The effect of electron beam irradiation on the chemistry of molybdenum hexacarbonyl on thin alumina films in ultrahigh vacuum

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Abstract

The interaction of incident electron beams with molybdenum hexacarbonyl ($Mo(CO)_6$) adsorbed on thin, dehydroxylated alumina films grown on a molybdenum substrate is studied in ultrahigh vacuum using primarily temperature-programmed desorption (TPD) and reflection–absorption infrared spectroscopies (RAIRS). It is found that electron beams induce decarbonylation, forming both subcarbonyls and a stable surface oxalate species, where it is found that a $Mo(CO)_2$ species is the precursor to the formation of oxalate species. A similar oxalate species is formed on dehydroxylated alumina by heating a $Mo(CO)_6$-covered surface to above $\sim$205 K, but the amount formed by electron beam irradiation is $\sim$3.5 times larger. It is shown that electron beam energies of $\sim$10 eV or greater are required to cause extensive decarbonylation and that the majority of the surface decomposition is caused by an electron dose of $\sim$6 mC/cm^2.
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1. Introduction

Catalysts synthesized by the reaction of molybdenum hexacarbonyl ($Mo(CO)_6$) with aluminum oxide are active for a number of reactions including alkene hydrogenation and metathesis [1–4]. A number of studies have been carried out on high-surface area substrates, primarily using infrared spectroscopy, to understand the nature of the catalytically active surface species [5–12]. Thin alumina films have been grown on refractory metal substrates to mimic these high-surface area oxides [13–23]. Molybdenum carbonyl on such thin alumina films desorbs from the surface below $\sim$250 K and also reacts to form strongly bound species, where these reaction pathways compete. The CO from the strongly bound surface species desorbs in two states in temperature-programmed desorption (TPD) with a profile that is very similar to that found on high-surface area substrates. This strongly bound species has been identified on aluminas with various degrees of hydroxylation as an ox-

alate species, where the first peak, centered at 320 K in the TPD spectrum, is associated with the loss of one CO from the surface oxalate species, and the high-temperature desorption state at $\sim$430 K with the desorption of a second. This results in the two desorption states having approximately equal areas [24–27]. Unfortunately, because of the kinetic competition between carbonyl desorption at $\sim$250 K and decomposition to form the surface species, only relatively small molybdenum coverage (a few percent of a monolayer) can be achieved in ultrahigh vacuum, even when dosing at higher temperatures [25]. This maximum coverage of these strongly bound species, which decompose to yield CO at 320 and 430 K, depends on the degree of hydroxylation, with hydroxylated alumina having a molybdenum coverage of $\sim$2% of a monolayer [25] and dehydroxylated alumina a coverage of $\sim$4% [27], where the coverages are referenced to the atom site density on the well-defined Mo(1 0 0) substrate. Recent theoretical calculations have emphasized the difficulties associated with $Mo(CO)_6$ dissociation on unreactive surfaces [28]. Because of this low density of potentially active catalytic sites, it is difficult to measure the catalytic activity of these model systems and to be able to correlate the nature of the surface species that can be formed and

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characterized in ultrahigh vacuum with their catalytic activities. In order to accomplish this, it is necessary to increase the coverage of strongly bound species without changing their nature. It has been shown previously that the coverage of surface species can be increased by repeatedly adsorbing $Mo(CO)_6$ on the alumina film at 80 K and heating [25]. Since each cycle of this procedure deposits a few percent of a monolayer of molybdenum, repeating it a number of times can, in principle, accumulate relatively high coverages of surface species. This, however, is clearly a tedious and inefficient process. It has been shown that $Mo(CO)_6$ can be decarbonylated when illuminated with ultraviolet radiation [29–31]. Since, at least, part of this effect is likely to be due to electrons photoemitted from the substrate, the work outlined in the following exploits the fact that our sample is in ultrahigh vacuum and therefore allows us to irradiate it directly with electrons. This strategy has a number of advantages. First, electrons can easily be obtained in ultrahigh vacuum from a heated filament. Second, the energy of the electrons can easily be varied by accelerating them through some potential and finally, the incident flux and electron dose can be monitored by measuring the current between the sample and ground. It is recognized that this strategy is difficult to implement with real catalytic systems. In those cases, catalysts could be prepared by photoactivation rather than by using electrons and the information available from studies of the effect of electrons in ultrahigh vacuum can provide a basis for the design of photoactivation protocols for high-surface area substrates in air.

The alumina substrate is modeled in this work by evaporating a thin aluminum film on a refractory metal substrate, which is then oxidized using water to form hydroxylated alumina [25,26]. The degree of hydroxylation can then be controlled merely by heating in vacuo. There are several advantages to this approach. First, the thin alumina sample allows electron-based spectroscopies to be used to interrogate the surface since the film is sufficiently thin that it does not charge [13–23]. Of course, other, non-electron-based techniques, such as reflection–absorption infrared spectroscopy (RAIRS) can also be used. Second, it is relatively easy to modify the oxide, for example by isotopic labeling, by forming the oxide with $H_2{}^{18}O$ or D_2O. Finally, the activity of the model catalyst can be measured without intervening exposure to air by moving it from ultrahigh vacuum into a high-pressure reactor incorporated in an ultrahigh vacuum system. This also allows any changes caused by the catalytic reaction to be monitored merely by moving the sample back into ultrahigh vacuum.

2. Experimental

Infrared data were collected using a system that has been described previously [32]. Briefly, the Mo(1 0 0) single crystal sample was mounted in a modified 2.75 in.(6.985 cm) six-way cross-equipped with infrared-transparent KBr windows. It could be resistively heated to 2000 K by electron beam heating, or cooled to 80 K. Infrared spectra were collected using a Bruker Equinox infrared spectrometer with a liquid-nitrogen-cooled, mercury cadmium telluride detector. The complete light path was enclosed and purged with dry, CO_2-free air. Data were typically collected for 1000 scans at $4 \, cm^{-1}$ resolution.

Temperature-programmed desorption data were collected in another ultrahigh vacuum chamber that has been described in detail elsewhere [32] where desorbing species were detected using a Dycor quadrupole mass spectrometer placed in line of sight of the crystal.

The Mo(1 0 0) sample was cleaned using a standard procedure, which consisted of argon ion bombardment (2 kV, $1 \, \mu A/cm^2$) and any residual contaminants were removed by briefly heating to 2000 K in vacuo. The resulting Auger spectrum showed no contaminants. Alumina films were deposited onto the Mo(1 0 0) single crystal substrate by sequences of cycles of aluminum evaporation/water oxidation (with H_2O or $H_2{}^{18}O$-enriched water) [24,25]. These cycles were necessary to ensure complete oxidation of the aluminum, which may be difficult to achieve with thicker aluminum layers. Oxidation was monitored using Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). Aluminum was evaporated from a small heated alumina tube, which was enclosed in a stainless steel shroud to minimize contamination of other parts of the system [33]. It was evaporated onto a Mo(1 0 0) single crystal held at 300 K for 40 s and then oxidized by water vapor at 550 K for 300 s. This procedure was repeated three times. This resulted in the formation of hydroxylated alumina and the film is sufficiently thick that no molybdenum signals from the substrate were detected by Auger electron spectroscopy. Partially dehydroxylated alumina was made by heating this sample in vacuo at 900 K for 10 s, and dehydroxylated alumina was formed by heating to 1200 K.

The sample was dosed with electrons from a heated filament mounted on a *z*-motion drive that allowed it to be moved close to, or away from, the sample. The energy of the electrons was controlled by applying a positive bias to the sample and the electron flux measured by monitoring the current between the sample and ground using a Keithly picoammeter.

The deionized water (H_2O) and ^{18}O-labeled water ($H_2{}^{18}O$ 10 at.%, Aldrich) used to grow the films were transferred to glass vials, which were connected to the gas-handling line of the chamber. Normal, deionized (H_2O) was generally used for surface oxidation. The water was purified using repeated freeze pump–thaw cycles. Molybdenum hexacarbonyl (Aldrich, 99%) was transferred to a glass vial, connected to the gas-handling line of the chamber and purified by repeated freeze pump–thaw cycles, followed by distillation, and its purity was monitored using mass and infrared spectroscopies. This was also dosed onto the surface via a capillary doser to minimize background contamination.

3. Results

Experiments were carried out with thin dehydroxylated alumina films formed on Mo(1 0 0) by sequential evaporation and water oxidation of aluminum on a Mo(1 0 0) single crystal substrate. The alumina was dehydroxylated by heating to 1200 K in ultrahigh vacuum and the resulting film characterized using Auger and X-ray photoelectron spectroscopy as described previously [25,26]. Dehydroxylated alumina was selected for these experiments since previous results have shown that larger coverages of stable surface species are formed on dehydroxylated alumina than on hydroxylated or partially dehydroxylated aluminas [27].

Fig. 1 displays a TPD spectrum of a dehydroxylated alumina surface exposed to 0.72 L ($1 L = 1 \times 10^{-6}$ Torr s) of $Mo(CO)_6$ at 160 K collected at 97 amu, following electron beam irradiation with a total dose of $3 mC/cm^2$, as a function of incident electron beam energy. Exposures are uncorrected for ionization gauge sensitivity. The spectrum displays a feature at ~245 K without electrons, which decreases in intensity and shifts to ~269 K with increasing electron beam energy. It has been shown previously that this feature is due to the desorption of molybdenum carbonyls
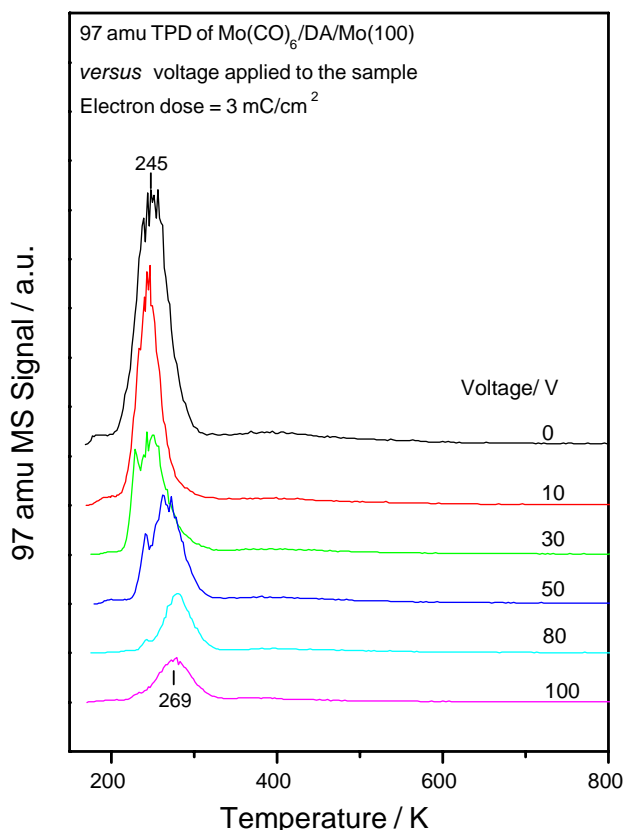

Fig. 1. Temperature-programmed desorption spectra collected at 97 amu following the adsorption of 0.72 L of $Mo(CO)_6$ on dehydroxylated alumina after electron irradiation at a current of 25 μA for 120 s ($3 mC/cm^2$ total dose) as a function of the electron energy. The spectra were collected using a heating rate of 10 K/s.
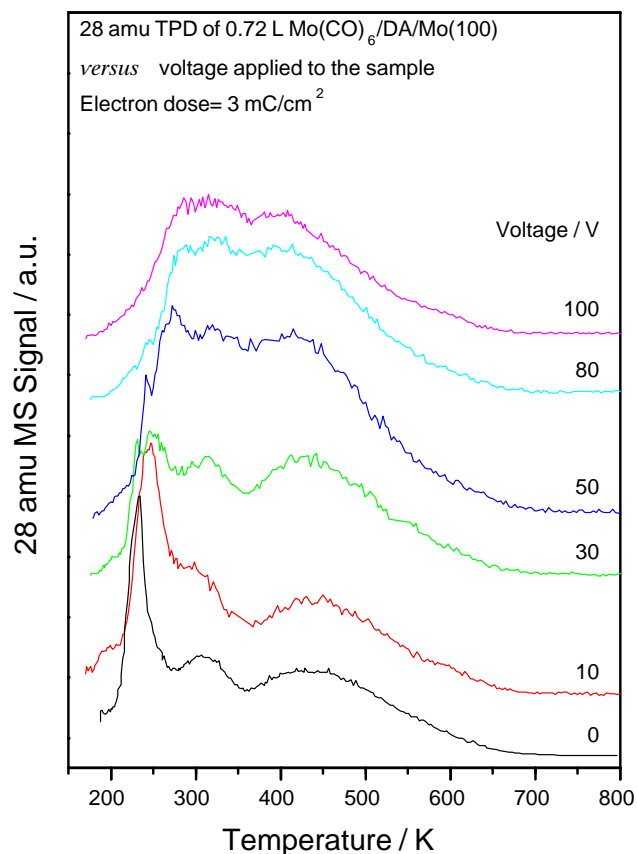

Fig. 2. Temperature-programmed desorption spectra collected at 28 amu following the adsorption of 0.72 L of $Mo(CO)_6$ on dehydroxylated alumina after electron irradiation at a current of 25 μA for 120 s ($3 mC/cm^2$ total dose) as a function of the electron energy. The spectra were collected using a heating rate of 10 K/s.

from the surface [25–27,34] and the decrease in intensity as a function of electron dose clearly indicates that carbonyls have undergone reaction under the influence of the electron beam. The corresponding series of 28 amu (CO) desorption spectra are displayed in Fig. 2. In this case, the sharp feature at ~245 K is a fragment of the feature shown in Fig. 1, which decreases in a similar manner as the 245 K feature in those spectra. The features at ~320 and 430 K in the absence of an electron dose are due to the thermal decomposition of stable surface species formed by the surface reaction of molybdenum hexacarbonyl [27]. These features grow with increasing electron energy indicating that the carbonyl removal shown in Fig. 1 results in the formation of additional, more stable surface species.

The total integrated 97 amu yield is plotted versus electron beam energy in Fig. 3, which clearly indicates that the electrons have a strong influence on the nature of the carbonyl species on the surface. The 97 amu desorption yield decreases rapidly for an electron beam energy of 10 eV and subsequently changes only slowly. This suggests that an ultraviolet photon energy of a few electron volts is likely to be similarly effective in inducing decomposition of adsorbed $Mo(CO)_6$, and has been borne out experimentally [29–31].

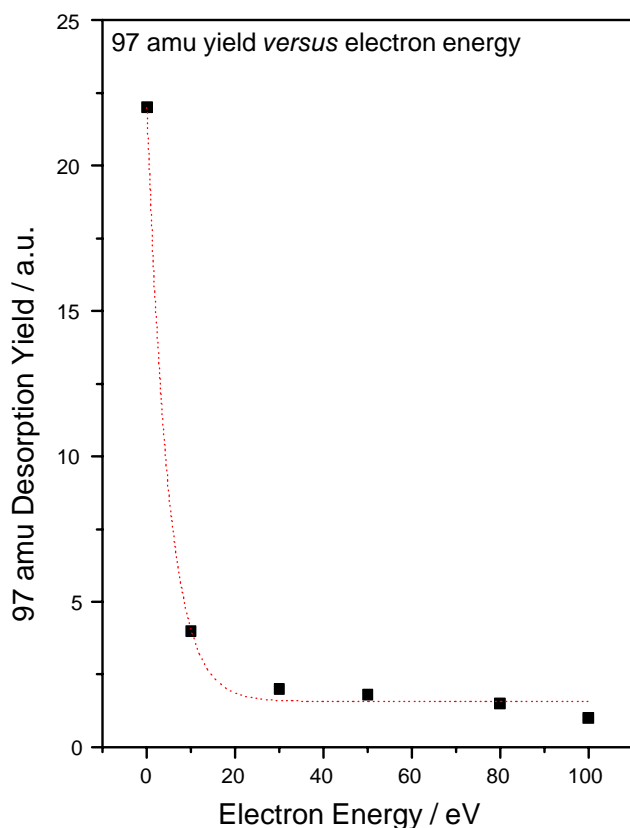Fig. 3. Plot of 97 amu yield as a function of electron beam energy (taken from the data of Fig. 1) for a $3\,mC/cm^2$ total dose.
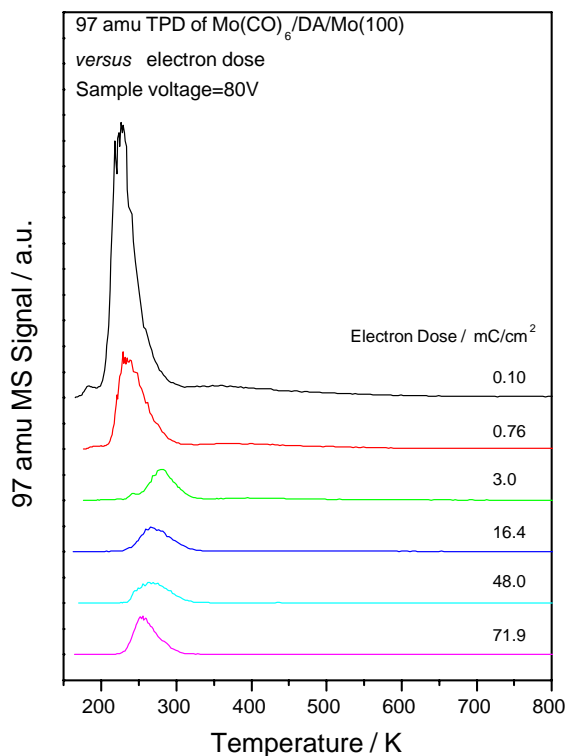

Fig. 4. Temperature-programmed desorption spectra collected at 97 amu following the adsorption of 0.72 L of $Mo(CO)_6$ on dehydroxylated alumina after electron irradiation at a beam energy of 80 eV for 120 s as a function of the incident current. The total doses are marked adjacent to the corresponding spectra, which were collected using a heating rate of 10 K/s.

An electron beam energy of 80 eV was selected for subsequent experiments.

Displayed in Fig. 4 is the effect of increasing electron dose on the nature of the surface species, monitored by the 97 amu carbonyl desorption signal. In this case, the dose was varied by adjusting the current for a fixed time of 120 s. The temperature-programmed desorption spectra show a similar behavior as found in Fig. 1 with the sharp feature at ~245 K decreasing in intensity and shifting slightly to ~269 K with increasing electron dose. The corresponding 28 amu spectra are displayed in Fig. 5 and again show a decrease in intensity of the 245 K feature mirroring the effects shown in Fig. 4. The integrated area of the high-temperature CO desorption states increases up to a total electron dose of between ~3 and $16\,mC/cm^2$, and shows little change with higher electron doses. The integrated intensities of the 97 amu TPD signals are plotted versus dose in Fig. 6, which shows that the signal decreases rapidly up to a total electron dose of ~$5\,mC/cm^2$.

A similar series of experiments was carried out by varying the exposure time at a fixed current of 25 μA to vary the total electron dose. The resulting 97 amu spectra are displayed in Fig. 7, which exactly mirror the data shown in Fig. 4. The corresponding 28 amu spectra are displayed in Fig. 8 and show the same behavior as seen in Fig. 5, confirming that no further change is found after a dose of ~$10\,mC/cm^2$.

It has been shown previously that slowly heating a $Mo(CO)_6$-covered alumina surface to ~250 K completely suppressed the formation of the stable surface species as evidenced by the absence of the ~350 and 425 K desorption peaks [27]. This indicated that the stable surface species were formed in kinetic competition with carbonyl desorption from the surface. In order to establish whether a similar effect was occurring with the stable surface species formed after electron beam irradiation, a similar series of slow heating rate experiments were performed and the results are displayed in Fig. 9. In this case, each sample was heated slowly at 3 K/s to some temperature and the 28 amu TPD spectrum subsequently collected using a heating rate of 10 K/s. The top spectrum is obtained following exposure of the dehydroxylated alumina sample to 0.72 L of $Mo(CO)_6$ without any further treatment. This displays a sharp feature at ~245 K due to carbonyl desorption and features at 350 and 425 K due to decomposition of the stable surface species as found previously [27]. The second spectrum shows the effect of irradiating with $3\,mC/cm^2$ of electrons at a beam energy of 80 eV. The sample was then heated slowly (at 3 K/s) to either 270 or 354 K, and the resulting TPD spectra (collected at 10 K/s) are also displayed, where the annealing temperatures are displayed adjacent to the corresponding spectrum. Clearly the effect of annealing is to remove that portion of the spectrum up to the annealing
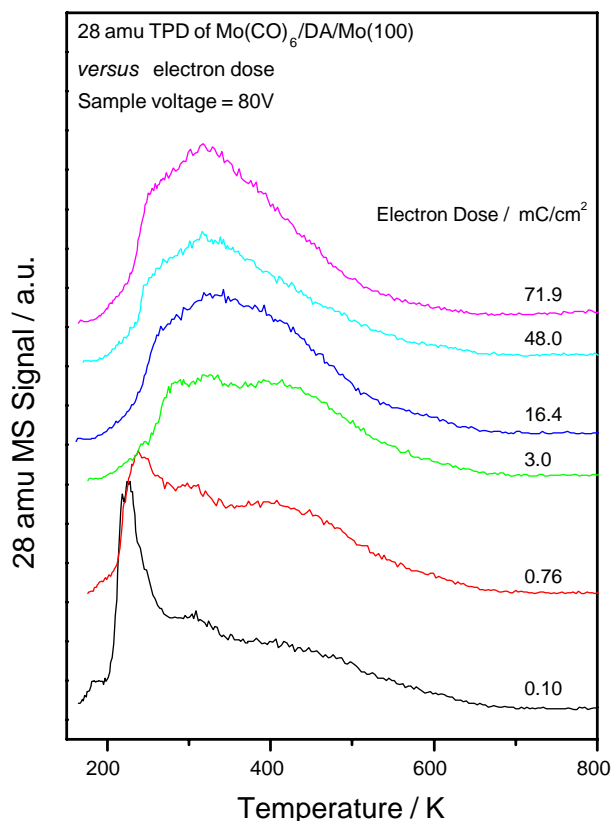
Fig. 5. Temperature-programmed desorption spectra collected at 28 amu following the adsorption of 0.72 L of Mo(CO)$_6$ on dehydroxylated alumina after electron irradiation at a beam energy of 80 eV for 120 s as a function of the incident current. The total doses are marked adjacent to the corresponding spectra, which were collected using a heating rate of 10 K/s.

Fig. 6. Plot of 97 amu yield as a function of electron dose (taken from the data of Fig. 4) using a beam energy of 80 eV.

temperature, while the shape of the spectrum above that temperature remains unaffected. This confirms that the surface species have already been formed under the influence of the electron beams.

In order to ascertain whether any of the CO evolved from the decomposition of the stable surface species derives from the alumina substrate, an alumina surface was grown using water containing 10% H$_2$^{18}O to make isotopically labeled, dehydroxylated alumina. This was then exposed to 0.72 L of Mo(CO)$_6$ and irradiated with 3 mC/cm^2 of electrons at an incident energy of 80 eV, and a TPD spectrum collected monitoring 28 (C^{16}O) and 30 (C^{18}O) amu. The resulting spectra are shown in Fig. 10, which reveal that the desorbing CO contains some oxygen from the substrate. The 30 amu signal has been multiplied by a factor of 10 so that a completely random distribution would yield a 30 amu feature identical to that at 28 amu. In fact, the 28 amu signal has been divided by a factor of 20 so that the majority of the CO derives from the original carbonyl with only a small proportion (a few percent) deriving from the oxide support. This is in contrast to the behavior for species formed thermally where the oxygen was incorporated equally from the substrate and the carbonyl [27].
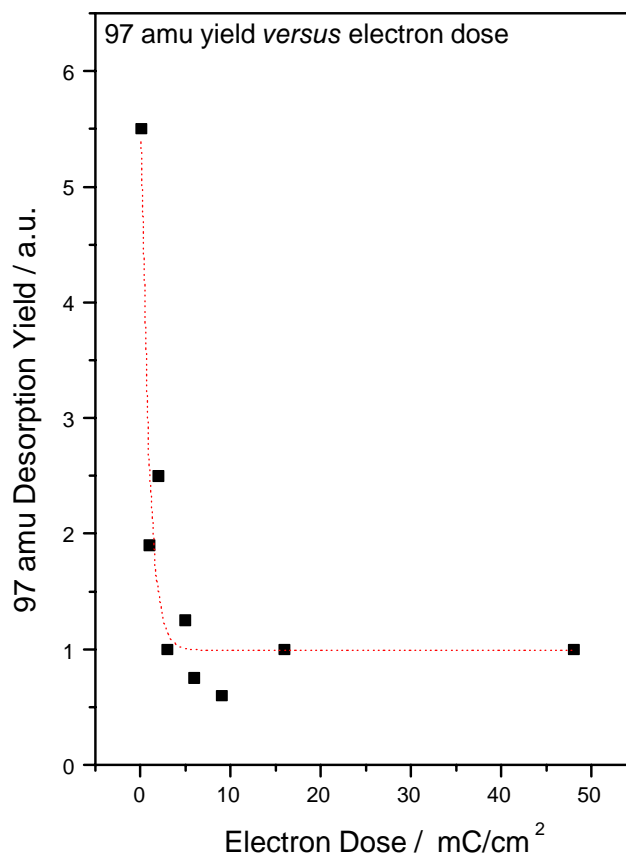
The RAIRS spectra showing the effect of electron irradiation on the surface species are displayed in Figs. 11 and 12. Fig. 11 displays the carbonyl stretching region between 1800 and 2200 cm^{-1}. The bottom three spectra are for increasing Mo(CO)$_6$ exposures, which, for low exposures, display features at 2028, 2002, and 1965 cm^{-1} and reproduce results found previously [27]. After a 2.7 L dose, the spectrum consists of a broad feature with discernible peaks at 2026, 2010, 1995, 1975, and 1957 cm^{-1}. Irradiating with 6.0 mC/cm^2 of electrons with 80 eV in energy yields a broad profile centered at ~1981 cm^{-1}, but without significant attenuation in intensity. Further irradiation with a total dose of 15 mC/cm^2 produces little further discernible change in accord with the results displayed in Fig. 6. Interestingly, the 97 amu TPD spectra following a similar treatment (Figs. 4 and 7) show that the amount of carbonyl on the surface has been substantially diminished, while the integrated infrared absorbance appears to increase. It may be that, as CO is lost from the surface, this results a lowering in symmetry, rendering more CO vibrations infrared active. Warming the surface to 205 K causes the features to become better defined having discernible peaks at 2007, 1996, 1976, and 1957 cm^{-1}. Heating to ~235 K causes all of the carbonyl modes to disappear coincident with carbonyl desorption in TPD (Figs. 4 and 7).

97 amu TPD of Mo(CO)$_6$/DA/Mo(100)

versus electron dose

Sample voltage = 80V

97 amu MS Signal / a.u.

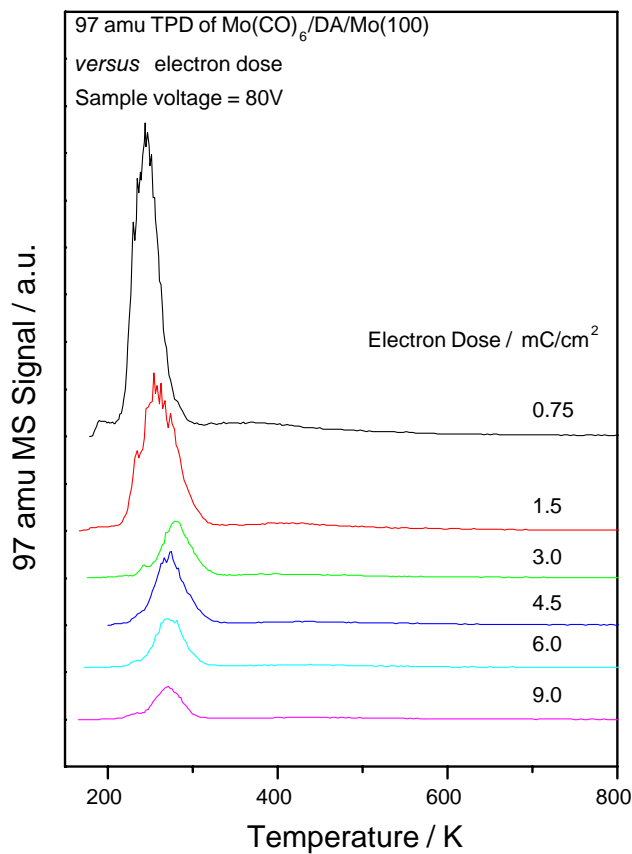Electron Dose / mC/cm^2

0.75

1.5

3.0

4.5

6.0

9.0

Temperature / K

Fig. 7. Temperature-programmed desorption spectra collected at 97 amu following the adsorption of 0.72 L of Mo(CO)$_6$ on dehydroxylated alumina after electron irradiation at a beam energy of 80 eV with a current of 25 μA, as a function of time. The total doses are marked adjacent to the corresponding spectra, which were collected using a heating rate of 10 K/s.

The corresponding spectra displayed between 1200 and 1800 cm^{-1} are shown in Fig. 12. No features are detected in this region following exposure to up to 2.7 L of Mo(CO)$_6$ indicating that it adsorbs as a carbonyl and forms no other stable surface species. This adsorption is accompanied by a negative excursion at ∼875 cm^{-1} (not shown). Since the spectra were collected using the alumina film as a background, and since alumina itself has a strong lattice mode at this frequency, this indicates that the alumina lattice is affected by carbonyl adsorption. As the surface is irradiated by 3 mC/cm^2 of electrons, features appear at 1725, 1465, and 1288 cm^{-1}. Further irradiation causes these features to increase in intensity. No additional changes are noted with additional irradiation in accord with the data displayed in Fig. 6.

The effect of heating this surface is displayed in Fig. 13, which shows that the intensities of the 1725, 1460, and 1288 cm^{-1} modes remain constant as the sample is heated to 275 K. Note that the carbonyl stretching modes disappear over this temperature range, which indicates that all of the carbonyls are lost by desorption and little, if any, appear to contribute to the thermal formation of the species exhibit-
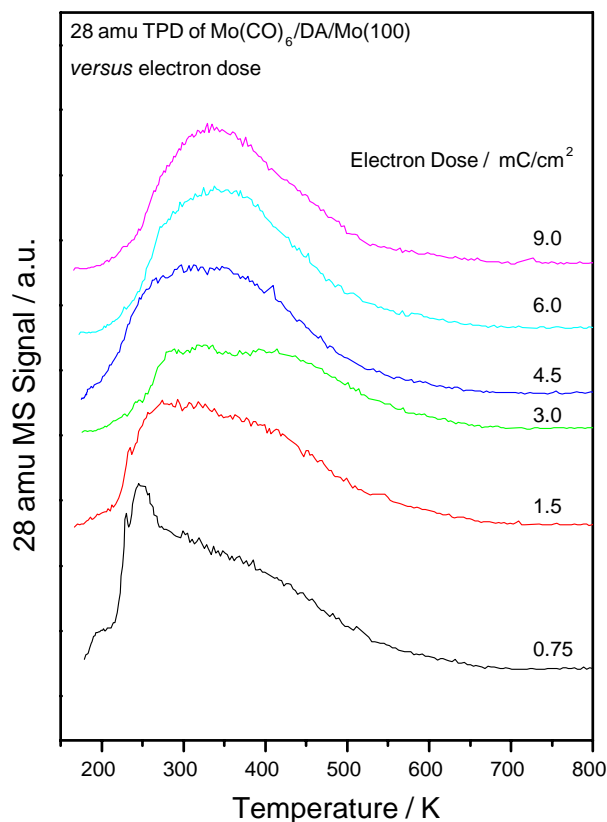
28 amu TPD of Mo(CO)$_6$/DA/Mo(100)

versus electron dose

28 amu MS Signal / a.u.

Electron Dose / mC/cm^2

9.0

6.0

4.5

3.0

1.5

0.75

Temperature / K

Fig. 8. Temperature-programmed desorption spectra collected at 28 amu following the adsorption of 0.72 L of Mo(CO)$_6$ on dehydroxylated alumina after electron irradiation at a beam energy of 80 eV with a current of 25 μA as a function of time. The total doses are marked adjacent to the corresponding spectra, which were collected using a heating rate of 10 K/s.

ing vibrational modes at 1725, 1460, and 1288 cm^{-1}. The 1725 and 1288 cm^{-1} modes decrease substantially in intensity on warming to 325 K coincident with the onset of CO desorption (Figs. 5 and 8). The intensity of the 1466 cm^{-1} mode also decreases, but less than that seen for the other two modes. This suggests that the 1466 cm^{-1} mode may be partially due to another surface species. Further heating to 350 K continues to reduce the 1466 cm^{-1} mode intensity and the surface shows no additional vibrational modes after heating to 425 K, indicative of total decomposition of all surface species, consistent with the TPD data (Figs. 5 and 8). The presence of molybdenum on the surface following this treatment is confirmed using Auger electron spectroscopy, which shows a Mo Auger signal that is significantly larger than that found on hydroxylated [25] and dehydroxylated [27] aluminas indicating that additional molybdenum has been deposited onto the surface by the electron beam treatment. Note that the alumina layer is sufficiently thick that no signal due to the molybdenum substrate is detected.

4. Discussion

Molybdenum hexacarbonyl adsorbed on alumina decomposes under the influence of an incident electron flux
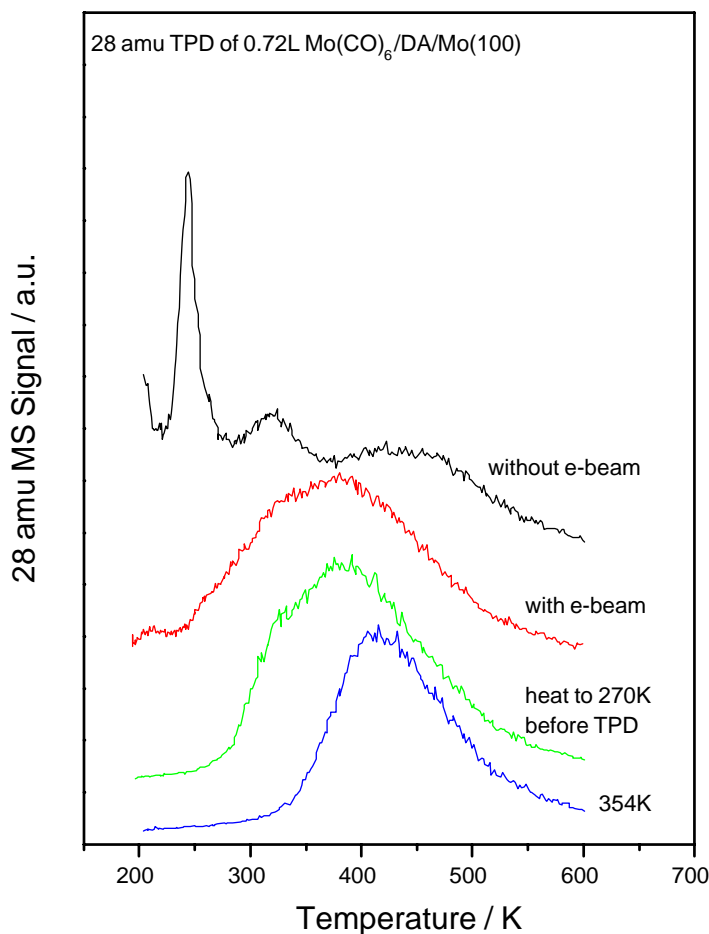
Fig. 9. Temperature-programmed desorption spectra collected at 28 amu following the adsorption of 0.72 L of $Mo(CO)_6$ on dehydroxylated alumina after irradiation with $3 \, mC/cm^2$ of electrons at a beam energy of 80 eV and then heated slowly (at 3 K/s) to various temperatures following which the temperature-programmed desorption spectrum was collected using heating rate of 10 K/s.

resulting in a decrease in carbonyl desorption (Figs. 1, 4 and 7) and a corresponding increase in high-temperature CO desorption due to the decomposition of stable surface species (Figs. 2, 5 and 8). The electron-induced reaction is complete after a dose of $\sim6 \, mC/cm^2$ (Fig. 6), corresponding to $\sim3.7 \times 10^{16}$ electrons/cm^2 incident onto the surface. A rapid decrease in the amount of carbonyl desorbing at ~250 K is found under the influence of an incident electron beam with an energy of 10 eV, with a much lower rate of decrease at higher energies. There is a corresponding increase in the amount of CO desorbing from the surface due to the thermal decomposition of stable surface species formed by the incident electron flux where the maximum CO desorption yield for electron energies greater than ~50 eV, and electron doses above $10 \, mC/cm^2$, is approximately 3.2 times larger than the CO yield from a dehydroxylated alumina surface not dosed with electrons (Figs. 2, 5 and 8). It is evident from RAIRS that the adsorbed carbonyl is modified by the incident electron flux (Fig. 11) and results in the formation of a stable surface species with features at 1725, 1466, and $1288 \, cm^{-1}$ (Fig. 12). The species initially formed by the adsorption of 0.9 L of $Mo(CO)_6$ on dehydroxylated alumina

(Fig. 11), with features at 2028, 2002, and $1965 \, cm^{-1}$ is assigned, by comparison with previous work by Reddy and Brown [9], to $Mo(CO)_{5(ads)}$. Irradiation by electrons with a dose of $\sim15 \, mC/cm^2$ leads to a broad feature centered at $\sim1981 \, cm^{-1}$, with a shoulder at $\sim2028 \, cm^{-1}$. Heating this surface to 205 K results in an envelope containing identifiable features at 2007, 1996, 1976 and $1957 \, cm^{-1}$. Reddy and Brown [9] have assigned vibrational modes at 2008, 1997, and $1955 \, cm^{-1}$ to $Mo(CO)_{3(ads)}$. These vibrational frequencies are identical to those formed by heating $Mo(CO)_6$ on dehydroxylated alumina to ~205 K, and the carbonyls desorb to yield a feature at ~245 K in TPD [27]. Presumably the residual feature in the 97 amu TPD spectrum after electron beam irradiation (Figs. 1 and 4) arises from these species. In addition, intense vibrations are noted at 1725, 1466, and $1288 \, cm^{-1}$ due to stable species formed under the influence of electrons. These features are identical to those found by thermally decomposing $Mo(CO)_6$ on dehydroxylated alumina [27]. This suggests that similar surface species are formed in both cases and that either thermal or electron-induced decarbonylation results in the same species even when decarbonylation is carried out using electrons at
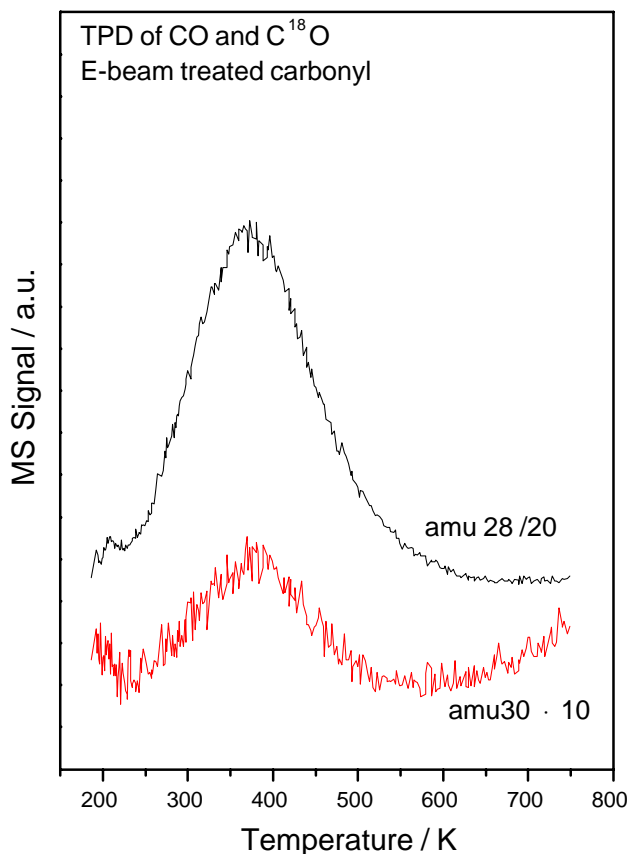
Fig. 10. Comparison of the temperature-programmed desorption spectra obtained following the adsorption of 0.72 L of $Mo(CO)_6$ on dehydroxylated alumina prepared using water containing 10% $H_2{}^{18}O$ following irradiation with $3\,mC/cm^2$ of electrons at a beam energy of 80 eV collected at 28 and 30 amu, using a heating rate of 10 K/s.

Fig. 11. Reflection–absorption infrared spectrum of $Mo(CO)_6$ adsorbed on dehydroxylated alumina at 160 K collected between 1800 and $2200\,cm^{-1}$ as a function of exposure up to a maximum of 2.7 L where the exposures are displayed adjacent to the corresponding spectra. The sample was then irradiated with electrons at a current of $25\,\mu A$ at an energy of 80 eV for various times, and the doses are displayed adjacent to the corresponding spectra. The sample was then annealed to various temperatures for 5 s and the infrared spectrum recorded.

a sample temperature of 160 K. Indeed, if the experiment is carried out at a sample temperature of 80 K (data not shown), this results in exactly identical vibrational frequencies, although the $1466\,cm^{-1}$ peak is relatively somewhat less intense than the 1725 and $1288\,cm^{-1}$ features. Heating the sample to 205 K does not detectably change the intensity of these features. This implies that the rate-limiting step in the formation of the more stable surface species is either thermal or electron-induced decarbonylation of the adsorbed molybdenum carbonyl and, once the appropriate subcarbonyl is formed, it reacts rapidly to form the stable surface species yielding vibrational frequencies at 1727, 1465, and $1293\,cm^{-1}$. These features have been previously associated with a surface oxalate species where the best agreement was found with a bidentate chelated species with the oxygen of two *cis* CO groups being coordinated to a single metal atom [27]. It was found, however, for thermally formed oxalates on hydroxylated alumina made with ^{18}O-enriched water, that the desorbing CO incorporated a statistical amount of oxygen from the alumina substrate, while the results of the isotope-labeling experiment shown in Fig. 10 indicate that relatively small amounts of substrate oxygen are incor-
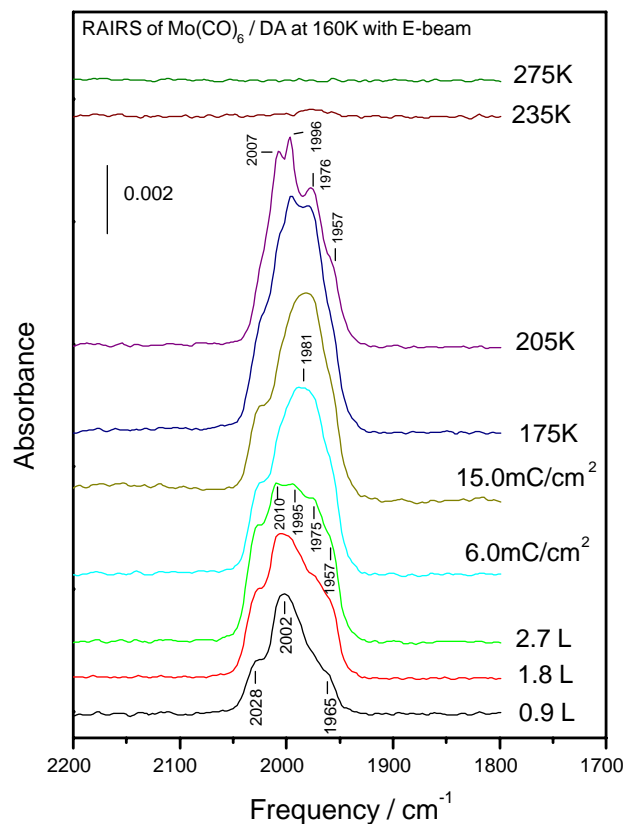
porated into the surface species when formed by electron irradiation. The origin of this difference is not clear but may imply that some of the CO dissociates to supply the additional oxygen, or that the structure of the oxalate species is somewhat different when formed by electron beam irradiation. The $1466\,cm^{-1}$ feature persists to slightly higher temperatures than the other two modes, which may suggest that this is also due to a different species formed on the surface. Certainly, this view is in accord with the observation that this feature is relatively less intense when the adsorbed $Mo(CO)_6$ is irradiated with electrons at a sample temperature at 80 K.

The detection of a stable $Mo(CO)_{3(ads)}$ species by RAIRS implies that this is not the precursor to oxalate formation, and suggests that the precursor is a $Mo(CO)_x$ species where $x \leq 2$. It should be mentioned that it has been found that removal of the last three CO ligands is difficult for $Mo(CO)_6$ adsorbed on metal surfaces [28]. Since the resulting oxalate species contains two carbons, it seems reasonable to assume that $x = 2$.

The absorbance of the $1725\,cm^{-1}$ feature is approximately 3.5 times larger for the electron-irradiated surface than for
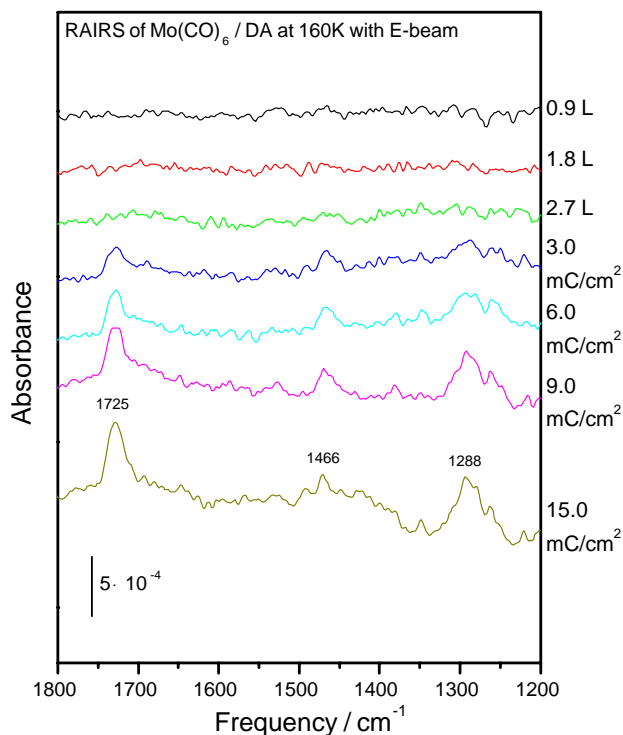
Fig. 12. Reflection–absorption infrared spectrum of $Mo(CO)_6$ adsorbed on dehydroxylated alumina at 160 K collected between 1200 and 1800 cm^{-1} as a function of exposure up to a maximum of 2.7 L where the exposures are displayed adjacent to the corresponding spectra. The sample was then irradiated with electrons at a current of 25 μA at an energy of 80 eV for various times, and the doses are displayed adjacent to the corresponding spectra.

Fig. 13. Reflection–absorption infrared spectrum of 2.7 L of $Mo(CO)_6$ adsorbed on dehydroxylated alumina at 180 K collected between 1200 and 1800 cm^{-1} following exposure then irradiated with electrons at a current of 25 μA at an energy of 80 eV for 120 s (resulting in a total dose of 3 mC/cm^2). The sample was then annealed to various temperatures for 5 s and the infrared spectrum recorded and the annealing temperatures are displayed adjacent to the corresponding spectrum.

the thermally formed species in accord with the relative CO yield in TPD (Figs. 2, 5 and 8). This indicates that electron beam irradiation provides a useful method for increasing the number of stable species on the surface and for potentially increasing the catalytic activity. Preliminary experiments comparing thermally and ultraviolet activated $Mo(CO)_6$ on high-surface area alumina using a mercury arc source indicate that the sample activated by ultraviolet radiation is more active for olefin metathesis than one that had been activated thermally. It has been shown that forming oxalate species thermally on dehydroxylated alumina leads to the deposition of ∼4% of a monolayer [27]. The RAIRS and TPD data suggest therefore that the oxalate coverage formed by electron beam irradiation is ∼14% of a monolayer.

Auger spectra collected after electron beam irradiating $Mo(CO)_6$-covered dehydroxylated alumina revealed the presence of molybdenum on the surface, where the molybdenum signal is larger for the electron beam-irradiated sample than for one that has been thermally activated, in accord with the larger coverage of oxalate species found in RAIRS and TPD. The state of the surface molybdenum is not known from these experiments, although it has recently been shown that Mo−Mo bonding occurs when $Mo(CO)_x$ species are present on the surface [35].
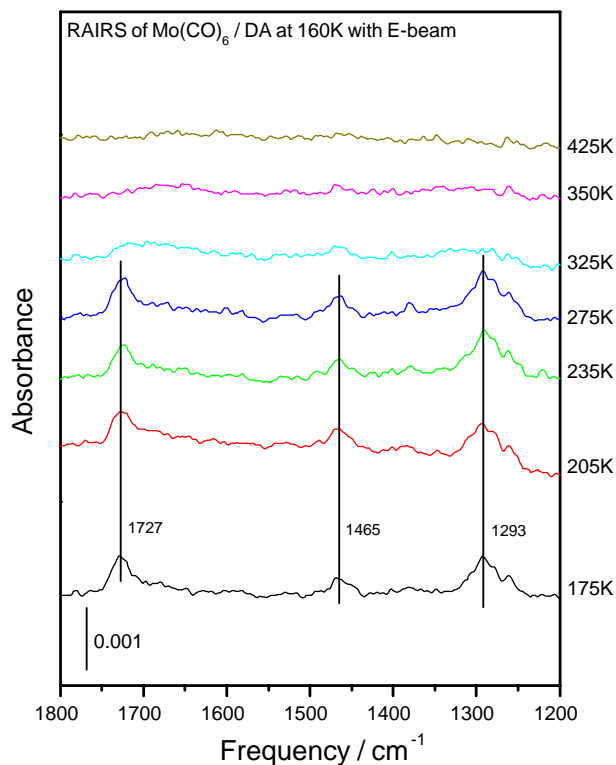
5. Conclusions

Molybdenum hexacarbonyl adsorbed on dehydroxylated alumina at ∼160 K decomposes under the influence of incident electrons, where electron energies larger than ∼10 eV and doses larger than ∼6 mC/cm^2 are required to cause the majority of the adsorbed carbonyls to decompose. Incident electrons decrease the carbonyl desorption yield and cause the CO yield, due to the decomposition of stable surface species, to increase correspondingly. Subcarbonyls are found using infrared spectroscopy, as well as a more stable surface species consisting of a surface oxalate species. The RAIRS spectrum of this surface species formed by incident electrons is identical to that formed thermally on dehydroxylated alumina, indicating that similar surface species are formed in either case. Both the CO desorption yield and the absorbance of the infrared features due to the stable surface species are approximately 3.5 times larger than when these species are formed thermally on dehydroxylated alumina. The oxalate coverage on dehydroxylated alumina formed by the thermal decomposition of $Mo(CO)_6$ was measured from the CO desorption yield to be ∼4% of a monolayer. This indicates that the corresponding coverage of the electron beam-induced oxalate is ∼14% of a monolayer.

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