

MORPHOLOGICAL EVOLUTION OF THE HYDROGEN REDUCED $\text{MoO}_{3-x}(010)$ SURFACE DURING REOXIDATION

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ABSTRACT

The reduction and reoxidation of the $\text{MoO}_3(010)$ surface have been studied with atomic force microscopy (AFM). Reduction in forming gas at 400 °C results in the formation of two surface modifying defects, crystallographic shear (CS) planes and surface voids. Reoxidation in air at 400 °C proceeds more slowly than reduction; it takes between 0.5 and 1.5 hours to completely oxidize the surface and annihilate the CS planes that were created during only 8 min of reduction. The surface voids persist through the oxidation treatments and, in fact, show morphological changes. Both the lateral and vertical dimensions of the voids increase and their bounding planes re-orient from mostly {101} to a combination of {001} and {100}.

INTRODUCTION

It is firmly established that the partial oxidation reactions catalyzed by molybdenum oxides are influenced by the structure of the crystal surface [1-10]. However, the development of mechanistic models to account for this surface structure sensitivity has been hindered by insufficient structural data. Determining the surface structure of these materials is complicated by the fact that the active surface is dynamic and evolves during redox processes. In the past, TEM studies have been carried out to study the structural evolution of MoO_3 during redox reactions [11,12]. These studies, which probe the through-thickness volume of small particles, have provided information about the evolution of the bulk defect structure from which surface information can sometimes be inferred. We have recently demonstrated that scanning probe microscopy can be used to probe the structural evolution of the $\text{MoO}_3(010)$ surface during reduction [13]. In addition to detecting bulk defect/surface intersections, consistent with the earlier TEM studies, our surface sensitive experiments provided additional information by revealing surface defects not detected in the TEM studies [13]. The objective of the present paper is to answer some remaining questions regarding the reversibility of the modifications that occur during the reduction reactions. For example, do the steps introduced at the surface by the CS defects persist after the material has been reoxidized? Do the surface voids remain unchanged through reoxidation? With these questions in

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mind, an AFM study was undertaken to explore the morphological evolution of the H₂ reduced (010) surface during reoxidation.

EXPERIMENTAL

The single crystals of MoO₃ utilized in this study were prepared by chemical vapor transport of powdered MoO₃ in evacuated, sealed quartz ampoules [13-15]. Each sample was mounted on a steel disc by spot-welding a thin strip of Ta foil across its (010) facet. Just prior to the reaction sequence, the single crystal sample was cleaved with adhesive tape to produce a fresh (010) surface.

After cleavage, samples were placed in a quartz reaction tube and reduced in a flow of forming gas at 400 °C. The gas had a nominal composition of N₂-10% H₂ (with 20 ppm H₂O) and it was flowed at 200 cc/min and 1 atm. After reacting the crystal for a pre-determined time at 400 °C, the sample was removed from the reactor and analyzed with AFM in the ambient atmosphere at room temperature. All of the observations reported here were reproducible over a time scale of hours to days. At least five characteristic areas on the crystal were imaged and their locations were noted so that they could be revisited after the oxidation treatments. Reoxidation was accomplished by heating the crystals in air in a muffle furnace at 400 °C. The sample described in this report was first reduced for 8 min, then it was oxidized for times of 10, 20, 60 and 120 min. After each of the intervals, the characteristic areas were re-examined.

EXPERIMENTAL RESULTS

Cleavage of MoO₃ produces an (010) surface characterized by large (up to 2500 square microns) atomically flat terraces, separated by steps or groups of steps (See Fig. 1). These steps have edges which are primarily oriented parallel to [001] and heights that are an integer multiple of 7 Å. (7 Å = 1/2 b). Steps smaller than 7 Å are never observed. The evolution of this surface during reduction in forming gas has been described, in detail, in an earlier report [13]. The elements of this earlier study that are relevant to the present paper are reviewed briefly below.

Within 30 s of reaction in H₂, small steps oriented parallel to [001] are found to cover the entire surface. These steps have an irregular spacing and heights on the order of 2 Å, far smaller than any step ever observed on the fresh cleaved surface. These defects are found on all surfaces heated above 350 °C for at least 30 s and with increasing reaction time, their density increases. Based on evidence presented in earlier publications, these steps (see Fig. 2a) have been identified as the lines along which crystallographic shear (CS) planes intersect the (010) surface [13, 15, 16]. CS plane formation in MoO₃ has been studied by others; the defects form to compensate the loss of oxygen that occurs when the molybdate reacts with H₂ to form H₂O and MoO_{3-x} [11,12]. According to the earlier TEM work, the defects nucleate at the surface and extend into the bulk of the crystal by climb of their bounding partial dislocations [11,12]. The AFM images are consistent with this result.

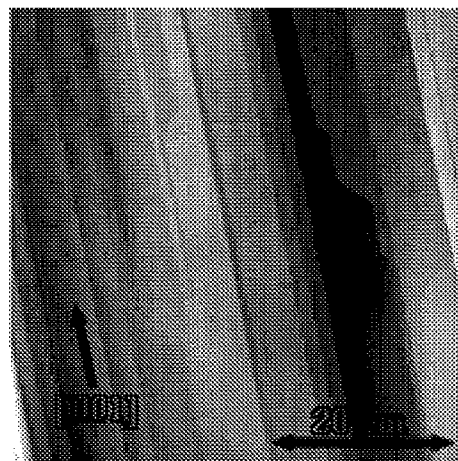


Figure 1. Topographic AFM image of a freshly cleaved $\text{MoO}_3(010)$ surface. Note the predominance of $[001]$ oriented steps edges in this region. The black-to-white contrast represents approximately 200 Å of vertical displacement.

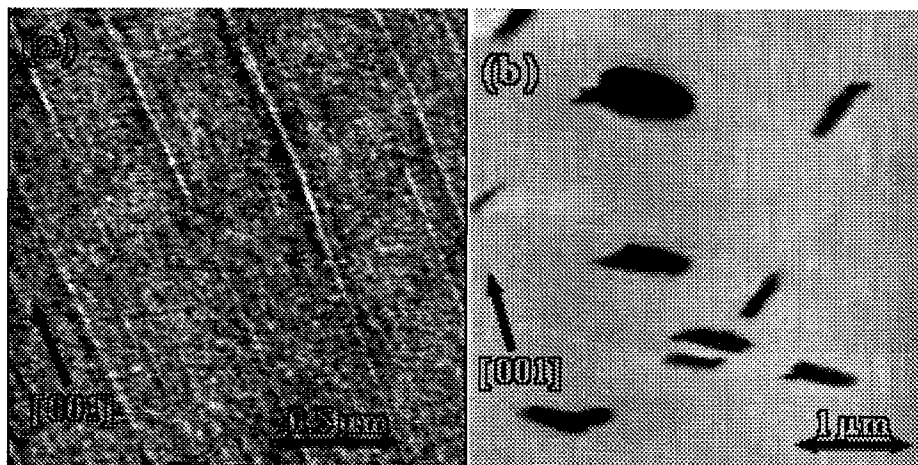


Figure 2. Topographic AFM images of the $\text{MoO}_3(010)$ surface after reaction with forming gas for 5 min at 400 °C. (a) Intersection of CS planes with the surface. (CS planes are the bright contrast parallel to $[001]$). The black-to-white contrast represents 6 Å of vertical displacement. (b) Black contrast indicates topographically lower positions on the surface, which we refer to as voids or pits. The black-to-white contrast represents approximately 100 Å of vertical displacement. Note the orientational order and high aspect ratio of these features.

The second change is that voids (pits) nucleate on the basal (010) terraces as well as at step edge sites. These voids are initially quite small, with diameters less than 400 Å and depths on the order of 50 Å. With increasing reaction time, the voids grow

(becoming larger and deeper) and their edges show a preferential orientation nearly parallel to $\langle 101 \rangle$ type directions (Fig. 2b). It has been shown that water vapor (present either as an impurity or a reaction product) catalyses this void formation and growth [13]. Below 350°C , the reaction with molecular H_2 is so slow that no changes in surface structure are observed, even after reaction times in excess of six hours. In the presence of atomic H, however, a low temperature reduction reaction does occur. The structural changes that accompany this reaction will be described in a forthcoming paper.

The reoxidation of reduced crystals caused morphological changes in both the CS planes and the voids on the (010) surface. The 10 and 20 min oxidation treatments at 400°C had no discernible effect on the surface structure of a crystal that was first reduced in flowing forming gas for 8 min at 400°C . Figure 3 shows the CS planes that remain on the surface after 30 min at 400°C in air. However, after the sample was heated for an additional hour at 400°C the CS planes had vanished from this area and, in fact, from all areas studied. A flat, featureless surface was left behind after the CS planes disappeared. Further study, however, will be necessary to identify the exact time that is required for the annihilation of the CS planes.

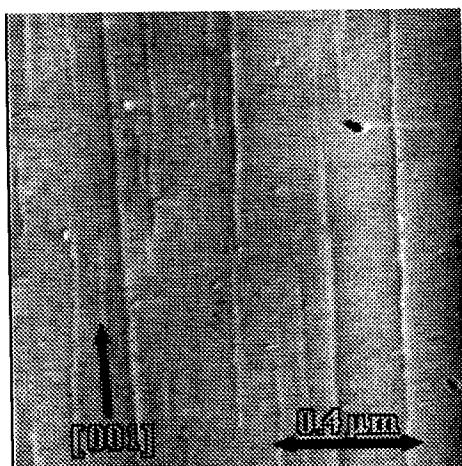


Figure 3. AFM topograph of reduced $\text{MoO}_3(010)$ after reoxidation in air at 400°C for 30 minutes showing the persistence of CS planes. The black-to-white contrast represents 10 \AA of vertical displacement.

As with the CS planes, very little change is evident in the voids after the first treatments of 10 and 20 minutes. However, after an additional hour at 400°C , distinct, morphological changes are apparent. The depths of the voids increase by up to 300 \AA and their edges begin to show faceting parallel to $\langle 001 \rangle$ and $\langle 100 \rangle$ directions. After an additional treatment for 2 hours at 400°C , the voids become larger (up to 6 microns in length) and deeper (up to 2000 \AA) and assume rectangular shapes bounded by $\{001\}$ and $\{100\}$ planes, as shown in Fig. 4. Additionally, step edges show signs of erosion and faceting to $\{001\}$ and $\{100\}$. Although the

void edges are oriented parallel to $\langle 001 \rangle$ and $\langle 100 \rangle$, there is a high aspect ratio and $\langle 001 \rangle$ edges are clearly preferred (Fig. 5). These results indicate that treatment in air at 400°C causes additional voiding, as well as a complete re-orientation of the void edges. Finally, we should note that when a fresh cleaved surface is heated in the same conditions, but without the reducing pre-treatment to nucleate the voids, the (010) surface is stable and no voids formed. Under these conditions, only a very small amount of the surface volatilizes in the vicinity of step edges and surface/dislocation intersections.

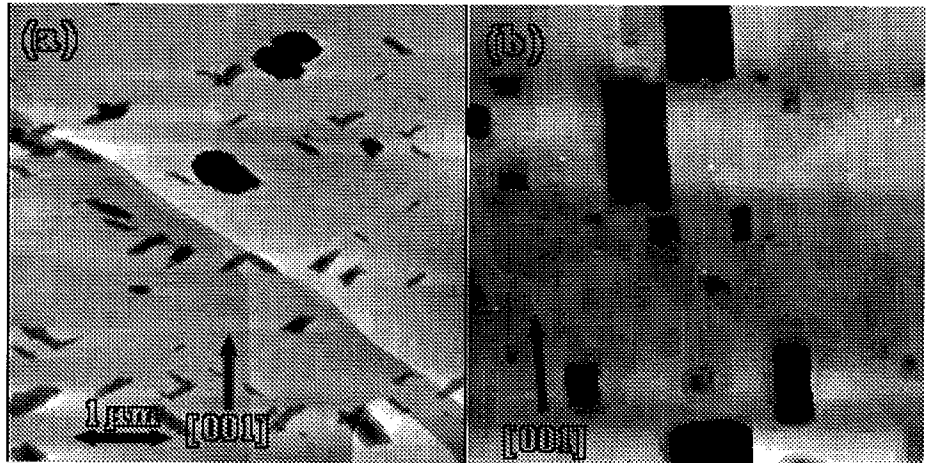


Figure 4. AFM topographs of the (010) surface illustrating the growth and faceting of voids during reoxidation. (a) shows an area after reduction in forming gas for 8 min at 400°C while (b) shows the same area after being oxidized in air at 400°C for 3.5 hours. Both images are 5×5 square microns. In (a), the black-to-white contrast represents 200 \AA of vertical displacement and in (b), 1000 \AA .

DISCUSSION

Reoxidation of H_2 reduced $\text{MoO}_3(010)$ surfaces in air results in distinct changes in the surface structure. Complete reoxidation takes up to 1.5 hours and results in the annihilation of the CS planes at the surface. The 2 \AA surface steps associated with the CS planes disappear when the defects are annihilated and the atomically flat (010) terraces, characteristic of the fresh cleaved surface, return. However, the terraces are not completely restored since the voids introduced during the H_2 reduction persist and, in fact, grow during the treatments in air.

The results of these reoxidation experiments show that reduction in forming gas proceeds more quickly than oxidation in air. It took between 0.5 and 1.5 hours in air at 400°C to reoxidize the defects created in 8 min at the same temperature in H_2 . The surface steps associated with the CS planes persist because the step can only be annihilated when the CS plane climbs out of the crystal. This non-conservative process requires O vacancies to diffuse from the line where the CS plane ends in the

bulk to the surface, where they are consumed by oxygen adatoms [11,12]. This is the reverse of the CS plane formation process, where oxygen vacancies are created at the surface and then diffuse to the end of the defect plane. Although there are certainly structural differences that might influence the rate of diffusion, we think that the slower oxidation kinetics are explained by the difference in driving force. During the reoxidation experiments, the chemical potential gradient is defined by lattice O in the crystal and O₂ in the surrounding gas phase. During reduction, on the other hand, the chemical potential gradient is defined by O in the crystal and H₂O in the gas phase. The latter gradient is certainly larger and is probably responsible for the faster reduction kinetics.

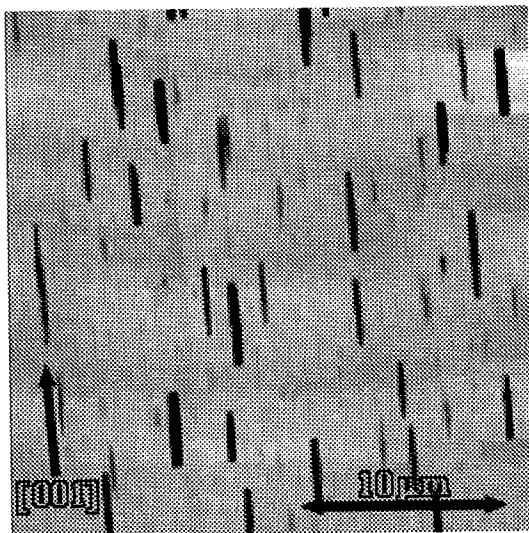


Figure 5. 50 x 50 μm² AFM topograph of the MoO₃(010) surface after reduction for 8 min at 400 °C and reoxidation for 3.5 hours at the same temperature. The black-to-white contrast represents 1000 Å of vertical displacement.

The persistence and growth of the surface voids during the air treatments conforms to the water-catalyzed evaporative process proposed earlier [13]. However, the reorientation of the void boundaries and faceting of irregular steps, to <001> and <100> directions, was not anticipated. This implies that the composition of the gaseous environment influences the relative stability of the different surfaces during volatilization.

Because water vapor cannot be completely excluded from the reactor (it will at least be present to some extent as a deep oxidation product), the voiding process described here will be active during reactions catalyzed at temperatures ≥ 400 °C. Therefore, mechanistic models for surface structure sensitivity must account for the presence of the new surface planes introduced by the voids. Since the volatilization

process does not occur below 350 °C, it may be possible to influence the selectivity of catalytic reactions occurring below this temperature through high temperature treatments that create the well-defined void structures described here.

CONCLUSIONS

Reoxidation of the H₂ reduced MoO₃(010) surface caused changes in both the CS planes and the surface voids created during the reduction reaction. Complete reoxidation in air takes at least four times as long as reduction in N₂ - 10% H₂ at the same temperature (400 °C) and is accompanied by annihilation of the CS planes at the surface. During reoxidation at 400 °C, surface voids continued to grow and their bounding planes are re-oriented from {101} to {100} and {001}.

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