Electron Spectroscopy of the Co–Mo–Al$_2$O$_3$ Catalyst System

Values of the energy levels of molybdenum and cobalt ions in Co–Mo–Al$_2$O$_3$ (in the oxide form) have been measured by electron spectroscopy (ESCA) and are reported here. The results, along with those obtained earlier (1–3), reveal more clearly the structural features of these two ions in this industrially important catalyst system used in hydrodesulfurization.

The spectra are shown in Fig. 1 and the corresponding binding energy values are compiled in Table 1. Significant features of Fig. 1 are: (a) the M_{IV} and M_V levels of Mo have practically the same binding energy in MoO$_3$, Mo–Al$_2$O$_3$, and Co–Mo–Al$_2$O$_3$; (b) while the M_{IV} and M_V peaks are narrow and well resolved in MoO$_3$, they are broad and merge into each other in the Mo–Al$_2$O$_3$ and Co–Mo–Al$_2$O$_3$ samples; (c) in Co–Mo–Al$_2$O$_3$, cobalt exists in at least three different energy states with binding energies of 780.5, 781.4, and 784.9 eV, for the L_{III} energy level.

The ESCA spectra of molybdenum or cobalt in Co–Mo–Al$_2$O$_3$ have so far not been published. The peak at 781.4 eV (Fig. 1) is evidently due to Co^{2+} in an environment similar to that in CoAl$_2$O$_4$ (781.2 eV). This value for CoAl$_2$O$_4$ is in excellent agreement with those of Ogilvie et al. (4), namely, 781.0 eV. Based on phase transformation studies, it was earlier suggested (1) that even though CoAl$_2$O$_4$ as a separate phase giving rise to its characteristic X-ray pattern may not exist in Co–Mo–Al$_2$O$_3$ samples, "spinel-like regions," wherein the short range order (say, of about 6–10 Å) around Co^{2+} is similar to that in CoAl$_2$O$_4$, might exist. The present ESCA results confirm this hypothesis. The peak at 780.5

eV cannot be assigned to the zero- or monovalent cobalt since both these oxidation states are not stable in presence of air or oxygen. Keeling (5) had earlier reported that the X-ray K-absorption edge for CoAl$_2$O$_4$ was somewhat higher than that for CoO. The peak at 780.5 eV is, therefore, assigned to Co^{2+} in an oxide phase, most probably, CoO. In fact, the presence of an oxide of cobalt on the catalyst surface had been postulated by us earlier (3) to account for the behavior of Co–Mo–

TABLE 1

BINDING ENERGY VALUES^a (eV)

Sample^b	Energy level		
	$^{Mo}M_{IV}$	$^{Mo}M_V$	$^{Co}L_{III}$
MoO$_3$	232.1	235.0	
Mo–Al$_2$O$_3$	232.5	235.2	
Co–Mo–Al$_2$O$_3$	232.2	235.1	780.5, 781.4, and 784.9
CoAl$_2$O$_4$			781.2

^{a} The electron spectra were recorded with a Vacuum Generators (ESCA 2) spectrometer equipped with Al anode and a Varian 1024C time averaging computer for accumulating repetitive scans. The binding energy values have been corrected for the "charging effect" using the carbon 1s line (283 eV) and are reproducible to ±0.3 eV.

^{b} MoO$_3$ was prepared from ammonium paramolybdate by decomposition at 550°C, its crystal structure being confirmed by X-ray diffraction; Mo–Al$_2$O$_3$ was obtained by impregnating gamma alumina (surface area = 220 m^2/g) with ammonium paramolybdate (13% by wt of MoO$_3$), drying at 110°C for 24 hr and calcining at 550°C for 24 hr; Gamma alumina was impregnated with a mixture of cobalt nitrate and ammonium paramolybdate (2.5% of Co as Co$_3$O$_4$ and 13% Mo as MoO$_3$) dried at 110°C and calcined at 550°C, to yield Co–Mo–Al$_2$O$_3$; CoAl$_2$O$_4$ was obtained by calcining at 900°C for 24 hr gamma alumina containing 2.5% Co as Co$_3$O$_4$.
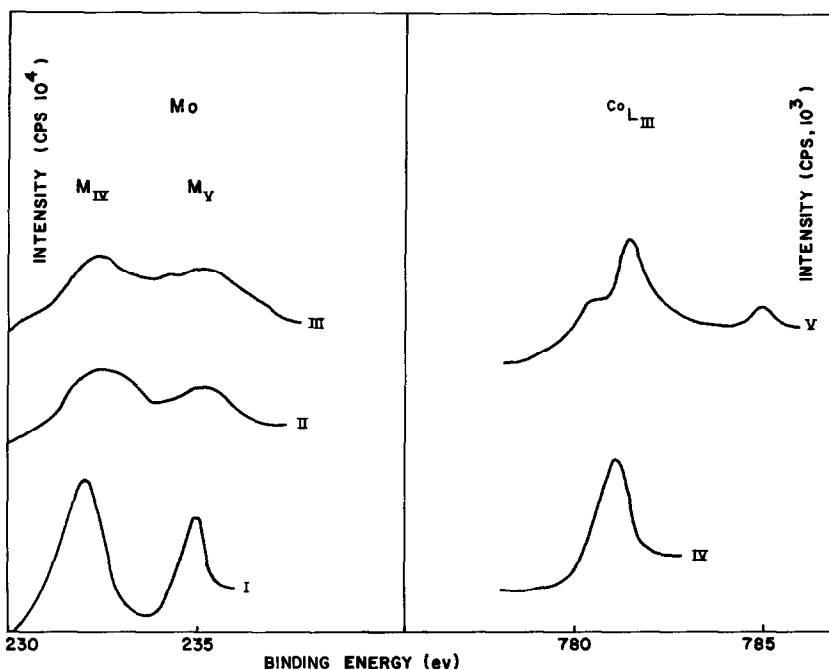
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FIG. 1. ESCA spectra: (I, II, and III) the M_{IV} and M_V energy levels of Mo in MoO_3, Mo–Al_2O_3 and Co–Mo–Al_2O_3, respectively; (IV and V) the L_{III} energy level of cobalt in $CoAl_2O_4$ and Co–Mo–Al_2O_3, respectively.

Al_2O_3 under reduction conditions. At first sight, the peak at 784.9 eV might be thought to arise from Co^{3+} ions, especially since their presence in some Co–Mo–Al_2O_3 has been reported (6) based on ESR spectral results. However, Jorgensen (7) reported a value of only 782.3 eV for the cobalt L_{III} level of Co^{3+} in Co_2O_3. Now, it is known both from our previous results (3) and those of Lipsch (8), that below 450°C, a small amount of strongly held water is present on the surface of Co–Mo–Al_2O_3 samples which cannot be removed even by reduction in pure H_2. It is probable that Co^{2+} ions in coordination with these strongly bound water molecules cause the peak at 784.9 eV. The observation by Jorgensen (7) of the L_{III} level of Co^{2+} in $Co^{II}(H_2O)_6$ $(ClO_4)_2$ at 788.0 eV lends additional support to this assignment.

The broadening of the Mo doublet (Fig. 1) had been observed also by Miller et al. (9) for Mo–Al_2O_3 samples. They ruled out,

quite rightly, the possibility that the broadening is due either to a change in the coordination number of Mo from 6 to 4 or to a change in the oxidation state of Mo. Based on the results of the kinetics of reduction, sulfidation and hydrodesulfurization reactions, it was earlier postulated (3) that on the surface of Mo–Al_2O_3 or Co–Mo–Al_2O_3 catalysts, in the oxide form Mo occurs in three different forms, viz, phase A, wherein chemical interaction with the support is so intimate that the Mo ions are not reduced in hydrogen even in high temperatures, phase B which has minimal interaction with the support and a high reducibility and phase C which is partially reducible in the presence of promoters like cobalt metal. The broadening of the peaks observed for both Mo–Al_2O_3 and Co–Mo–Al_2O_3 is attributed to the presence of molybdenum in these different energy states, the energy levels lying too close together to permit resolution in the ESCA spectra.

The ESCA results, thus lend considerable support to our earlier postulates about the nature of molybdenum and cobalt in Co–Mo–Al$_2$O$_3$ systems.

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