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NOTE

Effect of Local Structure on the UV–Visible Absorption Edges of Molybdenum Oxide Clusters and Supported Molybdenum Oxides

Recent studies from a number of research groups (1–8) have characterized the average particle sizes of domains of transition metal oxides or sulfides by means of an analysis of the optical bandgap energy, E_g, determined from the position of the low energy rise in the material's UV–visible spectrum. The characterization relies upon a relation between E_g and the domain size of an insulator or semiconductor (9–11). As in the case of a particle-in-a-box, where the separation between energy levels decreases with increasing box size, the bandgap energy of a real system decreases as the domain size increases. An analytical function has been developed that models the bandgap behavior of particles in the size range from about 100 nm down to about 2 nm (11).

Here, reanalysis of published spectra of molybdenum polyoxometalates has yielded a correlation between the optical bandgap energies and the average number of adjacent molybdenum cations in very small oxide clusters (≤ 1 nm). This empirical aggregation–energy relation is shown to be only slightly dependent on the nature of the charge-compensating cations or the presence of a support. When applied to the spectra of silica- and alumina-supported molybdenum oxide samples, the correlation indicates that the average sizes of the molybdenum oxide domains increase with increased metal loading. However, a large range of average aggregation size is seen even among samples containing molybdenum at concentrations substantially below monolayer coverage.

Diffuse reflectance spectra from nine sources (12–20) were carefully photoenlarged and digitized. The fidelity of the digitization was ensured by repeated measurements; accuracy was checked by comparing the positions of the peaks to those reported in the papers and was thereby estimated to be about ±2% (ca. ±0.05 eV). While peak position is the typical way of indexing the electronic spectra of catalyst samples, this measurement suffers the limitation that it is influenced by the structure of the vibrational states of the sample. Within the assumptions of conventional theory (21), the optical bandgap energy of an insulator or semiconductor is better represented by the energy of the absorption edge. Here, the positions of the absorption edges (Fig. 1) were determined in the classical fashion for allowed transitions (21–23) by finding the energy intercept of a straight line fitted through the low energy rise in the graphs of $[F(R_\infty) \times h\nu]^2$ vs $h\nu$, where $F(R_\infty)$ is the Kubelka–Munk function for an infinitely thick sample and $h\nu$ is the energy of the incident photon. In the cases presented below, the estimated edge position was insensitive (±0.02 eV) to any reasonable choice of the fitting region, even for those spectra in which the shape of the rise could scarcely be called linear.

A set of calibration spectra were taken from samples of polyoxomolybdates having well-defined structures (12, 14). A second set of spectra were taken from catalyst samples containing supported molybdenum oxides (13–18). The latter samples had been prepared both by grafting and by impregnation; their areal molybdenum loadings were in the range 0.1–6.3 μmol/m^2 (0.06–3.8 Mo/nm^2), and the spectra were all obtained from samples after calcination in air or oxygen (typically at 773 K) with efforts made to minimize rehydration. Regrettably, the spectra of some interesting samples could not be included fully in this set either because the low energy edge of the spectra was not presented (24–26), the spectra contained a peak in the typically smooth absorption edge (13, 18), or the areal loading of the metal was not specified (20).

The absorption edges of the series of isopolymolybdates are found to span a 1.6 eV range, with the larger aggregates having the smaller energies (Fig. 2). The results are reminiscent of the shift to lower bandgap energies that accompany the growth of semiconductor particles (2–8, 11, 27, 28). A continuum model of the valence electronic structure is not appropriate (and does not fit the data well) in the case of these cluster compounds. Instead, the energy differences should be compared to the results of molecular orbital calculations (6, 11). Here in lieu of those calculations, the edge energies, E, have been compared simply with N_{Mo}, the average number of nearest Mo neighbors in the clusters (i.e., the number of next nearest neighbors). The result (Fig. 3) is an empirical, linear correlation between edge energy and this measure of the local degree of aggregation of the clusters: $N_{Mo} = 16 - 3.8 \times E$. Like peak position (12, 14), this correlation does *not* distinguish between tetrahedral and octahedral site symmetry since all the compounds are fit well by the same line. Both the dependence of the spectra on the size of the aggregate

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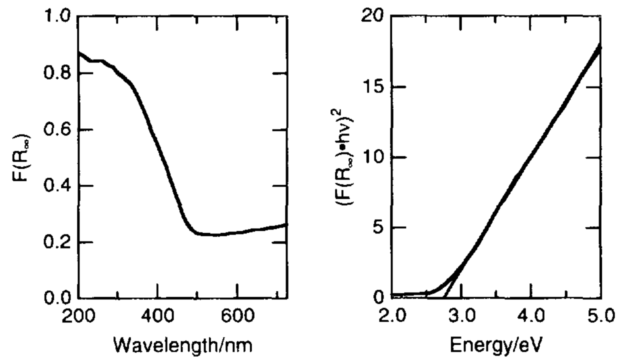

FIG. 1. Transformation of a spectrum to obtain the absorption edge energy. Left: ultraviolet diffuse reflectance spectrum of $Na_3PMo_{12}O_{40}$ supported on silica, after (19). Right: least-squares fit of a line through the low energy edge of the transformed spectrum (edge is located at 2.72 eV).

and the independence of the spectra on local symmetry around the Mo cations have been predicted by Masure *et al.* (29), on the basis of extended Hückel calculations, although they focused their attention on changes in the position of the absorption maximum, as was done in the spectroscopic study by Fournier *et al.* (12), rather than the edge energy, as is done here.

More distant neighbors also affect the edge energy, but for oxides it appears that the effect of these neighbors decreases rapidly with increasing domain size. For example, in the case of titania, the optical bandgap energy falls to within 0.4 eV of its value for the bulk for particles whose diameter is greater than or equal to roughly 1.5 nm (8). In the case of polyoxometalates, changes in charge-compensating cation or the presence of a support have a similarly small effect (Table 1), which would lead to a modest change in any prediction of aggregate size inferred from the correlation presented in Fig. 3.

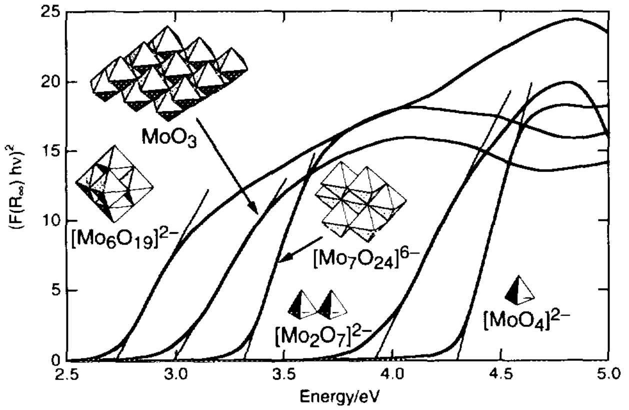

FIG. 2. UV absorption edges of standard compounds: $(tetrabutylammonium)_2Mo_6O_{19}$ (12), MoO_3 (14), $(NH_4)_6Mo_7O_{24}$ (14), $(tetrabutylammonium)_2Mo_2O_7$ (12), and Na_2MoO_4 (14).

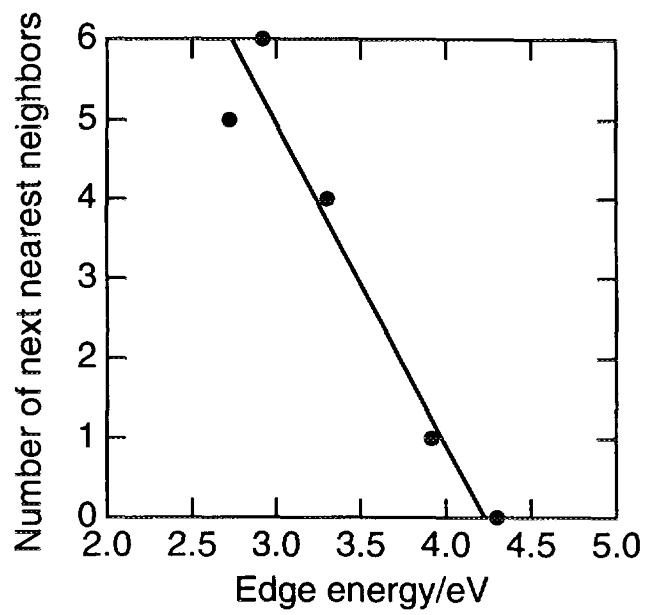

FIG. 3. Correlation between edge energy and the size of the molybdenum domain, calculated as the average number of nearest molybdenum neighbors for the compounds shown in Fig. 2.

Edge energies for the catalyst samples (Fig. 4) range from 4.3 eV for some of the least concentrated samples, i.e., as high as that measured for $[MoO_4]^-$, to 3.1 eV, which approaches that of bulk MoO_3 (2.97 eV). The results show the expected trend that the edge energy decreases—and by inference, that the estimated average degree of aggregation increases—with increased loading. The trend is most clear within each family of samples. Between families, however, there is a large range of edge energies (average size of the molybdenum oxide aggregates) even for the samples that contain very low loadings of molybdenum, likely indicating the sensitivity of the samples to the details of their preparation protocols or to variations among the supports (e.g., density of hydroxyl groups, impurities). There is a small difference between samples prepared by grafting and those prepared by im-

TABLE 1

Effect of Cations and Support on the Electronic Spectra of Bulk Samples Containing $[SiMo_{12}O_{40}]^{4-}$

Cation, support	Edge position (eV)	Reference
H^+, none	2.5	(12)
H^+, silica	2.7	(12)
Na^+, silica	2.7	(19)
$[NH_2C(NH_2)_2]^+$, none	2.6	(12)
$[N(C_4H_9)_4]^+$, none	2.7	(12)
$[N(C_{18}H_{37})_4]^+$, none	2.7	(12)

pregnation (Table 2): for comparable loadings, the impregnated samples exhibit slightly higher edge energies. The data are too limited to exhibit any systematic differences in edge energies between silica- and alumina-supported samples of comparable loadings.

TABLE 2

Comparison of Samples Prepared by Grafting and by Impregnation

Loading (μmol m^{-2})	Edge position (eV) Grafted sample	Edge position (eV) Impregnated sample	Support	Reference
0.12	4.26	4.34	Silica	(13)
0.23	4.06	4.23	Silica	(13)
0.46	4.02	4.11	Silica	(13)
0.18[a], 0.19[b]	3.60	3.84	Silica	(14)
5 wt%[a,c], 6 wt%[b,c]	2.73	3.21	Alumina	(20)

[a] Loading for grafted sample.

[b] Loading for impregnated sample.

[c] Mass loading.

The empirical correlation presented in Fig. 3. gives an estimate only of the degree of aggregation of the absorbing species and does not provide any information about the number distribution of the species that contributes to that average. Thus, a sample whose UV absorption edge lies at some intermediate energy, and therefore appears to contain medium size aggregates, may in fact contain a mixture of isolated molybdenum monomers and bulk MoO_3 or other, highly condensed polyoxomolybdates, as has been suggested from the results of other spectroscopic examinations of these and similar samples (13, 14, 24–26, 30). In principle, the number distribution of such species in a sample could be estimated by deconvoluting its spectrum using the spectra of model compounds as basis functions. This procedure, however, would require accurate measurements of the intensities of all the species' absorption curves, which is feasible (31), but which involves tedious attention to concentrations, particle size, sample placement, etc.

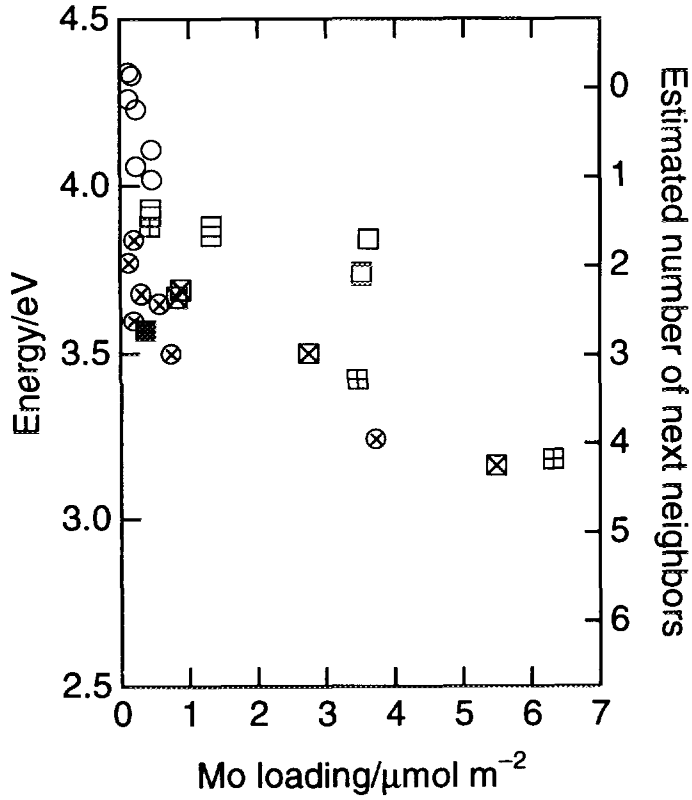

FIG. 4. Energies of the UV absorption edges of catalyst samples. (○) 0.1–0.9 μmol Mo/M^2 SiO_2 (13); (⊗) 0.1–3.7 μmol Mo/m^2 SiO_2 (14); (□) 0.4–3.6 μmol Mo/m^2 Al_2O_3 (15); (⊞) 0.4–6.3 μmol Mo/m^2 Al_2O_3 (16); (⊠) 0.8–5.5 μmol Mo/m$_2$ Al_2O_3 (17); (■) 0.4 μmol Mo/m^2 Al_2O_3 (18).

It is not clear at this stage how edge energy depends on the bonding of the molybdenum oxides to a support. The similarity between the edge energies of bulk and silica-supported Keggin ions shown in Table 1 may only mean that the cluster–support interaction is negligible in this case. On the contrary, the small differences between edge energies of impregnated and grafted samples shown in Table 2 are consistent with the idea that grafting can alter the electronic structure of a supported cluster as has been suggested recently (32). But the edge results presented here are also consistent with the grafted samples containing aggregates that are slightly larger, on average, than those formed by impregnation at the same areal loading. The latter view is consistent with the results of a number of spectroscopic and chemical characterizations of supported molybdenum oxides (17, 30, 33) while the former view derives principally from X-ray absorption studies (18, 32, 34). The juxtaposition in Fig. 4 of edge data from the UV spectra of samples from many camps suggests that the different structures inferred for these precursors of oxidation catalysts could well arise from significant variations in the samples themselves, even when they have been prepared according to apparently similar recipes.

By extension of the theory that applies to the bandgap energies of larger ensembles (1, 9–11), the edge energies of molecularly sized clusters should track with the extent of spatial delocalization of the molecular orbitals involved in the electronic transition associated with the UV–visible edge. If so, then the degree of aggregation estimated from edge energies according to the correlation presented in Fig. 3 need not be strictly comparable with other measures of the exposure or geometric structure of the oxide domains. For example, oxygen uptake counts uptake sites but does not tell their proximity; EXAFS and Raman spectroscopy can give more direct measures of local structure, but both techniques are liable to underestimate the sizes of the domains of metal oxides when samples exhibit static disorder.

The energy of an absorption edge, moreover, need not correspond directly to energies measured through thermally excited processes such as electron tunneling and chemical reaction since, during an optically excited electronic transition, structural relaxation of the absorbing species does not have time to occur (35). For example, the difference between an optical and a thermal bandgap energy can be on the order of 1 eV (36). Electron spin resonance (ESR) spectroscopy (37) and superparamagnetism measurements (38, 39) can give estimates of electron delocalization but these two techniques are also only complementary to the edge measurements in the case of Mo oxides since the magnetic measurements must be done on partially reduced samples which may have undergone structural rearrangement. For reduced Keggin ions, where the gross structure of the anion is known to be preserved upon reduction (40, 41), ESR indicates that the frontier electrons can delocalize over the entire cluster (40–43), in satisfactory agreement with the edge measurements on oxidized clusters given in Table 2 which suggest that the excitation involves about 8 of the 12 Mo centers in this very compact structure.

Finally it should be pointed out that, because these edge measurements were performed *ex situ*, their implications for the structures of the samples under reaction conditions are, *a priori*, as uncertain as those that come from the usual application of the other physical methods like those just mentioned.

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