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The Environment of Mo(V) in Supported Molybdena Catalysts

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Supported molybdenum catalysts are of great current interest because of their importance in hydrodesulfurization and coal hydrogenation. These catalysts have been studied using ESR in order to delineate their structure–function relationship. As a result of these studies, an ESR signal observed in reduced supported molybdenum catalysts has been ascribed to the Mo(V) ion which was envisioned as being surrounded by an octahedron of O^{2-} ions with one O^{2-} ion removed so as to give a square pyramidal environment of C_{4v} symmetry. We wish here to reinterpret the local symmetry assignment of the Mo(V) ion in these catalysts based mainly on the strength of new crystallographic and spectroscopic evidence that has recently appeared in the literature.

An ESR signal was first observed in alumina-supported molybdenum catalysts by Boreskov *et al.* (*1*), and the signal was assigned to a Mo(V) ionic species. This assignment is reasonable because even if Mo(IV) were paramagnetic, its signal would not be observable at room temperature due to the fact that it is an ^3F state ion with a large zero field splitting and fast relaxation. By the same reasoning Mo(III) can be eliminated as a source of this signal. In subsequent work Ashley and Mitchell (*2*) on basis of X-ray and optical reflectance spectra suggested that the molybdenum ion in Co–Mo–Al_2O_3 catalysts is present in a tetrahedral environment but did not rule out the possibility of an octahedral environment. Asmolov and Krylov (*3*) suggested that for low content Mo/γ-Al_2O_3 catalysts, Mo(VI) is present in a tetrahedral environment but later (*4*) concluded that in the reduced catalyst, Mo(V) is in a square pyramid of C_{4v} symmetry. This is in agreement with other workers' assignment (*5–7*). In (*5,6*) MoO_3 supported on alumina gave an ESR signal with observable peak-to-peak line width of about 80 G and an average g-value of 1.93. The signal was asymmetric with a broad tail. The signal obtained from bismuth molybdates supported on silica (*7,8*) had a broad tail with a double minimum and was about 40 G wide when measured between points at the maximum and the first up field minimum. These lines have been described in terms of an axially symmetric Hamiltonian that can be written as:

$$\hat{\mathscr{H}} = g_{\parallel} H_z S_z + g_{\perp}(H_x S_x + H_y S_y),$$

with values for $g_{\parallel}$ and $g_{\perp}$ ranging from 1.92 to 1.95 and 1.87 to 1.94, respectively (*5–8*).

Crystal field symmetry considerations reveal that the d-orbital energy level splitting for different symmetries are as shown in Fig. 1. It is clear from Fig. 1 that while a crystal field of C_{4v} symmetry around the ion would yield a ground state orbital singlet, a field of tetrahedral symmetry with tetragonal distortion would also result in an orbital singlet for the lowest energy

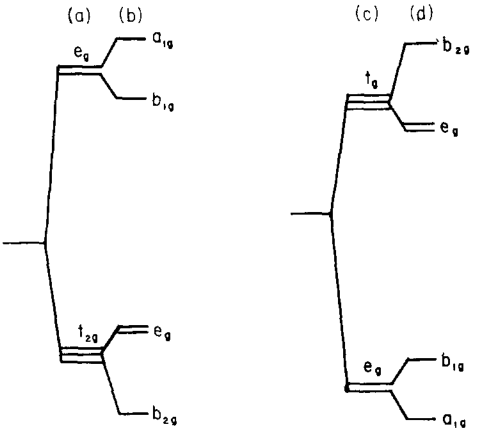
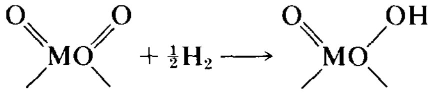


FIG. 1. *d*-orbital splitting of the Mo(V) ion in (a) octahedral field, (b) octahedral with tetragonal distortion (C_{4v}), (c) tetrahedral field, and (d) tetrahedral with tetragonal distortion.

level; this would make it possible to observe the ESR spectrum at room temperature while maintaining the essentially tetrahedral environment.

Recently the crystal structure of $Bi_2(MoO_4)_3$ has been published (*9*). The environment of the molybdenum ion in this catalyst was determined to be tetrahedral. In light of this information, we propose that the spectra of bismuth molybdate catalysts published in (*7,8*) are due to Mo(V) ions in a tetragonally distorted tetrahedral environment rather than one of C_{4v} symmetry as has been proposed. This is further evidenced by the fact that the spectra of Mo(V) ions obtained from molybdena supported on silica (*8*) and the product of the vacuum decomposition of $Mo(CO)_6$ at 150°C on porous Vycor glass (*10*) have similar ESR spectral characteristics to those in (*7,8*). That is, since the molybdenum ions are known to substitute in vacant silicon ion sites, though to a very small extent, and knowing that the coordination of these ions is tetrahedral, it is reasonable to conclude that the similar signal of (*7,8*) originates from the same species—i.e., Mo(V) in a distorted tetrahedral environment.

Furthermore, we hold that the spectra of Mo/γ-Al_2O_3 catalysts reported in (*5,6*) are also due to Mo(V) ions in tetragonally distorted tetrahedral symmetry. Lipsche and Schuit (*11*) have observed a strong ir band due to tetrahedrally surrounded molybdenum in a calcined mixture of γ-Al_2O_3 and MoO_3; and Stork, Coolegem and Pott (*12*) have demonstrated, by X-ray luminescence, the formation of $Al_2(MoO_4)_3$, in which Mo(VI) is tetrahedrally coordinated, from γ-Al_2O_3 impregnated with ammonium heptamolybdate and then calcined. In addition, recent ESR evidence obtained in our laboratory supports this view. An X-band (9.5 GHz) spectrum of our 8% Mo/γ-Al_2O_3 reduced under hydrogen has similar characteristics to those reported in (*5,6,13*). *Q*-band (35 GHz) spectra of the same samples, however, are radically different. The line shape in our 35 GHz spectra is similar to that in (*7,8*) with a line width of 160 G, compared to 40 G for the *X*-band spectra reported in (*7,8*). This is explained by the fact that the inhomogeneously broadened ESR line of our Mo(V) sample was resolved into a $g_{\parallel}$ (1.94) and $g_{\perp}$ (1.91) component at *Q*-band, allowing a more accurate "line width" determination and revealing a line shape that is the same as that reported for the Mo(V) ion in bismuth molybdates. This new evidence strengthens our conclusion that the ion in both of the catalysts is in the same environment. Our picture of the formation of the Mo(V) center is, then,



where the bonds at the bottom link to O–Al of the support. This interpretation is in accord with work presented elsewhere (*14,15*).

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