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On the Relationship between 3d Binding Energy and Oxidation State in Molybdenum Oxides

The assignment and interpretation of the experimentally determined values of the binding energies (BE) for 3d levels in molybdenum oxides is a problem of much current interest and discussion (*1*, *2*). For this reason, Broclawik *et al.* (*3*) initiated theoretical calculations for a series of models of increasing complexity for the Mo oxides. In the first of these studies (*3*), calculations employing the SCF-SW-Xα method (*4*, *5*) were made for a simple model of MoO_6^{6-}, MoO_6^{7-}, MoO_6^{8-}, and MoO_6^{10-} clusters in order to try to establish which of the published interpretation (*1*, *2*) of the Mo 3d BE data (*2*) in terms of the oxidation state of Mo is more probable.

Recently Cimino and De Angelis (*6*) (CA) have commented upon the relationship between 3d BE and oxidation number (ON) of the Mo in Mo oxides and on the theoretical calculations. On the basis of a newer measurement for MoO_2 (*7*), they contend that the experimental relationship for the three known oxide systems (MoO_3, MoO_2, and Mo metal) is not a linear one as found originally by Swartz and Hercules (*8*). This relationship is useful in interpreting the process of reducing MoO_3 to MoO_2 by following the changing nature of the 3d XPS spectrum (*2*). Haber *et al.* (*2*) made such measurements, found three stages, the initial form (MoO_3), an intermediate form (I), and the final form (II or MoO_2), and interpreted their data for the latter two forms on the basis of isolated Mo^{4+} (form I) and paired Mo^{4+} (form II or MoO_2) ions. They associate forms I and II with oxidation numbers 4 and 2, respectively, on the assumption of a linear relationship between 3d BE and oxidation number. CA reject this interpretation because the relationship is a nonlinear one and instead interpret the data on the basis of Mo^{5+}(I) and Mo^{4+}(II) ions. At this point, it is important to realize that CA and Haber *et al.* are discussing different oxidation numbers: the former a formal oxidation number (FON) and the latter an apparent or effective oxidation number (AON). These two concepts coincide for the two end points Mo metal (0) and MoO_3 (+6) but differ in the case of MoO_2 and the intermediate form I. It is interesting to note that the new measurement for MoO_2 (*7*) improves the linear relationship of 3d BE vs AON with the opposite effect for 3d BE vs FON [for the Hercules data (*7*, *8*)]. Furthermore, it is implicit that CA assume that 3d BE vs FON is linear for MoO_2, form I and MO_3 in order to arrive at the interpretation in terms of Mo^{5+} ions for form I, i.e., the nonlinearity arises only when the metal is included.

CA contend (*6*) that the theoretical model was constrained to give a *linear* relationship and that the calculations neglected relaxation effects. The aim of the theoretical studies was to use models which describe the properties of the molybdenum

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oxides by including the influence of the surrounding lattice and the changes in the oxidation state of the metal itself. The calculations with the simple octahedra were intended to investigate the nature of the BE vs ON relationship only but linearity was not forced by the model. The results do show a linear correlation to a good degree of approximation. Since the +2 oxidation number of Mo in MoO_2 has been interpreted in terms of double Mo–Mo bond formation (*2*) we have studied (*9*) a more sophisticated model mentioned in the first paper (*3*), namely, clusters composed of two Mo–O octahedra joined by a corner (MoO_3) and by an edge (MoO_2). The results of these calculations are in substantial agreement with the previous interpretation of the Mo 3d BE changes and give a clear picture of the Mo–Mo bond. Calculations are in progress with more elaborate models.

Contrary to the statement of CA final state relaxation effects were taken into account in the calculation of the ionization energies by means of Slater's transition-state technique (*10*). Thus the intracluster part of the relaxation is properly treated. We agree with CA that a rigorous treatment should include any possible effects of screening by itinerant electrons. The theory of metallic screening is still in its developmental stages (*11–13*). Preliminary indications are that the screening process is a relatively complicated one involving changes in nearly all of the valence orbitals. For instance in our transition state calculations we found that the Mo atom had very nearly the same charge as in the ground state; that is, the positive charge is not localized on the molybdenum atom but rather spread out throughout the intersphere and extracluster regions. The effects of adding a screening electron is thus to restore charge neutrality, not to the molybdenum but rather to its near environment. A more adequate cluster model for this effect would include the shell of first-neighbor molybdenum atoms and such calculations are planned for the near future.

REFERENCES

1. Cimino, A., and De Angelis, B. A., *J. Catal.* **36,** 11 (1975).
2. Haber, J., Marczewski, W., Stoch, J., and Ungier, L., *Ber. Bunsenges. Phys. Chem.* **79,** 970 (1975).
3. Broclawik, E., Foti, A. E., and Smith, V. H., Jr., *J. Catal.* **51,** 580 (1978).
4. Johnson, K. H., *Advan. Quant. Chem.* **7,** 143 (1973).
5. Slater, J. C., and Johnson, K. H., *Phys. Rev.* **B5,** 844 (1972).
6. Cimino, A., and De Angelis, B. A., *J. Catal.* **62,** 182 (1980).
7. Patterson, T. A., Carver, J. C., Leyden, D. E., and Hercules, D. M., *J. Phys. Chem.* **80,** 1700 (1976).
8. Swartz, W. E., Jr., and Hercules, D. M., *Anal. Chem.* **43,** 1774 (1971).
9. Broclawik, E., Foti, A. E., and Smith, V. H., Jr., to be published.
10. Slater, J. C., *Advan. Quant. Chem.* **6,** 1 (1972).
11. Williams, A. R., and Lang, N. D., *Phys. Rev. Lett.* **40,** 954 (1978).
12. Messmer, R. P., personal communication (1978).
13. Salahub, D. R., personal communication (1979).

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