
ADSORPTION INTERACTION OF OXYGEN WITH Mo(110) SURFACE: KINETICS, STRUCTURE, AND CHEMICAL TRANSFORMATIONS

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The formation of an oxide layer on the Mo(110) surface is investigated with the help of low-energy electron diffraction (LEED), Auger spectroscopy, thermodesorption spectroscopy, and the contact potential difference method. The potential barrier for oxygen atoms moving in the subsurface region is calculated in the framework of the density functional theory (DFT). The DFT calculations have shown that oxygen penetrates under the surface layer near step boundaries. An oxide monolayer is formed at a temperature of approximately 800 K under conditions of a sufficient surface concentration of oxygen.

1. Introduction

The adsorption of oxygen at the surfaces of transition metals and the formation of oxide layers play an important role in corrosion processes and surface catalytic reactions. For example, it is known that the Ru(0001) surface is rather passive with respect to the catalytic reaction of CO oxidation, whereas ruthenium oxide represents one of the best catalysts of this reaction [1]. In turn, Mo oxides are widely used as catalysts of various oxidation reactions of hydrocarbons [2] and, though there are no convincing evidences of their activity as respects to CO oxidation, the compounds based on molybdenum oxides are promising for this catalytic reaction as well.

The Mo(110) surface of a Mo crystal is the most close-packed one, which results in its high stability with respect to the surface reconstruction. Thus, the structure of this surface remains practically invariable in the case of the adsorption of hydrogen and various electropositive elements (i.e. those resulting in the reduction of the work function). In the case of the oxygen adsorption at a substrate temperature lower than 700 K, the surface also is not reconstructed in spite of the strong interaction (the oxygen adsorption energy at low coverages θ amounts to 6.99 eV [3]), which determines the dissociative character of oxygen adsorption even at the liquid-helium temperature [4]. At the same time, at large exposures

of oxygen and at temperatures higher than 750 K, one observes the formation of a surface layer of molybdenum oxide that evidently has a structure corresponding to the (100) surface of MoO₂ [5].

A large interest in the surfaces of Mo oxides gave rise not only to versatile experimental investigations of their properties but also to theoretical calculations of the optimal structures of the interface between the Mo(110) surface and the MoO₂ epitaxial layer. Nevertheless, the important peculiarities of the oxygen-surface interaction require further investigations aimed at the clarification of regularities of the formation of the oxide layer and its catalytic properties. In particular, according to the generally accepted concepts, oxygen does not dissolve in the bulk of Mo, but the formation of oxide at the surface calls for the penetration of oxygen at least under the Mo surface layer. Such a penetration seems to be surprising with regard for the fact that oxygen adsorbed at the Mo(110) surface desorbs (in the atomic form) at a very high temperature (~ 2000 K), but no oxides are formed in this case [6].

In this work, we investigate the formation of an oxide layer on the Mo(110) surface with the help of diffraction, Auger spectroscopy, thermodesorption spectroscopy, and the contact potential difference method and also present the results of DFT calculations of the potential relief for the motion of oxygen atoms in the subsurface layer.

2. Procedure

The investigations were performed in an ultrahigh-vacuum metal device that allows one to measure thermodesorption spectra in the “black camera” mode, i.e. molecules reflected from the walls of the device cannot get to the collector of a quadrupole mass spectrometer. In order to observe the low-energy electron diffraction, we used a three-grid hemispherical system, while Auger spectra were obtained with the help of a

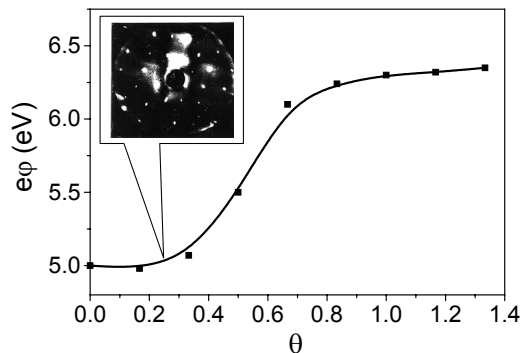


Fig. 1. Dependence of the work function on the O covering at the Mo(110) surface. The inset shows the LEED image of the $c(2 \times 2)$ structure corresponding to the covering $\theta = 0.25$

cylindrical mirror analyzer. A detailed investigation of the structural transformations in the system and the corresponding changes in the work function were fulfilled in a sealed-off glass device equipped with an analogous LEED system and a mobile electron gun for precision measurements of the contact potential difference. The clamping construction of samples in the both devices allowed us to cool them to the liquid-nitrogen temperature and to heat up to 2400 K. The residual gas pressure in the both devices was 10^{-11} Torr. The purity of the Mo(110) surface was controlled with the help of Auger spectroscopy and confirmed by a high quality of the LEED images. The oxygen source in the device used to study the adsorption allowed us to obtain a well-collimated molecular beam directed immediately onto the sample surface.

The calculations were performed in the framework of the DFT (ABINIT software packet [7]) with the use of GGA-pseudopotentials [8, 9]. The quality of the potentials was verified, by estimating the lattice constant for the Mo crystal as well as the bond length and the binding energy in an oxygen molecule. The convergence of the total energy with respect to the number of special points in the Brillouin zone and the number of plane waves in the expansion of the wave function was not worse than 0.002 Ry. In order to estimate correctly the energy of an oxygen atom, whose ground state corresponds to the triplet state, and the binding energy in an oxygen molecule, the calculations were performed with regard for the spin polarization. The obtained value of the binding energy in the molecule, 5.33 eV, corresponds well to the known experimental value of 5.13 eV [9].

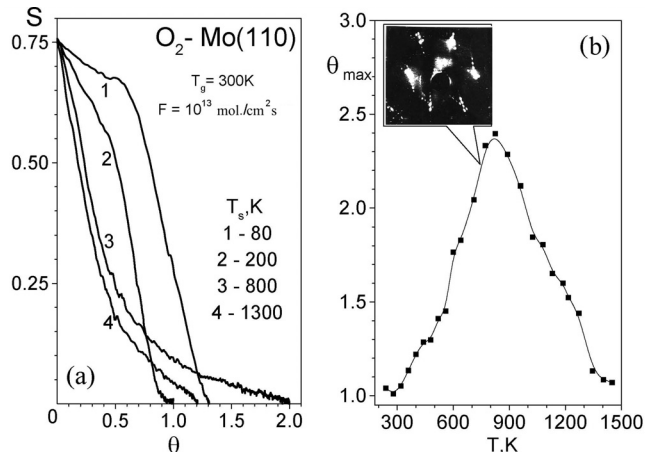


Fig. 2. (a): Dependence of the sticking coefficient on the O coverage on the Mo(110) surface. (b): Limiting covering of oxygen as a function of the surface temperature. The inset shows the LEED image typical of the formed oxide layer

3. Results and Discussion

The adsorption of oxygen results in an increase of the work function (except for the region of initial coverages below $\theta = 0.2$, where one observes a slight reduction of the work function) (Fig. 1). In the case of the gradual growth of the oxygen coverage degree, a number of structures (investigated in detail in [10–12]) are formed at the Mo(110) surface, by starting with the $c(2 \times 2)$ structure that is easy-to-use for the determination of the coverage degree, since it corresponds to $\theta = 0.25$ (its diffraction image is demonstrated in the inset in Fig.1) and by finishing with the formation of a complete monolayer with the structure (1×1) ($\theta = 1$). It is worth noting that the oxygen adsorption at 77 K does not result in the formation of ordered structures. Apparently, it is caused by the restricted mobility of atoms on the surface. That is why the formation of structures requires the heating of a sample approximately to room temperature. The long-term adsorption of oxygen at a sample temperature higher than 750 K results in the formation of a LEED image typical of a molybdenum oxide film at the Mo(110) surface [5] (see inset in Fig. 2).

The results of investigations of the adsorption kinetics obtained with the use of the molecular beam technique at various temperatures of the surface and the constant flow of oxygen $F = 1.5 \times 10^{13}$ molecules/($\text{cm}^2 \cdot \text{s}$) (which corresponds to the adsorption of nearly 0.02 monolayers per second) are presented in Fig. 2, a in the form of a series of dependences of the sticking coefficient S on the coverage. The initial sticking coefficient S_0

does not depend on the substrate temperature in a wide temperature range. This fact probably testifies to the direct or Langmuir character of adsorption without participation of intrinsic pre-states. At a surface temperature between 300 K and 1300 K, the direct type of adsorption is also conserved at large coverages, which is confirmed by the form of the dependences $S(\theta)$ typical of the Langmuir isotherms for dissociative adsorption ($S \approx (1 - \theta)^2$). At a temperature of 77 K, the reduction of S with increase in the coverage essentially decelerates, and there appears a characteristic shoulder at the $S(\theta)$ curve typical of the adsorption with participation of extrinsic pre-states. At a temperature of 200 K, the dependence $S(\theta)$ still differs substantially from the Langmuir one.

Thus, the deviation from the direct type of the adsorption toward that with participation of pre-states is observed exactly at the temperatures, at which the mobility of oxygen adatoms on Mo(110) is restricted (according to our LEED data). Probably, the restriction of the mobility of adsorbed oxygen atoms creates such conditions, under which an essential part of the surface remains free and is consequently available for the dissociation of oxygen molecules with their further adsorption. This fact also explains an increase of S at low temperatures as compared to its values at room one. Such a behavior of the system can be explained by the temporary capture of oxygen molecules from the gas phase to the so-called extrinsic pre-states that correspond to the adsorption of oxygen molecules over a monolayer of chemisorbed oxygen atoms [13]. At a temperature of 77 K, the lifetime of a molecule captured in an extrinsic pre-state is small, since the corresponding peak of thermodesorption is observed at a temperature close to 45 K [13]; nevertheless, it can be sufficient for a molecule moving along the surface to find a place for dissociation. At a higher temperature, this time shortens, which results in a decrease of the sticking coefficient [14]. In the case where oxygen getting to the surface cannot find free centers for adsorption, S decreases up to zero, and the molecular flow coming from the surface becomes equal to that falling onto the surface. In this case, a certain limiting coverage that essentially depends on the surface temperature at a given flow of incident molecules is reached (Fig. 2,b).

The formation of a surface oxide layer requires that oxygen atoms penetrate under the surface Mo(110) layer. This layer is formed only in the case of heating above 750 K, which is proved by the LEED results (see the inset in Fig. 2), and the presence of desorption peaks of oxides in the region above 1000 K (Fig. 3). Such a

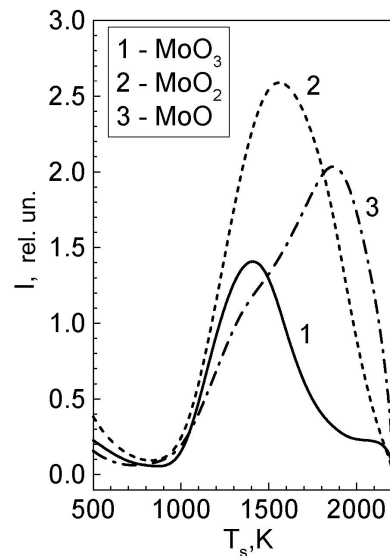


Fig. 3. Thermodesorption spectrum of molybdenum oxides

penetration under the surface results in the appearance of an additional channel for the capture of oxygen atoms, which can explain an essential increase of the boundary coverage at this temperature (Fig. 2,b). It is important to mention that, at $T = 800$ K, the desorption of an oxide layer, which results in a decrease of θ_{\max} at high temperatures, is still absent (Fig. 3).

In order to clarify the mechanism of penetration of oxygen atoms under the Mo(110) surface, we calculated the potential barriers in the framework of different models. First of all, we tested the possibility of the penetration through the ideal surface. Primarily, oxygen atoms were located at the centers with the threefold symmetry, which is optimal for all structures of oxygen adsorbed on Mo(110) [3]. After that, oxygen atoms were forcibly shifted (with an increment of 0.2 Å) toward the crystal bulk. In this case, we optimized the structure after each movement, so that the atoms of three Mo(110) subsurface layers had a possibility for the relaxation, and calculated the energy of the system. After surmounting the 4.9-eV potential barrier mainly caused by the shift of the atoms of the upper Mo(110) layer due to the repulsion by the oxygen atom, oxygen atoms settle at places with the threefold symmetry that correspond to the most energy-gained positions. The further penetration of oxygen to the bulk of the crystal appears to be practically impossible, as the corresponding deformation of the second Mo layer requires very high power inputs. At the same time, the estimated barrier for the diffusion of oxygen atoms along the surface below the upper Mo layer amounts to only

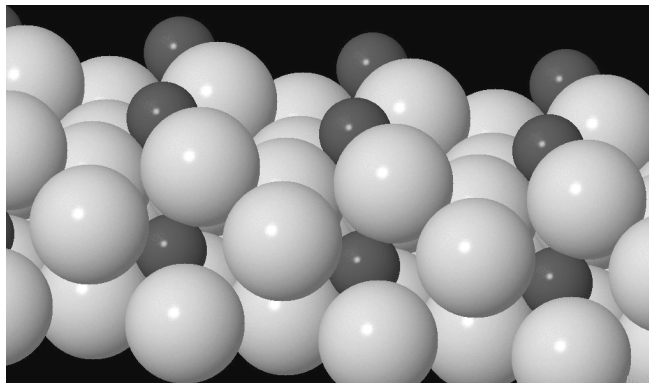


Fig. 4. Calculated equilibrium structure of the oxide layer formed by the O monolayer under the Mo(110) surface and the adsorbed oxygen monolayer. Small dark-grey balls depict O atoms, large light grey – Mo ones

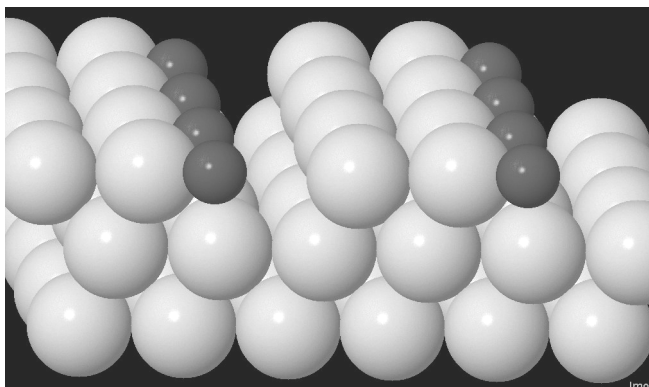


Fig. 5. Steps on the Mo(110) surface with oxygen atoms located near them

0.13 eV. This means that, after the penetration under the Mo surface, oxygen atoms can fill the whole interface monolayer that forms, together with the monolayer of adsorbed oxygen, the surface oxide layer (Fig. 4). The total concentration of oxygen atoms in the latter corresponds to $\theta = 2$, which agrees with the experiment.

Obviously, oxygen atoms can penetrate under the surface at places, where the necessary shift of Mo atoms requires a less energy, for example, at the boundaries of atomic terraces. In order to simulate the penetration of oxygen under the surface, we chose a periodic system of Mo(110) steps with oxygen atoms located near them (Fig. 5). The potential barrier for the motion under the surface layer of a step appeared to be ~ 3.5 eV. However, the immersion of oxygen atoms located at a step close to its edge turned out to be even more convenient. In this case, the extreme molybdenum atom shifts along the surface setting the way for the oxygen atom free

and after that moves in the opposite direction somewhat shifting from the surface and covers the immersed oxygen atom. The height of the potential barrier for this way of the penetration amounts to only 2.8 eV, and its surmounting by oxygen atoms at a temperature of 800 K is quite possible.

4. Conclusions

According to the LEED data, an oxide layer is formed at a temperature close to 800 K under the condition of a sufficient surface concentration of oxygen. The calculations with the help of the density functional technique have demonstrated that oxygen penetrates through a surface layer near the boundaries of terraces, subsequently propagates along the surface, and forms the interface necessary for the creation of an oxide layer. An important role in the processes of penetration under the surface and diffusion of oxygen under the upper Mo(110) layer is played by the corresponding shift of Mo surface atoms.

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АДСОРБЦІЙНА ВЗАЄМОДІЯ КИСНЮ З ПОВЕРХНЕЮ
Mo(110): КІНЕТИКА, СТРУКТУРА, ХІМІЧНІ
ПЕРЕТВОРЕННЯ

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Резюме

Представлено результати дослідження формування оксидного шару на поверхні Mo(110) за допомогою дифракції повільних

електронів (ДПЕ), оже-спектроскопії, термодесорбційної спектроскопії, контактної різниці потенціалів, а також розрахунків (в рамках теорії функціонала електронної густини) потенціального бар'єра для руху атомів кисню в приповерхневій області. Розрахунки методом функціонала електронної густини показали, що кисень проникає під поверхневий шар поблизу границь атомних терас. Оксидний шар утворюється при температурі близько 800 К за умови достатньої поверхневої концентрації кисню.