

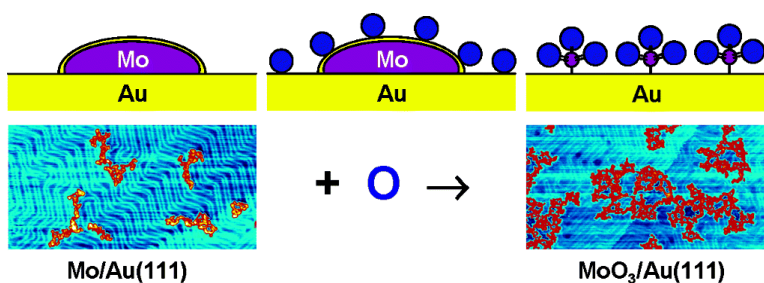
Article

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*J. Am. Chem. Soc.*, **2003**, 125 (26), 8059-8066 • DOI: 10.1021/ja034862m • Publication Date (Web): 10 June 2003

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## Molecular Level Study of the Formation and the Spread of MoO<sub>3</sub> on Au (111) by Scanning Tunneling Microscopy and X-ray Photoelectron Spectroscopy

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**Abstract:** The formation of MoO<sub>3</sub> and its spontaneous spread over an Au (111) surface have been studied by X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). Metallic Mo clusters grown by Mo(CO)<sub>6</sub> chemical vapor deposition (CVD) have a constant size independent of the Mo coverage. Molecular oxygen does not react with low coverage of Mo, probably due to the encapsulation of the Mo clusters by Au. At higher coverage, O<sub>2</sub> reacts with Mo, partially transforming the metallic Mo to Mo<sup>4+</sup>. NO<sub>2</sub> can oxidize Mo efficiently to Mo<sup>6+</sup> and Mo<sup>5+</sup> species at all coverages investigated. XPS experiments show that the integrated intensity of the Mo 3d peaks increases by a factor of 2 upon the oxidation, suggesting the spread of the MoO<sub>3</sub> over the surface. The STM study confirms this suggestion and provides the mechanistic details of the spreading. Mo oxide forms ramified two-dimensional islands covering a substantially larger fraction of the Au surface than the metallic Mo. We propose that the morphology change starts with the diffusion of oxide clusters (ramified-cluster-diffusion mechanism), followed by their breakdown to highly disordered two-dimensional islands of molecular MoO<sub>3</sub>.

### Introduction

Nanoscale particles and ultrathin films are important in many areas because of their unique electronic, optical, and chemical properties that are different from those of the corresponding bulk materials. It has been found that many metal oxides and salts are able to spontaneously spread over supports and form monolayer species. This behavior has been applied extensively in the preparation of heterogeneous catalysts.<sup>1–3</sup> Careful study of the spreading mechanism can lead to a better understanding of many fundamental problems on surface diffusion, which controls the growth of nanoparticles, nanowires, and epitaxial layers on surfaces.

MoO<sub>3</sub> has many interesting and unique properties. It can be used in H<sub>2</sub> sensing, electrochromic coloration, and solid-state thin film batteries as the cathode material. Supported MoO<sub>3</sub> is widely used as a catalyst in the petroleum and chemical industry. A number of papers have reported the spontaneous spread of MoO<sub>3</sub> on various oxides surfaces<sup>3–17</sup> or in sieve pores<sup>1,2</sup> upon thermal treatment.

The spreading behavior of the MoO<sub>3</sub> has been studied by numerous methods. Xie and co-workers were the first to report the MoO<sub>3</sub> spontaneous spreads on oxide supports.<sup>4,5</sup> The investigation of the physical mixtures of MoO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> by X-ray diffraction analysis (XRD) showed the disappearance of the MoO<sub>3</sub> bulk features upon a thermal treatment around 670–770 K. The X-ray photoelectron spectroscopy (XPS) measurement supported their assumption on the monolayer spread of MoO<sub>3</sub> over the support surface. This spontaneous spread of MoO<sub>3</sub> was further proved by ion scattering spectroscopy,<sup>6,7</sup> scanning electron microscopy,<sup>8</sup> Raman spectroscopy,<sup>9–11</sup> FT infrared spectroscopy,<sup>9</sup> extended X-ray absorption fine structure,<sup>12</sup> and scanning photoemission microscopy<sup>13,14</sup> measurements. The transport of MoO<sub>3</sub> across an alumina surface could occur over several hundred micrometers.<sup>10</sup> In situ high-

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temperature Raman spectroscopy<sup>15</sup> suggested that the actual spreading phase was surface molten MoO<sub>3</sub>, consisting of MoO<sub>3</sub> monomers and small oligomeric species. It was also shown in the above studies that ambient gas, especially water vapor, could promote the spread of MoO<sub>3</sub>. It is generally suggested that the driving force for this spreading is to reduce the surface free energy. The interaction of MoO<sub>3</sub> with the substrate influences the spreading behavior.<sup>8,16,17</sup>

Three mechanisms (transportation via gas phase (GP), unrolling carpet (UC), and free surface diffusion (SD))<sup>18</sup> have been suggested to explain the spreading phenomenon. However, because of the limitation of the above-mentioned measurements, there are many open questions remaining, such as the morphology and atomic structure of the spread species, and the molecular level mechanism that leads to the mobility and diffusion.

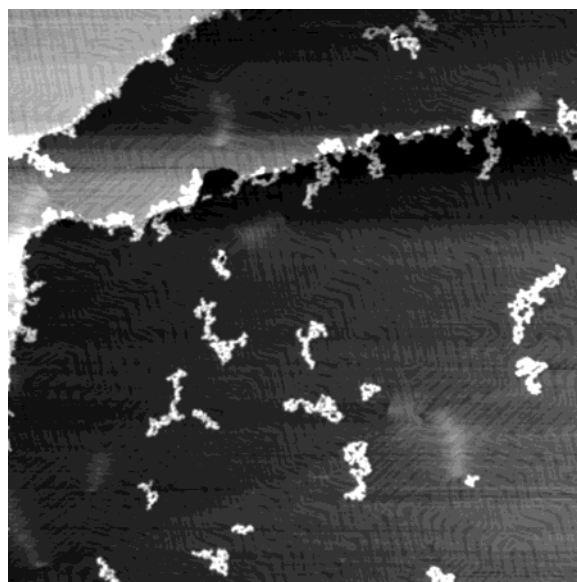
In the present study, we prepared samples of Mo nanoparticles on Au (111) by chemical vapor deposition (CVD) growth of metallic Mo from a Mo(CO)<sub>6</sub> precursor. The samples were then oxidized in situ to form MoO<sub>3</sub> on Au. Gold is used as a substrate in this experiment because, on one hand, it is chemically inert and, on the other hand, the surface free energy of Au is near that of Al<sub>2</sub>O<sub>3</sub>, which is used as a support for MoO<sub>3</sub> in industrial catalysts, and had been extensively studied for the MoO<sub>3</sub> spreading behavior. We believe that important insight into the spreading mechanism can be obtained even when using Au as a support. In this study, we used XPS measurement to monitor the formation of the MoO<sub>3</sub>, and scanning tunneling microscopy (STM) to get nanometer-level information on the MoO<sub>3</sub> morphology and structure. Surprisingly, the MoO<sub>3</sub> wetting layer on Au does not have a compact structure; instead, the three-dimensional Mo clusters are transformed to two-dimensional ramified MoO<sub>3</sub> islands. The mechanism for the spreading and the structure of the MoO<sub>3</sub> islands are discussed at a molecular level.

## Experimental Section

The XPS experiments were performed in a UHV chamber (base pressure < 5 × 10<sup>-10</sup> Torr) that is a part of the U7A beam line of the National Synchrotron Light Source. The chamber is equipped with a hemispherical electron-energy analyzer with multichannel detection. The spectra of the Mo 3d and Au 4f core levels and the corresponding valence bands were recorded at a photon energy of 370 eV, whereas the O1s spectra were recorded at a photon energy of 625 eV. The binding energy scale in the photoemission data was calibrated by measuring the position of the Fermi edge. The coverage of Mo is defined as the ratio of the number of Mo atoms over that of the surface Au atoms. In the XPS measurement, the Mo coverages are estimated from the intensities of Mo 4d and Au 5d valence band spectra.

The STM experiments were carried out in a separate UHV chamber (base pressure < 4 × 10<sup>-11</sup> Torr) equipped with a variable temperature STM (Omicron). STM images were acquired at room temperature using a tungsten tip. A preparation chamber used for CVD was isolated by a gate valve from the STM chamber. The Mo coverage estimates in the STM study are based on the molecular resolution images of MoO<sub>3</sub>, assuming that the oxidation does not induce any Mo loss from the Au surface.

The Au (111) surface was cleaned by cycles of Ne<sup>+</sup> sputtering (600 eV, 2 μA) at room temperature followed by 900 K annealing. The Au samples were deemed clean when STM images exhibited extended domains of the periodic herringbone reconstruction or no impurity is



**Figure 1.** STM image of 0.13 ML Mo on Au (111) deposited by Mo(CO)<sub>6</sub> CVD at 500 K, and then annealed to 600 K. The details of this CVD growth have been described in refs 19, 20. Image size: 364 × 364 nm<sup>2</sup>.

detectable by XPS. Molybdenum was deposited on the Au (111) surface by exposing the surface to a pressure of ~1 × 10<sup>-7</sup> mbar Mo(CO)<sub>6</sub> at 500 K, followed by annealing in a vacuum at 600 K.

An Au (111) surface covered by 0.13 ML Mo is shown in Figure 1. Detailed descriptions of the CVD growth of Mo on Au (111) have been reported elsewhere.<sup>19,20</sup> Briefly, at small coverages of Mo (<0.15 ML), no carbon and oxygen contamination was detected by XPS. At larger Mo coverages (~0.5 ML), only traces of C were found on the surface. The growth of Mo clusters is self-limited, with diameters of ~1.8 nm. These three-dimensional clusters aggregate without coalescence, forming ramified islands with the branches extending preferentially along the fcc troughs and the domain boundaries of the Au (111) reconstruction. The size of the island increases with Mo coverage as new clusters form and migrate to expand the existing islands, keeping the number density of the island constant within the coverage range investigated. In the following text, we use the term “island” to indicate the Mo islands that are composed of Mo clusters.

Molybdenum was oxidized at elevated temperatures by backfilling the chamber with O<sub>2</sub> or using a capillary array doser for NO<sub>2</sub> exposures.

**Safety Note.** Both Mo(CO)<sub>6</sub> and NO<sub>2</sub> are highly toxic and should be handled with extreme caution. Gas lines for NO<sub>2</sub> handling should be carefully leak-tested, and carbonyl should be transferred in a glovebox using UHV-compatible vials with a shutoff valve.

## Results and Discussions

**XPS Measurements.** As we reported previously,<sup>19–22</sup> the Mo clusters on Au are probably capped by a layer of Au and have therefore low reactivity toward O<sub>2</sub>, CO, and C<sub>2</sub>H<sub>4</sub>. The limited oxidation by O<sub>2</sub> shows that the encapsulation affects the Mo clusters at low Mo coverage more than at higher coverage. In Figure 2, the Mo 3d spectra for two Mo coverages (0.05 and 0.22 ML) before and after exposure to O<sub>2</sub> at elevated temperatures are compared. The inset STM images (I and II) show that the Mo islands are growing by capturing more nearby

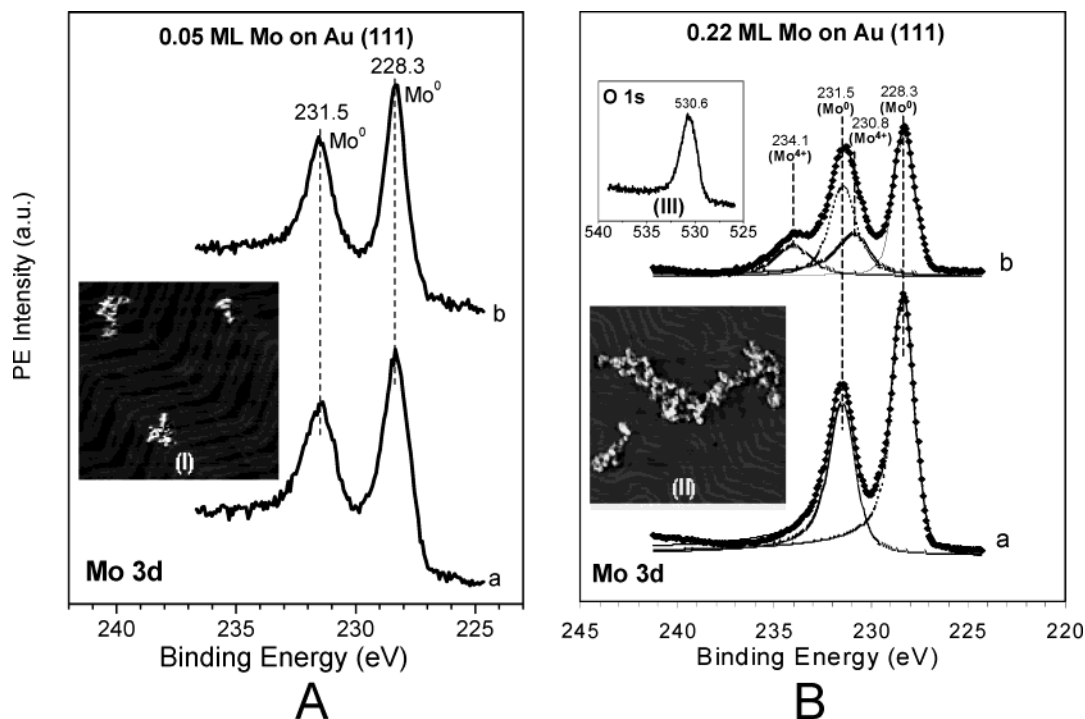
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**Figure 2.** Mo 3d XPS spectra taken from two samples with Mo coverages of  $\sim 0.05$  (A), and  $\sim 0.22$  (B) ML before (curve a) and after (curve b) oxidation. The oxidation temperatures are 850 and 600 K for the 0.05 and 0.22 ML Mo samples, respectively. The dosages of O<sub>2</sub> are about 20 L for both. (I) STM image of  $\sim 0.03$  ML of Mo on Au(111) by Mo(CO)<sub>6</sub> CVD. Image size:  $60 \times 60$  nm<sup>2</sup>. (II) STM image of  $\sim 0.13$  ML Mo on Au(111) by Mo(CO)<sub>6</sub> CVD. Image size:  $65 \times 65$  nm<sup>2</sup>. (III) O 1s spectrum for the 0.22 ML Mo sample after the oxidation.

equally sized clusters as the Mo coverage increases.<sup>20</sup> Before oxidation, the Mo 3d<sub>5/2</sub> and 3d<sub>3/2</sub> doublets in the XP spectra are at 228.3 and 231.5 eV, respectively, for both of the samples (curve a in both Figure 2A and B), implying a metallic character of the Mo clusters on Au grown by Mo(CO)<sub>6</sub> CVD.<sup>23</sup> After oxidation by 20 L O<sub>2</sub> at temperatures up to 850 K, neither oxidized Mo species nor the intensity change of the Mo peaks can be found on the 0.05 ML Mo sample (curve b in Figure 2A). For the 0.22 ML Mo sample, after an oxidation by 23 L O<sub>2</sub> at 600 K, a shoulder appears at the higher binding energy side of the Mo 3d<sub>5/2,3/2</sub>, and the intensity ratio of the 5/2 to 3/2 peaks decreases (curve b in Figure 2B). Using curve fitting, we found an additional set of Mo 3d doublets at 230.8 and 234.1 eV, binding energies typically assigned to MoO<sub>2</sub>.<sup>23</sup> The inset (III) in Figure 2B shows the corresponding O 1s peak from this sample, confirming the formation of oxide on the surface.

The above result implies that the larger Mo islands are probably not fully covered by Au and can react with oxygen. The reason for this is still unknown. One possible explanation could be as follows: our previous STM study<sup>20</sup> on the CVD growth of Mo on Au (111) displays that the Mo clusters preferentially decorate the step edges (Figure 1). It is assumed that the step edges could be the source of free metal atoms migrating on terraces to form two-dimensional metal gas. These free Au atoms could be those to cover on the Mo clusters. Site exchange of Mo with the substrate Au has probably not occurred here, because no change of the Au reconstruction is found. For a larger coverage of Mo on Au, Mo can decorate the entire step edges, and, as a result, not enough Au atoms are available to fully

cover the Mo clusters. A cluster-size-dependent reactivity of Mo cannot explain the coverage-dependent reactivity of Mo, because the cluster size does not change with the coverage. This result also shows that the reactivity of molecular oxygen is not high enough to oxidize the Mo clusters fully.

To remove the capping layer of Au on the Mo cluster, we used NO<sub>2</sub> to cover the surface with chemisorbed atomic oxygen.<sup>24</sup> Dissociative adsorption of NO<sub>2</sub>, NO<sub>2(gas)</sub>  $\xrightarrow{T > 300\text{K}}$  NO<sub>2(gas)</sub> + O<sub>ads</sub>, is facile on metal surfaces and is often used as a source of atomic oxygen. Wang and Koel<sup>25</sup> found that only atomic O remains on the Au surface above room temperature after reaction with NO<sub>2</sub>. Jirsak et al.<sup>26</sup> reported that, at room temperature, the reaction of NO<sub>2</sub> with Mo(110) leads to the oxidation of the Mo surface and generates also a small amount of atomic N in the surface layer. The reaction of NO<sub>2</sub> and Mo(110) at elevated temperature produces pure films of MoO<sub>2</sub>. The stronger interaction of O with Mo than with Au provides the driving force for Mo surface segregation, and a high reactivity of atomic oxygen leads to a complete oxidation of molybdenum metal.

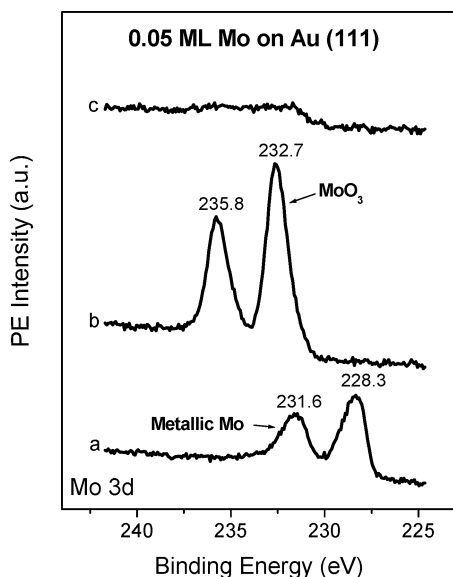
Figures 3 and 4 show two sets of XPS data from samples with Mo coverages of 0.05 and 0.10 ML. After oxidation by NO<sub>2</sub> at 500 K, metallic Mo (curves a in both figures) is converted mainly to MoO<sub>3</sub> (curve b in Figure 3, c in Figure 4), and the Mo doublet is shifted to higher binding energy by 4.3 eV with the Mo 3d<sub>5/2</sub> peaks at 232.7 eV.<sup>23</sup> The asymmetry of the Mo core levels after oxidation suggests the presence of an additional doublet at lower binding energy due to Mo species at a lower oxidation stage. The areas of the Mo 3d peaks increase

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**Figure 3.** Mo 3d XP spectra taken from a 0.05 ML Mo covered Au (111) sample (a) before oxidation, (b) after oxidation in 0.5 L NO<sub>2</sub> at 500 K, and then (c) annealing the oxidized sample to 700 K.

by a factor of 2 for both of the Mo coverages. No nitrogen-containing species were detected after the oxidation by NO<sub>2</sub>.

We believe that the 2-fold increase of the Mo peak intensity cannot be explained by, for example, the changes of the photoelectron cross-section or surface diffraction. A plausible explanation is the MoO<sub>3</sub> spreading over the surface that leads to the increase of the surface Mo species, therefore eliminating the self-attenuation of the photoemission signal as for the three-dimensional Mo clusters. As the size of the Mo clusters stays constant for different coverages, the expansion factor of the islands after the spreading from a three-dimensional to a two-dimensional morphology has a constant value for different coverages, as is expected. The fact that different Mo coverages have the same expansion factor confirms the self-limited growth of Mo in the Mo(CO)<sub>6</sub> CVD.<sup>20</sup>

Among molybdenum oxides, MoO<sub>3</sub> is known to sublime easily at moderate temperatures. Figures 3 and 4 show that the desorption temperature of MoO<sub>3</sub> from Au is coverage dependent. On the 0.05 ML Mo sample, the MoO<sub>3</sub> desorbs upon annealing to 700 K (curve c in Figure 3), whereas on the 0.10 ML Mo sample, the desorption of MoO<sub>3</sub> occurs only after annealing to 800 K (curve e in Figure 4). Although it is known that larger clusters have a lower vapor pressure that induces the so-called Ostwald ripening phenomenon, this mechanism might not dominate the temperature-dependent desorption process here. One of the reasons is that (as we will show below) the MoO<sub>3</sub> islands have ramified shape, which indicates limited interactions among the particles within the islands as compared to compact islands, which are used for the size-dependent vapor pressure modeling. We suggest that the temperature-dependent desorption is related to a disordered structure (amorphous state) of the MoO<sub>3</sub> islands (see below).

In addition to the Mo<sup>6+</sup> species, a lower oxidation state of Mo is visible with the Mo 3d<sub>5/2</sub> and 3d<sub>3/2</sub> peaks at 231.5 and 234.6 eV, respectively, especially in the initial oxidation stage and after annealing the oxidized sample to 700 K (curves b and d in Figure 4 Mo 3d spectra, respectively). This lower oxidation state can be assigned to Mo<sup>5+</sup> species.<sup>27</sup> We therefore

assume that the oxidation of metallic Mo to MoO<sub>3</sub> proceeds via the Mo<sup>5+</sup> state. However, even with the excess exposure of NO<sub>2</sub> when the Mo 3d core levels are dominated by the photoemission signal from Mo<sup>6+</sup> (Figure 4, curve c), the Mo<sup>5+</sup> species are still present.

The fraction of Mo<sup>5+</sup> state increases due to partial reduction after annealing. From the intensity ratio of Mo<sup>6+</sup> and Mo<sup>5+</sup>, we estimate that this reduction of the oxide should lead to about a 2% decrease of O concentration on the surface. However, a 50% decrease of the O 1s intensity has been found after annealing the sample to 700 K (curve d in O 1s spectra, Figure 4). The sample preparation temperature was chosen above the desorption temperature of CO from the Mo/Au(111) surface. In addition, we have shown<sup>19</sup> that, at Mo coverage below 0.15 ML, no residual C can be detected by synchrotron-based photoelectron spectroscopy. Therefore, the O 1s decrease caused by heating the sample from 500 to 700 K cannot be attributed to the oxygen loss due to desorption of CO or to the residual carbon reaction with oxygen. We propose that the decrease of the O 1s peak is due to desorption of the large concentration (~0.3 ML) of atomic O present on Au surface after exposure to NO<sub>2</sub>. The atomic O is known to desorb from the Au (111) surface between 500 and 600 K.<sup>24,25</sup>

**STM Measurements.** The STM measurements provide a direct view of the MoO<sub>3</sub> spreading on the Au (111) surface upon the oxidation by NO<sub>2</sub>. Molecular resolution images display the structure of the spread MoO<sub>3</sub> layer.

Figure 5A and B displays a Au (111) surface covered by 0.13 ML Mo after oxidation by 6 L NO<sub>2</sub> at 500 K. Two major changes of the Mo islands morphology upon the oxidation can be identified (cf., Figure 1): first, the size of the islands increases. Figure 5C compares the island size distribution before and after oxidation. The maximum of the distribution increases by ~200 nm<sup>2</sup> from ~50 to ~250 nm<sup>2</sup> upon the oxidation. XPS experiments have shown that, at this oxidation stage, all Mo has been oxidized into Mo<sup>6+</sup> and Mo<sup>5+</sup> species (Figure 4, curve b). The STM observation confirms our suggestion based on the XPS data that the increase of the island size is due to the spread of molybdenum oxides over the Au surface.

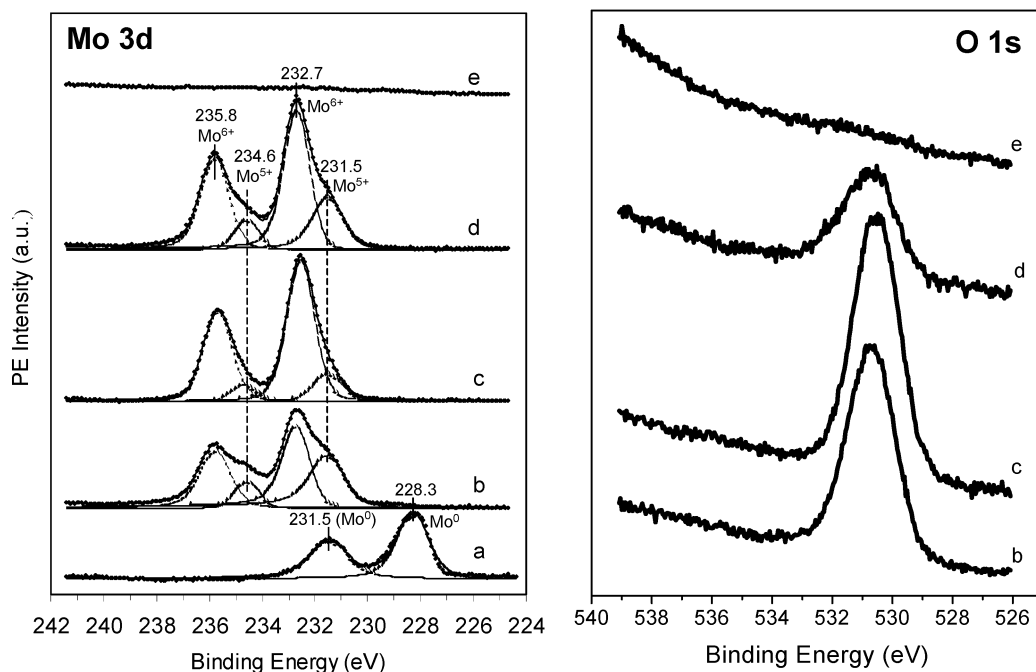
The second change in the islands upon oxidation is that there is an obvious height difference within the islands. At the STM sample bias voltage of -1.8 V, a large fraction of the islands have an apparent height of ~0.2 nm. However, there are a few bright features on the islands with an apparent height up to 0.8 nm. The metallic Mo cluster's apparent height at the same bias voltage is lower than 0.3 nm (Figure 1). Therefore, the bright features in the islands shown in Figure 5 can be associated with the oxidized Mo species that have not yet spread out.

The zoomed image (Figure 5B) shows clearly that the spreading of the MoO<sub>3</sub> species leads to a ramified island morphology. The branch widths of the islands are in the range of 2–6 nm, comparable to that of the original metallic Mo ramified island (Figure 1), whereas the lengths of the branches have increased, resulting in the increase of island size. It is known that there is a reflective wall at the edge of a terrace, the Ehrlich–Schwoebel (ES) barrier, which hinders the descent of atoms to lower levels.<sup>28</sup> The fact that only the branch length

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## 0.10 ML Mo on Au (111)



**Figure 4.** Mo 3d and O 1s XP spectra taken from a Au (111) sample covered by 0.10 ML Mo. (a) Before oxidation; (b) after oxidation in 2 L NO<sub>2</sub> at 500 K; (c) after oxidation in 23 L NO<sub>2</sub> at 500 K; (d) annealing the oxidized sample to 700 K; (e) annealing the oxidized sample to 800 K.

rather than the width of islands increases upon the spreading of the oxides indicates that the ES barrier is anisotropic. STM images shown in Figure 5 reveal that the spreading of the islands seems to follow the fcc troughs (the energy valley of the Au (111) surface<sup>29</sup>) and the orientation domain boundaries of the Au reconstruction, similar to the metallic Mo island growth directions. This indicates that the diffusion energy along the preferential directions on the Au surface could be lower than that toward other directions.

Upon additional oxidation of the sample at a higher temperature, 600 K, the islands spread further over the surface (Figure 6A). According to the XPS result, after this oxidation, the islands contain mainly MoO<sub>3</sub>. The size of the islands increases significantly, and they even connect to each other. More branches are found on the islands, and the spreading direction of the branches seems random at this temperature. The islands become flatter as compared to the earlier oxidation stage (Figure 5A). It is noticeable that the island is still composed by small particles but with much smaller size ( $\sim 1.1$  nm) (the inset of Figure 6A). This implies that the diffusing particles are MoO<sub>3</sub> clusters. This result is consistent with the in situ high-temperature Raman spectroscopy study,<sup>15</sup> which found the existence of amorphous oligomeric species in the molten phase during the MoO<sub>3</sub> spreading.

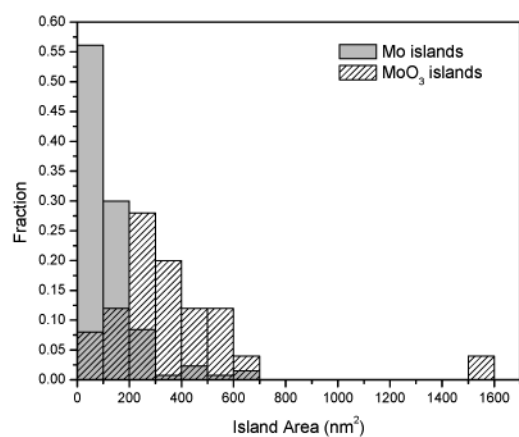
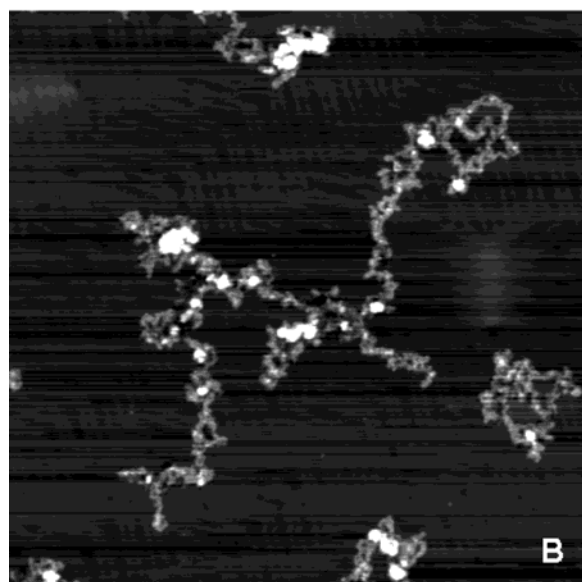
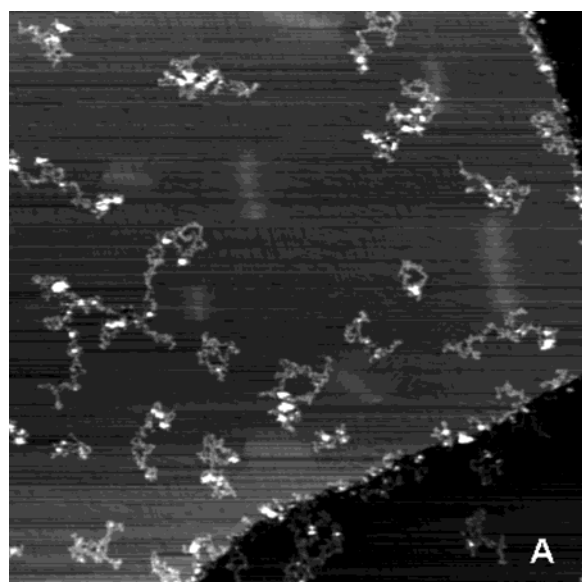
All images taken after oxidation by NO<sub>2</sub> with thermal treatment below 600 K have many fuzzy lines, possibly due to the presence of atomic O on the surface. Figure 6B shows the image of the sample after annealing in UHV to 700 K, which is free of fuzzy lines and shows clearly the Au substrate structure. The morphology of the islands displays a higher density of connected branches (networklike structure) than that in Figure 6A. This morphology change of the MoO<sub>3</sub> islands is

caused by diffusion of the MoO<sub>3</sub> on the surface upon heating in the absence of ambient gas.

To prove that surface diffusion in the absence of ambient gas can occur for MoO<sub>3</sub>, we carried out the following experiment. A Mo/Au (111) sample was oxidized at 500 K in NO<sub>2</sub> introduced by background dosing. Using this dosing method, we found that the flux of NO<sub>2</sub> molecules on the sample is much lower than that via a directional tube. Figure 7A shows a 0.08 ML Mo covered Au (111) surface. After oxidation in  $2 \times 10^{-7}$  Torr NO<sub>2</sub> at 500 K for 10 min, the predominantly vertical growth of the islands limits the ability of the STM tip to image the tall islands correctly (Figure 7B). The inset in Figure 7B is a differential image of this surface, showing clearly the herringbone structure of Au substrate together with the morphology of the bright features, indicating the tip quality does not change when taking this image. The similar shapes of bright features in Figure 7B are actually convolution images of the islands and the STM tip, due to the tiplike parts on the MoO<sub>3</sub> islands. At the sample bias of  $-1.8$  V, parts of the islands can be as high as 1.8 nm. This result implies that the low flux of NO<sub>2</sub> results in a low spreading rate of MoO<sub>3</sub> over the Au surface. This surface was then annealed in UHV ( $5 \times 10^{-11}$  Torr) at 750 K for 20 min (Figure 7C). The tall islands spread out, becoming much flatter and larger than the metallic ones. The spread of the islands has preferential directions along the energy valleys of the Au (111) reconstruction (inset of Figure 7C). Because the annealing temperature is rather high, defects of the Au reconstruction can be observed near the MoO<sub>3</sub> island regions.

Figure 8 is a molecular resolution image of the MoO<sub>3</sub> islands. The black dots highlight the ball-like feature in the islands. It is clear that MoO<sub>3</sub> is in a highly disordered amorphous state. The ramified and disordered flat structure indicates that the spread-out islands are in a single layer. There is no short- or

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**Figure 5.** STM images of the 0.13 ML sample oxidized in 6 L NO<sub>2</sub> at 500 K. (A) 350 × 350 nm<sup>2</sup>; (B) 152 × 152 nm<sup>2</sup>; (c) island size distributions before and after the oxidation in NO<sub>2</sub>. The size of the islands increases upon oxidation by extending the branches along preferential directions.

long-range order among the ball-like features, and with the average distance between two neighboring features of  $0.38 \pm 0.10$  nm, we assume that each individual feature is an image of a single MoO<sub>3</sub> molecule. Raman spectroscopy studies<sup>2,9,11</sup> found substantial decreases or even a disappearance of the crystal lattice related vibrations at 670 and 821 cm<sup>-1</sup> due to the spread, and these were assigned to doubly and triply coordinated oxygen (Mo<sub>2</sub>-O and Mo<sub>3</sub>-O) stretching modes, typical of the corner- and edge-sharing MoO<sub>6</sub> octahedra. In all of the Raman studies on the spread MoO<sub>3</sub> species, the peak at 950–1000 cm<sup>-1</sup>, the stretching mode of a free (nonlattice) O bonded to Mo (Mo = O) was preserved. On the basis of these results and our STM observations, we assume that the MoO<sub>3</sub> is molecularly adsorbed on the Au surface and has a weak interaction with nearest neighbors. The coverage of the original metallic Mo clusters can thus be obtained.

**The Spreading Mechanism of MoO<sub>3</sub>.** The results of previous studies of the MoO<sub>3</sub> spreading on several oxide surfaces were explained by three transport mechanisms:<sup>18</sup> gas-phase transportation (GP), unrolling carpet (UC), and free surface diffusion (SD).

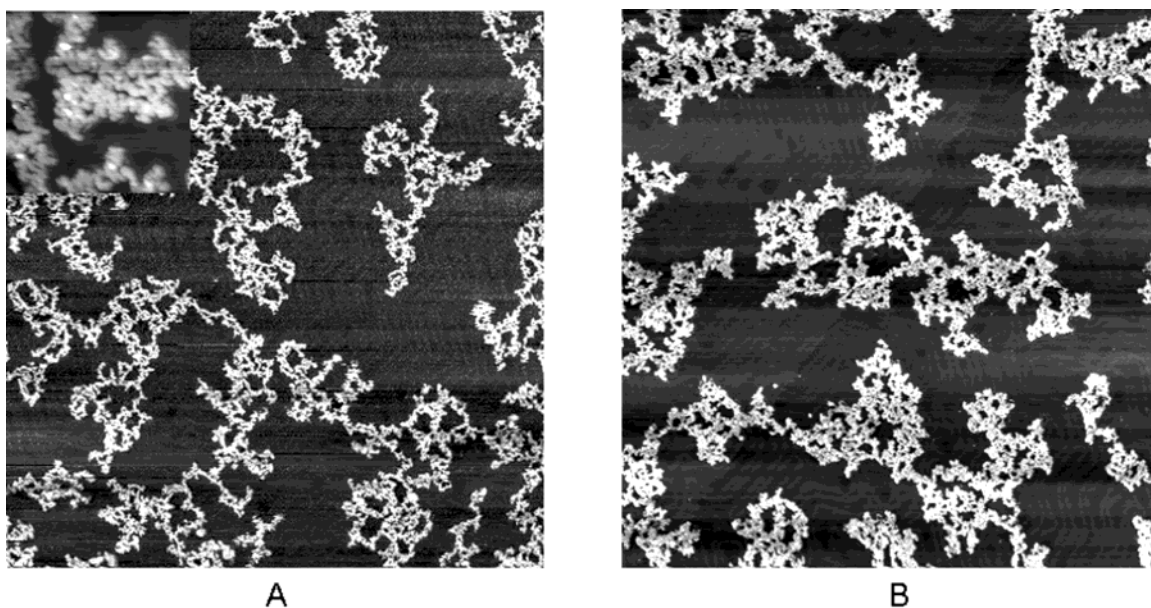
The spreading via the GP mechanism can be excluded according to the results in this study. The idea of the GP mechanism is that the MoO<sub>3</sub> molecules, volatilized into the presence of carrier gas, re-adsorb at the surface. Our experiments are conducted under UHV conditions where a mean free path of the gas-phase molecules is much larger than the chamber dimensions. All MoO<sub>3</sub> molecules would be lost by adsorption on the chamber walls.

The presence of ambient gas enhances the MoO<sub>3</sub> spreading, as has been shown in several experiments. For example, the water vapor and O<sub>2</sub> gas promote the spreading of MoO<sub>3</sub>.<sup>10,15</sup> As shown above, NO<sub>2</sub> is also efficient for the enhancement of this process. The spreading rate of MoO<sub>3</sub> in NO<sub>2</sub> is much faster than that in UHV.

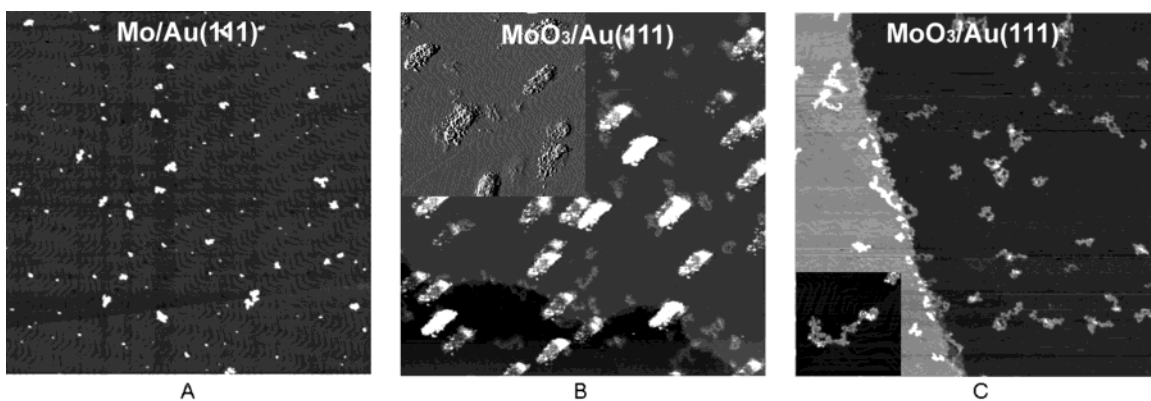
MoO<sub>3</sub> crystals are built from distorted MoO<sub>6</sub> octahedral units. As the Raman study<sup>11</sup> showed, the thermally unstable MoO<sub>3</sub> particles decreased in size on heating to 773 K, indicating a destruction of the MoO<sub>3</sub> lattice. It is worth mentioning that in those measurements the MoO<sub>3</sub> crystals were dispersed in alumina or silica particles. A complementary experiment showed that, for a bulk MoO<sub>3</sub>, thermal treatment at 550 K transforms amorphous MoO<sub>3</sub> to the crystalline state.<sup>30</sup> We assume that the presence of an ambient gas makes the destruction of the MoO<sub>3</sub> crystal structure irreversible by reaction of the gas molecule with a dangling bond generated by the destruction of the MoO<sub>3</sub> lattice. Molecules such as H<sub>2</sub>O can react directly with MoO<sub>3</sub> to form [MoO<sub>4</sub>]<sup>2-</sup> and therefore destroy the lattice. Thus, MoO<sub>3</sub> or MoO<sub>3</sub> clusters may separate from the bulk crystal and diffuse away. The destruction of the MoO<sub>3</sub> crystal structure is probably the rate-determining step in the spreading, and the enhancement of this process will increase the spreading rate.

The different spreading behaviors of MoO<sub>3</sub> at 500 and 600 K in the presence of NO<sub>2</sub> indicate that the spreading is a thermally activated process. As reported above, the spreading is mainly along the existent island branches or the troughs and orientation domain boundaries of the Au reconstruction at 500 K. At 600 K, the spreading of MoO<sub>3</sub> is more random; many

(30) Julien, C.; Khelifa, A.; Hussian, O. M.; Nazri, G. A. *J. Cryst. Growth* **1995**, *156*, 235.



**Figure 6.** (A) An STM image ( $205 \times 205 \text{ nm}^2$ ) of the 0.13 ML sample oxidized in 18 L  $\text{NO}_2$  at 600 K. The inset image ( $30 \times 30 \text{ nm}^2$ ) shows the islands are composed by clusters with a size of  $\sim 1.1 \text{ nm}$ . (B) An STM image ( $200 \times 200 \text{ nm}^2$ ) of the sample (B) being annealed in UHV at 700 K for 10 min. The width of the branches increases upon annealing, indicating a spreading in the absence of ambient gas.



**Figure 7.** STM images of (A) a Au (111) sample covered by 0.08 ML Mo, image size:  $400 \times 400 \text{ nm}^2$ ; (B) sample (A) being oxidized at 500 K by background dosing  $2 \times 10^{-7} \text{ mbar NO}_2$  for 10 min, image size:  $400 \times 400 \text{ nm}^2$ ; inset in (B) differential image  $200 \times 200 \text{ nm}^2$ ; (C) sample (B) being annealed in UHV at 750 K for 20 min, image size:  $400 \times 400 \text{ nm}^2$ ; inset in (C)  $64 \times 64 \text{ nm}^2$ .

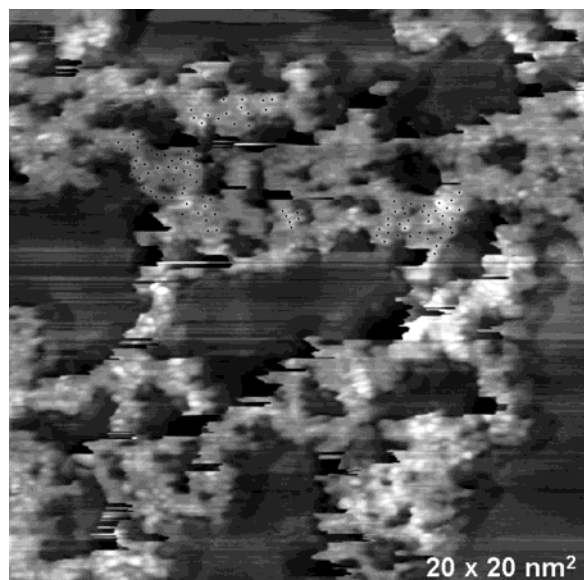
more branches are generated with no preferred orientation with respect to the substrate reconstruction. These results strongly support the idea of the spreading via an anisotropic activation barrier at the edge of the islands. As has been shown in the STM observation,  $\text{MoO}_3$  diffuses in the form of a whole cluster. These clusters could still contain several  $\text{MoO}_6$  octahedral units and keep this three-dimensional arrangement during the diffusion. When they get to the Au surface, they spread to two-dimensional islands, as shown in Figure 8.

The observed spreading behavior is consistent with the unrolling carpet (UC) mechanism in terms of the continuity of the spread islands. The UC mechanism was proposed to explain the results of the Raman spectroscopy of the molten phase of  $\text{MoO}_3$  during annealing.<sup>15</sup> Günther et al.<sup>14</sup> have claimed that the results of their measurement of the  $\text{MoO}_3$  spreading by scanning photoemission microscopy are incompatible with the UC mechanism. Their conclusion was based on an observation of  $\text{MoO}_3$  spreading to coverages less than 1 ML, which was assumed to be a discontinuous spread layer. However, they

cautioned that the UC mechanism could play a role if the layer morphology was a ramified one with the branch width smaller than the lateral resolution of the instrument. It is obvious from the present study that this is exactly the case. The ramified islands are a consequence of the cluster diffusion and the anisotropic diffusion potential. From the highly disordered and ramified  $\text{MoO}_3$  island structure, one can conclude that the interactions between  $\text{MoO}_3$  molecules/clusters are weak; as a result, the  $\text{MoO}_3$  clusters could have a high mobility on top of the  $\text{MoO}_3$  islands, which enable the branches to propagate quite a long distance.

The present STM study also provides direct evidence for a free surface diffusion (SD) mechanism, which means that the diffusion can occur without an ambient gas. The thermal treatment was carried out in a UHV chamber at  $\sim 10^{-11}$  Torr, and the annealing time is on the order of 10 min. During this time and in this vacuum range, the influence of the residual gases in the chamber can be neglected. The spreading can be ascribed exclusively to the free surface diffusion of  $\text{MoO}_3$  clusters.





**Figure 8.** Molecular resolution of the MoO<sub>3</sub> islands spread on the Au (111) surface. This image is a zoomed image of Figure 6B, and the black dots are used to highlight the ball-like features in the islands.

The three mechanisms proposed for explanation of the MoO<sub>3</sub> spreading are mutually exclusive, and none alone is capable of explaining all of the experimental results. The present study confirms that each mechanism describes different aspects of the spreading process. We suggest a more complex mechanism, the ramified-cluster-diffusion mechanism, which can explain the process of spreading on a nanoscale for the most of the results in this and previous studies: bulk MoO<sub>3</sub> spread in a ramified way in the form of a cluster over the surface. The diffusion of MoO<sub>3</sub> is a thermally activated process. The shape of the

dispersed islands can be strongly influenced by the diffusion barrier at the edge of the islands toward different directions. An ambient gas can accelerate the spreading rate by enhancing the destruction of the MoO<sub>3</sub> crystal lattice, assumed to be the controlling step for the spreading.

### Conclusions

We have compared O<sub>2</sub> and NO<sub>2</sub> oxidations of Mo clusters deposited on Au (111) via Mo(CO)<sub>6</sub> CVD. The results show that the Mo clusters on Au are probably encapsulated by gold. The smaller the Mo islands, the more complete the encapsulation, and, therefore, the lower the reactivity toward O<sub>2</sub>. NO<sub>2</sub> can remove Au capping and oxidize the Mo cluster.

The MoO<sub>3</sub> spread spontaneously over the Au (111) surface. A ramified-cluster-diffusion mechanism has been proposed. The spread of the MoO<sub>3</sub> is via the diffusion of the MoO<sub>3</sub> clusters. This diffusion is a thermally activated process, and an anisotropic diffusion barrier at the edge of the island results in a ramified shape of the spread islands. MoO<sub>3</sub> could have a high mobility on top of the MoO<sub>3</sub> islands. When the MoO<sub>3</sub> clusters step down from the islands, they form two-dimensional islands, in which the MoO<sub>3</sub> molecules adsorb on Au without any ordering. The average distance between two adjacent molecules is ~0.38 nm. Free surface spread can occur, and ambient gases can promote the spreading by enhancing the destruction of the MoO<sub>3</sub> crystal lattice, which could be the controlling step for the spreading.

**Acknowledgment.** This research was supported by the U.S. Department of Energy, Division of Chemical Sciences, under Contract DE-AC02-98CH10886.

JA034862M