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NOTE

The High Energy Photoelectron Spectra of Molybdenum in Some Mo/Al_2O_3 Systems

In this note we present preliminary investigations of the use of high energy photoelectron spectroscopy in elucidating the surface structure of some Mo/Al_2O_3 systems. We consider this to be a necessary prelude to further planned work on typical hydrodesulfurization catalysts where additional complications arise due to the incorporation of Co into the system. We present below results which indicate that a possible stable surface structure involves the creation of electron accepting sites on the alumina followed by electron donation from the molybdenum, thus providing chemical shifts in the molybdenum $3d_{5/2}$ and $3d_{3/2}$ levels.

High energy photoelectron spectroscopy is based on the study of the energy distribution of electrons which are ejected when materials are bombarded with monochromatic X-radiation. The technique has been described in detail by Siegbahn *et al.* (*1*) and the instrument used for these investigations was an A.E.I. Electron Spectrometer. Briefly this consists of a conventional X-ray source (Al $K\alpha$ for this work) which is used to irradiate the sample. The photoejected electrons then pass through an electrostatic field which brings the electrons to a focus according to their energy before they are collected on an electron multiplier. The energy distribution of characteristic photoelectron peaks is obtained by scanning the electrostatic analyzer voltage and an X-Y recorder is used to display the spectrum.

The discrete peaks observed in the spectra arise from photoejected electrons which have not suffered any inelastic scattering on escaping from the material. This means that the electrons will originate from a depth in the surface layer which is dependent on their kinetic energy, e.g., electrons which have only 70 eV of kinetic energy will escape collision free from $\lesssim 5$ Å (*2*) while electrons of 1000 eV of kinetic energy will escape collision free from 50 to 100 Å (*1*).

The energy relationship for the peaks observed is as follows:

$$E_{\mathrm{kin}} = h\nu - E_b$$

where E_{kin} is the measured energy of the ejected electrons; $h\nu$ is the energy of the exciting radiation (Al $K\alpha = 1487$ eV); E_b is the binding energy of the electron ejected from the atoms by the elements under investigation. E_b is not constant, and differences in the precise positions of characteristic electron peaks (i.e., chemical shifts) give information about the chemical environment of the atoms concerned. The particular peaks examined in these investigations arose from the $3d$ levels of molybdenum (where E_b for $3d_{3/2} = 230$ eV and for $3d_{5/2} = 227$ eV).

The materials under study were in the form of powders and each sample was presented to the spectrometer as a thin layer pressed on a phosphor bronze gauze. The materials were prepared as follows:

Pseudoboehmite (*3*) was precipitated from sodium aluminate and aluminium sulfate solutions and ammonium molybdate or molybdic oxide was added in the process between filtration and calcination. The quantities used were sufficient to give a final product containing 15% MoO_3. In a number of cases the resulting material was further calcined after the addition stage. The cobalt molybdate used was precipitated from cobalt nitrate and ammonium molybdate solution at pH 7, washed and dried at 100°C. This material gave charge transfer bands at 37,000 cm^{-1} and $31,600^{-1}$ when examined by diffuse reflectance spectroscopy and these are indicative of Mo(VI) in an octahedral environment (*4*). The molybdic oxide and sodium molybdate were A.R. grade. The ammonium molybdate solution used was commercial grade, containing approximately 25% (w/w) MoO_3, and was made by dissolving technical grade molybdic oxide in aqueous ammonia.

Our results indicate a distinct change in the electron binding energy spectra when mixtures of molybdenum compounds and pseudoboehmite or γ-alumina are calcined at 365°C or above. Material which had not been calcined after mixing gave well resolved peaks for the $3d_{3/2}$ and $3d_{5/2}$ level of molybdenum (Fig. 1). Heating mixtures of molybdenum compounds with pseudoboehmite or γ-alumina at 366, 453, or 600°C gave unresolved peaks for these levels. The transition to this pattern appeared to begin at approximately 360°C (Fig. 2).

The following alumina-free reference samples gave well-resolved peaks:

1. molybdic oxide;
2. cobalt molybdate (a) dried at 100°C; (b) dried at 100°C and calcined at 600°C;
3. sodium molybdate;
4. ammonium molybdate solution (a) evaporated and dried at 100°C; (b) evaporated and dried at 100°C and calcined at 600°C;
5. 1:1 mixture of sodium and cobalt molybdates.

That the effect on calcination is due to interaction between molybdenum and the alumina is demonstrated by the spectra of, for example, cobalt molybdate where the peaks are well resolved in both the dried and calcined states.

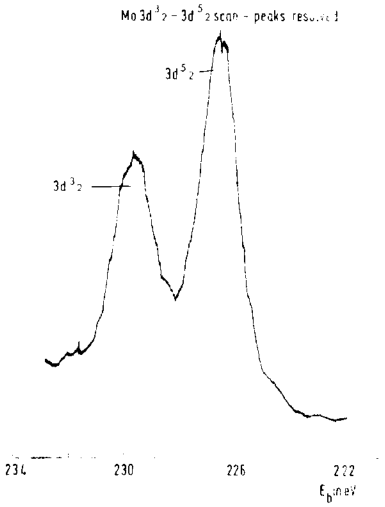

Fig. 1. Typical spectrum of Mo in an uncalcined or reference sample.

Three possible explanations have been considered for the change in the Mo/Al_2O_3 spectrum on calcination above 360°C:

1. A change in coordination number of the molybdenum. The results on the reference samples indicate that this is not the case. Cobalt molybdate and molybdic oxide have the molybdenum octahedrally coordinated with oxygen (*4, 5*) while in sodium molybdate, the oxygen is arranged tetrahedrally about the molybdenum atoms (*6*). The mixture of sodium and cobalt molybdates did not yield broadened peaks which

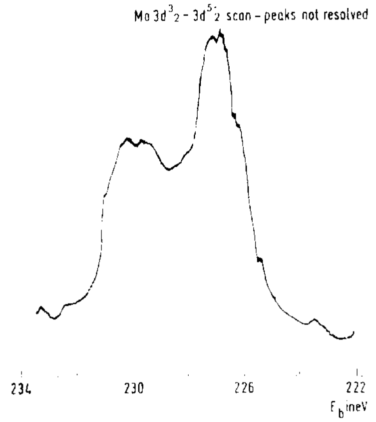

Fig. 2. Typical spectrum of Mo in a sample calcined above 360°C.

would have been expected if the coordination number of molybdenum caused the chemical shift.

2. Change in oxidation state. The spectral evidence indicates that a higher oxidation state than 6 would be involved to account for the observed chemical shift to higher binding energies. To the best of our knowledge there is no previous evidence for the existence of such an oxidation state for molybdenum.

3. Electron donor/acceptor process. A plausible explanation for the effect observed would involve the alumina acting as an electron acceptor from the molybdenum. The observed chemical shift of the molybdenum peaks, although surprisingly large, would support this explanation. However, not all the molybdenum present is involved with active sites on the alumina because more than one state of molybdenum is indicated in the unresolved doublets obtained from calcined materials. Flockhart *et al.* (*8*), have shown that alumina has electron acceptor properties which are developed at 320°C.

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REFERENCES

1. Siegbahn, K., Nordling, C., Fahlman, A., Nordberg, R., Hamrin, K., Hedman, J., Johansson, G., Bergmark, T., Karlsson, S., Lindgren, I., and Lindberg, B., "ESCA." *Nova Acta Regiae Soc. Sci. Upsal.* Ser. IV **20,** Uppsala 1967.

2. Palmberg, P. W., and Rhodin, T. N., *Appl. Phys.* **39,** 2425 (1968).

3. Papée, D., Tertian, R., and Biais, R., *Bull. Soc. Chim. Fr.* **1950,** 1301.

4. Ashley, J. H., and Mitchell, P. C. H., *J. Chem. Soc.* **1968,** 2821.

5. Smith, G. W., and Ibers, J. A., *Acta Crystallogr.* **19,** 269 (1965).

6. Wells, A. F., "Structural Inorganic Chemistry," 3rd ed., p. 468. Oxford Univ. Press, London/New York, 1962.

7. Wells, A. F., "Structural Inorganic Chemistry," 3rd ed., p. 445. Oxford Univ. Press, London/New York, 1962.

8. Flockhart, B. D., Scott, J. A. N., and Pink, R. C., *Trans. Faraday Soc.* **62,** 730 (1966).

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