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The Decomposition of Molybdenum Hexacarbonyl on Thin Alumina Films at High Temperatures: Formation and Reduction of Carbides

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Film growth by reaction of molybdenum hexacarbonyl with an alumina film deposited onto a Mo(100) substrate is investigated under ultrahigh vacuum where a significant deposition rate is found only for substrate temperatures above ∼670 K. Auger and X-ray photoelectron spectroscopy measurements reveal that a monolayer of molybdenum carbide (MoC) is deposited onto the alumina surface forming a monolayer after an exposure of ∼40 L. This layer is reduced to the metal by heating to ∼1500 K by reaction with the alumina substrate to evolve CO and form metallic molybdenum. The carbide can be re-formed by heating the metal-covered alumina sample in ethylene at 900 K, and the carbide can once again be reduced to the metal by heating to 1500 K. This process can be repeated so that the carbide can be regrown by reaction with ethylene and reduced by annealing *in vacuo* **to 1500 K.** © 2000 Academic Press

Key Words: **alumina; thin films; molybdenum hexacarbonyl; molybdenum carbides; X-ray photoelectron spectroscopy; Auger spectroscopy; temperature-programmed desorption.**

INTRODUCTION

The adsorption of molybdenum carbonyl on alumina has been extensively studied because these form catalysts that are active for a range of reactions including olefin metathesis (1, 2), alkene hydrogenation (3–5), and isomerization (6). Molybdenum hexacarbonyl adsorbed on hydroxylated alumina in ultrahigh vacuum at 80 K has been studied previously (7). In the following, we investigate the thermal decomposition of $Mo(CO)_6$ at higher sample temperatures, also on thin alumina films grown on Mo(100). The resulting films no longer consist of a molybdenum oxide (7), but molybdenum carbide. This class of materials has been extensively studied because group VI transition metal carbides have been suggested to have catalytic properties similar to those of the group VIII metals (8–11). Furthermore, molybdenum carbides incorporated into zeolite lattices have been shown to convert methane into benzene (12, 13). Recent surface science studies have demonstrated that methyl species adsorbed onto a carbided molybdenum single crystal can form ethylene (14) and similar results have been found on oxygen-modified molybdenum (15). Catalytic reactions carried out using alkenes on oxygen overlayers on molybdenum and model molybdenum oxides have demonstrated that the alkene dissociates forming surface CH_x species which polymerize to form high hydrocarbons (16–19), in accord with this surface chemistry (20–22).

EXPERIMENTAL

The growth and characterization of the alumina films formed on Mo(100) have been discussed in detail elsewhere (7). Briefly, the films are deposited by sequences of cycles of aluminum evaporation/water oxidation (with H_2O or $H_2{}^{18}O$-enriched water) to ensure complete oxidation of aluminum. Oxidation is monitored using Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) and the film is then heated to 450 K *in vacuo* to desorb any remaining molecular water and yield fully hydroxylated alumina (7). Aluminum is evaporated from a small heated alumina tube enclosed in a stainless-steel shroud to minimize contamination of other parts of the system (23). Experiments were carried out in a vacuum system that has been described in detail elsewhere (7). Briefly, the 12-in.-diameter, stainless-steel vacuum chamber operated at a base pressure of $\sim 5 \times 10^{-11}$ Torr following bakeout and was equipped with a double-pass, cylindrical mirror analyzer, an X-ray source, and a quadrupole mass analyzer. Auger spectra were collected using an electron beam energy of 3 keV and the first-derivative spectrum obtained by numerical differentiation. XPS data were collected using the double-pass, cylindrical mirror analyzer operating at a pass energy of 50 eV. Mg $K\alpha$ radiation was furnished by a water-cooled source operating at a power of 120 W. The chamber also contained a retractable, electron-beam heating filament which is used to heat the molybdenum substrate to ∼2100 K for cleaning. Temperature-programmed desorption spectra were collected at a heating rate of 30 K/s and the desorbing species were detected using a quadrupole

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mass spectrometer interfaced to a microcomputer which allowed up to five masses to be monitored sequentially.

The deionized water and ^{18}O-labeled water ($H_2{}^{18}O$, 10 at.%, Aldrich, 95%) used to grow the films were transferred to glass bottles. Normal (H_2O) water was generally used for surface oxidation. ^{18}O-Labeled water was used in experiments to distinguish between oxygen coming from the substrate and from adsorbates. The water was purified using repeated freeze–pump–thaw cycles. Molybdenum hexacarbonyl (Aldrich, 99%) was transferred to a glass vial and purified by repeated freeze–pump–thaw cycles, followed by distillation, and its purity monitored using mass and infrared spectroscopies. The $Mo(CO)_6$ was also dosed onto the surface via a capillary doser to minimize background contamination.

RESULTS

Table 1 displays the rate of molybdenum deposition on alumina following carbonyl exposure from the dosing source with a background pressure of 5×10^{-9} Torr. The dosing source has a pressure enhancement factor of 200 (see below) so that the effective pressure at the sample is $\sim 1 \times 10^{-6}$ Torr. The molybdenum coverage was measured from the peak-to-peak ratio of the Mo MNN Auger signal relative to that of the aluminum LVV peak from the alumina substrate. The calibration of the signal due to a monolayer of molybdenum is described below. Substrates were prepared by oxidizing aluminum evaporated onto a Mo(100) substrate and the film was sufficiently thick that there were no residual signals arising from the substrate. The alumina sample was annealed at 450 K to remove any residual water so that experiments performed at higher temperatures result in further dehydroxylation where it has been shown that approximately 50% of the surface hydroxyls are removed by heating to 900 K (7). There is little molybdenum deposition below 500 K and Mo is deposited at a significant rate only for sample temperatures above 670 K.

In view of these results, subsequent films were grown at a sample temperature of 700 K where the deposition rate is significant. Figure 1 displays a series of Auger spectra for an initially hydroxylated alumina sample exposed to $Mo(CO)_6$ as a function of exposure in langmuirs (1 langmuir (L) $= 1 \times 10^{-6}$ Torr · s). To avoid excessive background contamination by molybdenum hexacarbonyl, it was dosed by means of a dosing source. The source was calibrated by comparing doses for CO on Mo(100), where the CO coverage was monitored using temperature-programmed desorption (24), and CO was dosed either from the source or by back-filling the chamber, yielding the enhancement factor of 200 used above. Pressures were not corrected for ionization gauge sensitivities in either case. The features due to molybdenum (at 186 and 221 eV kinetic energy) and carbon (at 273 eV kinetic energy) grow together. Shown for comparison is the Auger spectrum of the alumina film showing the Al LVV and O KLL peaks. The kinetic energy of the Al LVV feature is sensitive to the aluminum oxidation state and the peak position at 52 eV kinetic energy confirms the presence of aluminum oxide. The ratio of the molybdenum and carbon Auger peaks can be used to estimate the molybdenum to carbon stoichiometry; using standard Auger sensitivity factors (25), this yields a Mo : C ratio of 0.95. Shown as an inset in this figure is an expanded depiction of the Auger KLL transition for the surface after exposure to 40 L of $Mo(CO)_6$ at 700 K which exhibits a typical carbidic lineshape.

TABLE 1

Rate of Molybdenum Deposition as a Function of Temperature

Temperature/K	Deposition rate/ML · s^{-1}
470	5.5×10^{-5}
570	1.2×10^{-4}
670	1.9×10^{-3}

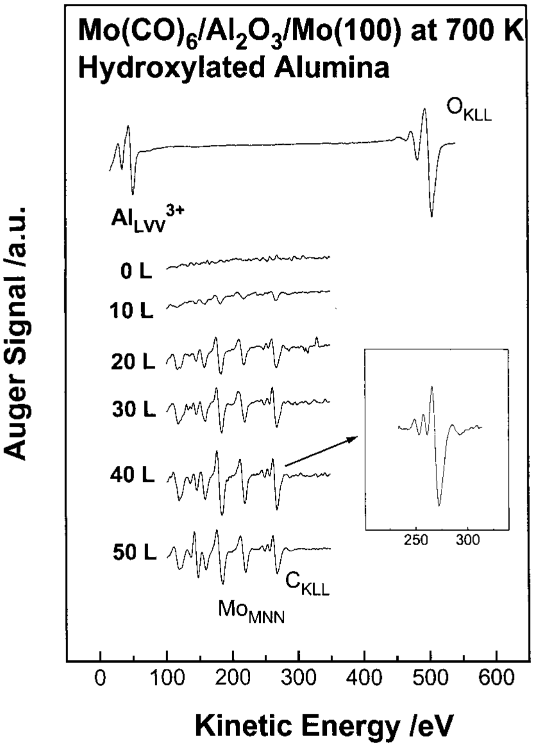

FIG. 1. Evolution of the Auger spectra following adsorption of $Mo(CO)_6$ on hydroxylated alumina as a function of exposure for a sample temperature of 700 K. The carbonyl exposures are marked adjacent to the corresponding spectrum and the spectrum of the alumina sample prior to carbonyl exposure is shown for comparison. Shown as an inset is an expanded version of the carbon KLL Auger feature after 50 L exposure at 700 K.

Figure 2 shows a plot of the relative molybdenum peak-to-peak intensity ratioed to the signal of the alumina

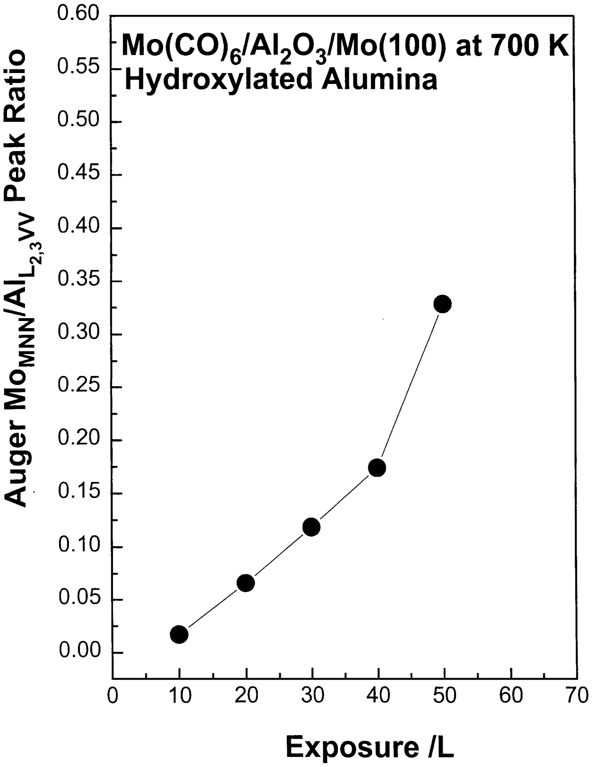

FIG. 2. Plot of the ratio of the peak-to-peak intensity of the Mo MNN Auger feature (at 221 eV kinetic energy) normalized to the aluminum LVV feature at 52 eV kinetic energy as a function of molybdenum hexacarbonyl exposure.

substrate versus molybdenum hexacarbonyl exposure. This increases linearly up to an exposure of ∼40 L and then increases more rapidly thereafter. This suggests that the carbonyl reacts more rapidly on the carbide surface so that ∼40 L is taken to correspond to the formation of a monolayer. The value of the molybdenum peak-to-peak intensity at this point is ∼0.175. Using standard electron escape depths (26) and the aluminum and molybdenum Auger signals for the alumina film and Mo(100) substrate, respectively, yields a molybdenum coverage of ∼0.9 monolayers in accord with the assertion that a 40 L exposure corresponds to the completion of a monolayer. Shown in Fig. 3a are the corresponding X-ray photoelectron (XP) spectra of the surface formed after a 50 L $Mo(CO)_6$ exposure at 700 K. Identical spectra were collected at different X-ray powers indicating that there are no shifts due to charging. The Mo 3*d* spectrum shows spin–orbit split peaks with the $3d_{5/2}$ peak at 228.6 ± 0.1 eV binding energy (BE) and the $3d_{3/2}$ feature at 231.8 ± 0.1 eV BE. The $3d_{5/2}$ feature is shifted ∼1 eV from that for metallic molybdenum and corresponds to an approximately +1 oxidation state. The C 1*s* spectrum shows two closely spaced features that are fit using a combined Lorentzian/Gaussian lineshape. This reveals the presence of two features at 285.0 ± 0.2 and 283.5 ± 0.1 eV BE. The 285 eV feature corresponds to elemental carbon and is probably due to some graphite deposited onto the surface (see below). The feature at 283.5 eV is assigned to the presence of carbide on the surface. The relative intensities of these features can also be used to estimate the stoichiometry of the surface species from the XPS sensitivities (27) for a double-pass, cylindrical mirror analyzer using Mg *Kα* radiation and this yields a Mo : C ratio of 0.92. These binding energies are slightly different (by ∼0.5 eV) from those for Mo_2C (28) likely due to the presence of a carbidic monolayer rather than a bulk carbide. All of these results taken together indicate that $Mo(CO)_6$ thermally decomposes at 700 K on alumina to form a molybdenum carbide.

Figure 4a displays a temperature-programmed desorption spectrum of an alumina film grown using 10% $H_2{}^{18}O$, so that the 10% of the oxide is isotopically labeled. This sample is exposed to 60 L of $Mo(CO)_6$ at 700 K. This yields an intense CO (28 amu) desorption feature at 1380 K where the corresponding 30-amu signal (due to $C^{18}O$) has been scaled by a factor of 10 to take account of the proportion of isotopically labeled CO in the water used to oxidize the film. This result indicates that the carbide formed on the surface reacts with the lattice oxygen to yield CO. A leading-edge analysis of the desorption peak yields an activation energy of 330 kJ/mol. Displayed in Fig. 3b is the Mo 3*d* XPS spectrum of the surface after the thermal desorption sweep (so after annealing to 1500 K) which shows a $3d_{5/2}$ peak at 227.7 ± 0.1 eV BE and a $3d_{3/2}$ feature at 230.9 ± 0.1 eV. This corresponds to the presence of metallic molybdenum (27) and confirms that the carbide has been reduced to the metal.

Figure 5a displays the corresponding Auger spectrum after annealing the carbide to 1500 K, confirming that the metal is retained on the surface. A small amount of carbon remains as evidenced by the weak feature at 273 eV kinetic energy which is likely due to the graphitic species detected by XPS after dosing molybdenum carbonyl at 700 K (Fig. 3a). Reacting this surface with 30 L of ethylene at 900 K yields a surface displaying the Auger spectrum shown in Fig. 5b. There is a substantial increase in the intensity of the C KLL Auger feature which is shown expanded in the inset. Once again, the Mo : C stoichiometry and the C KLL lineshape indicate that the carbide has been re-formed by this procedure. This conclusion is confirmed by the XPS data of Fig. 3c which show Mo 3*d* and C 1*s* features consistent with carbide formation on the surface and are essentially identical to the spectra displayed in Fig. 3a. Note that the oxide in this case was also made using ^{18}O-enriched water and the temperature-programmed desorption spectrum taken monitoring 28 ($C^{16}O$) and 30 ($C^{18}O$) amu is displayed in Fig. 4b. Again, CO desorbs at 1300 K and the presence of $C^{18}O$ confirms reaction between the carbide and the oxygen of the alumina substrate. Note also that the originally hydroxylated surface will have undergone substantial dehydroxylation during the desorption sweep to 1500 K.

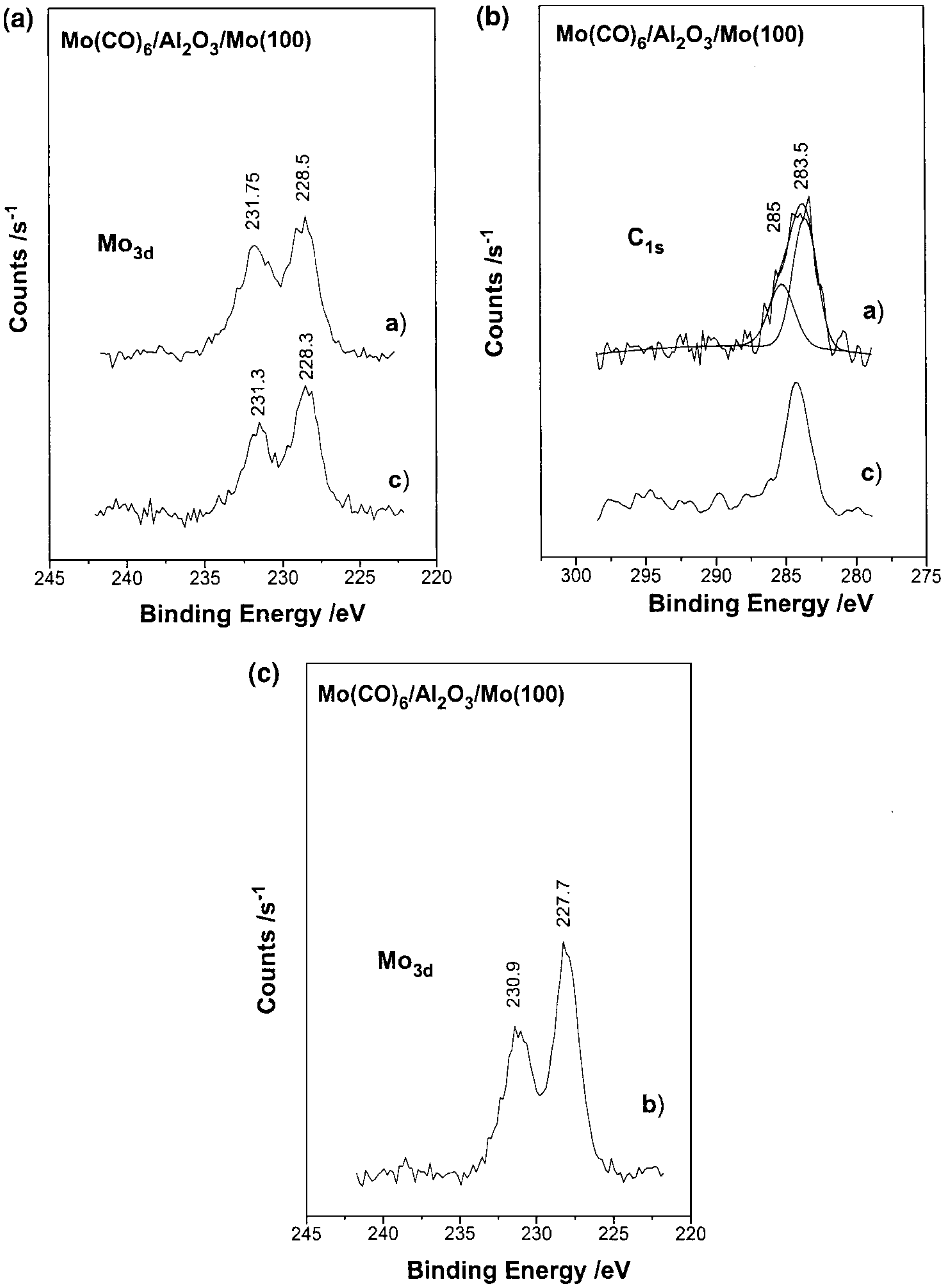

FIG. 3. (a) Molybdenum 3*d* and C 1*s* XPS following 50 L $Mo(CO)_6$ exposure to alumina at 700 K; (b) the molybdenum XPS peak after heating the surface to 1500 K and (c) then exposing the surface to 30 L of ethylene at 900 K.

The similarity between the TPD spectra in Fig. 4 suggests that this process is not unduly affected by the degree of hydroxylation of the surface although some slight changes are noted, presumably due to a reduction of the oxide. The Auger spectrum of the sample after the desorption sweep is displayed in Fig. 5c and confirms the removal of carbon from the surface except for the presence of some residual graphite. Note also that the intensities of the molybdenum features (at 186 and 221 eV kinetic energy) in Figs. 5a and 5c are essentially identical, further confirming that no molybdenum has been lost from the surface by this high-temperature treatment.

Finally, shown in Fig. 5d is the Auger spectrum collected after carbide formation by reaction with ethylene (Fig. 5b) and heating to 1500 K to reduce the carbide (Figs. 5c, 6, and 7) which is once again exposed to 30 L of ethylene at 900 K. This again reveals the presence of a carbide and indicates that the carbonylation/decarbonylation cycle can be repeated. This process has been repeated reversibly four times.

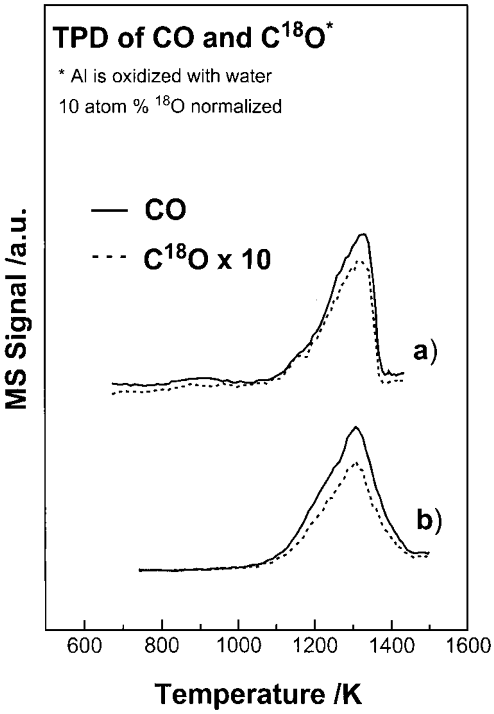

FIG. 4. Temperature-programmed desorption spectra collected at 28 amu ($C^{16}O$) and 30 amu ($C^{18}O$) for (a) a surface exposed to 60 L of $Mo(CO)_6$ on an alumina film grown using $H_2{}^{18}O$ and (b) then exposed to 30 L of ethylene at 900 K. The heating rate was 30 K/s.

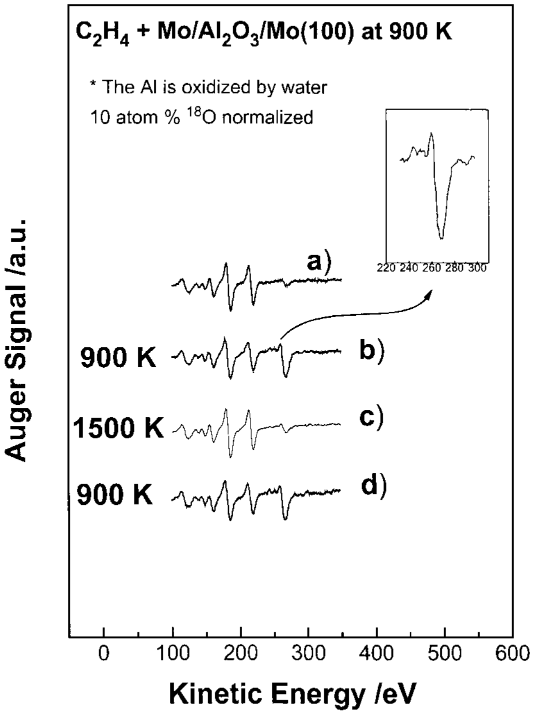

FIG. 5. Auger spectra collected (a) following the temperature-programmed desorption spectrum displayed in Fig. 4, (b) after exposure to 30 L of ethylene at 900 K, (c) annealing *in vacuo* to 1500 K, and (d) exposing, once again, to 30 L of ethylene at 900 K.

DISCUSSION

Molybdenum hexacarbonyl reacts slowly with alumina at 470 K and at an appreciable rate above 670 K to form a film that consists of a molybdenum carbide. There are two forms of carbide, namely Mo_2C and MoC (29). The approximately 1 : 1 stoichiometry measured using both Auger and X-ray photoelectron spectroscopy suggests that MoC is formed. The amounts of carbide on the surface increases approximately linearly with carbonyl exposure up to ~40 L and increases more rapidly thereafter. This suggests that a monolayer of the carbide forms at ~40 L and the Mo/Al Auger ratio is consistent with this view. The carbide is reduced by reaction with the lattice oxygen of the alumina substrate above ~1200 K (Fig. 4) to re-form the metal where the activation energy for this process is ~330 kJ/mol.

The molybdenum metal can be recarbided by reaction with ethylene at 900 K (Figs. 3 and 5b) and reduced to the metal, once again by reaction with the oxide (Fig. 3). This indicates that the alumina is only partially reduced. It also appears that the surface can be repeatedly reduced and recarbided without substantial loss of molybdenum from the surface.

CONCLUSIONS

Molybdenum hexacarbonyl reacts with a hydroxylated alumina surface under ultrahigh vacuum at an appreciable rate only above 670 K to form MoC where the rate of carbide formation is linear with exposure up to completion of the monolayer and increases thereafter. The carbide reacts with oxygen from the alumina substrate to evolve carbon monoxide leaving metallic molybdenum on the surface with no loss of molybdenum. The carbide can be re-formed by heating the adsorbed metal in ethylene at 900 K. This can be reduced once again, without loss of molybdenum, by reaction with the alumina substrate.

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