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A study of $Co/Mo/Al_2O_3$ hydrodesulphurization catalysts and related model compounds by XPS and x-ray absorption spectroscopy (XANES and EXAFS)

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Abstract. A detailed investigation of sulphided $Co/Mo/Al_2O_3$ catalysts, their oxide precursors and several model oxides and sulphides of cobalt and molybdenum has been carried out using x-ray photoelectron spectroscopy and x-ray absorption spectroscopy (XANES and EXAFS). Octahedrally coordinated Co(II) and Mo(IV) are shown to be present in a sulphidic environment on the surfaces of these catalysts. The surface species contain an excess of sulphur, probably involving disulphide linkages. The surface compositions of the catalysts examined conform to the general formula $Co^{II}\,Mo^{IV}_{2n}\,(2n+3)\,S_2^{2-}\,(2n-2)S^{2-}$.

Keywords. Hydrodesulphurization; cobalt-molybdenum catalysts; EXAFS; XANES.

1. Introduction

Cobalt-molybdenum catalysts, widely used commercially for the hydrodesulphurization of petroleum feedstocks, are nominally composed of cobalt oxide (CoO) in the concentration range of 3–5 % and molybdenum oxide (MoO_3) in the range of 12–15 % and are usually supported on alumina. The concentration ranges of Co and Mo in these catalysts make it possible to examine them under non-reactor conditions by x-ray photoelectron spectroscopy (XPS), x-ray absorption spectroscopy and a variety of other techniques (Thomas and Lambert 1980). Structural chemistry of these catalysts has been investigated by a number of workers (Ratnaswamy and Sivasankar 1980). Despite several investigations, it has not yet been possible to establish the nature of the active sites in these catalysts. At least four distinct models have been proposed hitherto, but none of these is capable of accommodating all the known facts. We therefore embarked on a systematic investigation of the oxide precursors and sulphided catalysts with a range of Co:Mo ratios as well as with several model compounds of cobalt and molybdenum. In order to examine the nature of the Co and Mo species present on the surfaces, we have utilised core-level binding energies of Co and Mo in x-ray photoelectron spectra, chemical shifts of K-absorption edges, spectroscopic transition energies and site-symmetries deduced from x-ray-absorption-near-edge-structure (XANES), as well as bond distances and coordination numbers evaluated from extended-x-ray-absorption-fine-structure (EXAFS).

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2. Experimental

MoO_3 was prepared by heating pure ammonium para-molybdate to 723 K for 12 hr. $Al_2(MoO_4)_3$ was obtained by heating a mixture containing the requisite amount of $Al(NO_3)_3$ and ammonium paramolybdate solutions to dryness, grinding them together and then heating the solid mixture to 900 K for 24 hr. $CoMoO_4$ was prepared similarly starting from an aqueous solution mixture of $Co(NO_3)_2$ and ammonium paramolybdate. $CoAl_2O_4$ was prepared starting from a solution mixture of $Co(NO_3)_2$ and $Al(NO_3)_3$. Co_3O_4 was obtained by heating $Co(NO_3)_2$ to 1000 K for 24 hr. CoO was prepared by heating Co_3O_4 at 1200 K in a CO_2 atmosphere for 48 hr. CoS and Co_3S_4 were prepared by heating stoichiometric mixtures of the pure elements inside a sealed tube at high temperatures. $Co:MoS_2$ samples were prepared by the so-called 'co-maceration method' in which MoO_3 and Co_3O_4 were co-digested in an aqueous ammonium sulphide solution for 6 hr at 350 K. The compounds obtained were subsequently heated in a H_2S-Ar atmosphere for 6 hr at 650 K. $Co/Mo/Al_2O_3$ catalyst precursors were obtained first by impregnating γ-alumina to pore-volume saturation with ammonium paramolybdate, drying at 400 K, and calcining at 900 K. This binary mixture, with the required proportion of Mo on alumina served as a support for introducing cobalt to different extents by a second pore-volume saturation impregnation step. These Co-Mo catalyst precursors were then dried at 400 K and calcined at 900 K. Sulphidation was carried out by heating the mixed oxide precursors in a stream of nitrogen at 650 K, followed by passing a mixture of H_2S and H_2 (10:90) over them at a flow rate of 30 ml/min for nearly 12 hr. The resulting sulphided catalysts were cooled to room temperature while the $H_2S:H_2$ mixture continued to flow. MoS_2 was made from $(NH_4)_2MoS_4$ by the method of Wildervanck and Jellinek (1964).

X-ray photoelectron spectra were recorded using an ESCA-3 Mark II spectrometer of V.G. Scientific Limited, U.K., fitted with a sample preparation chamber. The operating vacuum was 10^{-10} torr. This chamber was fitted with an argon ion gun and a quadrupole mass spectrometer. The radiation employed was AlK_α (1486·6 eV). The spectrometer was calibrated with reference to the binding energy of Au ($4f_{7/2}$) at 83·7 eV. The spectra were analysed in terms of relative intensities (peak areas) and relative changes in binding energies of Mo($3d$), Co($2p$), S($2p$) and Al($2p$) lines. Peak separations and satellite structure have also been used in the case of the Co($2p$) band. Decomposition of Mo($3d$) and Co($2p$) bands were attempted assuming the peaks to be gaussian. A bent-crystal spectrograph of diameter 1000 mm with a mica crystal (the $\bar{2}01$ planes of which serve as the analyzer) was employed to record x-ray absorption spectra. Sealed x-ray tubes with Cu and Mo targets were used as sources of continuous radiation. Uniform absorbing screens of the compounds were prepared by sandwiching them as fine powders between two thin cellophane adhesive tapes. The energy analysis of the spectra was carried out with the aid of a Carl-Zeiss MD 100 microdensitometer. In order to obtain finer details of the spectra, 200 × magnification scans were taken on the densitometer for each compound. The densitometer plots which represent the transmitted intensity as a function of the energy of the x-ray photon were converted into absorption coefficient *vs* the energy of the x-ray photon after determining the photodensities. The absorption edge was taken as the inflection point (mid-point of the steeply rising linear part of the plot) on the microdensitometer plots. The uncertainties in the measurements of absorption edge positions were found to be within $\pm 0·5$ eV. In order to determine spectroscopic transition energies corresponding to the various peaks in the edge spectra (Sankar *et al* 1983), first derivative curves were calculated by fitting a third-order polynomial around each point of interest over a total range of about 2 eV (Eccles 1978) and differentiating the polynomial at that point. The uncertainties in the measurement of transition energies were ± 0·4 eV and ± 0·9 eV in the energy separations (3*d*–4*s*, 3*d*–4*p*, 4*d*–5*s*, 4*d*–5*p*). Extended x-ray absorption fine structure spectra of some of the compounds were recorded using absorbing screens of different thickness in order to get a clearly visible fine structure. We were able to observe EXAFS clearly up to ~ 550 eV. To analyse the raw EXAFS data (Parthasarathy *et al* 1982), the background substraction procedure due to Lytle *et al* (1975) and the method of minimization of termination errors due to Via *et al* (1979) were used. Fourier transforms were obtained by performing the integration using Simpson's rule (Eccles 1978). The bond distances in the catalysts were determined from the positions of the peaks in the Fourier-transformed spectra using the phase shifts obtained from the model oxides and sulphides. The background substracted absorption data were fitted to a parametrized form of an equation suggested by Cramer *et al* (1976) and the least-squares fits of these were done for model compounds as well as for the catalysts using optimization techniques (Himmelblau 1972). The coordination numbers in the catalysts were determined (Cramer *et al* 1976) by comparing the parameters of the least-squares fits of the catalysts with those of the model compounds.

3. Results and discussion

3.1 *Model Co and Mo Compounds*

In table 1, we have listed, for some of the model cobalt compounds, chemical shifts of the cobalt K-absorption edge, spectroscopic transition energies of Co from XANES and Co($2p_{3/2}$) binding energies from XPS. Spectroscopic transition energies show changes with oxidation state and vary with the effective atomic charge of the metal as described recently by Sankar *et al* (1983). XANES also provides the site symmetry (Belli *et al* 1980) of the absorbing atom. Thus, we see from figure 1 that in $CoAl_2O_4$, where cobalt has tetrahedral coordination, the peak due to the 1*s* → 3*d* transition (Shulman *et al* 1976) is

Table 1. XPS and K-absorption edge data on model cobalt compounds.

Absorber	Transition energy (eV)			Chemical shift† of Co K-edge, (eV)	Binding energy Co($2p_{3/2}$) (eV)	Co(2*p*) Spin-orbit splitting (eV)
	1*s* → 3*d*	1*s* → 4*s*	1*s* → 4*p*			
Co metal	7713·1	—	7728·1	—		
CoO	7713·2	7722·7	7730·7	8·0	781·5*	16·1
$CoAl_2O_4$	7713·0	7723·0	7730·5	8·9	781·1*	15.2
$CoMoO_4$	7712·9	7723·9	7732·4	9·3	781·2*	16·0
CoS	7711·0	7720·0	7726·5	5·9	778·8	15·2
Co_3S_4	7711·3	7721·3	7728·8	7·2	778·8 (broad)	15·2

* Indicates the presence of an additional satellite 6–6·2 eV away from the main peak.
† Shift measured with respect to the K-edge of cobalt metal.

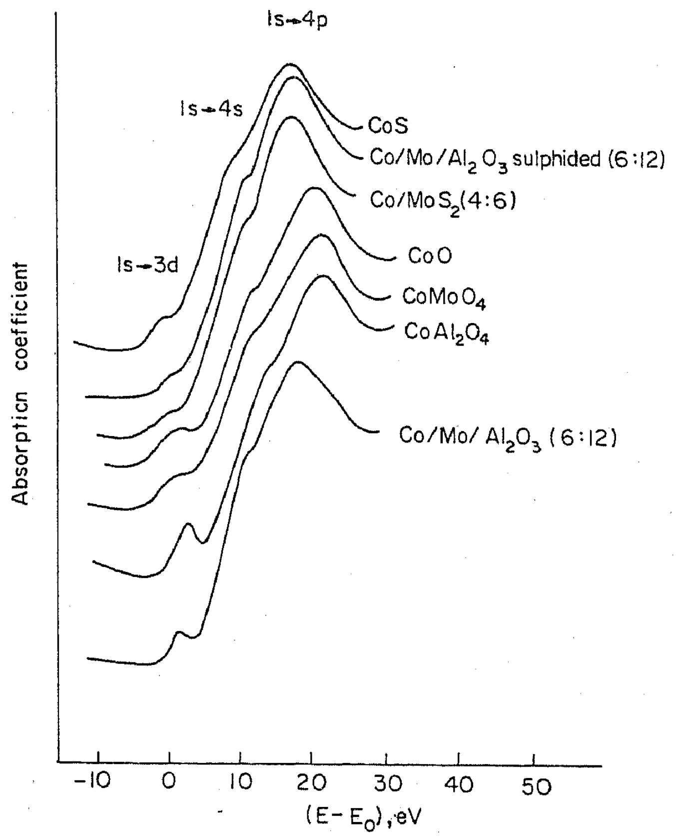


Figure 1. X-ray K-edge absorption spectrum of cobalt in cobalt oxides, sulphides and Co-Mo catalysts. E is the x-ray photon energy and E_0, the zero of photon energy scale, taken at the first maximum of the derivative spectrum of the cobalt metal ($E_0 = 7709{\cdot}6$ eV).

more intense than it is in CoO, CoS and CoMoO$_4$ where the Co has octahedral coordination. If there are different species present on the surface and in the bulk, XANES would give an average of the two features. In the present study, however, we find only one kind of Co or Mo species since these metal ions are dispersed on the alumina surface. The Co K-edge chemical shifts for Co(II) states in the oxides are between 8·0 and 9·3 eV while in the sulphides they lie between 5·9 and 7·2 eV; moreover, the Co($2p_{3/2}$) binding energies are in the range, 781–781·5 eV in the oxides, but in the range, 778·9 ± 0·1 eV, in the sulphides.

In table 2 are shown the chemical shifts of the Mo K-absorption edge, spectroscopic transition energies from XANES and Mo($3d_{5/2}$) binding energies from XPS of some of the model compounds containing molybdenum. The Mo K-edge chemical shifts for the Mo(VI) state in the oxides lie between 12·2 and 14·8 eV while for the Mo(IV) state in the oxides, they fall between 9·6 and 12·3 eV. MoS$_2$, however, shows a lower chemical shift of 6·3 eV due to the smaller effective atomic charge of the metal in the sulphide. The Mo($3d_{5/2}$) binding energies are in the range 232·0–232·4 eV for the Mo(VI) state and in the 228·5–229·0 eV range for the Mo(IV) state. From the XANES shown in figure 2(a) and (b), we see that the first peak due to the $1s \rightarrow 4d$ transition is very weak in compounds like MoO$_3$, CoMoO$_4$ and MoS$_2$ where Mo has a six-fold coordination; on the other hand, this peak is strong in SrMoO$_4$ and (NH$_2$)$_2$MoS$_4$ where Mo has tetrahedral coordination.

Table 2. XPS and K-absorption edge data on model molybdenum compounds.

Absorber	Transition energy (eV) $1s \rightarrow 4d$	$1s \rightarrow 5s$	$1s \rightarrow 5p$	Chemical shift† of Mo K-edge, (eV)	Binding energy $Mo(3d_{5/2})$ (eV)
$SrMoO_4$	20009·5	20028·7	20041·1	13·9	232·2
MoO_3	20010·0	20029·6	20041·2	14·8	232·3
$Al_2(MoO_4)_3$	20009·5	20028·8	20041·0	12·2	232·0
$CoMoO_4$	20009·0	20028·0	20041·0	12·6	232·2
$H_{1.0}MoO_3$	20008·5	20027·0	20037·1	12·5	—
$GdMoO_4$	20008·6	20027·0	20037·1	12·6	231·7
MoO_2	20007·9	20025·5	20034·0	12·3	228·8
$SrMoO_3$	20007·8	20025·0	20034·0	11·4	—
$ZnMoO_3$	20007·8	20025·0	20034·1	9·6	—
$(NH_4)_2MoS_4$	20008·0	20025·0	20036·0	8·5	229·6
MoS_2	20006·0	20021·0	20029·0	6·3	228·5

† Shift measured with respect to the K-edge of molybdenum metal.

3.2 *Co : MoS_2*

In table 3, we have listed the Mo(3*d*) and Co(2*p*) binding energies of the binary sulphides, Co : MoS_2. It is clearly seen that Mo exists in two different oxidation states, Mo(IV) and Mo(VI). The $Mo(3d_{5/2})$ peak with a binding energy of 228·8 eV can be ascribed to Mo(IV) as in MoS_2 while the higher binding energy $Mo(3d_{5/2})$ peak at 232 eV can be assigned to Mo(VI). We also see two different oxidation states for cobalt, the $Co(2p_{3/2})$ peak in XPS around 778·8–779·0 eV with a spin-orbit splitting of ~ 15 eV and with no satellite structure being associated with sulphided Co(II). The $Co(2p_{3/2})$ peak around 781·8–782·2 eV with a spin-orbit splitting of ~ 16 eV and with a pronounced satellite structure can be ascribed to oxidic Co(II) as in CoO. Our studies of pure CoS do indeed confirm that there is no satellite structure in the Co(2*p*) band and that the spin-orbit splitting is ~ 15 eV. The percentages of Mo(IV) and sulphided Co (with respect to the total Mo and Co contents) increase with increasing cobalt concentration in these catalysts. XANES studies show that Co and Mo in Co : MoS_2 samples are both in octahedral coordination (figure 1 and figure 2(b)); the various spectroscopic transition energies of Co and Mo are comparable to those of CoS and MoS_2 respectively.

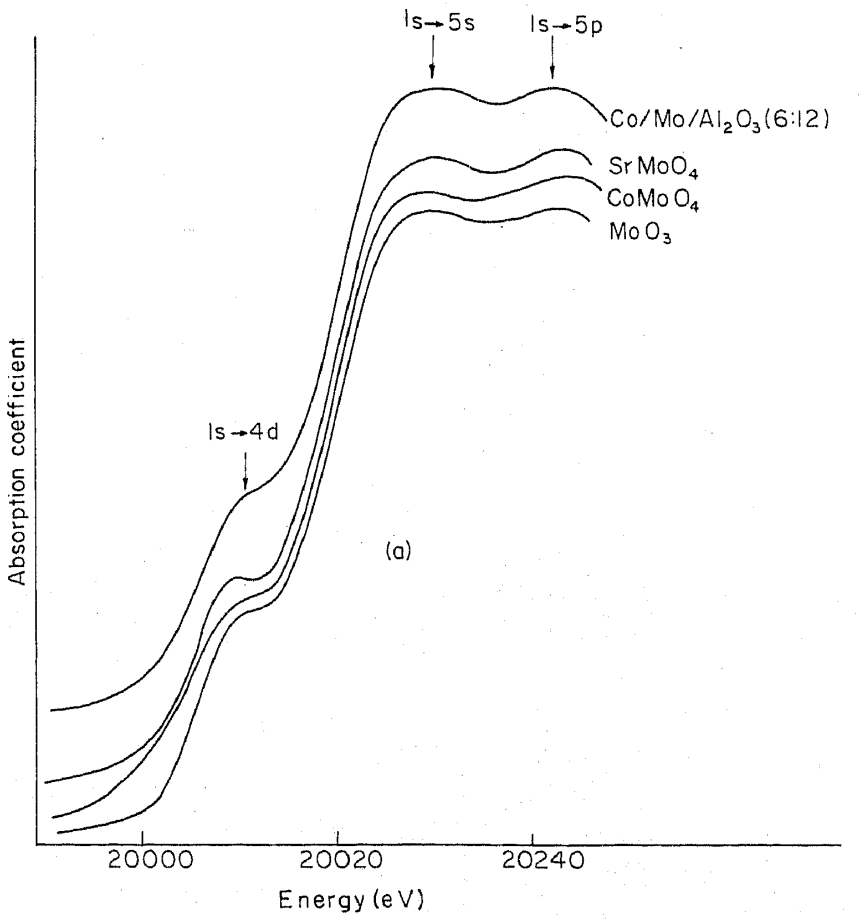
Making use of the EXAFS data, we have found the coordination numbers of both Co and Mo to be six in the different Co : MoS_2 samples. From EXAFS, we compute the Co-S distance to be about 2·30 Å while the Mo-S distance is 2·32 Å. The Co-S distance in CoS is 2·39 Å (Wyckoff 1961) and the Mo-S distance in MoS_2 is 2·41 Å (Semiletov 1961).

3.3 *$Co/Mo/Al_2O_3$ precursors*

A variety of samples over a wide range of concentrations with the Co : Mo ratio varying between 3 : 12 and 6 : 12 were examined by XPS as well as K-edge measurements on Co and Mo. The results of these measurements are shown in table 4. The results obtained on a commercial catalyst precursor are also given in this table. We see that Mo is mainly present as Mo(VI) and Co as Co(II) in these catalyst precursors. Thus, the $Mo(3d_{5/2})$

binding energy of the Mo(VI) state in these samples is 232·3 ± 0·1 eV with a spin-orbit splitting of 3·1 ± 0·1 eV for the Mo(3d) band. The Co($2p_{3/2}$) peak has a binding energy of around 781·7 ± 0·1 eV with a pronounced satellite structure around 6·2 eV away from the main peak. The spin-orbit splitting for the Co(2p) band in these oxides is found to be ~ 16 eV. The Mo(3d) and Co(2p) binding energies from XPS show negligible change with changing Co/Co + Mo ratio, but we find that the K-edge chemical shifts of both Co and Mo increase slightly with the increasing Co content on the surface. Spectroscopic transition energies of Co and Mo in Co/Mo/Al_2O_3 samples obtained from XANES are similar to those of Co(II) and Mo(VI) oxides respectively. The peaks due to the $1s \rightarrow 3d$ transition in the case of Co and the $1s \rightarrow 4d$ transition in the case of Mo show that Co and Mo have tetrahedral and octahedral coordinations respectively. Accordingly, the $1s \rightarrow 3d$ transition of Co in Co/Mo/Al_2O_3 (6 : 12) is similar to that of $CoAl_2O_4$ while that of the $1s \rightarrow 4d$ transition peak of this sample is similar to that of MoO_3 (see figures 1 and 2).

Mo(3d)/Al(2p) intensity ratios (from XPS) in these catalysts are plotted against the cobalt concentration in figure 3. Not unexpectedly, we see that the intensity ratio decreases as the cobalt content increases, but we also find that the full width at half-maximum of the Mo(3d) band is slightly broader than in pure MoO_3. The Al(2p) band width, on the other hand, increases with increasing binding energy of the Al(2p) band probably due to effects of sample charging.



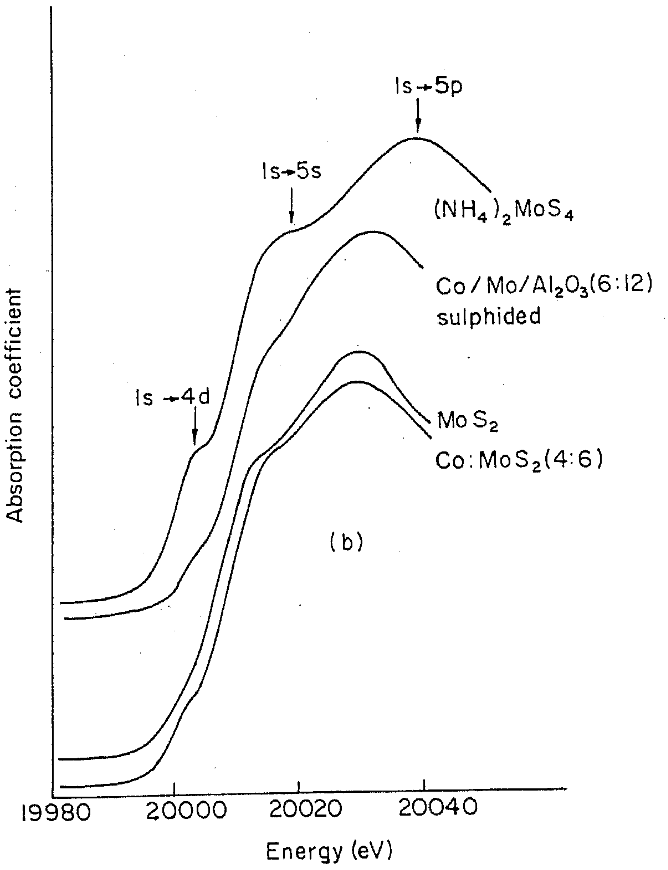


Figure 2. (**a**) X-ray K-edge spectrum of molybdenum in molybdenum oxides and Co-Mo catalyst precursor. (**b**) x-ray K-edge spectrum of molybdenum in molybdenum sulphides and Co-Mo catalyst.

Table 3. XPS and K-absorption edge data on Co:MoS$_2$ samples.

	Chemical shifts (eV)				
Co:MoS$_2$	Co K-edge	Mo K-edge	B.E. (eV) Co($2p_{3/2}$)	Co($2p$) spin-orbit splitting (eV)	B.E. (eV) Mo ($3d_{5/2}$)
2:8	—	7·1	782·2* (60)	16·0	232·0 (20)
			778·8 (40)	15·2	228·8 (80)
3:7	6·7	8·0	781·8* (15)	16·2	232·0 (10)
			778·8 (85)	15·2	228·8 (90)
4:6	6·9	8·0	779·0	15·0	228·8

* Indicates the presence of a satellite 6–6·2 eV away from the main peak. Values in parenthesis stand for the percentage of the species present on the surface.

Our studies of a commercial catalyst precursor reveal that Mo is present as Mo(VI) and Co as Co(II) in this material as well. The Mo($3d_{5/2}$) and Co($2p_{3/2}$) binding energies as well as the Mo K-edge and Co K-edge chemical shifts of the catalyst precursor are close to those of the 4:12 Co/Mo/Al$_2$O$_3$ catalyst (see table 4 and figure 3).

Table 4. XPS and K-absorption edge data on Co/Mo/Al_2O_3 samples.

	Chemical shifts (eV)		B.E. (eV)	Co(2*p*) spin-orbit	B.E. (eV)
	Co K-edge	Mo K-edge	Co ($2p_{3/2}$)	splitting (eV)	Mo ($3d_{5/2}$)
3:12	6·9	—	—	—	—
4:12	7·0	12·5	781·8*	16·0	232·4 (2·4)
5:12	7·1	12·6	781·6*	16·0	232·3 (2·5)
6:12	7·9	13·0	781·8*	16·0	232·2 (2·6)
Catalyst precursor	6·4	12·4	781·8*	16·2	232·2

* Indicates the presence of a satellite 6–6·2 eV away from the main peak. Values in parenthesis are the corresponding FWHM values in eV.

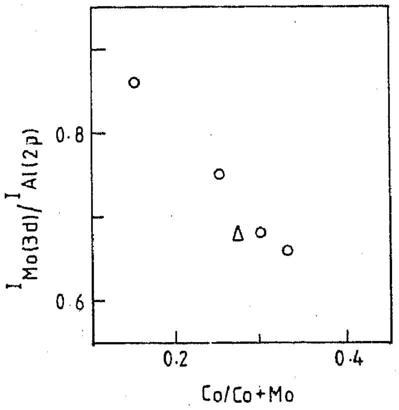


Figure 3. Variation of the intensity ratio of Mo(3*d*) to Al(2*p*) bands in the x-ray photoelectron spectra of Co/Mo/Al_2O_3 precursors as a function of cobalt concentration. The value for a commercial catalyst precursor is indicated by a triangle.

From EXAFS data of the 4:12 and 6:12 Co/Mo/Al_2O_3 samples, the coordination number of Co turn out to be four and of Mo to be six; the Co-O distance from EXAFS is close to 2·0 Å while the Mo-O distance is ~ 1·8 Å (table 5). These may be compared with the Co-O distance of 2·12 Å in CoO (Holgersson and Karlsson 1929) and Mo-O distances of 1·98 Å and 1·86 Å in $CoMoO_4$ and MoO_3 respectively (Smith and Ibers 1965; Anderson and Magneli 1950).

3.4 *Sulphided Co/Mo/Al_2O_3*

We have studied the sulphided Co/Mo/Al_2O_3 catalysts over a wide range of composition with the Co : Mo ratio varying between 2:12 and 12:12. Our results on these catalysts are summarised in table 6. Chemical shifts of the Co K-edge and the Mo K-edge do not show appreciable changes with the Co : Mo ratio. In XPS, we see two different oxidation states for Mo, Mo(IV) and Mo(VI), just as in some of the Co : MoS_2 samples. The Mo($3d_{5/2}$) peak with a binding energy of 228·9 ± 0·1 eV can be ascribed to Mo(IV) as in MoS_2 while the 232 eV peak is close to that due to Mo(VI) as in oxides. Similarly, Co exists in two states just as in some Co : MoS_2 samples, the Co($2p_{3/2}$) peak

Table 5. Bond distances from EXAFS.

	Co EXAFS(a)	Mo EXAFS(b)
$Co/Mo/Al_2O_3$ (6:12)	1·99 Å (Co-O)	1·81 Å (Mo-O)
$Co/Mo/Al_2O_3$ (6:12) Sulphided	2·32 Å (Co-S)	2·29 (Mo-S)
$Co:MoS_2$ (4:6)	2·30 Å (Co-S)	2·31 (Mo-S)

(a) Model compounds employed were: CoO(Co-O, 2·12 Å) and CoS (Co-S, 2·39 Å).

(b) Model compounds employed were: $CoMoO_4$ (Mo-O, 1·98 Å), $SrMoO_4$ (Mo-O, 1·76 Å); $(NH_4)_2MoS_4$ (Mo-S, 2·18 Å) and MoS_2 (Mo-S, 2·41 Å).

Table 6. XPS and K-absorption edge data on sulphided $Co/Mo/Al_2O_3$ samples.

Sample	Chemical shifts, eV		B.E. eV $Co(2p_{3/2})$	Co(2*p*) spin-orbit splitting, eV	B.E. eV $Mo(3d_{5/2})$
	Co K-edge	Mo K-edge			
2:12	—	7·9	—	—	232·2 (60)
					229·0 (40)
4:12	6·0	8·1	781·8* (60)	16·0	232·0 (50)
			778·8 (40)	15·2	228·6 (50)
5:12	6·4	7·9	—	—	—
6:12	5·9	8·1	781·6* (40)	16·2	232·0 (40)
			778·8 (60)	15·2	228·8 (60)
8:12	6·2	7·9	—	—	—
12:12	6·4	7·9	—	—	—
Spent catalyst	5·1	9·2	781·8* (40)	16·2	232·0 (50)
			779·0 (60)	15·2	228·6 (50)

* Indicates the presence of a satellite 6–6·2 eV away from the main peak. Values in parenthesis indicate the percentage of the species present on the surface.

at 778·8 eV with no satellite structure (spin-orbit splitting $\sim$ 15 eV) being due to Co(II) as in the sulphides. The higher binding energy peak at 781·8 eV associated with pronounced satellite structure and a spin-orbit splitting of 16 eV is similar to the features of Co(II) found in CoO. The oxidic peaks of Co(II) and Mo(VI) may be ascribed to the surface oxide which has not been sulphided. A sample of a spent industrial catalyst examined by us showed $Mo(3d_{5/2})$ and $Co(2p_{3/2})$ binding energies and K-edge chemical shifts similar to those of 4:12 or 6:12 sulphided catalysts.

We have examined the S(2*p*)/Mo(3*d*) intensity ratio from XPS as a function of increasing cobalt concentration (figure 4a) and, again, unsurprisingly, find that the ratio increases with the cobalt concentration. In figure 4b, we have plotted the Mo(3*d*)/Al(2*p*) intensity ratio from XPS as a function of increasing cobalt concentration; it shows an increase. This behaviour is in contrast to the decreasing trend observed in the oxide precursors (figure 3). In figure 5, we have plotted the Mo(IV) per cent and sulphided Co per cent (with respect to the total Mo and Co content on the surface

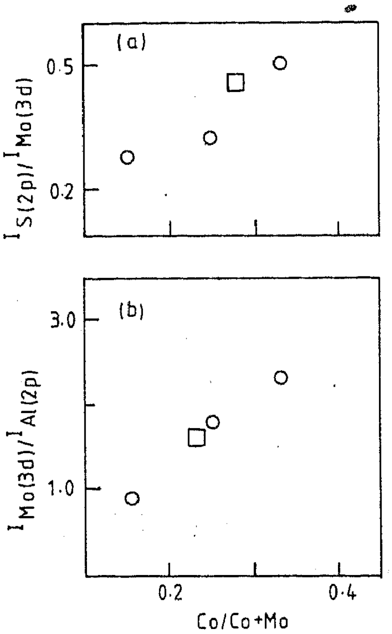


Figure 4. Variation in the intensity ratio of (**a**) S(2*p*)/Mo(3*d*); and (**b**) Mo(3*d*)/Al(2*p*) bands in the x-ray photoelectron spectra of sulphided Co/Mo/Al_2O_3 catalysts. The values for the spent catalyst are indicated by squares.

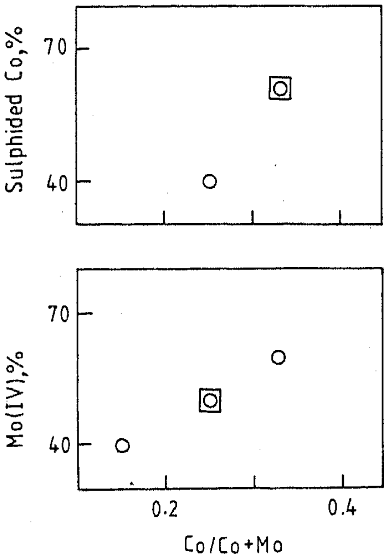


Figure 5. Percentages of Mo(IV) and sulphided Co present in the sulphided Co/Mo/Al_2O_3 catalysts shown as a function of cobalt concentration. The values for the spend catalyst are indicated by squares.

respectively) as functions of cobalt concentration. Both the quantitites increase with increasing cobalt content on the surface.

From the above discussion it is clear that Mo(IV) and Co(II) species are present in the sulphided form on the catalyst surfaces. In addition, Mo(VI) and Co(II) associated with higher core-level binding energies, are also found due to oxidic species arising from incomplete sulphidation or, alternatively, due to the presence of a complex Co-Mo-Al-O-S phase on the surface.

XANES of cobalt in the sulphided samples (figure 1) is similar to that of bulk CoS, indicating that Co has an octahedral coordination. The transition energies are also comparable to those of CoS. Transition energies of Mo in these catalysts are similar to those in MoS_2 in agreement with the observations of Clausen *et al* (1981). EXAFS data also show that the coordination numbers of both Co and Mo are six. Based on the EXAFS data (table 5), we obtain a Co-S distance of 2·33 Å and a Mo-S distance of 2·29 Å in the sulphided catalysts and these distances are comparable to those in the model sulphides studied by us (figure 6 and table 5). There is little doubt, therefore, that cobalt is present in sulphided form and not as a free metal as suspected earlier by Brinen and Armstrong (1978).

Although the positions of the first peak in the Mo EXAFS (due to back-scattering from sulphur) of the 4 : 12 and 6 : 12 samples are similar to the feature exhibited by crystalline MoS_2, the amplitudes are different. The first peak amplitude for the 4 : 12 catalyst is less than that for the 6 : 12 catalyst which in turn is less than that for crystalline MoS_2 (figure 7). Assuming that Mo in the catalysts has the same coordination number and a Mo-S distance as in bulk MoS_2 (Clausen *et al* 1981), the decrease in peak amplitude may be accounted for by a decrease in the Debye-Waller factor. The smaller Debye-

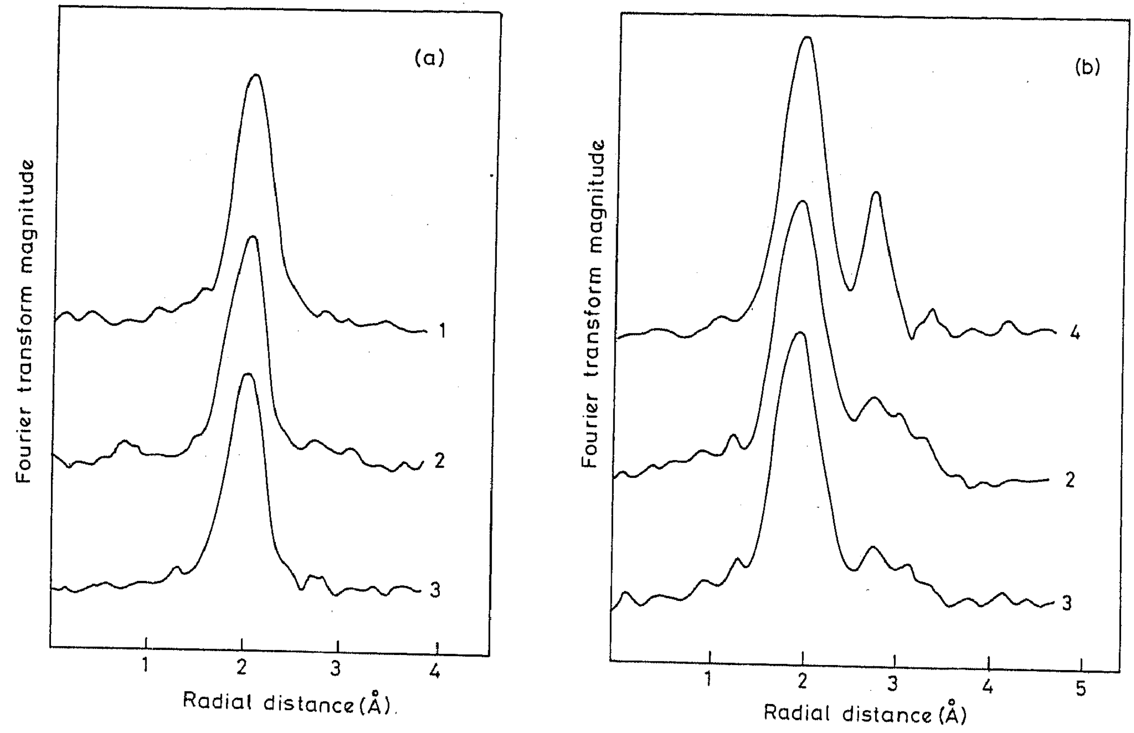


Figure 6. Plots of the Fourier transform magnitude against the radial distance from EXAFS: (**a**) Co; (**b**) Mo. 1. CoS; 2, Co:MoS_2(4:6); 3, Co/Mo/Al_2O_3 sulphided (6:12); 4, MoS_2.

Waller factor for the 4:12 catalyst as compared to the 6:12 sample suggests that the ordered or crystalline MoS_2-like domains may be smaller on the surface of the former catalyst.

Using the literature Hartree-Slater subshell photoelectric cross section values (Scofield 1976), we have obtained relative concentrations of the various species present in the 4:12 and 6:12 sulphided catalysts on the basis of the XPS core level intensities (table 7). In the 4:12 sulphided catalyst, the gross composition works out to be $CoMo_5S_9$; charge balance can be attained only if we assume the presence of oxygen, independent of whether Mo is in 4+, 5+ or 6+ state. In the 6:12 sulphided sample, the gross composition works out to be $CoMo_2S_6$ which would be charge-balanced if we take Mo to be in 5+ state (average of 4+ and 6+ states). If we prescribe Mo to be in the 4+ state, as indeed suggested by our XPS and other studies, there would be some sulphur excess. If we assign the high energy peaks in XPS to the precursor oxides, then again we end up with a considerably larger excess of sulphur. The surface composition works out to be roughly $CoMo_6S_{22}$ and $CoMo_2S_{10}$ respectively in the case of the 4:12 and the 6:12 sulphided catalysts. The excess of sulphur on the surface may be due to disulphide or polysulphide ions (and not due to free sulphur as found from XPS). The general formula for these surface sulphides can be written as $CoMo_{2n}(2n+3)S_2^{2-}(2n-2)S^{2-}$; we believe that this may be a significant observation.

4. Concluding remarks

We shall now examine our results in relation to the various models proposed to explain the activity of Co-Mo hydrodesulphurization catalysts. One of the earliest models was

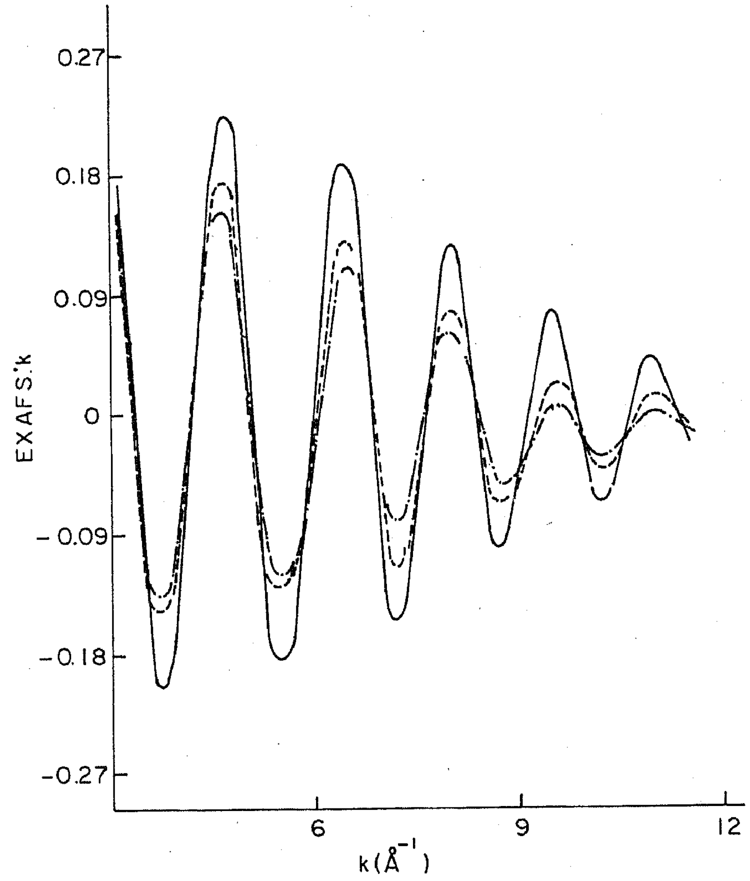


Figure 7. Fourier filtered EXAFS data of the first coordination shell of crystalline MoS_2 (——), the 6:12 sulphided catalyst (– – – –) and the 4:12 sulphided catalyst (–·–·–·–).

Table 7. Relative intensities of various bands from XPS of sulphided $Co/Mo/Al_2O_3$ samples.

	2:12	4:12	6:12
Mo(3d)/Al(2p)	0·90	1·85	2·30
S(2p)/Mo(3d)	0·28	0·32	0·50
S(2p)/Al(2p)	0·25	0·59	1·15
Co(2p)/Mo(3d)	—	0·42	0·91

the monolayer model originally applied to the oxide precursor but later modified to account for the sulphided catalysts (de Boer and Schuit 1976; Gates *et al* 1979). According to this model, in proceeding from the bulk to the surface, the compositions are supposed to pass from γ-Al_2O_3, to a Co-containing Al_2O_3, to a layer containing Co and Mo bound below to oxygen atoms and above to sulphur atoms and finally to a layer of sulphur atoms. Our XPS results do not agree with this monolayer model especially since the Mo binding energies are not different for the supported and unsupported catalysts. The attractive intercalation model (Farragher and Cossee 1973) which ascribes the catalytic activity to the pseudo-intercalation of Co in MoS_2 is also not entirely in line with our observations. There may be no actual intercalation of Co in MoS_2 and furthermore, the Mo dispersion increases with increasing Co content (figure 4). The contact synergism model (Grange and Delmon, 1974) explains the catalytic activity as due to a contact between MoS_2 and Co_9S_8. Our XPS binding energies and chemical shifts of K-absorption edges are not consonant with this model as there is no obvious evidence for electron transfer between cobalt and molybdenum.

On the basis of a gravimetric study, Chung and Massoth (1980) found the existence of three possible phases in sulphided Co-Al_2O_3 catalysts: (i) a non-sulphidable Co-Al_2O_3 phase, (ii) a dispersed CoS surface phase, and (iii) a bulk sulphided Co phase (possibly Co_9S_8). In sulphided Co/Mo/Al_2O_3 catalysts they found (i) and (ii) and a third phase involving interaction between Mo and Co. Topsoe *et al* (1981) and Wivel *et al* (1981) based on their Mössbauer study suggest the presence of a 'Co-Mo-S' phase in addition to cobalt sulphide in the unsupported catalyst. In the supported catalyst, they suggest the presence of Co located in alumina and the 'Co-Mo-S' phase. They do not find evidence for Al or oxygen in the 'Co-Mo-S' phase. Results of the present study are qualitatively similar to those of Topsoe *et al* (1981) as well as to those of Chung and Mossoth. Since the chemical shifts in both XPS and in x-ray K-absorption edges of unsupported and supported catalysts are similar, we believe that the 'Co-Mo-S' type phase is present on both the surfaces. We do not find Co_9S_8 as such, but we do have evidence for the presence of a cobalt sulphide. (It should be noted, however, that we have studied Co/Mo ratios less than 0·5). The high core level binding energies found in the sulphided catalysts may arise from non-sulphidable species in γ-Al_2O_3. Topsoe *et al* (1981) rule out the presence of oxygen or Al in the 'Co-Mo-S' phase on the basis of their isomer shifts, but we have some evidence suggestive of the presence of oxygen on the basis of analysis of XPS core-level peak intensities. We are unable to give the exact composition for such a species and cannot be certain if Al is also associated with the 'Co-Mo-S' species. Our results, however, establish the presence of cobalt in the oxidation state $2+$ and molybdenum in the oxidation state $4+$ (certainly not higher than $5+$), both having a six-fold coordination in the sulphided catalysts. Particularly significant is the possibility of disulphidic linkages. Cobalt and such cations which may be present at the edges of MoS_2 sheets (Pecorano and Chiannelli 1981) would favour formation of disulphide linkages. The latter provide pathways for the hydrodesulphurization reaction by the facile making and breaking of S–S bonds. The disulphide ion would be stabilized since the $\mathrm{Mo}(d_{z^2}^{2})$ band is, energetically, above the disulphide ($3p^6$) band (Goodenough 1982). The $S^{2-}(3p^6)$ band overlaps the highest filled d band in the case of group VIII elements such as Co. Furthermore, with filled t_g-orbitals, group VIII cations do not form strong π bonds as in MoS_2 and would favour the disulphide linkage. It is, therefore, possible that the hydrodesulphurization reaction is most favoured on a surface containing disulphide ions. The role of the group VIII cations may be to stabilize such a surface.

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