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## BINDING ENERGIES FOR CO ON CLEAN AND OXYGEN-MODIFIED Mo(110) SURFACE

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*The interaction of CO molecules with clean and oxygen-modified Mo(110) surface has been investigated by means of density functional (DFT) calculations. It has been found that on both clean and oxygen-covered Mo(110) surfaces CO molecules are tilted with respect to the normal to the surface and adsorbed near hollow sites. The presence of oxygen substantially reduces the binding energy of CO molecule with the Mo(110) surface and on oxygen-saturated surface the adsorption of CO occurs completely blocked. The presence of the preadsorbed oxygen atoms on the Mo(110) surface results in the appearance of the 19 eV peak in local densities of states. The peak position corresponds to the chemical shift of the 2s oxygen line with regard to the electron states pertinent to oxygen atom in CO molecule.*

### INTRODUCTION

The adsorption of CO on the transition metals and related oxides is one of the elementary steps of many catalytic reactions such as the car exhaust catalysis and Fischer-Tropsch synthesis. The molybdenum oxide is the most widely used catalyst and, due to the variety of oxidation states of Mo, the reactivity of the surface can be easily controlled by changing the concentration of oxygen and other modifiers.

The CO adsorption on clean and oxygen-modified molybdenum surfaces has been studied experimentally by temperature-programmed desorption (TPD), high-resolution electron energy loss spectroscopy (HREELS), and the infrared absorption spectroscopy (IRAS) [1–3]. In thermal desorption spectroscopy (TDS) studies for CO on Mo(110) surface, two main peaks has been observed. These two peaks have been attributed to two different forms of adsorption, namely, the low-temperature peak about 300–400 K was explained as desorption from a molecular CO state (called the  $\alpha$  state) while the high-temperature (~900–1500 K) peak (the  $\beta$  state) corresponds to an associative desorption of preliminary dissociated CO [4]. It has been shown that the low-temperature  $\alpha$  state appears only for sufficiently high CO coverages whereas the multiple  $\beta$  state is a characteristic of low coverages and should be attributed to a precursor to CO dissociation [5]. On the other hand, on a Mo(112) surface, the similar behaviour of TPD spectra have been explained basing on DFT calculations on binding (chemisorption) energies, local densities of states

(LDOS), and CO vibrational frequencies for various configurations of equilibrated layers without involving the CO dissociation [6].

The preadsorbed oxygen significantly affects the properties of transition metal surfaces with respect to adsorption of CO. In particular, the binding energy for CO on Mo(112) surface is found to be strongly dependent on the presence of oxygen. With increasing oxygen coverage, the low-temperature spectral peak shifts from 305 to 280 K, and a new peak arises at 220 K. On the  $p(1\times 2)$ -O/Mo(112) surface (with oxygen coverage  $\theta_{\text{O}}=1$ ) only the high temperature peak (280 K) was observed and the binding energy for CO in this adsorption state was estimated as 0.75 eV [1]. For the coadsorbed CO and oxygen on W(110) and W(113) surfaces, a similar decrease in the heat of adsorption of CO with increasing oxygen concentration was reported [7].

The coadsorption of oxygen and CO on Ru(0001) surface has been studied with thermal desorption spectroscopy, LEED, and HREELS [8, 9]. It has been shown that for the lower-coverage phases of oxygen ( $\theta_{\text{O}}=0.5$  ML), CO adsorbs on the surface, and the bond between CO and Ru is weakened by the coadsorption with oxygen as indicated by the significant decrease of the CO desorption temperature [8, 9]. For the oxygen coverage close to 1.0 ML, for which the CO oxidation rate has been assumed to be optimal, the adsorption of CO is nearly prohibited [10]. In contrast, CO molecules prefer to desorb as CO<sub>2</sub> from the oxygen-modified Pt(111) (with the activation energy of the oxidation reaction about 0.5–1.1 eV [11–15]).

In the present paper, the adsorption of CO on clean and oxygen-modified Mo(110) surface is studied by means of density-functional (DFT) calculations of favorable structures, binding (adsorption) energies and local densities of states (LDOS). It has been found that the presence of oxygen on the Mo(110) surface substantially reduces the binding energy of the CO molecule and on the oxygen-saturated surface the adsorption of CO occurs completely blocked.

#### METHOD OF CALCULATIONS

The DFT semirelativistic calculations were carried out using ultrasoft pseudopotentials [16] and generalized gradient approximation (GGA) in Perdew-Burke-Ernzerhof form [17]. The surfaces were simulated within the supercell approach with CO and O adsorbed on one side of the slab. The surface unit cells were chosen to be (1×1) and (2×1) for Mo(110). The thickness of the slab was of 7 Mo(110) layers and the vacuum gap was about 10 Å. The positions of oxygen atoms, CO molecules and Mo atoms of three surface layers were optimized (using BFGS [18] optimization procedure) until the forces on atoms converged to less than 0.03 eV/Å. The local densities of states were calculated using the linear interpolation scheme. The efficiency of the Brillouin zone sampling, using various k-point lattices, was carefully verified by increasing the number of k-points until the required 0.01 eV convergence of total energies and about 0.005 Å accuracy of atomic positions were achieved (the 6×6×1 Monkhorst-Pack [19] set of special k-points was found sufficient). All calculations were performed with cut-off energy of 340 eV.

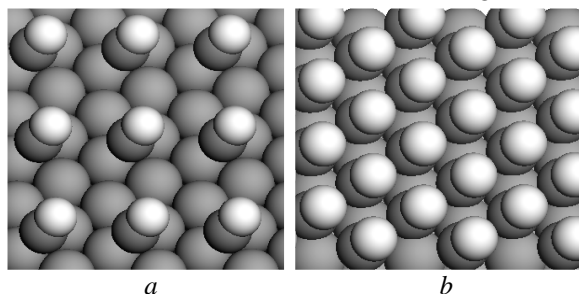
The optimization of atomic positions for a clean Mo(110) surface, in agreement with results of other calculations [4, 20], resulted in the ~5% contraction of the topmost Mo surface layer with respect to the related interplane distance in a bulk Mo (the estimated lattice constant of the bulk Mo was of 3.15 Å). Only minor relaxation shifts were found for the second and the third layers. Before depositing CO and oxygen atoms, the slabs were relaxed, i.e., all the atoms were allowed to adjust their positions to minimize the total energy of the system. Optimization of atomic positions of adsorbed oxygen atoms along with Mo atoms of the three surface layers led, on average, to a "backward" relaxation shift of the Mo(110) surface.

The binding energies (positive) of CO were defined as  $-E_b = E - E_{Substr} - E_{CO}$  where  $E$ ,  $E_{Substr}$ , and  $E_{CO}$  are total energies of the adsorption sys-

tem, the total energy of the substrate (Mo(110) surface or O+Mo(110) surface), and a CO molecule, respectively. These energies were determined taking into account the relaxation of the oxygen-covered molybdenum surface as well as the CO-induced surface relaxation. The coverage  $\theta$  for all species was defined with respect to the number of substrate atoms in the surface unit cell.

#### RESULTS AND DISCUSSION

**Structures and binding energies for CO on a clean Mo(110) surface.** The favorable adsorption positions for CO molecules on the Mo(110) could be atop Mo atoms, in short-bridge and long-bridge sites, and in triply-coordinated hollow sites. In a (2×2) structure ( $\theta=0.25$ ) the most favorable for CO molecules are found to be nearly hollow sites (Fig. 1a). The CO molecules are tilted by ~30° and the estimated binding energy of CO in these positions is of 2.0 eV. The long-bridge and on-top sites are less favorable and the short-bridge sites are found to be unfavorable for all CO coverages.



**Fig. 1.** Favorable CO structures on Mo(110) at  $\theta=0.25$  (a), 1.0 (b). Carbon atoms are shown dark grey, O – white, and Mo – light grey

The hollow sites remain favorable also for  $\theta=1.0$  and therefore for coverages up to 1 ML, CO molecules should occupy predominantly these sites (Fig. 1b). In the forming p(1×1) CO structure the distance between neighboring CO molecules is of 3.15 Å. As the binding energy decreases (by ~0.2 eV) with respect to that for  $\theta=0.5$ , at these distances the lateral interaction (repulsive) becomes significant and leads to a decrease in the tilting angle to 24°. The estimated lateral interaction can explain the split of the high-temperature TPD peak for high CO coverages but definitely not the appearance of the 380 K peak that corresponds to the 0.7 eV binding energy. The low-temperature peak appears only for sufficiently high CO exposures and, as follows from the estimate of binding energy for p(1×1) CO structure ( $\theta=1.0$ ), should be attributed to a desorption from the second CO layer. The formation of CO bilayer was modeled for  $\theta=1.5$

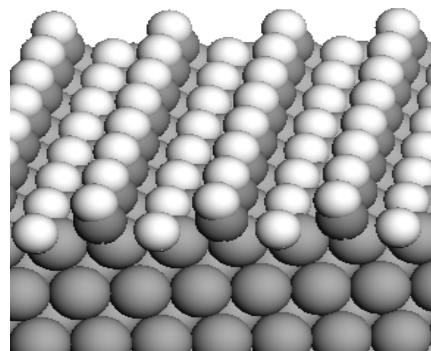
and 2.0. The optimized structures may be considered as curved C–O–C–O chains and C<sub>2</sub>O<sub>2</sub> complexes. Desorption of a CO molecule corresponds to a break of the bond between two CO fragments, so that the upper CO molecule of the chain desorbs while the other remains on the surface.

**Structure and binding energy for CO on oxygen-modified Mo(110) surface.** The LEED studies of structures of oxygen layers on the Mo(110) surface [21–23] have shown that oxygen forms various structures, starting from  $c(2\times 2)$  O at  $\theta=0.25$  and finishing with  $(1\times 1)$  O at  $\theta_0=1.0$ . Previous DFT calculations [24] suggest that triply coordinated hollow sites of the Mo(110) surface are strongly favorable for oxygen atoms for all coverages and the  $p(2\times 1)$ O structure, forming at  $\theta_0=0.5$ , is found to be favored with regard to other possible structures.

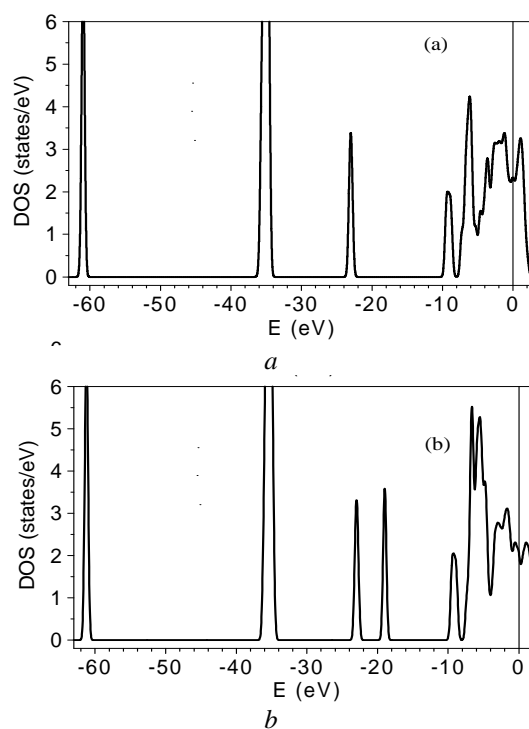
To obtain the optimal CO structure on the oxygen-modified molybdenum surface, the CO molecule was placed in various possible positions in the unit cell. On the O/Mo(110) surface, such sites are quasi-threefold, two-fold, and atop Mo atoms. The CO adsorption on the oxygen-modified Mo(110) surface has been simulated for two concentration of oxygen atoms. It was found that the CO molecule does not stick to the oxygen-saturated Mo(110) ( $\theta_0=1.0$ ) surface. Evidently, this is due to the fact that adsorption of the oxygen monolayer on the Mo(110) surface causes a complete poisoning of the molybdenum surface that leads to the blockage of the CO adsorption. The adsorption of CO becomes possible when the Mo(110) surface is only partly covered with oxygen. Under optimization (along with two molybdenum and oxygen layers), CO molecules initially deposited at arbitrary positions at the surface, move towards hollow sites on Mo surface. The strong preference of the hollow sites with respect to the others results in the forming of a  $p(2\times 1)$  CO structure (Fig. 2). The adsorbed CO molecules in this configuration are tilted by  $15.72^\circ$  with respect to the normal to the surface and do not noticeably affect the position of the adsorbed oxygen atoms, so that bond lengths of O atoms with substrate atoms remain constant within  $\sim 0.02$  Å. The obtained binding energy for CO molecules is found to be of 1.05 eV which is by  $\sim 1.0$  eV less than that of CO with a clean Mo(110) surface (2.0 eV).

**Density of states.** To reveal the difference in electronic structure of the adsorption systems, the local densities of states (LDOS) have been calculated for the CO/Mo(110) and CO/O/Mo(110) structures.

The estimated LDOS for the CO/Mo(110) and CO/O/Mo(110) surfaces presented in Fig. 3a,b were constructed for the surface layer consisting of adsorbed species and two Mo atoms of the upper layer.



**Fig. 2.** Optimized CO structures on the  $(2\times 1)$  O/Mo(110) ( $\theta_0=0.5$  ML,  $\theta_{CO}=0.5$  ML)

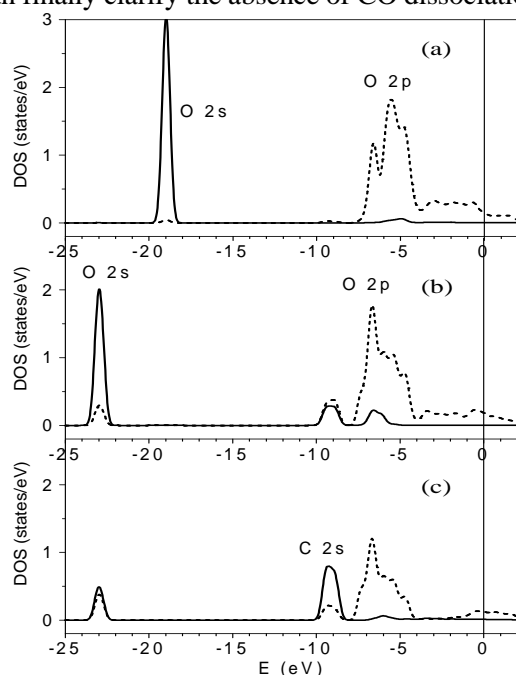


**Fig. 3.** The calculated density of states for the  $(2\times 1)$  CO/ Mo(110) (a) and for the  $(2\times 1)$  CO/O/Mo(110) (b) structures

The peaked structure in the range from  $E_F$  to  $-5$  eV and peaks  $-36$  eV,  $-61$  eV are originated by Mo electron states while the other peaks in the spectra are originated from CO and O states.

To reveal the contribution of different states to the net spectrum, the partial densities of states have been calculated. The corresponding LDOS on the adsorbed O as well as on O and C atoms in adsorbed CO molecule are shown in Fig. 4 a–c. For adsorbed oxygen atom (Fig. 4a) the O 2s-derived peak is at  $-19$  eV while the character-

istic peaks at -6.5 and -5 eV are originated predominantly by the interaction of O 2p electrons with Mo surface. In contrast, the O 2s peak for the oxygen atom of adsorbed CO molecule is at -23 eV, (Fig. 4b). The 2p O states still contribute to LDOS in the region from  $E_F$  to -7 eV. Such a significant difference in the position of the oxygen 2s peak for adsorbed oxygen atom and the oxygen atom of a CO molecule is due to the bonding either with Mo or with C atom, respectively. This feature can serve as a decisive argument in the vital discussion about the form of CO adsorption on Mo surfaces, namely, it is the position of the O 2s peak in photoemission spectra that can finally clarify the absence of CO dissociation.



**Fig. 4.** The calculated partial local densities of states for the CO/O/Mo(110) on adsorbed oxygen atom (a), oxygen atom of adsorbed CO molecule (b), and carbon atom in adsorbed CO molecule (c)

The carbon atom of adsorbed CO gives rise to the peak at -9 eV which originates from the 2s states of the carbon (Fig. 4c). The trace of this peak is visible in the spectrum of the oxygen atom in CO molecule (See Fig. 4b) while the peaks -5, -7 and -23 eV in the partial DOS localized on the carbon atom are induced by oxygen atom in adsorbed CO molecule.

#### CONCLUSION

Results of present calculations have shown that on a clean as well as on oxygen-covered Mo(110) surface CO molecules are adsorbed near hollow sites and are tilted with respect to the normal to the sur-

face. The presence of oxygen substantially reduces the binding energy of the CO molecule with the Mo(110) surface, so that on oxygen-saturated surface the adsorption of CO occurs completely blocked. The presence of the preadsorbed oxygen atoms on the Mo(110) surface results in the appearance of the -19 eV peak in local densities of states. The position of the peak corresponds to the chemical shift of the 2s oxygen line with regard to the electron states pertinent to the oxygen atom in CO molecule.

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## Енергія зв'язку CO з чистою та модифікованою киснем поверхнею Mo(110)

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В рамках теорії функціонала електронної густини досліджено взаємодію молекули CO з чистою та модифікованою киснем поверхнею Mo(110). Показано, що як на чистій, так і на вкритій киснем поверхні Mo(110) молекула CO адсорбується під кутом до нормалі до поверхні і займає положення поблизу осей симетрії третього порядку. Наявність кисню на поверхні істотно зменшує енергію зв'язку молекули CO з поверхнею Mo(110), а насичення поверхні киснем призводить до повного блокування адсорбції молекул CO. Наявність кисню на поверхні Mo(110) обумовлює появу піку  $-19$  eV в спектрі густини станів. Положення цього піку відповідає хімічному зсуву  $2s$  лінії кисню в порівнянні з електронними станами, притаманними атому кисню в адсорбованій молекулі CO.

## Энергия связи CO с чистой и модифицированной кислородом поверхностью Mo(110)

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В рамках теории функционала электронной плотности исследовано взаимодействие молекулы CO с чистой и модифицированной кислородом поверхностью Mo(110). Показано, что как на чистой, так и на покрытой кислородом поверхности Mo(110) молекула CO адсорбируется под углом к нормали к поверхности и занимает положение вблизи осей симметрии третьего порядка. Наличие кислорода на поверхности существенно уменьшает энергию связи молекулы CO с поверхностью Mo(110), а насыщение поверхности кислородом приводит к полной блокировке адсорбции молекул CO. Наличие кислорода на поверхности Mo(110) приводит к появлению пика  $-19$  эВ в спектре плотности состояний. Положение этого пика соответствует химическому сдвигу  $2s$  линии кислорода по сравнению с электронными состояниями, характерными для атома кислорода в адсорбированной молекуле CO.