

An investigation of the chemistry of molybdenum hexacarbonyl on thin dehydroxylated alumina films in ultrahigh vacuum

Y. Wang^a, F. Gao^a, M. Kaltchev^b, D. Stacchiola^a, and W.T. Tysoe^{a,*}

^aDepartment of Chemistry and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, Milwaukee, WI 53211, USA

^bDepartment of Physics and Chemistry, Milwaukee School of Engineering, Milwaukee, WI 53202, USA

Received 26 June 2003; accepted 2 September 2003

The adsorption of molybdenum hexacarbonyl on thin dehydroxylated alumina films grown on an Mo(100) single-crystal substrate is studied in ultrahigh vacuum using primarily temperature-programmed desorption and reflection-absorption infrared spectroscopy. Subcarbonyls are detected using infrared spectroscopy at low temperatures and desorb at ~ 245 K. A portion of the subcarbonyls decomposes to form an oxalate species on the surface, which thermally decomposes to evolve CO in two states at ~ 320 and 450 K. The coverage of the oxalate species is larger on dehydroxylated alumina than on hydroxylated or partially dehydroxylated alumina.

KEY WORDS: reflection-absorption infrared spectroscopy; temperature-programmed desorption; chemisorption; molybdenum hexacarbonyl; alumina thin films.

1. Introduction

The reaction of molybdenum hexacarbonyl with alumina is extensively used to synthesize active catalysts for a range of reactions including alkene hydrogenation and olefin metathesis, where the activity for a particular reaction depends on the pretreatment conditions [1–4]. A substantial amount of work has been carried out using a number of techniques to explore the species that are formed from $\text{Mo}(\text{CO})_6$ on high-surface-area alumina supports [5–12]. More recently, planar oxide films have been grown on refractory metal substrates in ultrahigh vacuum [13–23]. This approach offers the advantage of allowing the full range of ultrahigh vacuum surface analytical techniques to be used to scrutinize the surface chemistry, while avoiding the charging problems that would normally occur when electron-based techniques are used with insulating samples. In addition, the cleanliness of the surface can be carefully monitored and controlled in ultrahigh vacuum and, since the films are grown *in situ*, they can be modified by, for example, isotopic substitution. Finally, when thin planar samples are used for infrared spectroscopy, adsorbate-induced features are not obscured by the substrate and the infrared selection rules can be used to yield information about adsorbate geometry. The surface chemistry of a number of alumina films has been explored in ultrahigh vacuum [20,21,24].

It has been shown previously that alumina films can be grown on a refractory metal substrate by sequentially

oxidizing evaporated aluminum thin films using water [13–23,25,26]. This leads to the formation of hydroxylated alumina, which can be dehydroxylated by heating the sample *in vacuo* to desorb water. The adsorption of $\text{Mo}(\text{CO})_6$ on hydroxylated (HA) and partially dehydroxylated alumina (PDA) has previously been studied in this way [25,26]. It was found that the majority of the molybdenum hexacarbonyl desorbs intact with only a small proportion (~ 2 percent) reacting to form strongly bonded surface species on HA. It is also found that partially dehydroxylating the surface increases the molybdenum coverage by about 50% [25]. These stable surface species decompose to yield carbon monoxide in two states, which contain approximately equal amounts of CO. These desorption spectra are similar to those found following the adsorption of $\text{Mo}(\text{CO})_6$ on high-surface-area alumina. In this case, the observation that equal proportions of CO desorbed in each state was taken to indicate the formation of an intermediate $\text{Mo}(\text{CO})_{3(\text{ads})}$ surface species [5,6]. The ability to probe lower-frequency modes using RAIRS enabled the stable surface species arising from molybdenum hexacarbonyl decomposition to be identified as an oxalate species, which decomposed to evolve CO and leave a formate species. These subsequently decompose at higher temperatures, also to yield CO [25,26]. This alternative model, therefore, was able to account for the equimolar amounts of CO desorbing in each state.

However, the relatively low coverage of the stable surface species formed in ultrahigh vacuum makes it difficult to use these samples as model catalysts. Since it was found previously that the molybdenum coverage

* To whom correspondence should be addressed.

E-mail: wtt@uwm.edu

increased on PDA compared to HA [25], the chemistry of $\text{Mo}(\text{CO})_6$ has been investigated, in the following, on dehydroxylated alumina (DA) to follow reaction with the Lewis acid sites present on this surface.

2. Experimental

Infrared data were collected using a system that has been described previously [27]. Briefly, the $\text{Mo}(100)$ -single-crystal sample was mounted in a modified $2\frac{3}{4}$ " 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 equipped 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 (TPD) data were collected in another ultrahigh vacuum chamber that has been described in detail elsewhere [27], where the desorbing species were detected using a Dycor quadrupole mass spectrometer placed in-line of sight of the sample.

The $\text{Mo}(100)$ sample was cleaned using a standard procedure, which consisted of argon ion bombardment (2 kV , $1\ \mu\text{A}/\text{cm}^2$), and any residual contaminants were removed by briefly heating to 2000 K *in vacuo*. The sample was deemed clean when the Auger spectrum revealed no contaminants. Alumina films were deposited onto the $\text{Mo}(100)$ -single-crystal substrate by sequences of cycles of aluminum evaporation/water oxidation (with H_2^{16}O or H_2^{18}O -enriched water) [25,26]. Oxidation was monitored using Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). Aluminum was evaporated from a small heated alumina tube [28] onto an $\text{Mo}(100)$ single crystal held at 300 K for 120 s which, from measurements of the resulting oxide film thickness using Auger spectroscopy, deposited ~ 1.5 monolayers [25,26]. Then, water was introduced into the chamber through a capillary dosing source to oxidize the aluminum at 550 K for 120 s. This resulted in the formation of hydroxylated alumina. Partially dehydroxylated alumina was made by heating this sample *in vacuo* at 900 K for 30 s, and dehydroxylated alumina formed by heating to 1200 K.

The deionized water (H_2O) and ^{18}O -labeled water (H_2^{18}O 10 atomic %, Aldrich, 95%) used to grow the films were transferred to glass vials, which were connected to the gas-handling line of the chamber. Normal, deionized water 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 monitored using mass and infrared spectroscopies. This was also dosed onto the surface *via* a capillary doser to minimize background contamination.

3. Results

Figure 1 displays the 28 amu TPD spectra collected following the exposure of various alumina surfaces to $\text{Mo}(\text{CO})_6$ (0.72 L , $1\text{ L} = 1 \times 10^{-6}\text{ torr s}$) at a sample temperature of 190 K collected using a heating rate of 10 K/s. The sharp feature centered at $\sim 245\text{ K}$ has been shown previously to be due to the desorption of molecular carbonyl, which contains fragments at higher masses, particularly at 97 amu [29], while the features at ~ 320 and 450 K are due to the decomposition of stable surface species. In the case of HA and PDA, it has been demonstrated that the areas under the two features are identical [25,26] and it is evident that the areas under the corresponding features for DA are also equal. It is clear that the total amount of CO desorbing in these high-temperature states is greater for DA than for both HA and PDA. It has been shown previously that the amount of molybdenum remaining on HA in these states corresponds to $\sim 2\%$ of a monolayer of molybdenum, and that on PDA is $\sim 3\%$. The relative areas of the ~ 320 plus 450 K states scale with these coverages for HA and PDA and this indicates that the corresponding molybdenum coverage on DA is $\sim 4\%$ of a monolayer.

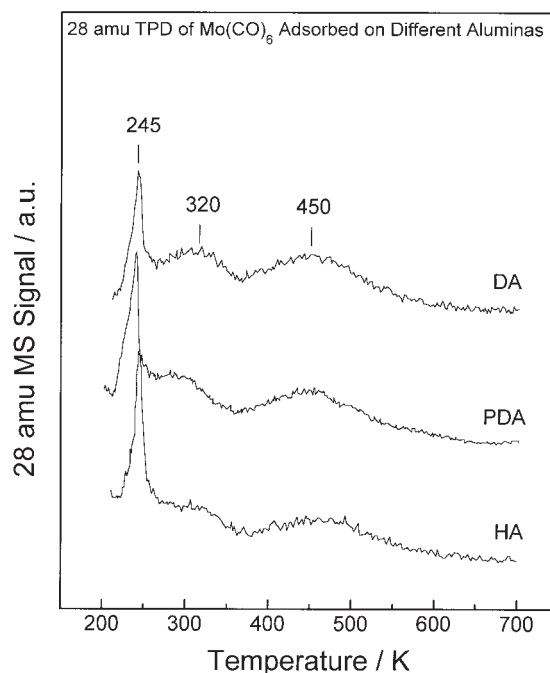


Figure 1. Temperature-programmed desorption spectra collected at 28 amu following the adsorption of 0.72 L of $\text{Mo}(\text{CO})_6$ on hydroxylated alumina (HA), partially dehydroxylated alumina (PDA) and dehydroxylated alumina (DA) at 190 K, collected using a heating rate of 10 K/s.

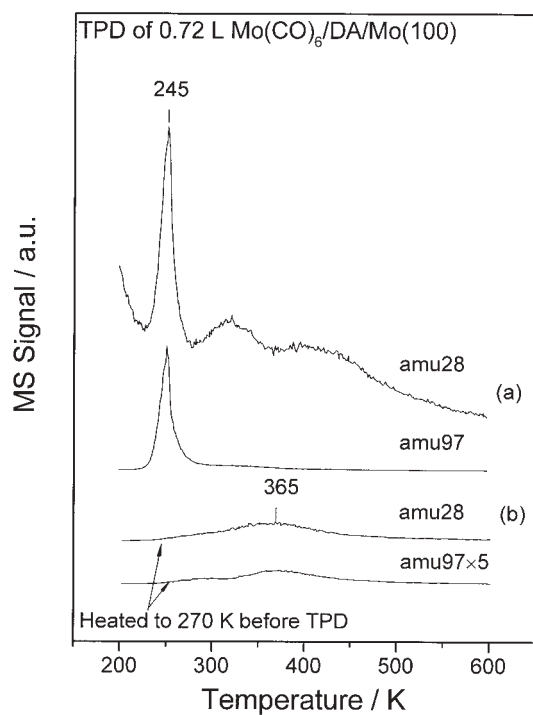


Figure 2. Temperature-programmed desorption spectra collected at 28 and 97 amu following the adsorption of 0.72 L of $\text{Mo}(\text{CO})_6$ on dehydroxylated alumina (a) following adsorption at 190 K and (b) after slowly heating at 3 K/s to 270 K, where the spectra were collected using a heating rate of 10 K/s. The masses are marked adjacent to the corresponding spectra.

Shown in figure 2(b) is the effect of annealing an $\text{Mo}(\text{CO})_6$ -covered DA surface to 270 K at a heating rate of 3 K/s, and then collecting the TPD spectrum monitoring 28 and 97 amu using a heating rate of 10 K/s. Shown for comparison (figure 2(a)) are the spectra formed by adsorbing $\text{Mo}(\text{CO})_6$ directly at 190 K. Slowly heating the surface to 270 K, just above the 245-K desorption state, results in the higher-temperature 28-amu states being almost completely attenuated, leaving a broad and relatively weaker state centered at ~ 365 K. This indicates that the ~ 320 - and 450-K states are not formed on the surface immediately following adsorption at 190 K, but are produced during the desorption sweep at a heating rate of 10 K/s. As this is lowered, the relative rates of desorption and decomposition are such that desorption is favored over decomposition leading to a much lower coverage of the stable surface species. The corresponding 97 amu spectra (figure 2(a)), due to carbonyl desorption [29], yields a sharp feature at 245 K, which corresponds to the 245-K feature detected at 28 amu (figure 1), confirming that this is, at least, partially due to carbonyl desorption. Slowly annealing the surface to 270 K (at 3 K/s) completely removes the 245-K, 97-amu feature as expected, and results in a weak feature appearing at ~ 365 K (which is enlarged by a factor of 5 in figure 2). This is identical in temperature to the 28-amu signal found after heating slowly to 270 K (figure 2) and

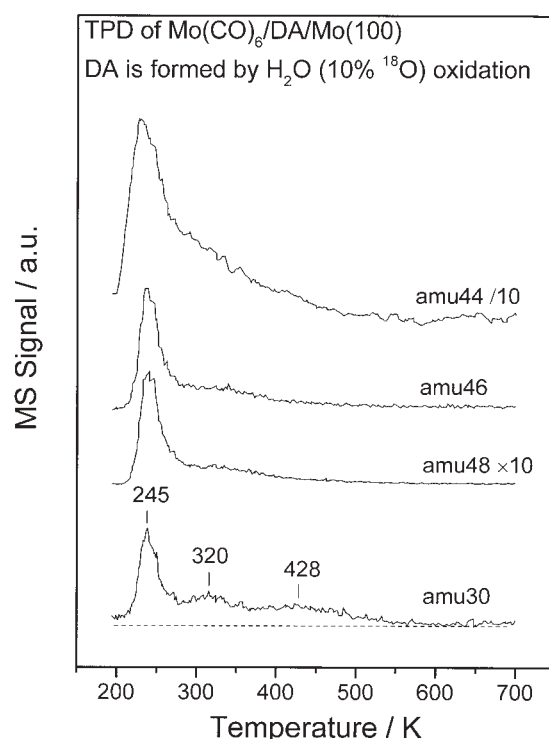


Figure 3. Temperature-programmed desorption spectra obtained following adsorption of $\text{Mo}(\text{CO})_6$ on a dehydroxylated alumina films grown with water containing 10% ^{18}O monitoring 30 and 44, 46 and 48 amu, where the masses are marked adjacent to the corresponding spectra.

implies that a different species, likely a subcarbonyl, is formed at these lower heating rates.

The temperature-programmed desorption spectra for $\text{Mo}(\text{CO})_6$ (0.72 L) adsorbed onto the DA grown using water containing 10% ^{18}O is shown in figure 3, taken using a heating rate of 10 K/s. The 30-amu spectrum (C^{18}O) is very similar to the 28-amu spectrum formed by $\text{Mo}(\text{CO})_6$ adsorption on a surface made using H_2^{16}O (figure 1) and this indicates that some oxygen from the substrate is incorporated into all of the desorption states. This behavior is different from that found on HA where no ^{18}O incorporation was detected [25]. As also shown in figure 4, some CO_2 desorption is found at ~ 245 K, coincident with features detected at 28 amu (figure 1) and 97 amu (figure 2). In this case, signals were monitored at 44 (C^{16}O_2), 46 ($\text{C}^{18}\text{O}^{16}\text{O}$) and 48 (C^{18}O_2) amu, where the 44-amu signal has been attenuated by a factor of 10, while that at 48 amu has been increased by the same factor. Since the original H_2^{18}O contains 10% ^{18}O , this indicates that the isotope is almost randomly incorporated into the CO_2 that is formed. It should be noted that no CO_2 was found when molybdenum carbonyl was adsorbed onto HA.

The corresponding RAIRS spectra collected following exposure of $\text{Mo}(\text{CO})_6$ at 80 K are shown in figure 4, and at 160 K in figure 5. Following the adsorption at 80 K, three features are detected in the CO stretching region at ~ 2030 , 2009 and 1963 cm^{-1} . When $\text{Mo}(\text{CO})_6$

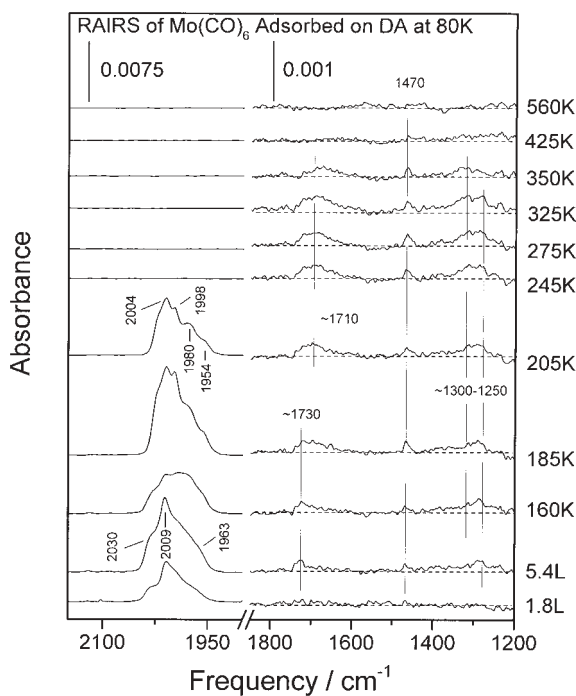


Figure 4. Reflection-adsorption infrared spectra following the adsorption of $\text{Mo}(\text{CO})_6$ on dehydroxylated alumina at 80 K and subsequently annealing to various temperatures. The exposures and annealing temperatures are marked adjacent to the corresponding spectra. Note the different absorbance scales for the two spectral ranges.

is adsorbed at 160 K, similar features appear at low exposures, at ~ 2026 , 2002 and 1970 cm^{-1} , but the shape changes considerably as the exposure increases, with the 2026-cm^{-1} feature becoming more intense and is accompanied by the appearance of a series of overlapping features at approximately 2006 , 1994 and 1980 cm^{-1} following a 3.6L exposure of $\text{Mo}(\text{CO})_6$ (figure 5). Further differences are seen between the behavior following adsorption at 80 and 160 K as the sample is heated. DA dosed with molybdenum hexacarbonyl at 80 K maintains the features at 2030 and 2009 cm^{-1} when the sample is heated to 185 K, but a broad feature appears at $\sim 1990 \text{ cm}^{-1}$, similar to that seen at higher exposures when dosing at 160 K (figure 5). Further heating to 185 K yields an intense absorption band containing features at 2004 , 1998 , 1980 and 1954 cm^{-1} . Heating to 205 K results in a reduction in intensity of this band, but with features at identical frequencies. Similar features are detected following adsorption at 80 K after annealing to 205 K (figure 4), with similar relative intensities. The peak absorbance of the feature found after heating to 205 K, however, is larger when the $\text{Mo}(\text{CO})_6$ is adsorbed at 160 K ($\sim 8.5 \times 10^{-3}$ absorbance units) than when it is adsorbed at 80 K, where the peak absorbance in this case is $\sim 7.4 \times 10^{-3}$ absorbance units. Thus, the final nature of the surface species is identical irrespective of whether the molybdenum carbonyl was adsorbed at 80 or 160 K. In

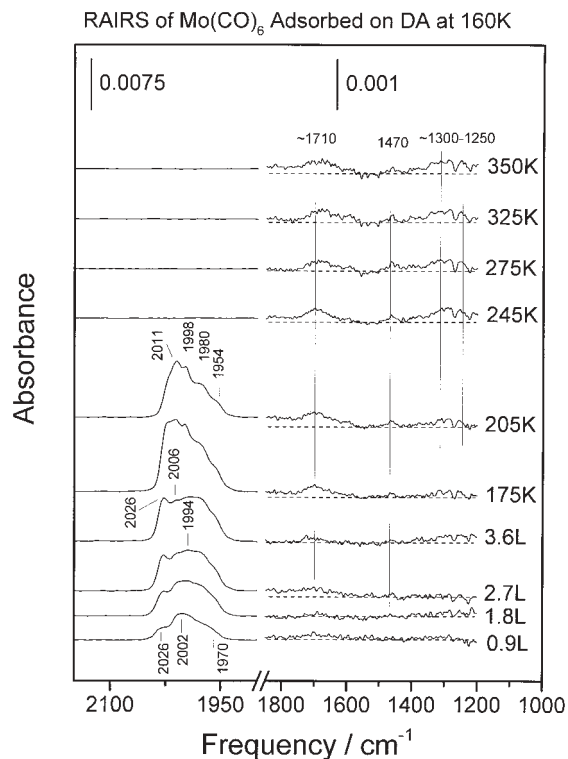


Figure 5. Reflection-adsorption infrared spectra following the adsorption of $\text{Mo}(\text{CO})_6$ on dehydroxylated alumina at 160 K and subsequently annealed to various temperatures. The exposures and annealing temperatures are marked adjacent to the corresponding spectra. Note the different absorbance scales for the two spectral ranges.

both cases, the CO stretching modes are completely removed on heating to 245 K corresponding to the low-temperature desorption state found in TPD (figures 1 and 2).

The corresponding low-frequency regions (between 1200 and 1800 cm^{-1}) are also displayed in figures 4 and 5. In addition, a larger negative excursion was detected at $\sim 875 \text{ cm}^{-1}$ in all the spectra (not shown). This has been found previously following $\text{Mo}(\text{CO})_6$ adsorption on HA and PDA [25,26], where the spectra were also collected using the alumina-covered surface as a background. The alumina film itself exhibits modes at $\sim 875 \text{ cm}^{-1}$ and the negative excursion at this frequency is due to the quenching of alumina lattice modes indicating a perturbation of the alumina surface due to bonding.

Initial carbonyl adsorption yields a broad feature at $\sim 1730 \text{ cm}^{-1}$, particularly evident after adsorption at 80 K. After annealing to 205 K, where the CO stretching data (figures 4 and 5) indicate the formation of identical species, the spectra in both the cases show broad features at ~ 1710 and between 1300 and 1250 cm^{-1} , with a sharper peak at $\sim 1470 \text{ cm}^{-1}$. These features grow slightly in intensity as the sample is warmed to 275 K and decrease as the sample is heated from 275 to 350 K, coincident with the broad desorption state centered at $\sim 320 \text{ K}$ (figure 1).

4. Discussion

Gas-phase $\text{Mo}(\text{CO})_6$ (O_h point group) has CO stretching modes with t_{1u} , e_g and a_{1g} symmetry where the first mode is infrared active (2003.0 cm^{-1}), while the latter two are Raman active (at 2019 and 2117 cm^{-1} respectively) [30]. If the carbonyl adsorbs weakly onto the surface via a CO group such that the symmetry is lowered to C_{4v} , the t_{1u} mode correlates with $a_1 + e$ modes, the a_{1g} with a_1 , and the e_g with $a_1 + b_1$ modes [31]. The a_1 and e modes are infrared active, where the e mode is generally more intense than the a_1 modes. When the carbonyl is weakly adsorbed, the modes are not likely to be strongly perturbed from the gas-phase values and therefore would have vibrational frequencies at ~ 2003 , 2019 and 2117 cm^{-1} . The absence of modes with these frequencies on alumina suggests that the carbonyl is strongly bonded and Brown *et al.* [9] have assigned vibrational modes at 2028 , 1998 with a shoulder at $\sim 1950\text{ cm}^{-1}$ to the presence of $\text{Mo}(\text{CO})_{5(\text{ads})}$ species, and the frequencies found following adsorption at 80 K and heating or at low exposures after adsorption at 160 K , are in reasonable agreement with these values. The shapes of the profiles at these two temperatures are somewhat different indicating the likely presence of other surface carbonyls. Heating a carbonyl-covered surface to 205 K produces essentially identical spectra irrespective of the initial adsorption temperature with features at $2004/2011$, 1998 , 1980 and 1954 cm^{-1} . Brown *et al.* [9] have assigned vibrational modes at 2008 , 1997 and 1955 cm^{-1} to $\text{Mo}(\text{CO})_{3(\text{ads})}$ suggesting further decarbonylation on heating to 205 K . These modes are accompanied by a feature at $\sim 1730\text{ cm}^{-1}$ (figure 4), and vibrational modes close to this value have been associated with interactions with Type II Lewis acid sites [9]. Heating above 205 K causes all of the carbonyl modes between 1800 and 2200 cm^{-1} to disappear, coincident with carbonyl desorption at 245 K (figures 1 and 2). The low-temperature 28-amu (CO) desorption state (figure 1) is slightly broader than the carbonyl desorption state at 97 amu (figure 3), presumably because of some additional CO evolution at these temperatures. As this occurs, features are detected at ~ 1710 , 1470 and $\sim 1300\text{ cm}^{-1}$. Clearly, these more stable surface species are formed from subcarbonyls. When the alumina is grown using ^{18}O -containing water, some of the ^{18}O appears to be incorporated into the desorbing carbonyl (figure 3).

The species having features at ~ 1710 , 1470 and $\sim 1300\text{ cm}^{-1}$ is present up to $\sim 350\text{ K}$ and its disappearance is associated with the evolution of CO at $\sim 320\text{ K}$, where this species also incorporates oxygen from the alumina since C^{18}O is detected when the alumina film is synthesized using H_2^{18}O (figure 3). Vibrational modes at ~ 1720 and $\sim 1290\text{ cm}^{-1}$ have been found following the adsorption of $\text{Mo}(\text{CO})_6$ on HA and PDA [25,26] and assigned to the presence of oxalate species. Table 1

Table 1

Vibrational frequency ranges for various types of oxalate species [32]

Type	Frequency range/ cm^{-1}		
Bidentate oxalate (Type 1)	1755–1765	1625–1640	1310–1325
Bidentate oxalate (Type 2)	1696–1720	1629–1670	1250–1276
Bidentate chelate	1672–1722	1388–1405	1236–1270
Tridentate	1629–1690	1410–1439	1250–1276
Tetradentate	1628–1650	—	1342–1348
$\text{Mo}(\text{CO})_6/\text{DA}$ alumina	1680–1720	1465	1280–1320

summarizes the vibrational frequency ranges for various types of oxalato organometallic species [32]. The agreement with the experimental data is best for the bidentate chelate species although there may be a range of species formed on the surface. It should be mentioned that the relative intensities of the vibrational modes of the oxalate species formed on DA are different from those for HA and PDA, where the $\sim 1300\text{ cm}^{-1}$ mode is the most intense and the 1720 cm^{-1} mode is very weak in the latter case. On the hydroxylated surface, the ~ 1710 and $\sim 1300\text{ cm}^{-1}$ modes have almost equal intensity. This may indicate different bonding geometries on surfaces that contain surface hydroxyl species. It should be mentioned that Brenner *et al.* [6] have identified an oxidized molybdenum species incorporating two CO molecules strikingly similar to the oxalate species suggested here.

The features due to the oxalate surface species disappear on heating above $\sim 350\text{ K}$ coincident with the evolution of CO in TPD (figure 1) indicating that the oxalate species decomposes to evolve CO. This incorporates oxygen from the alumina (figure 3) in contrast to the behavior found on HA, where no incorporation of oxygen from the alumina substrate was found using similar isotope-labeling experiments. This further argues for different oxalate adsorption geometries on HA and DA. No infrared features are detected on the surface above $\sim 425\text{ K}$, while CO is evolved in TPD above this temperature indicating that surface species are still present (figure 1). A broad feature between 1580 and 1660 cm^{-1} was detected on HA assigned to a $\text{O}-\text{C}=\text{O}$ species bonded to two surface hydroxyl groups [25,26]. It may be that a similar species formed on DA has a $\text{C}=\text{O}$ bond lying closer to parallel to the surface, so that it is infrared forbidden in RAIRS.

5. Conclusions

Molybdenum hexacarbonyl adsorbs on dehydroxylated alumina forming subcarbonyls, where $\text{Mo}(\text{CO})_{5(\text{ads})}$ and $\text{Mo}(\text{CO})_{3(\text{ads})}$ are identified from their CO stretching frequencies. The subcarbonyls and some CO desorb at $\sim 245\text{ K}$ to leave a more strongly bound species on the surface. This decomposes in two stages at ~ 320 and 450 K , where the total CO yield in

these two states is larger than for hydroxylated and partially dehydroxylated alumina, and suggests that ~4% of a monolayer of molybdenum is deposited onto the surface. This species is identified as an oxalate species similar to that found on hydroxylated and partially dehydroxylated alumina.

Acknowledgments

We gratefully acknowledge the support of this work by the Chemistry Division of the National Science Foundation under grant number CTS-0105329.

References

- [1] A. Brenner, *J. Mol. Catal.* 5 (1979) 157.
- [2] E. Davie, D.A. Whan and C. Kemball, *J. Catal.* 24 (1972) 272.
- [3] J. Smith, R.F. Howe and D.A. Whan, *J. Catal.* 34 (1974) 191.
- [4] R. Thomas and J.A. Moulijn, *J. Mol. Catal.* 15 (1982) 157.
- [5] A. Brenner and R.L. Burwell Jr., *J. Am. Chem. Soc.* 97 (1975) 2565.
- [6] A. Brenner and R.L. Burwell Jr., *J. Catal.* 52 (1978) 353.
- [7] R.F. Howe, *Inorg. Chem.* 15 (1976) 486.
- [8] A. Kazusaka and R.F. Howe, *J. Mol. Catal.* 9 (1980) 183.
- [9] K.P. Reddy and T.L. Brown, *J. Am. Chem. Soc.* 117 (1995) 2845.
- [10] A. Zecchina, E.E. Platero and C.O. Areán, *Inorg. Chem.* 27 (1988) 102.
- [11] R.F. Howe and I.R. Leith, *J. Chem. Soc., Faraday Trans.* 1 69 (1973) 1967.
- [12] W.M. Shirley, B.R. McGarvey, B. Maiti, A. Brenner and A. Cichowlas, *J. Mol. Catal.* 29 (1985) 259.
- [13] P.J. Chen and D.W. Goodman, *Surf. Sci.* 312 (1994) L767.
- [14] H.H. Madden and D.W. Goodman, *Surf. Sci.* 150 (1985) 39.
- [15] P.J. Chen, D.W. Goodman and J.T. Yates Jr., *Phys. Rev. B* 41 (1990) 8025.
- [16] B.G. Frederick, G. Apai and T.N. Rhodin, *Surf. Sci.* 244 (1991) 67.
- [17] T.N. Rhodin, B.G. Frederick and G. Apai, *Surf. Sci.* 287 (1993) 638.
- [18] C. Brüesch, R. Kötz, N. Neff and L. Pietronero, *Phys. Rev. B* 29 (1984) 4691.
- [19] C. Xu, W.S. Oh, G. Liu, D.Y. Kim and D.W. Goodman, *J. Vac. Sci. Technol. A* 15 (1997) 1261.
- [20] T.N. Rhodin, R.P. Merrill, P.J. O'Hagan, S.C. Woronick, N.D. Shinn, G.L. Woolery and A.W. Chester, *J. Phys. Chem.* 98 (1994) 2433.
- [21] B.G. Frederick, G. Apai and T.N. Rhodin, *Surf. Sci.* 277 (1992) 337.
- [22] A.J. Maeland, R. Rittenhouse, W. Lahar and P.V. Romano, *Thin Solid Films* 21 (1974) 67.
- [23] F.P. Mertens, *Surf. Sci.* 71 (1978) 161.
- [24] M.G. Kaltchev and W.T. Tysoe, *Surf. Sci.* 430 (1999) 29.
- [25] M. Kaltchev and W.T. Tysoe, *J. Catal.* 193 (2000) 29.
- [26] M. Kaltchev and W.T. Tysoe, *Top. Catal.* 13 (2000) 121.
- [27] M.G. Kaltchev, A. Thompson and W.T. Tysoe, *Surf. Sci.* 391 (1997) 145.
- [28] W.J. Wytenburg and R.M. Lambert, *J. Vac. Sci. Technol. A* 10 (1992) 3597.
- [29] Mass Spectrometry Data Center, EPA MS number 156817, National Institute of Standards, Gaithersburg, MD, USA.
- [30] A. Zecchina and C.O. Areán, *Catal. Rev.—Sci. Eng.* 35 (1993) 261.
- [31] F.A. Cotton, *Chemical Applications of Group Theory* (John Wiley & Sons, New York, 1967).
- [32] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part B* (John Wiley & Sons, New York, 1997).