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The X-Ray Photoelectron Spectra of Heterogeneous Catalysts[1]

III. Catalysts Derived from Dimeric Molybdenum(II) Carboxylates on Silica and Their Reactions with Carbon Monoxide, Nitric Oxide, and Hydrogen

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The X-ray photoelectron spectra (XPS) have been recorded for a series of molybdena-silica catalysts (containing 4 or 10% Mo). These catalysts were prepared from the molybdenum(II) carboxylates $Mo_2(O_2CR)_4$, where R = H, CH_3, CF_3, or C_6H_5, which contain a quadruple Mo–Mo bond. The Mo $3d_{\frac{3}{2},\frac{5}{2}}$ and O 1s binding energies were measured for the calcined catalysts before and after their reaction with NO and CO. XPS evidence supports the presence of a mixture of Mo(VI), Mo(V), and Mo(IV) sites on the surface of the calcined catalysts, while treatment with NO and CO leads to the formation of Mo(VI) and Mo(V), respectively. The redox characteristics of the catalyst (i.e., Mo(VI) $\rightleftarrows$ Mo(V)) induced by NO and CO treatments are reversible as shown by cycling of the NO and CO in various sequences. ESR spectroscopy indicates that the surface changes monitored by XPS are also typical of the bulk, namely, Mo(V) with $g = 1.93$ is formed upon CO treatment but disappears in the presence of NO. The present XPS results are compared to relevant literature data for supported molybdena catalysts prepared from more conventional starting materials. It is suggested that Mo-SiO_2 prepared from $Mo_2(O_2CR)_4$ may have different metal–support interactions from other molybdena systems.

INTRODUCTION

The existence of transition metal compounds containing *pairs* or *clusters* of metal atoms has attracted considerable interest because of their utilization as models for chemisorption and heterogeneous catalysis (*2*). While attention has mostly centered on organometallic molecules (*3–5*) there has remained the important question of whether other species, such as low oxidation state metal halides and carboxylates, which contain very strong metal–metal bonds (triple or quadruple bonds) (*6*, *7*) might be catalytically active. This is a particularly intriguing possibility because of the coordinatively unsaturated, highly reducing nature of many such species. Consequently, we have been exploring various aspects of the chemistry of derivatives of molybdenum and rhenium which contain these bonding units (*8–11*). Of relevance to our interests was the recent observation that supported $Mo_2(O_2CCH_3)_4$ and $Mo_2(O_2CCF_3)_4$ (see Structure I) will, when suitably activated,

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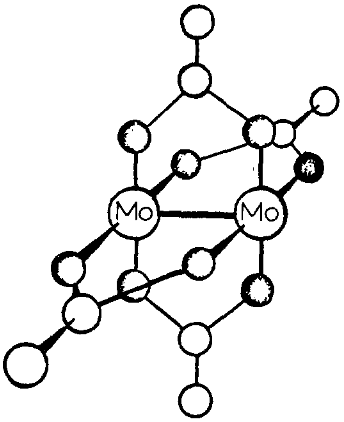

Structure I

catalyze the disproportionation (metathesis) of propene (*12*). This report prompted the present investigation.

The starting materials which have been used previously in the preparation of supported molybdenum catalysts for such important processes as olefin metathesis and hydrodesulfurization range in oxidation state from Mo(VI) to Mo(O). These include $MoO_2(OH)_2$ (*13*), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (*14*), MoS_2 (*15*), $Mo(C_3H_5)_4$[3] (*3, 5, 16, 17*), $Mo_2[CH_2Si(CH_3)_3]_6$ (*12*), $Mo_2[CH_2C(CH_3)_3]_6$ (*12*), and $Mo(CO)_6$ (*13, 18–21*). The use of $Mo_2(O_2CCH_3)_4$ and $Mo_2(O_2CCF_3)_4$ (*12*) constitutes the only report of a molybdenum (II) starting material.

Since the original discovery by Banks and Bailey (*22*) that linear olefins of three to eight carbon atoms can be converted to homologs of shorter and longer chain lengths, there has been tremendous interest in reactions of this type. The subject has been thoroughly reviewed (*23, 24*) and much interest currently centers on the mechanistic aspects of these reactions (*25*). From the recent work of Smith *et al.* (*12*) it appears that the complexes $Mo_2(O_2CCH_3)_4$ and $Mo_2(O_2CCF_3)_4$ on silica, when activated at 300°C, are about as active as $Mo(CO)_6$, $Mo_2[CH_2Si(CH_3)_3]_6$, and $Mo_2[CH_2C(CH_3)_3]_6$ after activation at 200°C. In this same paper, the observation was made that "in order to account for Mo(V) signals observed in the ESR spectra of $Mo(CO)_6$ catalysts, *and also in molybdenum alkyl and acetate complexes*, oxidation must take place on the support. The nature of this oxidation is unknown, but may involve the interaction of coordinatively unsaturated molybdenum with further hydroxo-groups." One means of following the fate of a complex such as molybdenum(II) acetate on silica and alumina supports is by the use of the technique of X-ray photoelectron spectroscopy (XPS or ESCA). Previous XPS investigations on molybdenum-containing catalysts constitute a reasonably successful application of this technique to the structural characterization of heterogeneous catalysts and encouraged us to pursue an XPS investigation of catalysts prepared from $Mo_2(O_2CR)_4$. The XPS of MoO_3–Al_2O_3 (*26–28*), MoO_3–SiO_2 (*27*), Co–Mo–Al_2O_3 (*29–35*), bismuth molybdate (*36–38*), and $Mo(CO)_6$–Al_2O_3 (*39*) catalysts have provided a wealth of data on the identification of the Mo $3d_{5/2,3/2}$ binding energies associated with Mo(VI), Mo(V), and Mo(IV) sites in oxide lattices (*33*).

Since XPS can provide important information on the chemical environment about a central metal and also monitor interactions between an "active" catalyst site (or catalyst precursors) and the support, we have investigated the XPS of systems derived from a series of molybdenum(II) carboxylates, $Mo_2(O_2CH)_4$, $Mo_2(O_2CCH_3)_4$, $Mo_2(O_2CCF_3)_4$, and $Mo_2(O_2CC_6H_5)_4$ on silica supports, and followed their subsequent reactions with gaseous NO, CO, and H_2.

Although the catalytic properties of these systems were not studied, we were able to obtain information concerning their surface structure and redox behavior. Additional information was obtained using ESR spectroscopy.

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[3] C_3H_5 represents the η^3-allyl ligand.

EXPERIMENTAL METHODS

The molybdenum carboxylates, $Mo_2(O_2CH)_4$, $Mo_2(O_2CCH_3)_4$, $Mo_2(O_2CCF_3)_4$, and $Mo_2(O_2CC_6H_5)_4$, were prepared according to the standard literature procedures (*40–42*). Catalyst preparation was performed using a procedure in which we followed as closely as possible that used to prepare $Mo_2(O_2CCH_3)_4$ and $Mo_2(O_2CCF_3)_4$ on silica and alumina (*12*). Due to the insolubility of these complexes in suitable solvents, the samples were dry ground under a nitrogen atmosphere into the silica (Cab-O-Sil, grade M-5) which had previously been calcined in air at a temperature of 600°C for a period of 24 hr. Sufficient quantities were used to produce samples containing either 4 or 10% molybdenum. The resulting light yellow powder was then placed via a porcelain boat into a glass tube which was subsequently evacuated. Samples were heated to a temperature of 300°C for 3 hr producing a dark blue powder. For the XPS studies, the resulting powder was then pressed at 843.0 kg/cm^2 to a 22-mm-diameter, 0.1 to 0.2-mm-thick self-supporting disc. Electron spin resonance (ESR) measurements were carried out on powdered samples at room temperature.

In the studies involving reactions of the molybdena catalysts with gaseous CO (Matheson, 99.5% min purity), NO (Matheson, 99.0% min purity), and H_2 (Matheson, 99.95% min purity), exposure to the atmosphere following reaction was minimized by use of the procedure described in our earlier report on chromia-silica catalysts (*1*).

Binding energy spectra were recorded using a Hewlett-Packard 5950A ESCA spectrometer. The Al $K_{\alpha 1,2}$ line (1486.6 eV) was used as the excitation source. The catalyst discs were placed in a recessed gold-plated copper blank which was in turn attached to the end of the instrument sample probe. An electron "flood-gun" was used to minimize surface charging effects (*43*) and peak deconvolutions were carried out using a Dupont 310 Curve Resolver employing a gaussian shape fit.

As has been discussed (*27*, *44*), the binding energies of a supported catalyst can be internally referenced to some suitable binding energy line of the support. This procedure is desirable if differences in surface charging effects between different catalyst samples are to be minimized. Accordingly, the Mo 3d, O 1s, and C 1s binding energies of $Mo_2(O_2CR)_4$ on silica were referenced to a Si 2p binding energy (*1*) of 103.7 eV for the silica support.

X-band ESR spectra of powders were recorded at room temperature with a Varian E-109 spectrometer.

RESULTS AND DISCUSSION

The XPS of the Calcined Catalysts

The XPS of the pure molybdenum(II) carboxylates, $Mo_2(O_2CR)_4$, where R = H, CH_3, CF_3, and C_6H_5, exhibit core Mo 3d binding energies in the ranges 232.4 to 231.9 ($3d_{3/2}$) and 229.3 to 228.8 ($3d_{5/2}$) eV. Accordingly, these values lie within the binding energy limits which were previously found (*9*, *33*, *45*) to be characteristic of nonorganometallic derivatives of Mo(II) which contain pairs or octahedral clusters of metal atoms. Dry grinding these compounds with the silica support does not lead to significant changes in the Mo 3d XPS. Likewise, the unchanged Mo(II) species are still dominant after evacuation of the catalyst mixtures at room temperature for several hours. These results are in accord with the moderate air stability of these complexes (*42*, *46*) and the absence of a rapid metal complex–support interaction in the solid state. However, upon calcining these mixtures *in vacuo* for 3 hr at 300°C, activation temperatures which Smith *et al.* (*12*) found gave the best activity for propene disproportionation, the XPS underwent a dramatic change.

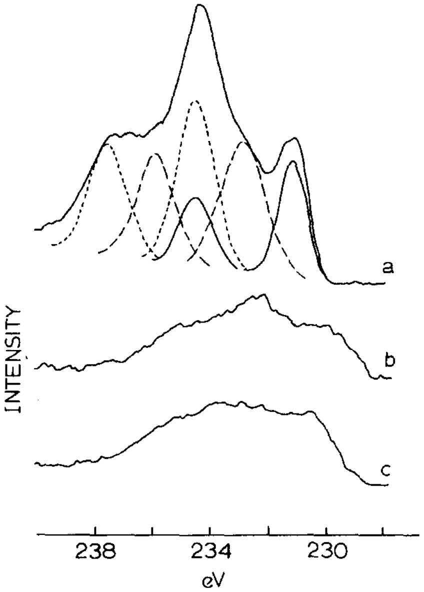


FIG. 1. Mo 3d binding energy spectra of $Mo_2(O_2CR)_4$-silica (10% Mo) calcined at 300°C for 3 hr: (a) $Mo_2(O_2CCH_3)_4$; (b) $Mo_2(O_2CH)_4$; (c) $Mo_2(O_2CC_6H_5)_4$.

The resulting spectra for the supported acetate, benzoate, and formate, which are shown in Fig. 1, demonstrate the formation of a mixture of high oxidation state molybdenum species. In the case of $Mo_2(O_2CCF_3)_4$-silica, large quantities of the yellow $Mo_2(O_2CCF_3)_4$ sublimed from the mixture, leaving behind a material whose XPS revealed very weak, ill-defined Mo 3d peaks. While there is no mention in the earlier report by Smith *et al.* (*12*) of such a problem exising with this system, our observations do not seem surprising in view of the known volatility of this class of molybdenum complexes (*42*, *46*). It therefore appears that the rate of sublimation of $Mo_2(O_2CCF_3)_4$ is significantly greater than the rate of its reaction with the SiO_2 support. Accordingly, we chose not to pursue an XPS study of this particular system, although we do note that molybdenum can be incorporated if calcination is carried out in the presence of air.

The Mo 3d XPS of the calcined catalysts containing 10% Mo, which were prepared from $Mo_2(O_2CH)_4$, $Mo_2(O_2CCH_3)_4$, and $Mo_2(O_2CC_6H_5)_4$, reveal some differences between each other. While the acetate gives rise to a reasonably well-defined spectrum (Fig. 1a) with peaks clearly located at 237.0, 234.2, and 231.0 eV, the formate and benzoate (Figs. 1b and c) produce more poorly defined spectra which, nonetheless, resemble one another.

The spectrum shown in Fig. 1a is of particular interest since the spectral profile and the peak separation between the two outermost peaks (~6.0 eV) resemble other published Mo 3d spectra for a variety of pertinent systems. These include (i) reagent grade MoO_2 which contains appreciable quantities of MoO_3 (*26*, *27*), (ii) materials arising from the H_2 reduction of MoO_3 (*26*, *27*), MoO_3–Al_2O_3 (*26*, *27*), MoO_3–SiO_2 (*27*), and Co–Mo–Al_2O_3 (*29*) under certain conditions, and (iii) $Mo(CO)_6$–Al_2O_3 after calcining and then exposing to air (*39*). Since XPS evidence has been presented in support of the presence of molybdenum oxidation states ranging from Mo(VI) to Mo(IV) in most of these systems (*26*, *27*, *29*), a similar conclusion would likely hold for calcined $Mo_2(O_2CCH_3)_4$ on silica. Indeed, the peak separation of 3.2 eV between the two lowest energy peaks (234.2 and 231.0 eV) in Fig. 1a is close to the chemical shift (3.2 to 2.9 eV) reported by others (*26*, *27*, *29*) for the Mo $3d_{\frac{5}{2}}$ peaks of MoO_3 and MoO_2. Deconvolution of this spectrum (Fig. 1a) provides good evidence for the presence of three types of molybdenum species, with Mo $3d_{\frac{5}{2}}$ binding energies of 234.2, 232.7, and 231.0 eV, the two higher energy sets of Mo 3d peaks being of comparable intensity and much more intense than the lowest energy Mo $3d_{\frac{3}{2},\frac{5}{2}}$ doublet by a factor of 2 to 3.

There is now reasonably good agreement in the literature concerning the values of the Mo 3d binding energies of the oxides MoO_3 and MoO_2 (*26*, *27*, *29*, *47*), provided a Au $4f_{7/2}$ value of 83.8 eV or a C 1s value of 285.0 eV for carbon contaminant is used as the binding energy reference (*48*). In addition, there is also good evidence that for supported molybdenum oxide catalysts of the types Mo–Al_2O_3, Mo–SiO_2, and Co–Mo–Al_2O_3, the Mo 3d binding energies associated with different molybdenum oxidation states are similar to those observed for the bulk oxides (*26*, *27*, *29*). As can be seen from Fig. 1a, if the lowest energy Mo $3d_{\frac{5}{2}}$ peak at 231.0 eV is correctly assigned to Mo(IV), and those at 232.7 and 234.2 eV are due to the Mo $3d_{\frac{5}{2}}$ components of Mo(V) and Mo(VI), respectively, then each of these peaks is shifted by approximately +1 eV relative to those previously reported for these oxidation states in both pure and supported oxides (*26*, *27*, *29*, *47*).

There are several possible reasons for this shift. First, our referencing procedure might not be compatible with that chosen by other workers (*26*, *27*, *29*, *47*), who used either a Au $4f_{7/2}$ (83.8 or 84.0 eV) or C 1s (285.0 eV for carbon contaminant) level as the reference. However, while this could be a contributing factor it does not appear to be the major one since, with our use of a Si 2p reference of 103.7 eV, we also find that for all the spectra presented in Fig. 1 the C 1s peak is at 285.0 ± 0.2 eV. Another possibility is that differential charging effects are prevalent and that the molybdenum is not in good electrical contact with the support. In view of this, efforts were taken to determine to what extent such charging phenomenon played a role in shifting the Mo 3d binding energies. From subsequent experiments dealing with different degrees of catalyst loading and electron "floodgun" currents, it was concluded that charging was not a significant factor. A third possibility is that the high Mo 3d binding energies result from a strong interaction with the support. Similar effects were noted on a chromia-alumina catalyst studied by Okamoto *et al.* (*49*), for which it was found that the binding energies of Cr(III) on the surface were considerably increased (1.0–1.4 eV) compared with those obtained for bulk Cr_2O_3. This fact was considered (*49*) to indicate the degree of electron flow from Cr_2O_3 to Al_2O_3. It is therefore possible that the shifts in binding energies we have observed arise in part from increased metal–support interactions which, in turn, result from use of unique starting materials and a different impregnation technique than in conventionally prepared molybdena catalysts. Whatever the explanation, it is clear that caution should be exercised in assigning peaks from supported catalysts since, as Delgass (*50*) has recently emphasized, poorly understood support interactions can be a major factor in complicating chemical shift interpretation. Nonetheless, it is apparent that these rather high Mo 3d binding energies are characteristic of our systems and we subsequently found that this property is retained during subsequent treatments of the catalysts, as we shall now describe.

The XPS of NO and CO Treated Catalysts

Reaction of the calcined $Mo_2(O_2CCH_3)_4$–silica (10% Mo) catalyst with CO gas at 300°C for 3 hr produced a material whose Mo $3d_{\frac{3}{2},\frac{5}{2}}$ spectrum consisted of a sharp doublet at 236.3 and 233.2 eV assigned to Mo(V).

The ESR spectra of both the calcined and CO-treated catalysts were very similar and clearly reveal the presence of Mo(V) in both systems, a species which has been shown by ESR spectroscopy to be present on other supported molybdena catalysts (*14*(a), *51–53*). The g value of 1.93 (Figs. 2a and b) is characteristic of this species. While it is not our intent to pursue a detailed investigation of the ESR spectra of these catalysts, a brief consideration of the intensities of the signals shown in Fig. 2 is appropriate. The spectra in the figure were recorded using the same instrumental settings with the exception of variations in the amplifier gain which were

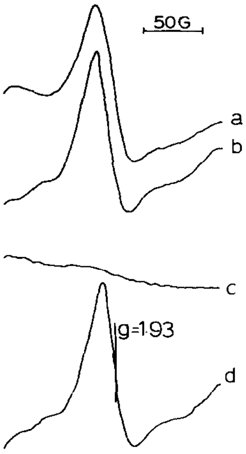


FIG. 2. The ESR spectra of $Mo_2(O_2CCH_3)_4$–silica (10% Mo) after calcination and reaction with CO and NO: (a) calcined catalyst; (b) sample from (a) reacted with CO; (c) sample from (a) reacted with NO; (d) sample from (c) reacted with CO.

as follows: (a) 3.2×10^3, (b) 8.0×10^2, (c) 8.0×10^3, and (d) 8.0×10^2. Accordingly, it is clear that there is an approximately fourfold increase in the concentration of ESR active Mo(V) species upon treatment of the calcined catalyst with CO. This result is in accord with the results of the XPS measurements (*vide supra*), namely, that the mixtures of Mo(VI), Mo(V), and Mo(IV) which are present in the calcined catalysts are converted to Mo(V) upon CO treatment.

A remarkable feature of the CO-treated catalyst is the absence of any XPS evidence for Mo(IV). The CO reduction of Mo(VI) to Mo(V) is to be expected, but the oxidation of Mo(IV) to Mo(V) might at first sight seem puzzling. One possibility is that CO_2, produced by the CO reduction of Mo(VI), oxidizes Mo(IV) to Mo(V). Some preliminary studies we have carried out involving the reaction of the calcined catalyst with CO_2 support this as a viable mechanism. After carrying out this reaction at 300°C for 3 hr, the resultant Mo 3d XPS reveals Mo(VI) and Mo(V) species (Mo $3d_{5/2}$ at ~234.0 and ~233.2 eV, respectively) but no significant amount of Mo (IV). The intensity of the Mo(V) ESR signal ($g = 1.93$) shows an approximately twofold increase after CO_2 treatment, consistent with an increase in the amount of Mo(V) due to the oxidation of Mo(IV); the Mo(VI) remains unaffected by this treatment.

Quite different results are obtained upon reacting the calcined catalyst at 300°C with NO instead of CO. Once again a sharp, Mo $3d_{3/2,5/2}$ doublet is produced but these peaks are now shifted to 236.8 and 233.8 eV and the ESR spectrum (Fig. 2c) reveals that no detectable paramagnetic molybdenum species are present. In view of the shift in binding energies and the ESR results, it is believed that diamagnetic Mo(VI) is formed upon the NO treatment. As observed by other workers (*27*, *47*), decomposition of the resulting Mo(VI) species was evident during prolonged data collection since the Mo 3d binding energies were lowered by approximately 0.5 eV. This problem was circumvented by lowering the X-ray flux by reducing the power to one-half of its original value of 1 kW.

In order to test the reversibility of these reactions with gaseous CO and NO, we cycled CO and NO over the molybdena catalyst as we have done previously with the chromia-silica catalyst system (*1*). Thus the Mo $3d_{3/2,5/2}$ binding energies produced upon reaction of the CO-treated sample with NO gas are analogous to those of the product formed by reaction of the calcined catalyst directly with NO. This indicates that Mo(V) has once again been oxidized to form Mo(VI). Further reaction of the NO-treated catalyst with CO gas produces Mo $3d_{3/2,5/2}$ binding energies of 236.3 and 233.2 eV and an ESR spectrum (Fig. 2d) indicative of Mo(V). These changes are quite reproducible, the same Mo 3d binding energies and ESR spectra which are characteristic of Mo(VI) and Mo(V) always being obtained upon treatment with NO and CO, respectively. The appropriate Mo 3d binding energies of the

TABLE 1

Mo 3d and O 1s Binding Energies (eV) of Calcined $Mo_2(O_2CR)_4$–Silica following Treatment with Carbon Monoxide and Nitric Oxide[a]

Experimental treatment[b]	Mo[c]		O 1s[c]
	$3d_{3/2}$	$3d_{5/2}$	
A. $Mo_2(O_2CCH_3)_4$–silica (10% Mo)			
(i) Reaction with CO	236.3 (1.3)	233.2 (1.2)	533.0 (2.0)[d]
			531.3 (1.3)
(ii) Reaction with NO	236.8 (1.1)	233.8 (1.1)	533.1 (1.6)[d]
			531.7 (1.2)
(iii) CO-treated product reacted with NO	236.8 (1.0)	233.8 (1.0)	533.2 (2.0)[d]
			531.7 (1.2)
(iv) CO–NO-treated product reacted with CO	236.3 (1.1)	233.2 (1.1)	533.1 (2.0)[d]
			531.2 (1.7)
B. $Mo_2(O_2CCH_3)_4$–silica (4% Mo)			
(i) Reaction with CO	236.7 (2.4)	233.7 (2.0)	533.2 (2.0)[d]
(ii) Reaction with NO	237.0 (2.2)	234.0 (2.0)	533.2 (1.7)[d]
(iii) CO-treated product reacted with NO	237.0 (2.0)	234.0 (1.8)	533.2 (1.6)[d]
(iv) CO–NO-treated product reacted with CO	236.6 (2.2)	233.6 (2.0)	533.2 (1.7)[d]
C. $Mo_2(O_2CH)_4$–silica (10% Mo)			
(i) Reaction with CO	235.9 (2.2)	232.9 (2.0)	533.2 (1.8)[d]
(ii) Reaction with NO	236.7 (1.9)	233.6 (1.9)	533.2 (1.6)[d]
(iii) CO-treated product reacted with NO	236.5 (1.8)	233.4 (1.7)	533.2 (1.7)[d]
(iv) CO–NO-treated product reacted with CO	236.1 (1.9)	233.0 (1.9)	533.2 (1.7)[d]

[a] C 1s binding energy at 285 ± 0.1 eV in all instances.

[b] Reactions with CO and NO carried out for 3 hr at 300°C.

[c] Full width at half maximum (fwhm) values given in parentheses.

[d] This O 1s binding energy is mainly due to the silica support.

products from these reactions are summarized in Table 1, and Fig. 3 illustrates several of the Mo 3d and O 1s spectra.

Several additional features of the XPS of the $Mo_2(O_2CCH_3)_4$–silica (10% Mo) catalysts merit comment. First, the Mo 3d peaks of the products resulting from the NO/CO treatments are unexpectedly narrow (full width at half maximum values of ~1.1 eV), a feature which is most unusual for supported catalysts, since these peaks are invariably broader than for the bulk oxides due to a variety of different metal–support interactions (*54*), as well as the possible occurrence of nonuniform surface charging effects due to the insulating properties of the support materials (*27*, *29*, *35*). Second, the O 1s spectra (Fig. 3) show a second O 1s peak in addition to that due to the silica support at ~533.2 eV. From the known values of the Mo 3d and 0 1s binding energies of the bulk molybdenum oxides (*29*, *47*) this O 1s peak (between 532 and 531 eV) must be associated with the molybdenum oxide-containing surface species. Accordingly, it appears that the XPS of this catalyst system is typical of that which is expected for "bulk molybdenum oxides" overlaying the supported molybdena. Evidence in support of this is provided by the weakness of the Si 2p signals and the high values of the I_{Mo3d}/I_{Si2p} intensity ratios (between 58 and 12) for the calcined and CO- and NO-treated catalysts. These ratios are one to two orders of magnitude greater than the values calculated by the model of Angevine *et al.* (*55*) in the limit of

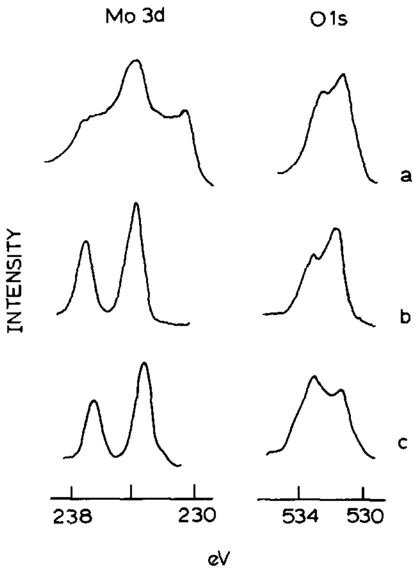


FIG. 3. Mo 3d and O 1s binding energy spectra of $Mo_2(O_2CCH_3)_4$–silica (10% Mo) after calcination and reaction with CO and NO: (a) calcined catalyst; (b) sample from (a) reacted with NO; (c) sample from (b) reacted with CO.

monatomic dispersion. With this condition, it has been proposed (*55*) that Eq. (1) should hold

$$I_m/I_s = \sigma_m N_m/\sigma_s \lambda_s(E_s) n_s S_{BET} \quad (1)$$

where $I_{m,s}$ = peak area of a particular XPS line in the active component (m) or support (s); $\sigma_{m,s}$ = effective cross-section for the production of electrons; $\lambda_s(E_s)$ = mean free path for the inelastic scattering of an electron from the support with kinetic energy E_s; n_s = number density of the support element chosen for reference; N_m = number of atoms of element m per gram of catalyst; and S_{BET} = support surface area, taken as the BET per gram of finished catalyst. In the case of molybdena on silica, Eq. (1) may be rewritten as (2)

$$I_{Mo3d}/I_{Si2p} = \sigma_{Mo3d} N_{Mo}/\sigma_{Si2p} \lambda_{Si}(E_{Si}) n_{Si} S_{BET} \quad (2)$$

from which we may calculate a value for the I_{Mo3d}/I_{Si2p} intensity ratio. Using values for σ_{Mo3d} and σ_{Si2p} of 9.50 and 0.82, respectively, from Schofield (*56*), and a $\lambda_{Si}(E_{Si})$ value of 25.7 Å from Penn's tables (*57*), the calculated I_{Mo3d}/I_{Si2p} value is approximately 1. Experimental values in excess of this, as we have observed in the present investigation, indicate a high concentration of molybdenum on the exterior surface of the silica particles.

An additional interesting observation stems from a consideration of the intensity changes of the O 1s peak as a function of reaction history (Fig. 3). After reaction of the NO product with CO, a decrease in intensity is seen in the oxygen peak associated with the surface molybdenum oxide component. Further reaction of this product with NO then results in an increase in intensity of this peak. Although the determination of a reaction mechanism for these reactions is beyond the scope of this work, these results may be in agreement with general proposed mechanisms for redox reactions occurring over metal oxide catalysts in which the reaction of NO produces a reduced NO species (such as N_2O). The O 1s XPS intensity data could be interpreted to mean that oxygen is transferred to the molybdenum resulting in a higher oxidation state species. Subsequent reaction of the NO-treated product with CO could then produce an oxidized CO species such as CO_2. Since the O 1s peak is now less intense after this step, it could be assumed that oxygen is transferred to the CO molecules producing a lower oxidation state molybdenum oxide (Mo(V)).

The preceding results for 10% loaded $Mo_2(O_2CCH_3)_4$–silica prompted us to investigate samples of lower loading. The appropriate Mo 3d and O 1s binding energies of a 4% loaded sample are presented in Table 1 and the resulting Mo 3d spectra are shown in Fig. 4. Calcination of the samples produces a Mo 3d spectrum which is similar to that of the 10% loaded samples derived from $Mo_2(O_2CH)_4$ and $Mo_2(O_2CC_6H_5)_4$ (Figs. 1b and c). Comparison of the binding energy data indicates that oxidation has occurred resulting in molybdenum of high oxidation states. The single O 1s peak at 533.1 eV is assigned to the oxygen of the support and, unlike the situation with the 10% loaded $Mo_2(O_2CCH_3)_4$ samples, there is no longer a lower energy O 1s peak of appreciable intensity. Reaction of the calcined catalysts separately with CO and NO or cycling these gases (i.e., CO–NO–CO etc.) over the heated catalyst gave products whose Mo 3d binding energies were similar, but not identical, to those observed with the 10% loaded samples. However, the Mo 3d peaks are now much broader than those encountered in the latter system (Table 1) by almost a factor of two, a result which is in accord with the supported nature of the molybdena which is being detected by the XPS technique (*27, 29, 35*). In addition, the Mo3d:Si2p peak intensity ratios are now significantly smaller than those encountered with the 10% loaded samples (*vide supra*). Experimental values for $I_{\mathrm{Mo3d}}/I_{\mathrm{Si2p}}$ of 0.6 to 0.2 are of the same order of magnitude as those calculated from Eq. (2), implying that the limit of monatomic dispersion is being approached (*55*). The Mo 3d Mo(VI)–Mo(V) chemical shift for the 4% loaded samples is slightly less than that encountered for the 10% Mo samples (0.4 versus 0.6 eV), a result which may reflect slight differences in the molybdena–support interactions. However, the molybdenum ESR spectra of the 10 and 4% loaded samples are virtually identical, implying a close similarity in the nature of the bulk Mo(V) sites and the redox characteristics of these materials.

In the case of the acetate-based catalysts, reactions with a 1:1 mixture of CO and NO gases resulted in a Mo 3d spectrum analogous to that obtained after reaction with NO alone. This result is in accord with the known chemistry of the second and third series where the formation of the highest oxidation state is favored in an oxidizing atmosphere even at high temperatures. This result may be contrasted with the behavior of the related chromia-silica system under comparable conditions (*1*).

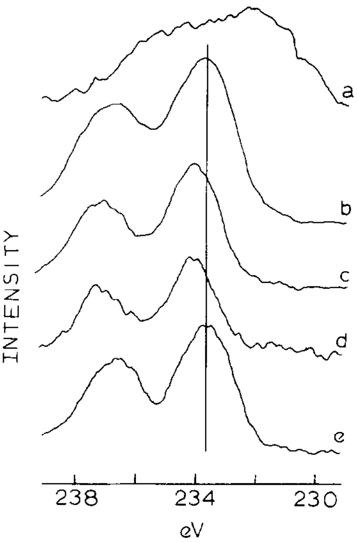


FIG. 4. Mo 3d binding energy spectra of $Mo_2(O_2CCH_3)_4$–silica (4% Mo) after calcination and reaction with CO and NO: (a) calcined catalyst; (b) sample from (a) reacted with CO; (c) sample from (a) reacted with NO; (d) sample from (b) reacted with NO; (e) sample from (d) reacted with CO.

The extension of the above studies to $Mo_2(O_2CH)_4$–silica (10% Mo) showed that this system resembles the 4% loaded $Mo_2(O_2CCH_3)_4$ samples in terms of its spectroscopic properties, with the exception of differences in the relative values of the Mo 3d binding energies (see Table 1). These are up to 0.8 eV lower than those encountered for $Mo_2(O_2CCH_3)_4$–silica containing 4% Mo. The reaction of CO with the calcined catalysts again produces Mo(V), with Mo $3d_{\frac{3}{2},\frac{5}{2}}$ binding energies of 235.9 and 232.8 eV, respectively, versus energies of 236.7 and 233.7 eV for the acetate-prepared samples. The Mo(VI) produced by reaction with NO gas shows a similar lowering in relative binding energy (Mo $3d_{\frac{3}{2},\frac{5}{2}}$ at 236.7 and 233.6 eV versus 237.0 and 234.0 eV obtained from the acetate sample), but the chemical shift

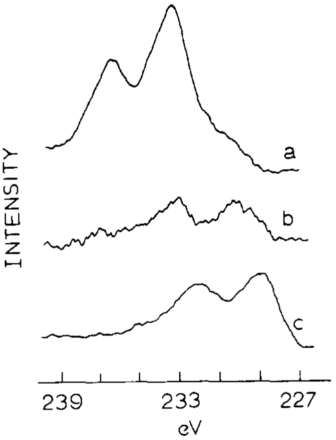


FIG. 5. Mo 3d binding energy spectra of $Mo_2(O_2CCH_3)_4$–silica (4% Mo) after reaction with H_2: (a) 400°C for 2 hr; (b) 500°C for 2 hr; (c) 600°C for 3 hr.

between Mo(VI) and Mo(V) remains close to 0.6 eV. These energy differences may reflect a weaker interaction between the metal and the silica support in the case of the catalysts prepared from molybdenum (II) formate.

While the Mo 3d spectrum of calcined $Mo_2(O_2CC_6H_5)_4$–silica (Fig. 1d) closely resembles that of the other calcined catalysts, the redox characteristics of the resultant product is dependent upon the calcining temperature. Reaction of the product calcined at 300°C with CO or NO affords a material whose Mo 3d$_{\frac{3}{2},\frac{5}{2}}$ binding energies are close to 236 and 233 eV, but the subsequent cycling of these gases over the "activated" catalysts produced little apparent change in the Mo 3d binding energies.

The ESR spectrum of this system also reveals important differences from those encountered with the other molybdenum(II) carboxylates. The spectrum of the sample calcined at 300°C shows evidence for two different Mo(V) environments (*14*(b), *50*). Other states may of course also be present but Mo(VI) is diamagnetic and Mo(IV) is difficult to observe at room temperature. Analysis of the ESR spectrum from the sample activated at 300°C and reacted with NO gas for 3 hr at 300°C reveals that Mo(V) is still present in contrast to the other catalysts which were calcined at 300°C. However, when a calcination temperature of 350°C is used, the ESR spectrum shows a single resonance at $g = 1.93$. This Mo(V) signal disappears upon reacting the catalyst with NO and reappears upon subsequent treatment with CO. These results may reflect the greater stability of the benzoate complex to oxidation compared to the other molybdenum(II) carboxylates. Hochberg *et al.* (*46*) have reported that the acetate complex is oxidized in a few days upon exposure to air while the corresponding oxidation of the benzoate complex requires about 2 months. It is concluded, therefore, that since the benzoate sample is less susceptible to oxidation, a higher temperature is required to afford complete reaction with the silica.

It should also be noted that in no case was there any XPS evidence for the formation of significant amounts of surface carbonate, nitrite, or nitrate species. The monitoring of nitrosyl (NO) species was thwarted by the presence of a rather broad Mo 3p$_{\frac{3}{2}}$ peak close to 400 eV.

Comparison of XPS Results with Those Reported for Conventionally Prepared Catalysts

As mentioned previously, XPS studies on supported molybdenum oxide catalysts have been reported by Cimino and De Angelis (*27*), Aptekar *et al.* (*26*), and Patterson *et al.* (*29*). When either silica or alumina is used, activation results in a complex Mo 3d spectrum which is very similar in profile to our spectra. The major difference is the binding energy data for the Mo(VI) and Mo(V) species which we have attributed to increased metal–support interactions. That the support does play a significant role in stabilizing a particular oxidation state has been noted by Cimino and De Angelis (*27*).

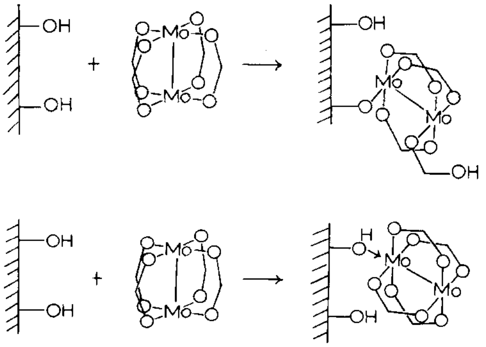
These workers have found that molybdenum is much more reducible with a silica support versus an alumina support, a difference which was attributed to the weaker interaction of MoO_3 with silica than with alumina. In fact the ease of reduction of molybdenum on silica was nearly the same as that of unsupported MoO_3. Although the study by Aptekar *et al.* (*26*) deals only with alumina-supported catalysts, their XPS results are in accord with those of Cimino and De Angelis (*27*). Other workers (*58*) reported that with catalysts obtained by thermal decomposition of ammonium molybdate and subsequently reduced with H_2, titration data indicate that molybdenum supported on silica is reduced to a greater extent than when Al_2O_3, CeO_2, or ZrO_2 is used as a support.

To compare our systems further with those described above, reactions of H_2 with $Mo_2(O_2CCH_3)_4$–SiO_2 samples containing 4% Mo have been carried out at temperatures of 400, 500, and 600°C. The resulting Mo 3d spectra are shown in Fig. 5. Higher reaction temperatures are required to produce increasing amounts of reduced molybdenum. From these results, it is clear that our system is not analogous to the catalyst samples prepared from ammonium molybdate and silica as reported by Cimino and De Angelis (*27*). These workers have identified significant quantities of a "metallic-like" species, MoO_x, upon reduction at 500°C for 2 hr. In our sample, however, similar reaction conditions produce largely Mo(IV) species. Reaction of our sample with H_2 at 600°C for 3 hr results in futher reduction producing Mo 3d$_{\frac{3}{2},\frac{5}{2}}$ peaks at 232.1 and 229.2 eV, which are known to be characteristic of the Mo(II) oxidation state (*33*). This result further illustrates the different properties of our system since under these reaction conditions reduction to metallic molybdenum might have been expected. In fact, this behavior appears to be quite similar to that observed by Yermakov (*3*) on catalysts obtained from the interaction of molybdenum π-allyl complexes with silica. He reported the formation of Mo(IV) upon reaction with H_2 at 450°C and Mo(II) at 550°C.

Although the specific mechanisms of interaction between an oxide support and an organometallic compound have not been determined, it is generally agreed (*5*) that interaction involves the surface hydroxyl groups and follows the general reaction

$$\text{support–OH} + MR_n \rightarrow \text{support–O–}MR_{n-1} + RH.$$

Such a mechanism would likely hold in the case of $Mo_2(O_2CR)_4$. Although there are a variety of reactions of $Mo_2(O_2CR)_4$ in which complete substitution of the carboxylate groups can occur (*6*), Garner and Senior (*59*) have evidence that in certain reactions involving molybdenum(II) trifluoroacetate, the carboxylate bridge may be opened thereby leading to products containing up to two "dangling" monodentate trifluoroacetate groups, *behavior which is not accompanied by disruption of the strong metal–metal bond.* In such an event, we can envisage attack of the surface –OH groups upon the carboxylate bridges with subsequent opening of one or more rings as shown in Scheme I.



Schemes I and II

Alternatively, the first step in anchoring the complex to the surface might involve coordination of –OH to one of the vacant axial coordination sites of the dimer (complexes of the type $Mo_2(O_2CR)_4L_2$ are known, as in $Mo_2(O_2CCF_3)_4$, 2py (*60*)) without the need initially for ring opening to occur (Scheme II).

Whatever the details of the mechanism for the $Mo_2(O_2CR)_4$–silica support interaction, the present XPS study has provided evidence that these systems have properties which are different from those of "conventional" molybdena-silica catalysts. It is hoped that our investigation will prompt further studies on the catalytic activity of molybdena catalysts prepared from molybdenum(II) carboxylates.

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