FORMATION OF A NANOLAYER OXIDE FILM ON THE Mo(110) SURFACE

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PACS 34.35.+a
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The process of formation of an oxide layer on the Mo(110) surface is investigated using the techniques of molecular beam (MB), temperature-programmed desorption (TPD), and Auger-electron spectroscopy (AES). It is established that this process consists of two stages: the fast and slow ones are characterized by exposures close to 100 L and those of the order of 10^4 L, respectively. At the first stage, a chemisorbed monolayer of oxygen atoms is formed. In this case, the TPD spectrum includes only atomic oxygen and inessential traces of oxides with a maximum at 2000 K. An oxide nanolayer starts to be formed after the end of the first stage, and only a small share of O_2 molecules incident to the surface (according to estimations, 10^{-8}–10^{-5} depending on the sample temperature) takes finally part in the formation of oxide molecules. The rate of formation of the oxide film grows, as the substrate temperature increases from 300 to 1000 K. At exposures $\geq 10^5$ L and a sample temperature of 900 K, we managed to form up to 4 oxide monolayers. This process goes on and shows no signs of complete saturation. In the TPD spectrum of the formed layer, one observes MoO, MoO_2, and MoO_3 oxides, whose peaks are located close to 1500 K, as well as a peak of atomic oxygen accompanied by a very insignificant oxide peak at 2000 K. The analysis of the TPD spectrum has revealed the first order of the desorption reaction, which testifies to the desorption of "ready" compounds, rather than their formation in the process of desorption with increase in the temperature. The presence of an oxide layer on the surface of the sample is also confirmed by the attenuation and bifurcation of the LMM Auger-peak of molybdenum.

1. Introduction

The "oxygen-molybdenum" adsorption system is the subject of a large number of works in the world scientific literature. Moreover, the interest in such systems and systems with other transition metals has significantly grown in the recent years (see for example [1–3]). It is due to the prospects of using metal oxides as a basis for the creation of effective catalysts. However, there remain a lot of unsolved problems concerning the process of formation of an oxide layer on the metal surface. For example, one has not yet established the exposures resulting in the formation of a large amount of oxide (of the order of a monolayer). There are available some contradictory data concerning this point.

For example, the authors of work [4], who studied the O_2-Mo(110) adsorption system with the help of the low-energy electron diffraction (LEED) technique, observed the formation of molybdenum oxide on the Mo(110) surface at exposures of 6000 L (1 L = 10^{-6} Torr·s). However, they did not adduce any data on the amount of the formed oxide. Work [5] is devoted to the investigation of the desorption kinetics of the atomic and oxide phases of the O_2–Mo(110) adsorption system depending on the exposure of a sample in the oxygen atmosphere. It is stated that, at exposures close to 300 L, there occurs the saturation of the amount of oxides formed on the Mo(110) surface. According to data [5], the number of oxide molecules formed in the saturation state is approximately equal to 10% of atomic oxygen on the surface in the same state. The composition of desorbed oxides was also established in this study: the thermodesorption spectrum includes MoO_3, MoO_2 is present in a somewhat less amount, whereas MoO is practically absent.

In [6], it is stated that nuclei of three-dimensional molybdenum oxides on Mo(110) are already observed at an exposure of 3.75 L. Here, the used investigation techniques were AES and LEED. But no information concerning the amount of the formed oxides is presented.

The authors of [7] believe the appearance of a new 740-cm^{-1} vibrational mode in the energy loss spectrum and the double increase of the ratio between the amplitudes of the Auger peaks O(KLL)/Mo(LMM) to be the evidences of the formation of an oxide layer in the case of the interaction of oxygen with the Mo(110) surface at 1000 K. This mode appears at exposures close to 1200 L, though no data on the amount of formed oxides are given in this study. No information of such a kind was also presented in [8], where the adsorptive O_2–Mo(110) system was investigated with the help of the diffraction of reflected high-energy electrons, AES, and LEED techniques.

In [9], the LEED, AES, and scanning tunneling microscopy (STM) techniques were used for the investigation of the initial stage of oxidation of Mo(110). The exposures of a sample in the oxygen atmosphere were close to 30 L at a temperature of the sample of 1250 K.
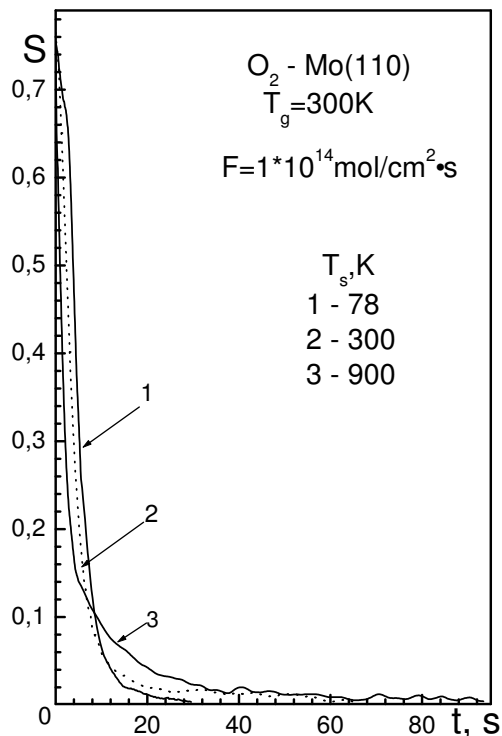
Fig. 1. Time dependences of the sticking coefficient $S(t)$

cess of formation of the oxide layer, remain urgent till now.

2. Experiment

We used a Mo(110) single crystal with a surface deviation from the (110) plane lower than $0.1°$. The sample was located in an ultrahigh-vacuum set-up of the "black chamber" type, where the residual gas pressure was lower than 10^{-10} Torr. The set-up allows one to apply the MB, TPD, LEED, and AES techniques. The construction of the set-up and the technique of experimental investigations are described in [13].

The Mo samples were first cleaned according to the standard procedure. It consists in the annealing of a sample in the O_2 atmosphere at a pressure of 1×10^{-6} Torr with the following flashes up to 2400 K necessary to remove oxygen and surface oxides [4]. The surface purity was controlled with the help of the AES and LEED techniques. The sample was heated, by bombarding its backside by an electron beam, whereas its temperature was measured with the help of a tungsten-rhenium thermocouple and an optical pyrometer. The temperature of the sample T_S in the process of adsorption was equal to some value in the range between 78 and 2400 K. During TPD, the linear heating rate of the sample with oxygen preliminary adsorbed at a certain exposure varied from 1 to 140 K/s.

The source of oxygen in the set-up allowed one to obtain a well-collimated molecular beam directed immediately at the surface of the sample. The intensity of the molecular beam was changed from 10^{12} mol/(cm^{2}s) to 3×10^{15} mol/(cm^{2}s). The temperature of the molecular-beam collimator T_g in the given investigations was constant and amounted to 300 K.

3. Results and Discussion

Figure 1 demonstrates the sticking coefficient S as a function of the adsorption time at the flow of oxygen molecules from the MB source equal to $\sim 10^{14}$ mol/(cm^{2}s) at several temperatures of the sample T_s. Similar dependences on the coverage of the surface were presented in our previous work [14]. Our apparatus allowed us to measure the sticking coefficients down to $S_{\min} \sim 10^{-3}$. That is why the decrease of the sticking coefficient to the indicated value can be considered as a saturation of the surface with oxygen (though conditional, as will be seen below). From Fig. 1, one can see that, at the flow of oxygen molecules from the MB source equal to $\sim 10^{14}$ mol/(cm^{2}s), the sticking coefficient falls

Moreover, there were observed LEED structures that were considered as those caused by an oxide layer (the same way as in the other adduced studies using LEED). Combining the LEED results with the analysis of STM images, the authors concluded that a layer of MoO_2 oxide was formed on the adsorbent surface. Works [9–12] stated that it is MoO_2 that is grown epitaxially on the Mo(110) surface.

As one can see from what was said above, there is no common opinion concerning the stage of oxygen adsorption on the Mo(110) surface, at which the oxide is formed, and the exposures of a sample in the oxygen flow resulting in the formation of a noticeable amount of the oxide. In all the considered works except for [5], there is no information on the amount of the oxide formed on the Mo(110) surface, as well as whether the process of its generation has attributes of saturation. The same uncertainty is inherent to the composition of the oxide film. For example, in [9–12], it is stated that the only compound that forms an oxide film on the Mo(110) surface is MoO_2, whereas the authors of [5] observed MoO_2 and MoO_3 within the thermodesorption technique (moreover, MoO_3 was observed in a larger amount). That is why the investigations of the O_2–Mo(110) adsorption system, in particular the pro-

to S_{min} during a rather short time interval dependent on T_s. For example, at $T_s = 78$ K, S_{min} is reached in 25 s, whereas at $T_s = 900$ K – in 90 s. For convenience, we called this stage of the adsorption fast. The analysis of the TPD spectra measured at this stage of the adsorption allows one to make several generalizing conclusions. The TPD spectra measured as functions of the adsorption time at all T_s manifest an increasing peak of atomic oxygen that reaches saturation as the sticking coefficient becomes equal to S_{min}. At the same time, TPD reveals a very inessential amount of molybdenum oxide molecules – <1% of the number of desorbed oxygen atoms. The TPD spectrum of the adsorbed film saturated with oxygen in such a way is given in Fig. 2. The considered spectra were obtained at the linear heating rate equal to 100 K/s.

The amount of oxide molecules was calculated taking several factors into account. First, the desorbed flow of oxides was detected for the Mo^{98} isotope, whose share in the isotopic composition of molybdenum amounts to 23.75% [15], and it was necessary to evaluate the shares of oxide molecules for the rest of Mo isotopes. Second, we should consider the difference between the probabilities of ionization of atomic oxygen and molybdenum oxide molecules in the ion source of a mass spectrometer. According to [16], the probability of electron impact ionization depends on the total number of electrons at atomic or molecular orbitals. The number of oxide molecules was approximately calculated with regard for these two factors.

Thus, at the oxygen flow from the MB source $\sim 10^{14}$ mol/(cm^{2}s), the formation of a chemisorbed layer of oxygen atoms takes approximately 90 s. Moreover, an increase of the exposure of the sample in the oxygen flow over 90 s does not result in the growth of the amount of desorbed oxygen atoms, i.e. the number of chemisorbed oxygen atoms reaches saturation. The exposure in the adsorbate flow will be determined in the Langmuir units (L). That is, an exposure equal to 1 L corresponds to the stay of the investigated surface in the adsorbate atmosphere with a pressure of 1×10^{-6} Torr during 1 s. According to [16], a flow equal to 10^{14} mol/(cm^{2}s) for oxygen corresponds to a pressure of 3×10^{-7} Torr. Thus, the saturation of the chemisorbed oxygen phase in our investigations is reached at the exposure of a Mo(110) sample in the oxygen flow close to 30 L. This result agrees with data in [5], where the saturation of the chemisorbed oxygen layer on the Mo(110) surface was observed at similar exposures.

Now let us return to the consideration of the oxide peaks (Fig. 2). One can see that their temperature posi-
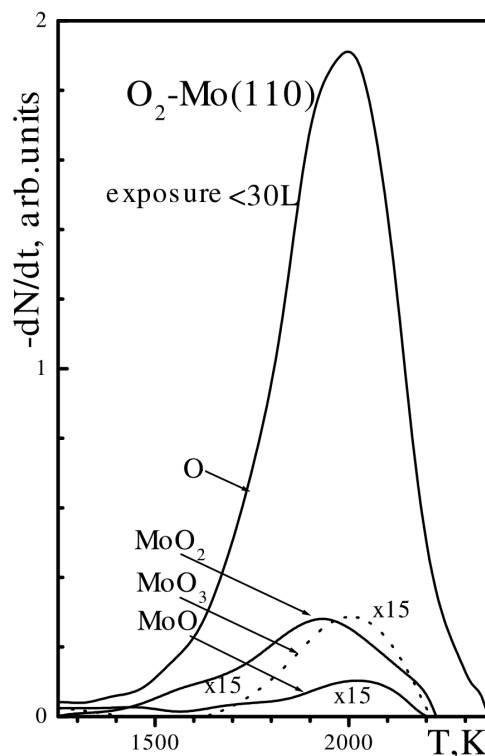

Fig. 2. TPD spectrum of the adsorbed film saturated with oxygen at exposures below 30 L. The linear heating rate is 100 K/s

tion coincides with that of the atomic oxygen peak, and the saturation of the latter corresponds to the saturation of the oxide peaks as well. We suppose that the appearance of these oxide peaks is caused by the interaction of some inessential part of oxygen atoms with molybdenum in the TPD process and the formation of molybdenum oxide molecules; however, they do not testify to the presence of oxides before the TPD process.

Thus, at exposures close to 30 L, we did not observe the formation of molybdenum oxides on the Mo(110) surface. Therefore, if they are still generated, the rate of their formation or the part of oxygen molecules participating in the process of oxide generation on the surface must be lower than 10^{-3}, i.e. lower than the limitedly possible measurable sticking coefficient. Under such conditions, a noticeable oxide film on the surface can be formed only in the case of an essential increase of the exposure.

The TPD spectrum of the oxide film formed at $T_s = 300$ K and an exposure of 4×10^5 L is presented in Fig. 3. The linear heating rate in the course of TPD was equal to 100 K/s. One can see that, in addition to the above-discussed peaks close to 2000 K, there appeared oxide peaks at a temperature close to 1500 K. One observes
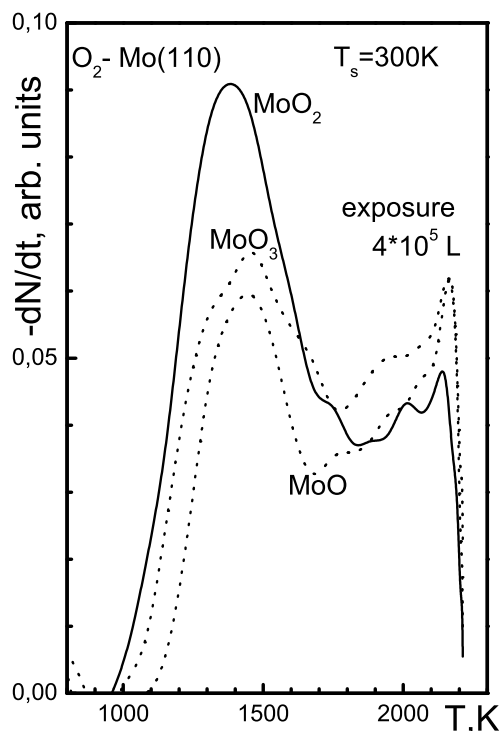
Fig. 3. TPD spectrum (oxides) of the film formed at an exposure of 4×10^5 L. The sample temperature T_s=300 K. The linear heating rate is 100 K/s
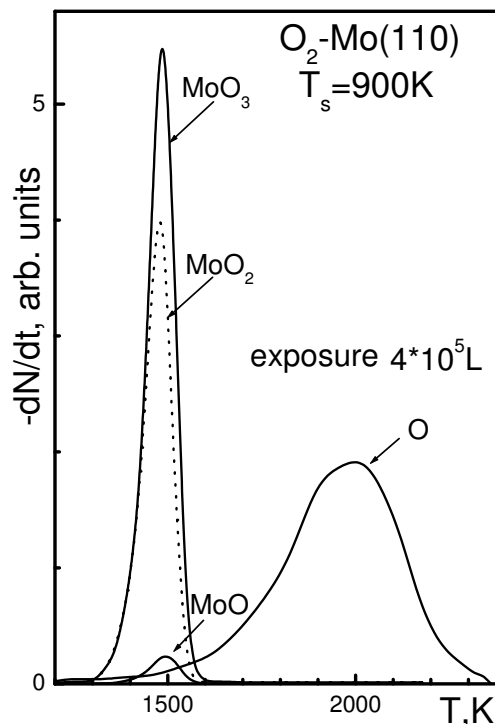

Fig. 4. TPD spectrum of the film formed at an exposure of 4×10^5 L. The sample temperature T_s=900 K. The linear heating rate is 100 K/s

desorption of three kinds of oxide molecules – MoO_3, MoO_2, and MoO. However, the number of desorbed oxide molecules in this case is also rather small – lower than 1% of the number of desorbed oxygen atoms. The calculated probability for the capture of oxygen molecules from the flow to this oxide state amounts to 10^{-8}.

An increase of the temperature of the sample results in an abrupt change of the situation. The TPD spectrum of the adsorbed film saturated with oxygen at $T_s = 900$ K and an exposure of 4×10^5 L is given in Fig. 4. One can see that the areas under the peaks of oxide molecules significantly increased and became comparable to that under the peak of atomic oxygen. We calculated that the number of oxide molecules formed at such an exposure and such a temperature of the sample exceeds the number of desorbed oxygen atoms approximately by a factor of 4. Moreover, a further increase of the exposure results in the growth of the number of desorbed oxide molecules, i.e. there is no limiting saturation of their amount (as it was for desorbed oxygen atoms). The calculated probability for the capture of oxygen molecules to the oxide state at a sample temperature of 900 K amounts to 10^{-5}. This value is one thousand-fold greater than that at $T_s = 300$ K. That is, the process of capture

of oxygen molecules to the oxide state of the adsorption is of activated nature.

An important question concerns the correspondence between the composition of thermodesorbed molybdenum oxides and that of the adsorbed oxide film. Does the observed composition of the oxides reflect the structure of the adsorbed layer or are the oxides formed with increase in the temperature during measurements of thermodesorption spectra? In our opinion, the answer to this question can be found by analyzing the TPD spectra of the oxides obtained from the Mo(110) sample saturated with oxygen at different exposures. If there occurs the thermodesorption of ready compounds, then it is worth expecting the first-order thermodesorption reaction. In the case of associative desorption, i.e. the formation of oxide compounds exactly in the desorption event, we obtain its second order. This order is characterized by a symmetric form of TPD curves regardless of the coverage of the surface (θ), while an increase of θ results in a shift of the TPD peak toward lower temperatures. At the same time, the first-order desorption is characterized by an asymmetric form of the curves and the independence of a position of the TPD peak on θ in the absence of lat-
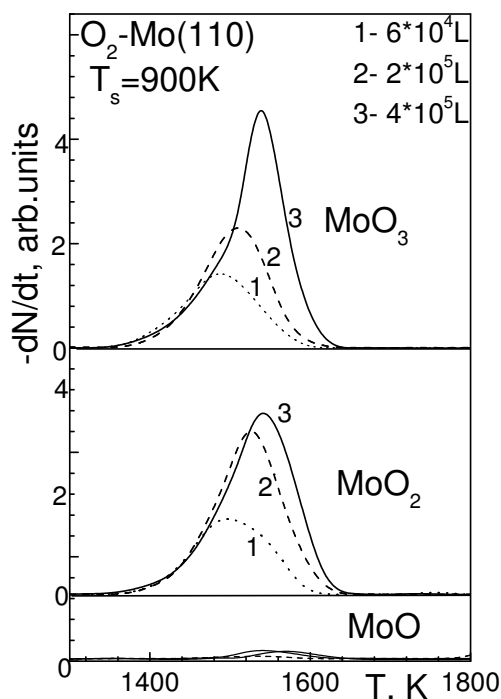
Fig. 5. TPD spectra for oxides depending on the exposure of the sample in the oxygen MB at $T_s = 900$ K. The linear heating rate is 100 K/s

Fig. 6. Auger spectra depending on the exposure of the sample in the oxygen MB at $T_s = 900$ K

eral interactions between adsorbate particles in the adlayer [17].

Figure 5 shows the TPD spectra of the oxides measured after various exposures of the sample at a temperature of 900 K in the oxygen flow. One can see that the TPD peaks of the oxides from the adsorbed layers formed at all exposures have an asymmetric form. With increase in the exposure of a sample in the oxygen flow (which is equivalent to the growth of θ), one observes that the oxide peaks in the corresponding TPD spectra shift toward higher temperatures, which testifies to the presence of lateral attractive interactions between oxide molecules in the adsorbed layer. Thus, we have grounds to state that the TPD spectrum reflects the composition of the adsorbed oxide film, and oxide molecules are desorbed in the same form they had on the surface before the TPD process.

The statement that oxides are formed on the surface in the process of adsorption rather than due to thermal transformations is also confirmed by the data of Auger investigations. Figure 6 demonstrates the Auger spectra obtained for the clean Mo(110) surface and those saturated in the oxygen flow at 30 L and at 5×10^5 L. One can see that the formation of a chemisorbed layer of oxygen atoms does not result in essential changes of
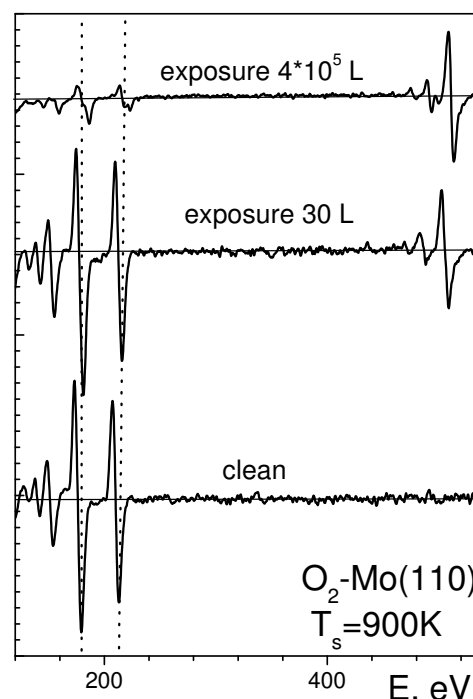
the Auger peaks of pure molybdenum. However, at an exposure of 5×10^5 L, the lines of pure molybdenum almost completely attenuate, which is explained by the screening of the Mo surface by several oxide monolayers. In turn, there appear Auger peaks that correspond, in our opinion, to Auger transitions of molybdenum in the oxide composition.

4. Conclusions

Thus, the performed investigations allow us to make the following conclusions.

– The process of formation of an adsorption film on the Mo(110) surface with participation of oxygen can be conditionally divided into two stages. The fast one (exposures below 100 L) which is characterized by the sticking coefficients from 0.75 to 0.001 corresponds to the formation of a chemisorbed layer; while the slow one (exposures of the order of 10^4 L) is the formation of Mo oxides. The latter stage of adsorption is characterized by the following sticking coefficients: $S = 10^{-8}$ at the substrate temperature $T_s = 300$ K and $S = 10^{-5}$ at $T_s = 900$ K.

– The TPD spectra of molybdenum oxides of an adsorbed film were obtained at various preliminary exposures varying from 0 to 10^5 L. Desorption of three

types of oxide molecules was observed – MoO_3, MoO_2, and MoO. At an exposure close to 10^5L, up to 4 layers of molybdenum oxides are formed on the Mo(110) surface. At all the used exposures, we did not observe any attributes of the limiting saturation of the amount of formed oxides.

– The analysis of the TPD spectra of the Mo(110) sample saturated with oxygen at increasing exposures has demonstrated that oxides are formed at the absorption stage rather than represent a product of the thermal transformation in the course of TPD. Such a conclusion is also confirmed by the data of AES investigations – attenuation and bifurcation of the LMM 186-eV peak of molybdenum caused by the screening of the Mo surface by several oxide monolayers, as well as the appearance of an Auger peak of molybdenum in the oxide composition.

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УТВОРЕННЯ НАНОШАРОВОЇ ПЛІВКИ ОКСИДУ НА ПОВЕРХНІ Mo(110)

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Р е з ю м е

Методами молекулярного пучка (МП), термодесорбційної мас-спектрометрії (ТПД), оже-електронної спектроскопії (ОЕС) досліджено процес формування оксидного шару на поверхні Mo(110). З'ясовано, що процес поділяється на дві стадії: швидку, для якої характерні експозиції близько 100 L, і повільну – експозиції порядку 10^4 L. На першій стадії формується хемосорбований моношар атомів кисню. Спектр ТПД при цьому містить лише атомарний кисень та незначні сліди оксидів з максимумом при 2000 K. Утворення оксидного наношару починається після завершення першої стадії, причому лише мала частка молекул O_2, що падають на поверхню (за оцінками 10^{-8}–10^{-5} залежно від температури зразка), в кінцевому результаті бере участь в утворенні молекул оксиду. Швидкість формування оксидної плівки збільшується при підвищенні температури підкладки від 300 до 1000 K. При експозиціях 10^5 L і температурі зразка 900 K вдалося сформувати до 4-х моношарів оксиду. Цей процес не виявляє ознак повного насичення, а продовжується і далі. У спектрі ТПД утвореного шару спостерігаються оксиди MoO, MoO_2, MoO_3, піки яких розташовані поблизу 1500 K, а також пік атомарного кисню в супроводі дуже незначного оксидного піка при 2000 K. Аналіз спектра ТПД виявив перший порядок реакції десорбції, що свідчить на користь десорбції "готових" сполук, а не їх утворення в процесі десорбції при підвищенні температури. Про наявність на поверхні зразка оксидного шару свідчить також згасання і розщеплення оже-піка LMM молібдену.