WORK FUNCTION STUDIES OF PROPYLENE, ACETYLENE, HYDROGEN AND NITROGEN CHEMISORPTION ON MOLYBDENUM

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The work function changes of vacuum deposited molybdenum films caused by the chemisorption of propylene, acetylene, hydrogen and nitrogen were measured using the Kelvin vibrating capacitor method. During the hydrocarbon chemisorption, the work function increased in a low surface coverage region but decreased at the higher surface coverages. The saturation values of the work function changes corresponding to complete coverage of the surface by chemisorbed propylene and acetylene equal $-0{\cdot}08$ eV and $-0{\cdot}42$ eV, respectively. The observed dependences of the work function change on surface coverage are interpreted by the dissociative chemisorption of hydrocarbons on a limited number of surface sites which are simultaneously the sites of preferred adsorption. The extent of dissociation decreases in the adsorption with the increasing surface coverage. The results of the study of the work function changes induced by the hydrogen and nitrogen chemisorption enabled to draw several conclusions on the surface topography of the used films.

One of the fundamental problems in the investigation of the gas molecule-solid surface interaction is connected with elucidation of the electronic structure changes of the molecules and surfaces, caused by the adsorption. It is the data of the work function change measurements of the metals which provide, among others, an information on the electron density transfer during a formation of the surface complex. In spite of the fact that a direct correlation between the work function and the density of electronic states on a surface is not yet known and that the measurements of the work function changes in adsorption do not usually lead to unambiguous conclusions on the bond character of the molecules adsorbed on the surface, the results of such measurements represent an important contribution to the solution of the above formulated problem and they can be applied also in other regions of surface-processes studies[1]. In this paper, the results are presented of investigation of the work function changes of polycrystalline molybdenum surfaces, caused by the propylene, acetylene, hydrogen and nitrogen chemisorption.

The work function changes of molybdenum for the propylene and acetylene adsorption were not yet published. Similarly, no reliable data on the effects of hydrogen and nitrogen are available since the published data[2-13] frequently widely differ. The investigation of the work function changes in the adsorption of hydrogen was interesting also from another point of view because the chemisorption of hydrocarbons on molybdenum surfaces is most probably accompanied by C—H bond dissociation and the resulting work function change can be therefore, in the first approximation, regarded as a superposition of the changes caused by the chemisorbed hydrogen and the fragments of hydrocarbon molecules[14,16].

It has been so far impossible to obtain direct and reliable experimental information concerning the surface topography of the polycrystalline films deposited under ultrahigh vacuum conditions — *i.e.* an information on the relative proportions of various crystal planes and the density of the defects present. This fact leads to many complications in an interpretation of the experimental data obtained from the chemisorption studies and studies of the catalytic reactions on surfaces of such films. An assumption is usually made that the film surface is formed predominantly by the most densely packed planes — *i.e.* by planes with the lowest surface energy per metal atom. For molybdenum, the density of packing decreases in a sequence $(110) > (100) > (211) > (111)$, that is the (110) plane exhibits the lowest surface energy.

The various molybdenum crystal planes differ in the process of hydrogen and nitrogen adsorption, by their activity, characterized by the value of the sticking coefficient[10]. The available results of the work function change studies for molybdenum (and the analogous metal tungsten which has been studied more frequently and with more reliable results) point also to a relatively high anisotropy[5,8,11–13]. These facts led us to an attempt to use the experimental data from this study of hydrogen and nitrogen adsorption for obtaining some information on the surface topography of the used films.

EXPERIMENTAL

The molybdenum films were deposited on glass supports under the vacuum $< 3 \cdot 10^{-7}$ Pa, at $T = 300$ K and annealed at 370 K for 30 minutes.

The work function changes were measured by means of the Kelvin vibrating capacitor method. A more detailed description of the experimental arrangement and measurement procedure used was given in the previous paper[14].

Propylene and acetylene (Fluka AG, Buchs, Switzerland, *puriss.* A) were purified directly in the vacuum apparatus by repeated vacuum distillation and resulting purity was checked by a mass spectrometric analysis.

Nitrogen (Technische Gase, Leipzig, DDR, Spectroscopic grade) was taken directly from a glass bottle without additional purification.

Hydrogen was generated in the vacuum apparatus by heating of titanium hydride. A mass spectrometric analysis carried out by means of a small quadrupole mass spectrometer connected directly to the apparatus detected no impurities in the nitrogen and hydrogen used. The gas pressure in a 10^{-3}—1 Pa range was measured by means of a thermal conductivity gauge. The measurements of the work function values and their changes were carried out (unless stated otherwise) at the temperature 298 K.

RESULTS AND DISCUSSION

The adsorption of the gases was carried out by a series of discrete doses which contained practically always (within gas-phase pressures 10^{-7}–10^{-2} Pa above the adsorbent), the same amounts of gas. The Figs 1–4 show the experimentally found dependences of the stationary work function changes $\Delta\phi$ on the relative surface coverage Q, for the range $0 < Q < 1{\cdot}2$. The relative coverage is defined as: $Q = Q_a/Q^*$, where Q_a is the amount adsorbed and Q^* is the adsorbed amount corresponding to the equilibrium gas-phase pressure $3 \cdot 10^{-3}$ Pa (more details are discussed in paper[14]).

Table I summarizes the experimental values $\Delta\phi_m$ – corresponding to the maxima on $\Delta\phi$ against Q plots – and the saturated values $\Delta\phi_s$ – corresponding to the work function change reached at the stationary gas-phase pressure ~5 Pa. For a comparison, Table I presents also the previously published data[14] on cyclopropane chemisorption. The value $n^*(H)$ is defined as $n^*(H) = Q^*(H_2)/Q^*(X)$, where $X = C_3H_6$, C_2H_2, cyclo-C_3H_6 and N_2, respectively. The quantity $2n^*(H)$ gives the number of sites required for the adsorption of one molecule of a given gas, assuming that: *1*) the adsorption of hydrogen in the surface coverage range $0 < Q \leqq Q^*$ is accompanied by a dissociation; *2*) all the gases studied are adsorbed on equivalent adsorption sites; *3*) all these sites have been just occupied at the moment when a Q^* surface coverage is reached. A fulfilment of the second and third of the above assumptions is, however, less probable. The quantity $n^*(H)$ has therefore a rather orientational meaning and its numerical value characterizes roughly the sorption

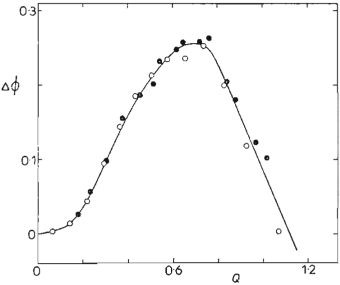

FIG. 1

The work function change $\Delta\phi$ (eV) (shown for two different molybdenum films) plotted against relative surface coverage Q, for adsorbed propylene

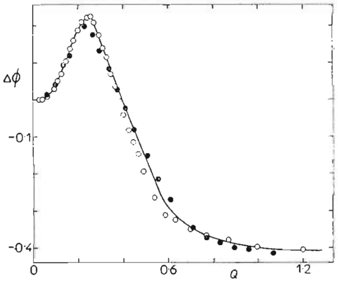

FIG. 2

The work function change $\Delta\phi$ (eV) (shown for two different molybdenum films) plotted against the relative surface coverage Q, for adsorbed acetylene capacity of the surface for a given gas (the sorption capacity decreases with the increase of its value). This conclusion is supported also by the high $n^*(H)$ value, observed in the adsorption of nitrogen.

The work function values presented in Table I correspond to average values calculated from the results of three independent experiments (four experiments in the case of cyclopropane). As can be seen from the given data, the characteristic work function change values ($\Delta\phi_m$, $\Delta\phi_s$) are very well reproducible.

Taking into account that the adsorbed hydrogen increases the work function of molybdenum, one can explain the initial increase observed during the chemisorption of hydrocarbons, by their dissociative chemisorption – which is significant especially in the low-coverage region. The work function decrease – observed after a maximum on the curve has been reached in the plot against increasing surface coverage – can be explained by a lesser extent of dissociation in the adsorption. The dependence of the extent of dissociative adsorption on surface coverage can be explained in three ways: *1*) the dissociative chemisorption can proceed only on a limited number of surface sites which are, simultaneously, the sites of preferred adsorption; *2*) the increasing surface coverage changes gradually the electronic structure of the surface which leads consequently to a change of the mode of chemisorption; *3*) the products of dissociative chemisorption are distributed on a surface in such a way that they prevent dissociation of the subsequently adsorbed molecules.

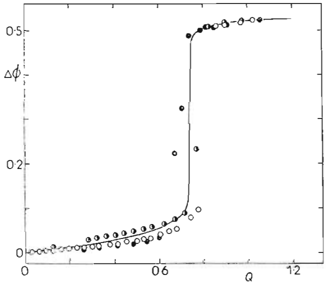

FIG. 3

The work function change $\Delta\phi$ (eV) (shown for three different molybdenum films) plotted against the relative surface coverage Q, for adsorbed hydrogen

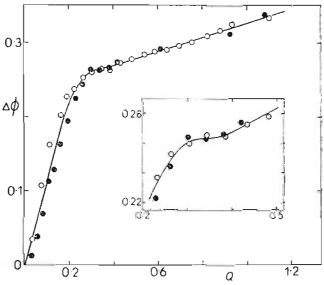

FIG. 4

The work function change $\Delta\phi$ (eV) (shown for two different molybdenum films) plotted against the relative surface coverage Q, for adsorbed nitrogen. The inflex region is shown in detail on the insertion

Our recent results seem to support the first of the above mentioned hypotheses. A question arises in this context about which sites on the surface are most active for the dissociative chemisorption. As it was shown in the previous papers of the present author[14-16] and in accordance with the literature[17,18], such sites are probably formed by the low-coordination metal atoms and by the surface regions containing such atoms. In agreement with this explanation, we would therefore expect to find an extensive dissociation of intramolecular bonds of hydrocarbon molecules on such metal crystal planes which are characterized by low density of the surface atoms and which, at the same time. exhibit low work function values $\phi_0(hkl)$ – *i.e.* work function values for the clean surface.

Thus, the energy barrier for dissociative chemisorption decreases with a decreasing work function of the clean surface. This correlation does not apply only to the chemisorption of hydrocarbons studied in this work, since, *e.g.* the extent of carbon monoxide dissociation on the W(110) plane (a plane with the highest work function value[1]) is substantially lower than on the W(100) plane – ref.[19]. In agreement with the given explanation are also the results of the hydrocarbon chemisorption studies on polycrystalline surfaces of nickel films deposited at different temperatures of glass substrate, which showed consequently different work function values[20].

One can argue that, sometimes, a change of the adsorption regime is observed with increased surface coverage also on the individual crystal planes – on which one would expect all the surface atoms to be equivalent. However, one must realize that even the single crystal planes – prepared in the usual way – contain a certain

TABLE I

The work function changes for the adsorption of propylene, acetylene, cyclopropane, hydrogen and nitrogen on the molybdenum film surfaces

Adsorbate	$\Delta\phi_m$[a], eV	Q_m[b]	$\Delta\phi_s$[c], eV	n^* (H)[d]
C_3H_6	0·26 ± 0·01	0·72	−0·08 ± 0·07	3·16 ± 0·2
C_2H_2	0·21 ± 0·01	0·25	−0·42 ± 0·01	1·56 ± 0·0
cyclo-C_3H_6	0·25 ± 0·03	0·83	−0·10 ± 0·02	5·32 ± 0·8
H_2	—	—	+0·54 ± 0·01	1·00
N_2	0·264	0·34	+0·37 ± 0·003	5·00 ± 0·0

[a] The work function change values corresponding to the maximum on a $\Delta\phi$ *vs* Q plot (for the case of nitrogen adsorption corresponding to the inflex on the $\Delta\phi$ *vs* Q curve – see Fig. 4); [b] the value of relative surface coverage corresponding to the same point as in [a]; [c] the saturated work function change value corresponding to the saturated chemisorption layer at equilibrium gas phase pressure 5 Pa; [d] the meaning of this quantity is explained in the text.

amount of defects not observable by the LEED technique applied in the the surface crystallography studies. It should be mentioned at this point that a concentration of these defects can be obtained from the measurements of the work function[21] and the work function changes during the adsorption, using a suitably selected adsorbate – most frequently hydrogen or carbon monoxide[22,23].

The reason for different adsorption properties of the surface metal atoms of lower coordination lies in the change of the electronic structure. According to one of the suggested explanations[24,25], the strong electric field gradients existing in the vicinity of such atoms polarize the bonds of the adsorbate molecule approaching the surface, facilitating in this ways a dissociation. Up to now, no rigorous self-consistent calculations have been carried out for real surfaces and it is, therefore, rather difficult to discuss in more detail the effect of the proximity of the metal surface on the individual bonds of hydrocarbon molecules. From a qualitative model one can only conclude that when a molecule has entered the region of electron-density above the surface, an additional screening of the Coulomb force fields weakens the intramolecular bonds. From thermodynamics it is evident that a dissociation of the C—H bonds (eventually C—C bonds) and a formation of the C—Mo and H—Mo surface bonds results in a net lowering of energy of the system, *i.e.* such process is energetically favourable. One can therefore expect that a highest activity will be found on those surface regions, on which the strongest C—Mo and H—Mo bonds are formed. Reliable values of C-metal bond energies for many metals are not available, however, it is known that Mo, unlike Pt and Pd, does form readily a stable carbide.

The analysis of the data published[26–29] on the heats of adsorption of hydrogen on metal surfaces and of their relation to the work function values[30,31] shows that, in most cases, the heat of adsorption decreases with the increasing work function value. The available experimental data[26,32] show a similar trend also for the adsorption heats of hydrocarbons. In this way we come back to the above stated conclusion that the dissociation of intramolecular bonds of hydrocarbon molecules is energetically favourable on transition metal surfaces with the low value of work function. Because the low work function regions on a heterogeneous surface contain atoms of low coordination, one can repeat that these atoms form the preferred adsorption sites for dissociative chemisorption.

The quantitative differences in the work function changes observed in the adsorption of propylene and acetylene (Figs 1, 2 and Table I) can be easily explained as a consequence of the lower hydrogen content and a stronger C—H bond in the acetylene molecule. The changes found for the chemisorption of propylene are not very different from those found for the chemisorption of cyclopropane.

Because the UV photoelectron difference spectra of molybdenum surfaces with adsorbed propylene and cyclopropane do not differ[15] very much, it is probable that in both cases similar surface complexes are formed.

The experimental results of the work function change measurements for the hydrogen and nitrogen adsorption allow, in connection with the published data[2-13], to draw some conclusions on the surface topography of the used molybdenum films. If a (100) plane would be the most abundant at the surface, then the work function should decrease during the chemisorption of nitrogen, in the low-coverage region, because nitrogen is adsorbed preferentially on this plane and decreases its work function value. Evidently, also a (110) plane is not prevailing. Most probably, the more open planes and a large concentration of defects are dominating at the surface of the films. In agreement with this conclusion, a more extensive dissociation of the C—H bonds of hydrocarbon molecules occurs on the surface than it corresponds to the UV-photoelectron spectra of surface complexes on a mohybdenum (110) plane – the most densely packed plane, with the highest work function value[1,15].

The work function value obtained for the clean surface film equals 4·0 ± 0·15 eV. If it is assumed that the film surface consists of equal areas of low-index planes, then, using the published values[1] for the work functions of individual crystal of molybdenum, one can obtain the average work function value, 4·5 eV. The presence of defects and planes with higher Miller-indexes leads, as a rule, to lower values of the work function.

The presented conclusions concerning the surface topography of the used molybdenum film are not unexpected, if one takes into account the high melting point of the molybdenum and the fact that the films were prepared and sintered at temperatures well below the Tamm's temperature of molybdenum. The observed dependence of the work function on the relative surface coverage with hydrogen (Fig. 3) is in agreement with the previously published results[5] and it points to a likely existence of three adsorption states of hydrogen. It is neither clear nor it does follow from the mentioned paper[5], which adsorption sites are responsible for the sharp increase of the work function at a relative surface coverage $Q = 0{\cdot}75$. It is interesting to mention that in this coverage region the adsorption proceeds with a very slow rate. One can therefore assume that the adsorption sites are gradually filled by a surface migration of atomic hydrogen formed by the dissociative chemisorption on other parts of the surface. The hydrogen, bound in this way is probably responsible also for an increase of the work function observed in the low-coverage region, in the chemisorption of hydrocarbons.

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