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Electron Spectroscopy for Chemical Analysis Spectra of Molybdenum Sulfides

Hydrodesulfurization reactions occurring over molybdenum sulfides have been widely studied because of their relevance to the CoMo–alumina system (*1*). Recent work with MoS_2 and MoS_3 using ir and X-ray techniques (*2*) led to some understanding of the structural relationship between these materials and we have investigated this further using electron spectroscopy for chemical analysis (ESCA). In this note we compare binding energies of the molybdenum and sulfur species in MoS_2 and MoS_3 in an attempt to gain more insight into the immediate environment of molybdenum in these sulfides and the chemical nature of the sulfur atoms.

ESCA spectra were measured on an AEI ES100 spectrometer. The data were plotted on an X–Y recorder and the parameters of the individual peaks (assumed Gaussian) were analyzed with an optimization programme.

Molybdenum disulfide was BDH laboratory reagent grade. MoS_3 was prepared by thermal decomposition of ammonium tetrathiomolybdate at 200°C and 10^{-1} Torr for 12 hr (*3*). Sample analysis gave $MoS_{2.95}$.

Mo(3*d*) and S(2*p*) peaks observed on MoS_2 and MoS_3 are shown in Figs. 1 and 2. The Mo(3*d*) signals were both well-defined doublets with S(2*s*) signals observed as shoulders on the higher kinetic energy side of the Mo($3d_{5/2}$) peak. Peak kinetic energies, half-widths and areas analyzed by computer deconvolution are listed in Table 1, together with values for the C(1*s*) impurity signal. The binding energies of the molybdenum and sulfur peaks were calculated assuming a value for C(1*s*) of 284.5 eV.

Certain features in the ESCA data are quite unexpected. In the Mo(3*d*) spectra the Mo(3*d*) binding energy in MoS_3 is 0.6 eV lower than in MoS_2. This is in marked contrast to the results reported for the oxides where the Mo(3*d*) binding energy in MoO_3 is 1.7 eV higher than in MoO_2 (*4*). This difference demonstrates unexpected valence and structural relationships between the sulfides.

Two possibilities were considered to account for this result:

i. That MoS_3 is an Mo(III) compound containing $(S–S)^{2-}$ ions.

ii. That MoS_3 is an Mo(IV) compound which has a different arrangement of ligands or different electrical properties from MoS_2 resulting in a small shift in the Mo(3*d*) binding energies of the surface atoms.

Infrared and laser Raman studies were carried out on the sample of MoS_3 in an attempt to detect S–S bridges. The strong Raman band associated with an S–S stretching vibration was not observed in the region 400–500 cm^{-1}. Well-defined bands attributed to Mo–S–Mo bend (125 cm^{-1}), S–Mo–S vibration (225 and 187 cm^{-1}) and Mo–S–Mo stretch (425 cm^{-1}) modes were observed and it was concluded that the sample of MoS_3 was an amorphous polymeric material.

Similarities between MoS_2 and MoS_3 were noted in recent radial electron distribution studies (*2*) where a similar immediate environment for molybdenum and sulfur ions was found in the two materials. However, the data do not provide conclusive evidence to show that MoS_3 is "a definite chemical compound rather than an intimate association of small fragments of

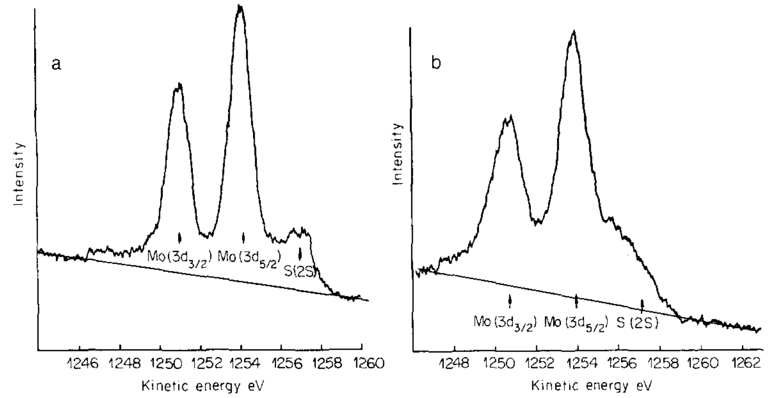

FIG. 1. Mo(3d) ESCA signals from (a) MoS_2 and (b) MoS_3.

MoS_2 layers and a stoichiometric amount of amorphous sulphur" (2). If this latter view of the structure of MoS_3 is correct we would expect to see little difference in Mo(3d) binding energy between Mo^{4+} ions in MoS_2 and MoS_3. We would also expect to observe two distinct forms of sulfur in the ESCA spectra due to S^{2-} as in MoS_2 and amorphous sulfur.

This seems to be the case. Figure 3a shows that the S(2p) signal from MoS_2 is readily deconvoluted into the spin components (2$p_{1/2}$) and (2$p_{3/2}$), whose parameters are listed in Table 1. The peaks derived from this deconvolution, however, cannot account for the S(2p) signals from MoS_3. In this case, a second set of S(2$p_{1/2}$) and S(2$p_{3/2}$) peaks must be included to obtain a satisfactory deconvolution. In the example shown as Fig. 3b, the sulfide signals were set at the values derived from MoS_2, and the amorphous sulfur spin components were allowed a maximum separation of 1.53 eV, a minimum individual width of 1.0 eV and any value for the separation from the sulfide peaks. The separation calculated between the sulfide and amorphous sulfur peaks was 1.1 eV which is compara-

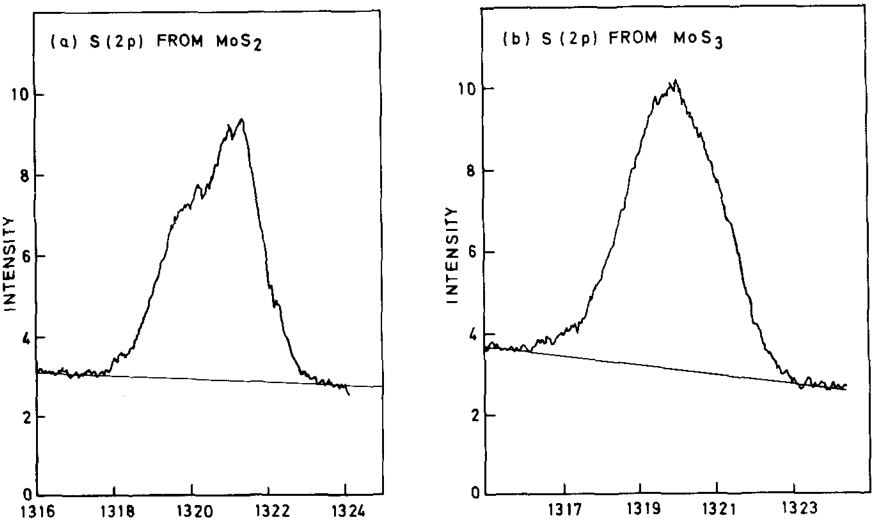

FIG. 2. S(2p) ESCA signals from (a) MoS_2 and (b) MoS_3.

TABLE 1

ESCA DATA FOR MoS_2 AND MoS_3; COMPUTER ANALYSIS OF Mo(3*d*) AND S(2*p*) SIGNALS

Peak	Compound		Binding energy (eV)	
	MoS_2	MoS_3	MoS_2	MoS_3
Mo($3d_{3/2}$) KE	1251.0	1250.7	232.5	231.9
Half-width	1.45	1.94		
Rel. area	12.8	13.8		
Mo($3d_{5/2}$) KE	1254.1	1253.9	229.4	228.7
Half-width	1.48	1.72		
Rel. area	19.1	20.7		
S($2p_{1/2}$) KE	1319.7	1318.2 1319.3	163.8	164.4 163.3
Half-width	1.45	1.45 1.7		
Rel. area	5.21	2.02 4.82		
S($2p_{3/2}$) KE	1321.2	1319.7 1320.8	162.3	162.9 161.8
Half-width	1.61	1.61 1.91		
Rel. area	10.41	4.04 9.64		
C(1*s*) KE	1199.0	1198.1	284.5	284.5

ble to the 1.4 eV separation between the S(2*p*) signals reported for S_8 and Na_2S (*5*).

We conclude that the S(2*p*) spectra from MoS_3 are consistent with the presence of two forms of sulfur, one similar to sulfide in MoS_2 and the other to sulfur in S_8. The structure of MoS_3 can then be regarded as an intimate association of subcrystalline MoS_2 and amorphous sulfur.

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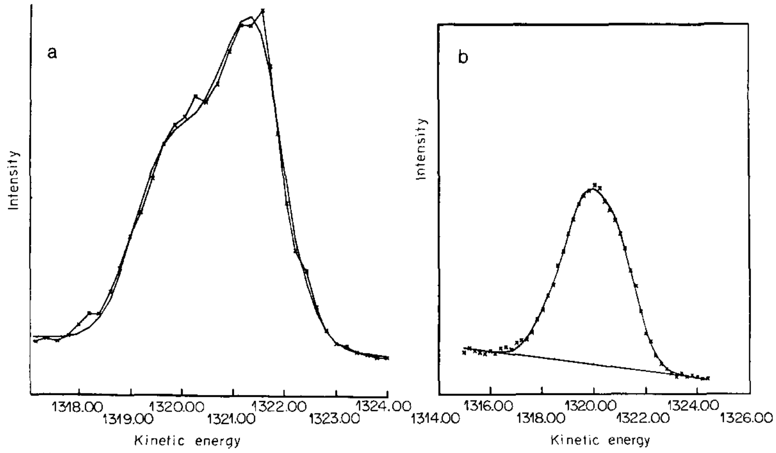

FIG. 3. Computer fit of S(2*p*) from (a) MoS_2 and (b) MoS_3; (×) experimental values; (—) computer fit.

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