necessary accuracy difficult. It is shown, however, that the distinction between Co–Mo–S and Co_9S_8 can be made also on the basis of the difference between the Co $2p_{3/2}$ BE and the S 2p BE (or any Mo BE), thus avoiding absolute BE determinations.

In unsupported catalysts the distinction between Co–Mo–S and Co_9S_8 can also be made on the basis of Co 2p peak shape differences, whereas in alumina-supported catalysts the presence of Co in the alumina complicates the analysis of peak shapes.

In previous XPS studies of sulfided Co–Mo catalysts no distinction has been made between Co–Mo–S and Co_9S_8. A reexamination of reported BEs for sulfided Co–Mo catalysts suggests that the Co–Mo–S phase may in fact have been present in some catalysts whereas Co_9S_8 may have dominated in others. The small XPS differences between Co–Mo–S and Co_9S_8 make it much more difficult to determine relative concentrations of the different Co-containing phases by means of XPS than by MES.

Although no attempt has been made in this work to explore the unique combination of surface and chemical sensitivity offered by XPS it is worth mentioning that important supplementary information about the depth distribution of the Co-containing phases may be obtained by analyzing simultaneously recorded Co peaks with very different BEs.

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