

## LETTERS TO THE EDITORS

## On the Relationship between Binding Energy and Oxidation State of Mo in Molybdenum Oxides

In a recent paper, Broclawik *et al.* (1) discuss the relationship between the binding energy of Mo and its oxidation states in Mo oxides and compare their theoretical results with some experimental data reported in the literature. Since their conclusions seem to contradict our previous work (2) we think it is appropriate to take up the subject again, in view of the fact that the problem is of general interest, as it relates to the interpretation of the XPS experimental data on oxides in general, and in particular to the surface characterization of oxide catalysts.

Binding energy (BE) values of the 3d levels for the different oxidation states of Mo have been reported by several authors (2-8). The data are in good agreement, with the exception of the MoO<sub>2</sub> value reported in Ref. (3), which is ~1.5 eV higher than the value reported by us. It should be noted, however, that a subsequent paper by Patterson *et al.* (7) gives a value 1.5 eV lower. The earlier higher value seems originated by an erroneous deconvolution of Fig. 3 of Ref. (3). The absolute values of BE can differ slightly depending on the choice of the reference, but there is no doubt, as pointed out by us (2), that the plot of the 3d BE vs oxidation number (ON) is not linear. A nonlinear plot was also obtained by Lepage *et al.* (5).

Haber *et al.* (6) studied by XPS the reduction of MoO<sub>3</sub> and interpreted their data on the basis of the presence of two different types of Mo<sup>4+</sup>, isolated and paired,

instead of Mo<sup>5+</sup> and Mo<sup>4+</sup>. A linearity of BE vs ON was assumed, so that the paired Mo<sup>4+</sup> came to have an apparent oxidation number of +2. Similar conclusions were drawn from the reduction of WO<sub>3</sub> (9).

While a linear relationship between BE and charge of ions has been observed in several cases, which involve compounds with closely related structures and similar types of bonding (10-12), a better approximation must include the electrostatic potential generated by the surrounding (potential model) and, finally, the relaxation energy. It should be noted that the ON is a formal quantity, not necessarily related to the effective charge. Thus the plot of Fig. 5 of Ref. (6) is really a plot aiming at defining the effective charge, not the ON.

It can be concluded that, experimentally, it is well established that the BE of the Mo 3d levels, in the metal, in MoO<sub>2</sub> and MoO<sub>3</sub>, are not on a straight line, the MoO<sub>2</sub> value falling 1 to 1.5 eV below. Linearity of BE vs ON has been observed in several cases, but, as a general rule, there is no theoretical reason why it should occur (10-12).

Recently, Broclawik *et al.* (1), from SCF-SW-X $\alpha$  calculations for MoO<sub>6</sub><sup>6-</sup>, MoO<sub>6</sub><sup>8-</sup>, and MoO<sub>6</sub><sup>10-</sup> clusters, concluded that the interpretation of Haber *et al.* (6) has to be preferred.

The model used by Broclawik *et al.* (1) does not take into account final state effects, assumes undistorted tetrahedra and

a constant Mo-O distance. These assumptions are not realistic (for example,  $\text{Mo}^{4+}$  and  $\text{Mo}^{6+}$  have different ionic radii), but once they have been made and relaxation effects are ignored, the only variable left is the charge on Mo, so that linearity of BE vs ON follows as a natural consequence, since it is built into the model itself. This type of model could be adequate for a series of compounds, like the chlorides of Mo, where final state effects can be considered reasonably constant. BE values for chlorides (5) confirm this fact and clearly point to the different behavior of  $\text{MoO}_2$ . This oxide is a conductor, itinerant 4d electrons being present. Extra-atomic relaxation has to be expected and must be taken into account.

The calculation of Broclawik *et al.* (1) can be considered a demonstration of the fact that if relaxation effects are ignored a linear BE vs ON plot is obtained. Similar results would be given by any MO-type calculation, but correct BE values are obtained only if relaxation energy is included, and this term can be particularly important in conducting oxides. The proper way to deal with the lowering of the BE in  $\text{MoO}_2$  and  $\text{WO}_2$  consists in taking into consideration final state effects (particularly extra-atomic relaxation).

The assignment to  $\text{Mo}^{5+}$  of the BE value between  $\text{Mo}^{4+}$  and  $\text{Mo}^{6+}$  seems the most logical conclusion. The objection that  $\text{Mo}^{5+}$  is not seen by ESR (6) is not stringent since in reduced  $\text{MoO}_3$  (and  $\text{WO}_3$ ) the presence of conduction electrons obscures the ESR signals. We also wish to note that the BE values for the 4f levels of W in W oxides reported in the literature (9, 13) give a nonlinear BE vs ON plot, as do our own data on Re oxides (14).

The presence of extra-atomic relaxation has been reported in  $\text{PbO}_2$  (15),  $\text{CdO}$  (16), and  $\text{Co}_3\text{O}_4$  (17). It is apparent that the occurrence of final state effects (relaxation)

in oxides is the rule rather than the exception, especially in compounds with conducting properties.

In the case of Mo and W oxides (6, 9) the linearity has been assumed. Such an assumption is untenable since it has no theoretical or experimental basis and leads to the introduction of an apparent oxidation number, which does not seem to fulfill any useful purpose and can be misleading.

We can summarize our discussion as follows:

(a) Published experimental BE values for 3d levels in Mo oxides and 4f values in W oxides are in substantial agreement and it is well established that they do not give a linear BE vs ON plot.

(b) The correct explanation of the deviation ( $\sim 1.5$  eV) from the straight line of the  $\text{MoO}_2$  (and  $\text{WO}_2$ ) value has to be sought in the increased extra-atomic relaxation due to the presence of conduction electrons (screening of the core hole by itinerant 4d electrons and 5d electrons).

#### REFERENCES

1. Broclawik, E., Foti, A. E., and Smith, V. H., Jr., *J. Catal.* **51**, 380 (1978).
2. Cimino, A., and De Angelis, B. A., *J. Catal.* **36**, 11 (1975).
3. Swartz, W. E., Jr., and Hercules, D. M., *Anal. Chem.* **43**, 1774 (1971).
4. Kim, K. S., Baitinger, W. E., Amy, J. W., and Winograd, N., *J. Electron. Spectrosc.* **5**, 351 (1974).
5. Lepage, F., Baillif, P., and Bardolle, J., *C.R. Acad. Sci. (Paris)* **280 C**, 1089 (1975).
6. Haber, J., Marczewski, W., Stoch, J., and Ungier, L., *Ber. Bunsenges. Phys. Chem.* **79**, 970 (1975).
7. Petterson, T. A., Carver, J. C., Leyden, D. E., and Hercules, D. M., *J. Phys. Chem.* **80**, 1700 (1976).
8. Aptekar, E. L., Chudinov, M. G., Alekseev, A. M., and Krylov, O. V., *React. Kinet. Catal. Lett.* **1**, 493 (1974).
9. Haber, J., Stoch, J., and Ungier, L., *J. Solid State Chem.* **19**, 113 (1976).
10. Siegbahn, K., Nordling, C., Fahlman, A., Nordberg, R., Hamrin, K., Hedman, J.,

- Johansson, C., Bergmark, T., Karlsson, S., Lindgren, I., and Lindberg, B., ESCA, Almovist and Wiksell, Uppsala, 1967.
11. Jolly, W. L., in "Electron Spectroscopy: Theory, Techniques and Applications" (C. R. Brundle and A. D. Baker, Eds.), p. 119. Academic Press, New York, 1977.
12. Gelius, U., *Phys. Scripta* **9**, 133 (1974).
13. De Angelis, B. A., and Schiavello, M., *J. Solid State Chem.* **21**, 67 (1972).
14. Cimino, A., De Angelis, B. A., Gazzoli, D., and Valigi, M., *Z. anorg. allg. Chem.*, in press.
15. Kim, K. S., O'Leary, T. J., and Winograd, N., *Anal. Chem.* **45**, 2214 (1973).
16. Gaarenstroom, S. W., and Winograd, N., *J. Chem. Phys.* **67**, 3500 (1977).
17. Haber, J., and Ungier, L., *J. Electron Spectrosc.* **12**, 305 (1977)

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