

# ESCA, A NEW TOOL FOR PROBING THE STRUCTURE OF CATALYSTS

P. RATNASAMY, *Indian Institute of Petroleum, Dehra Dun, U.P.*

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Electron spectroscopy has been applied to probe the surface structure of di- and trisulphides of molybdenum and a commercial ultramarine catalyst. Differences in the oxidation state of molybdenum in the di- and trisulphides are reflected in the lower binding energies of the electrons of sulphur originating from the former compared to the latter. The presence of sulphur dioxide in the ultramarine sample is inferred from its ESCA spectra. These results illustrate the type of information that may be obtained from an application of ESCA to the study of catalysts.

## INTRODUCTION

ESCA, or electron spectroscopy for chemical analysis (cf. Siegbahn *et al.* 1967; and Delgass *et al.* 1970) is one of the latest tools to join the arsenal of the catalyst chemist in his attempts to understand the mechanism of heterogeneous reactions. For a proper understanding of the mechanism of any molecular process that goes on the surface of a solid, a prime requirement is the detailed knowledge about the structure of the surface and the nature of the atoms therein, since these are the atoms, which, along with those of the adsorbed molecules form the activated complex for the particular kinetic route.

In ESCA, the surface of the solid is bombarded by X-ray photons. Due to this impact the valence and core electrons of the surface atoms are excited and ejected. By analysing and estimating the kinetic energy of these electrons, their original binding energy in the surface atoms can be evaluated. These B.E. values serve as a fingerprint for the electronic energy state of the surface atoms.

All these effects are confined to a depth called 'The escape depth' of electrons, of about  $5\text{\AA}$  (for dense matrices) to as much as  $100\text{\AA}$  (for light material) from the surface of the solid (Siegbahn *et al.* 1967).

## THEORY

When atoms in a gas are excited by X-ray photons of energy,  $h\nu$ , the kinetic energy of the emitted electrons  $E_{kin}$  is given by

$$E_{kin} = h\nu - E'_b \quad \dots (1)$$

where  $E'_b$  is the binding energy of the electrons in the particular electron shell from which it was emitted, with respect to an electron at rest in complete vacuum. For solid samples, since they are in electrical contact with the spectrometer, additional work (proportional to the work function of the spectrometer) has to be done by the ejected electrons before arriving at the analyser. Thus

$$E_{kin} = h\nu - E'_b - W \quad \dots (2)$$

Here  $E'_b$  is measured with respect to an electron at rest at the Fermi level. Since, for a given radiation and a spectrometer,  $h\nu$  and  $W$  are known and constant,  $E'_b$  values can be calculated from the  $E_{kin}$  values measured from the chart of the electron spectrum. Different peaks in the spectrum correspond to different energy levels in the surface atoms.

#### EXPERIMENTAL

Three catalysts were chosen, molybdenum trisulphide, molybdenum disulphide and a commercial ultramarine catalyst.  $\text{MoS}_3$  was prepared according to the methods of Maldvaski *et al.* (1933).  $\text{MoS}_2$  was prepared from  $\text{MoS}_3$  by reduction in a flowing stream of dry hydrogen at  $1000^\circ\text{C}$  for 24 hr and its crystal structure confirmed by its X-ray pattern. The ESCA studies were done with the ESCA 2 spectrometer of Vacuum Generators Ltd., England.  $\text{AlK}\alpha$  lines were used to eject the photoelectrons which were analysed by an electrostatic focussing technique. The spectra were calibrated using the carbon ( $K$ ,  $283 \pm 0.4$  eV) and gold ( $N_{vi}$ ,  $86.4 \pm 0.4$  eV  $N_{vii}$ ,  $82.8 \pm 0.52$  eV) lines. The analyser voltage was kept constant at 180 volts and the retarding potential on the sample was varied to analyse the photoelectrons of varying energy. The samples were studied in the form of powdered particles pressed to the tip of the sample probe of the instrument.

#### RESULTS AND DISCUSSION

Figs. 1 and 2 show the electron spectra of  $\text{MoS}_3$ ,  $\text{MoS}_2$  and ultramarine respectively. The sulfide ions in  $\text{MoS}_2$  have lower binding energies than those in  $\text{MoS}_3$ . This difference arises due to the fact that in  $\text{MoS}_2$ , the  $\text{S}^{2-}$  ions are attached to  $\text{Mo}^{4+}$  ions whereas in  $\text{MoS}_3$  they are bounded to  $\text{Mo}^{6+}$  ions. A similar difference is also seen in the binding energy values for the molybdenum ions. The electrons of  $\text{Mo}^{4+}$  (in  $\text{MoS}_2$ ) have a lower binding energy than those of  $\text{Mo}^{6+}$  (in  $\text{MoS}_3$ ). Again these differences are due to the different oxidation states.

The B.E. values are accurate to about  $\pm 0.5$  eV. The major features of interest are the two peaks at 232.9 eV and 158.4 observed for the sulphur  $L_I$  and  $L_{II,III}$  levels. The binding energies in eV of the sulphur  $L_I$  and  $L_{II,III}$  levels in some compounds of interest are (1)  $\text{S}_8$  (162.2),  $\text{Na}_2\text{S}$  (160.8),  $\text{SO}_2$  (168.0),  $\text{Na}_2\text{SO}_3$  (165.8) and  $\text{Na}_2\text{SO}_4$  (167.7), respectively. While quantitative interpretation of ESCA results is far from a satisfactory position, in the present case it may nevertheless be concluded that the sulphur in ultramarine exists in at least two forms, one (158.4 eV) in which there is a net negative charge and another (167.8 eV) in which there is a positive charge on the sulfur atoms. Now, previous investigations (4) on ultramarines using radial electron distribution and infrared techniques indicate the presence of  $\text{SO}_2$  as well as polysulfide species such as  $\text{S}_3^{2-}$  and  $\text{S}_6^{2-}$ . Accordingly the peak at 167.8 eV is assigned to the sulfur atom in  $\text{SO}_2$  while the peak at 158.4 eV is due to the polysulfide species. The amount of  $\text{SO}_2$ , in any case is very small as evidenced from the lower intensity of the peak at 167.8 eV.

The above examples illustrate some of the types of information that can be obtained by using the Esca technique. A major problem encountered in the application of this technique to catalysts is charging of the usually insulator or semiconductor sample due to depletion of electrons in the sample by the photo-electric

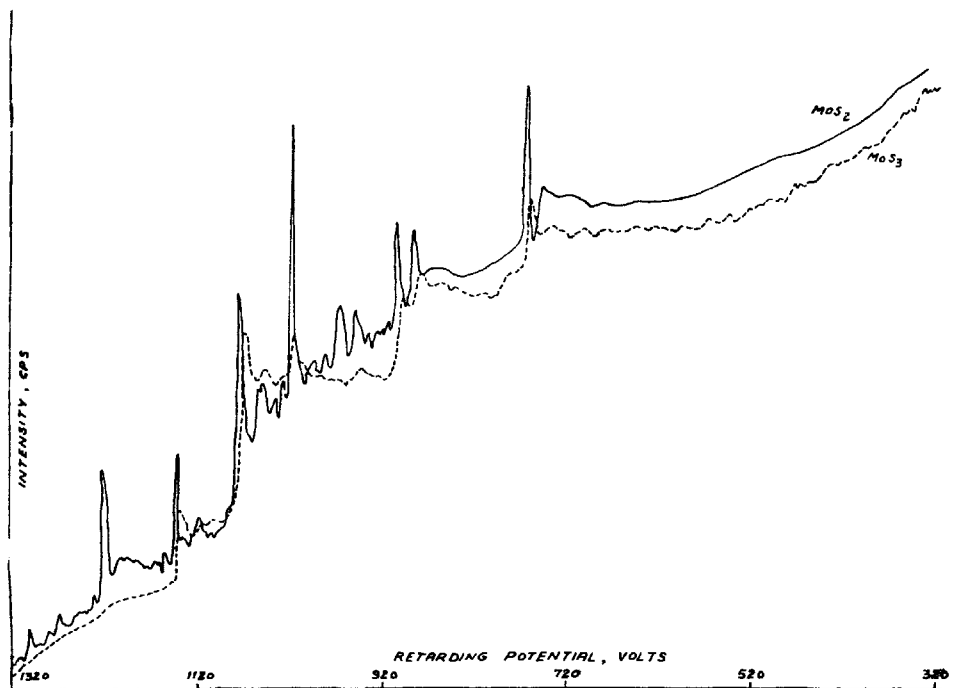


FIG. 1. Electron spectra of  $\text{MoS}_3$  and  $\text{MoS}_2$ .

ULTRAMARINE

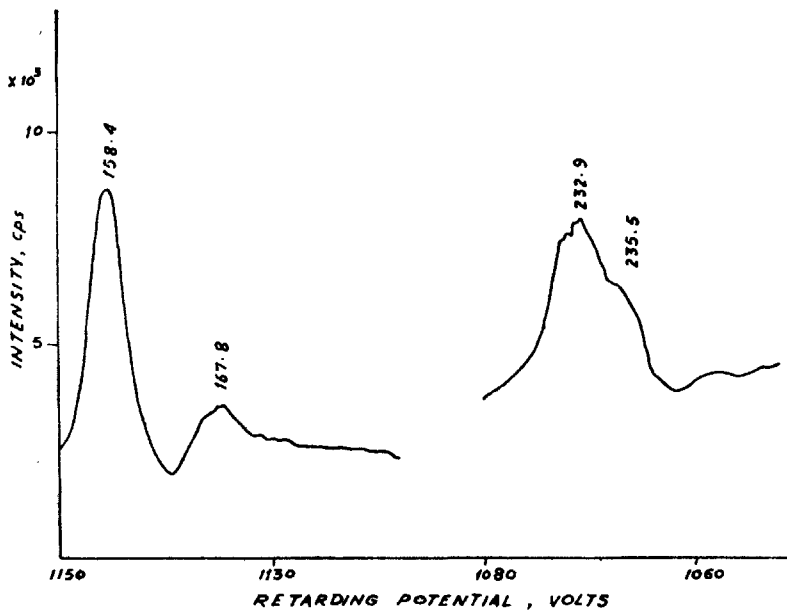


FIG. 2. The sulphur energy levels in ultramarine.

effect. In such cases the measured, binding energies have to be corrected for the drag on the ejected electrons due to the positively charged surface. This is usually done (as has been done in the present investigation) by using as a calibration standard the carbon (1S) line from the molecules of the pump oil which invariably form a thin film coating on the catalyst surface in actual use in the spectrometer. Charging of the sample affects all electron levels equally and is sensitive to factors such as temperature and hydration which affect the conductivity of the sample.

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