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Kinetics of Dissociative Adsorption on Stepped Surfaces of Platinum

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Abstract—The kinetics of dissociative adsorption of oxygen was studied by the Monte Carlo method for a model which supposed that absorption occurs with a high rate only on steps and that O_{ads} may migrate from steps onto terraces and backward. At the relatively low activation energy of diffusion from steps onto terraces $E_{dif} \sim 75$ kJ/mol (E_{dif} is lower by 4 kJ/mol in the back direction), the function $\log(s(\Theta))$, where s is the sticking coefficient and Θ is the surface coverage by oxygen atoms, is almost linear at 300 K; that is, the Roginskii–Elovich adsorption equation is obeyed. If it is supposed that the bonding energy of adatoms on terraces is slightly higher than that on steps, and the sticking coefficient is constant and equal to s_0 up to high degrees of coverage as well as in the model of the kinetics of adsorption with a precursor state.

INTRODUCTION

The adsorption of O_2 and H_2 on stepped facets of platinum Pt_s occurs at rates higher than the rates on the close-packed facet Pt(111) by ~2 orders of magnitude. The initial sticking coefficient of O_2 on Pt_s is $s_0 \sim 0.1$–0.5; on the Pt(111) facet, $s_0 \sim 10^{-3}$ [1–4]. In the initial stage, adsorption occurs in steps: the 2(1D) structure is formed, and then the (2×2)O structure is formed on terraces. That is, the steps play the role of "active" centers in chemisorption. It is important that the O_2 adsorption rate exceeds the adsorption rate on Pt(111) not only on steps, but also on Pt_s terraces. Hopster *et al.* [2] and Bonzel [3] showed that s_0 depends on the step concentration at Pt_s. The study of the kinetics of adsorption on recrystallized platinum foil Pt_s at 300 K by thermal desorption spectroscopy (TDS) and Auger spectroscopy showed [5] that the curve $s(\Theta)$ consists of two portions: rapid initial adsorption $s_0 = 0.2$ until $\Theta = 0.04$ (adsorption on steps) and a portion with a low rate of adsorption ($s = 5 \times 10^{-2}$–1×10^{-2}), where the function $\log(s(\Theta))$ is approximately linear. It was found [6, 7] for Pt(111) that the function $\log(s(\Theta))$ is linear, and, in the range T = 300–360 K, $\log(s(\Theta))$, curves are almost independent of the adsorption temperature. Salanov and Savchenko [5] proposed an adsorption scheme where the O_2 adsorption occurs on steps ($s_0 = 1.0$) and then O_{ads} can migrate from steps to terraces (and back) at T = 300–400 K. The calculations using this model showed [8] that, at a sufficiently high rate of diffusion, the function $\log(s(\Theta))$ is almost linear; that is, the Roginskii equation is satisfied, although only two types of centers connected by the diffusion of adsorbed particles are involved in the model. However, the calculations in [8] were basically carried out by the integration of simple differential equations. This supposes that, after the transition of particles from steps to terraces, the particles instantaneously scatter over the whole terrace. The calculation by the Monte Carlo method in [8] made for the $(100) \times (100)$ lattice was qualitative, because quantitative data of $s(\Theta)$ cannot be obtained through fluctuations. Of course, the Monte Carlo method makes it possible to obtain more detailed data on the adsorption of kinetics as a function of the surface structure than the simple differential equation method. However, it is necessary to carry out the calculations for the 1000×1000 lattice, and this calculation is time-consuming.

It is generally believed that oxygen is locally absorbed on platinum; that is, it does not migrate on the surface, because the activation energy of O_{ads} diffusion determined by the field-emission microscopy method [9, 10] is fairly high, E_{dif} = 100–110 kJ/mol. However, E_{dif} on the smooth Pt(111) surface (and Pt_s terraces) can be lower. Ivanov *et al.* [11] found $E_{dif} \sim 80$ kJ/mol from the induction period of formation of the (2×2)O structure on Ir(111) at 300 K. The value of E_{dif} on Pt(111) is still lower. Furthermore, at a small width of terraces on Pt_s, several "jumps" of O_{ads} performed in a time comparable to the adsorption time will suffice to level the concentration over the terrace surface.

The aim of this work is to study in detail the kinetics of oxygen adsorption, $s(\Theta)$, on the stepped surfaces depending on the energy characteristic of adsorption and the geometry of the surface (steps–terraces) by the Monte Carlo method for the 1000×1000 lattice.

MODEL AND ALGORITHM OF CALCULATION

The modeling was performed for a square lattice (1000×1000 centers) with periodic boundary conditions. Oxygen was adsorbed on the pure surface with an

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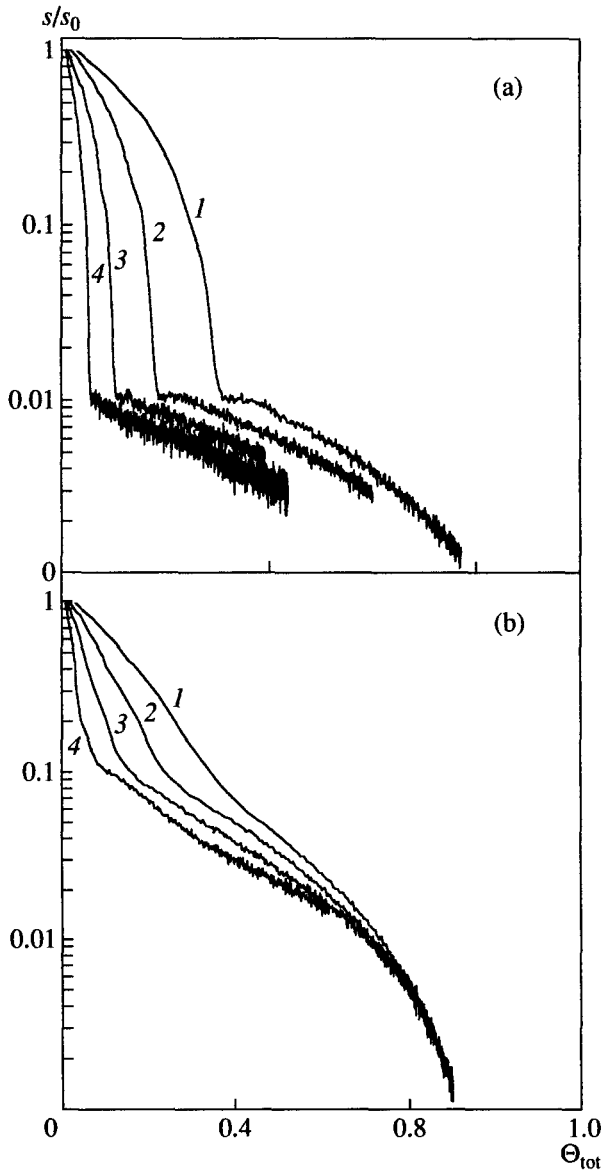

Fig. 1. The s/s_0 vs. Θ_{tot} plot for O_2 adsorption on a stepped Pt surface in the cases of almost localized adsorption: (a) $N_{dif} = 1$ and (b) $N_{dif} = 40$. $st = 1$, $ter = (1)$ 2, (2) 4, (3) 8, and (4) 16.

assigned geometry of the lattice (the width of steps and terraces).

Adsorption. It was supposed that oxygen is adsorbed only on free centers of the steps with the sticking coefficient $s_0 = 1.0$, and, then, O_{ads} atoms may overflow from steps onto terraces and backward onto steps [4, 6]. The sticking coefficient on steps can be taken to be lower, for example, $s_0 = 0.1$, which does not affect the quantitative character of $s(\Theta)$ curves and the conclusions of the work. The adsorbtion probability (at one center per 1 s) was estimated from the number of molecular impacts at 10^{-6} Torr and the number of centers per 1 cm^2 $n = 10^{15}$. At $s_0 = 1.0$, this value is $p_{ads} = 1.0$.

Diffusion. The diffusion act was simulated as a jump of a particle onto one of the accidentally selected nearest free places with the probability $p_{dif} = \nu\exp(-E_{dif}/RT)$, where $\nu = 10^{13}$ s^{-1} and E_{dif} ($E_{dif(s \to t)}$, $E_{dif(t \to s)}$, $E_{dif(s \to s)}$, $E_{dif(t \to t)}$) are the activation energies of diffusion from steps (s) onto terraces (t) and backward and over steps and terraces. Because of a dramatic difference in the time scales, diffusion was considered not as an alternative process to O_2 adsorption, but as a supplementary artificial procedure that facilitates the space mixing of the adsorbate. For this purpose, in the program, a cycle of diffusion was inserted to the basic cycle of adsorption as an internal cycle. The number of actuations of the diffusion cycle N_{dif} per one act of adsorption, i.e., per one Monte Carlo step, was assigned at the beginning of the program and varied from $N_{dif} = 1$ to $N_{dif} = 100$ for all surfaces.

Algorithm. Random selection of a center was simulated by the generation of two integer random numbers in the range from 1 to 1000 (coordinates of the center). If the center was free, an adsorption act proceeded on it with the probability p_{ads}. Thereafter, the possibility of diffusion was considered on the conditions described above. Next, another center was randomly selected until the calculations were performed for the number of centers that corresponds to the lattice size (10^6 centers). This procedure corresponded to one Monte Carlo cycle (step) (*MC*). The sticking coefficient was determined as the $\Delta\Theta/MC$ ratio for a given surface to the $\Delta\Theta/MC$ value for a completely stepped surface at $\Delta\Theta$ near zero, i.e., at $s_0 = 1.0$.

RESULTS AND DISCUSSION

Case 1.The bonding energy of adsorbed particles is higher on steps than on terraces. The activation energy of diffusion over terraces was taken equal to $E_{dif(t \to t)} =$ 75 kJ/mol; and over steps, $E_{dif(s \to s)} = 80$ kJ/mol. We performed the calculation assuming that the bonding energy of O_{ads} on steps E_s exceeds the bonding energy on terraces E_t by 4 kJ/mol, that is, $E_{dif(s \to t)} - E_{dif(t \to s)} =$ 4 kJ/mol.

To clarify the effect of surface structure on the kinetics of absorption, the ratio between the sizes of steps and terraces on the surface was varied. Figures 1 and 2 show the data for surfaces on which monoatomic steps (the number of rows in a step is equal to $st = 1$) alternate with terraces with various width. We set the number of atomic rows in terraces to $ter = 2$, 4, 8, and 16. In this case, the ratio of centers on steps to the total number of centers $\Theta_s = st/(st + ter)$ was 0.33, 0.2, 0.11, and 0.059, respectively. The calculations of the rate shown in Fig. 1a for all considered variants were performed at $N_{dif} = 1$, which almost corresponds to localized adsorption. In the initial stage of adsorption, oxygen is dissociatively adsorbed on steps and, as the coverage increases, the sticking coefficient normalized to unity, s/s_0, dramatically decreases from 1.0 to ~ 0.01 as Θ varied from 0 to Θ_s. After the adsorption of oxygen on

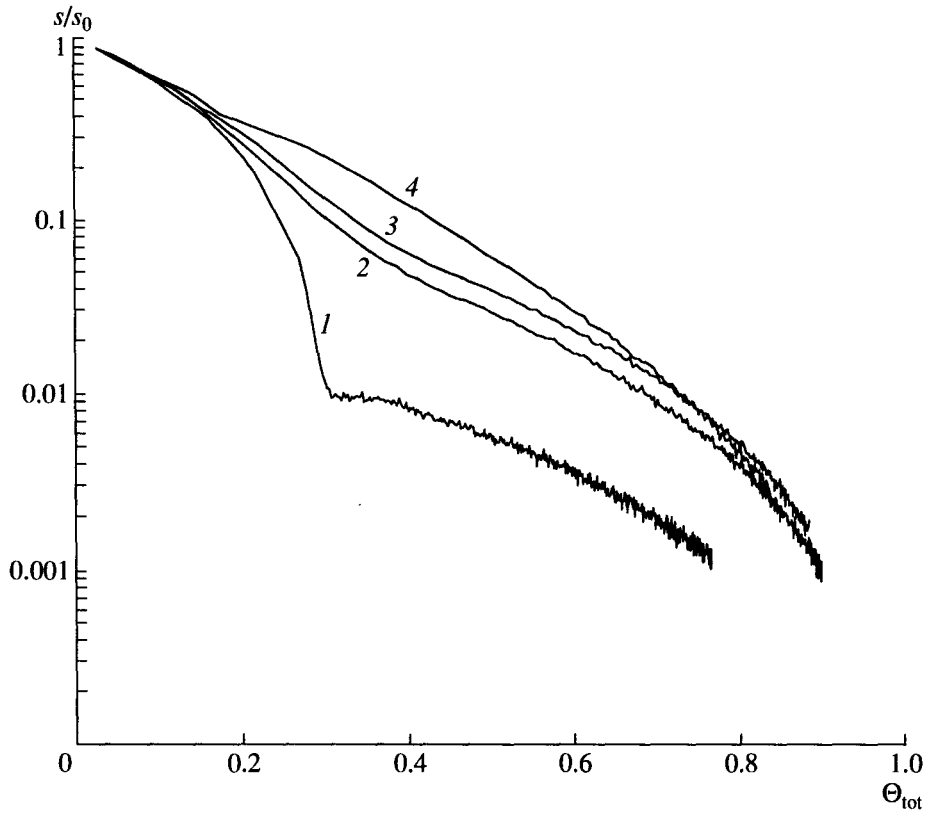

Fig. 2. The s/s_0 vs. Θ_{tot} plot for O_2 adsorption in the case of the alternating of monoatomic steps ($st = 1$) with terraces having the size of two atomic rows ($ter = 2$) at $N_{dif} = (1)$ 1, (2) 20, (3) 40, and (4) 100.

steps at $N_{dif} = 1$, the diffusion rate is low, and O_{ads} practically does not overflow on to terraces, $s/s_0 < 0.01$ (Fig. 1a).

For the above surfaces ($st = 1$, $ter = 2$, 4, 8, and 16), the adsorption rates were calculated at the values of N_{dif} from 1 to 100, i.e., with increasing rates of diffusion of adsorbed particles from steps on terraces (and backward) according to the probabilities determined by the activation energies $E_{dif(s \to t)}$ and $E_{dif(t \to s)}$. Figure 1b illustrates the data for $N_{dif} = 40$. As can be seen, adsorption initially occurs on steps, but then the curves $s/s_0(\Theta)$ are flatter than the curves in Fig. 1a, because O_{ads} diffuses on to terraces, and the total rate of adsorption increases in this case. For the surface with narrow terraces ($st = 1$, $ter = 2$), the curve $\log(s/s_0(\Theta))$ becomes smooth, approaching a straight line (curve *1*, Fig. 1b).

As can be seen in Fig. 1, the surface structure has a determining effect on the kinetics of adsorption. Because the fraction of centers on the steps is equal to $st/(st + ter)$, the broader the terrace, the lower the fraction of centers adsorbing oxygen with a high rate $s = 1.0$ and the lower is the fraction of boundary atoms (step/terrace) from which O_{ads} atoms can "run down" on to terraces. A direct observation of Monte Carlo patterns demonstrates that, in the case of Fig. 1a, atoms are primarily adsorbed on the steps, only a small amount overflow onto terraces, and they are concentrated near the step/terrace boundary. In the case of Fig. 1b, especially for the surface with narrow terraces, O_{ads} are uniformly distributed over steps and terraces. The calculations carried out at $N_{dif} = 100$ showed that Θ_t/Θ_s is equal to $\exp(-(E_s - E_t)/RT)$ during the entire adsorption time; i.e., an equilibrium distribution of particles between steps and terraces exists. This is consistent with the published data [8].

Figure 2 shows the kinetic data for one surface structure ($st = 1$, $ter = 2$) and various $N_{dif} = 1$–100. It can be seen that at $N_{dif} = 1$, adsorption proceeded only on steps, and the rate sharply decreases at $\Theta = 0.33$, whereas at $N_{dif} = 100$, the function $\log(s/s_0(\Theta))$ is approximated by a straight line. Note that, for the model under discussion, N_{dif} can be taken equal to 100, because a further increase in N_{dif} up to 1000 practically does not influence the character of the dependence. A similar linear function $\log(s/s_0(\Theta))$ was obtained earlier [8] by integration of a system of simple differential equations.

It was of interest to correlate the adsorption rates at the same ratio between the fractions of sites on the steps to the total amount of sites $st/(st + ter)$, but at various widths of steps, i.e., at various numbers of atomic rows on the steps. Figure 3a shows $\log(s/s_0(\Theta))$ curves for surfaces 1–8 (one row on a step and eight rows on a terrace), 2–16, 3–24, and 5–40. The fraction of adsorbtion sites on steps of the total amount of centers on all sur-

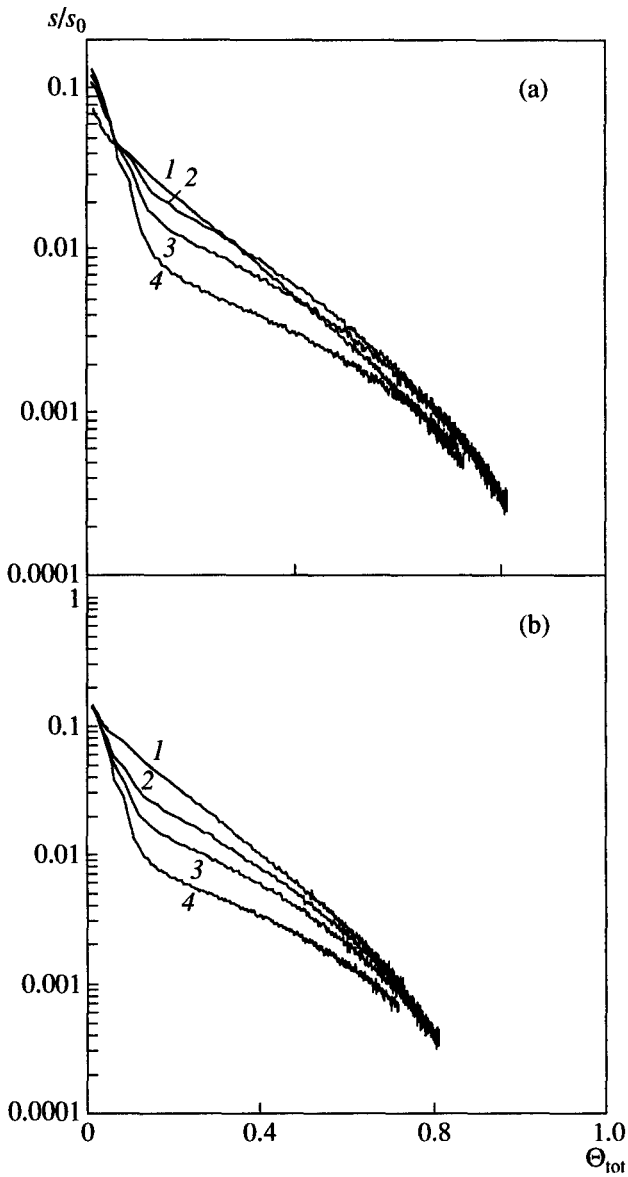

Fig. 3. The s/s_0 vs. Θ_{tot} plot for O_2 adsorption in the case of a constant ratio of the fraction of sites on steps to the total number of sites ($st/(st + ter) = 1/9$) and a change in the number of rows on steps: $st = (1)$ 1, (2) 2, (3) 3, and (4) 5; (a) data obtained in terms of the given model, (b) data corrected taking into account the difference in the probabilities of dissociative adsorption on steps with various widths. The data are given for $N_{dif} = 100$.

faces is equal to 1/9. The calculations were performed at $N_{dif} = 100$. It can be seen in Fig. 3a that the smaller the terrace size, the smoother the curve $\log(s/s_0(\Theta))$, because the number of step/terrace boundary atoms increases. This is also consistent with Fig. 1b. The function $\log(s/s_0(\Theta))$ for surface 1–8 is practically linear. Note that, as the step size decreases (5–40, 3–24, 2–16), the rate increases naturally, (for curve 1–8, this tendency is somewhat impaired) and, except the range $\Theta = 0.1$–0.25, the adsorption rate on surface 1–8 is lower than that on 2–16. The reason for this is probably the difference of probabilities of dissociative adsorption on the steps with different widths. Suppose that an O_2 molecule is adsorbed at the center inside a broad step (3–5 rows). Around this center, four unoccupied centers exist, and the second atom of the molecule can be adsorbed at any one of them. Let the adsorption probability be 1.0 in this case. If O_2 is adsorbed at a boundary step/terrace site, the number of neighboring vacant sites on the step is equal to 3 and the probability is 3/4. If the step is unidimensional, only two adsorbtion centers exist alongside the center of O_2 adsorption, and the probability of adsorption is equal to 2/4 = 0.5. It is not difficult to estimate the average probability of dissociative adsorption on all centers of a step with a given configuration. Thus, for a step of width in five atomic rows, $p_{av} = (3 + 3/2)/5 = 0.9$; in three atomic rows, $p_{av} = (1 + 3/2)/3 = 0.833$; in two atomic rows, $p_{av} = 0.75$; and in one row, $p_{av} = 0.5$. Let us correct the data of Fig. 3a by dividing them by p_{av}. We obtained a "normal" course of curves (Fig. 3b); that is, indeed, the difference in the course of the curves in Fig. 3a associated with the difference in the probability of dissociative adsorption on steps with various widths.

Thus, at $E_s > E_t$, after adsorption on the steps, atoms at small N_{dif} practically remain on the steps. At large $N_{dif} = 50$–100, adsorbed particles rapidly "drain down" and "scatter" over terraces. We can say this with reasonable confidence about a proportional distribution of adsorbed particles over terraces during the adsorption for the curves whose linearity corresponds to the Roginskii–Elovich equation. Moreover, we can also say this about the equilibrium distribution of particles between steps and terraces. Even at $T = 320$ K, during the adsorption, as new portions of O_{ads} enter the steps from a gas phase, the equilibrium distribution of O_{ads} between the surfaces of steps and terraces has a chance to be attained. Linear dependence $\log(s/s_0(\Theta))$ at large $N_{dif} = 50$–100 (Figs. 1b, 2) was also obtained earlier [8] by the integration of the simple differential equation system. This is somewhat surprizing because the logarithmic equation by Roginskii–Elovich suggests a linear function of the distribution of centers by bonding energy. In the model, we assign two types of centers; i.e., the surface is discretely inhomogeneous, and the near-logarithmic dependence results from the diffusion coupling between the centers on steps and terraces.

Case 2. The bonding energy of adsorbed particles is higher on terraces than on steps. Note that if the heat of adsorption on steps exceeds the heat of adsorption on terraces by more than 4 kJ/mol, the linear function $\log(s/s_0(\Theta))$ becomes steeper than curve *1* in Fig. 1b. In contrast, with decreasing $(E_s - E_t)$, the function $\log(s/s_0(\Theta))$ becomes flatter. If we suggest that the adsorption energy on the terraces exceeds the adsorption energy on steps by 5–10 kJ/mol, as can be seen in Fig. 4, although the adsorption proceeds only on steps, O_{ads} tend to "roll down" on to terraces, and, as a result, the sticking coefficient remains almost constant up to $\Theta \sim 0.8$–0.9. The shape of curves $\log(s/s_0(\Theta))$ is practically identical with the shape for the known model of the kinetics with a precursor state [12, 13]. In our model, oxygen dissociatively adsorbed on steps, which

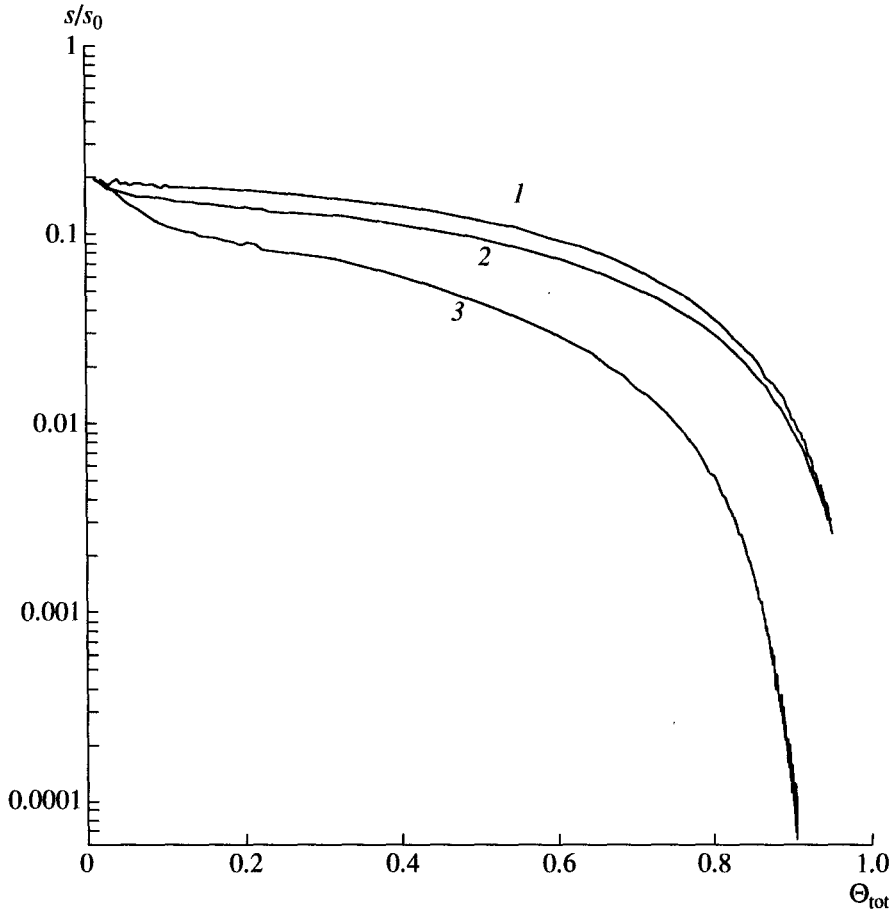

Fig. 4. The s/s_0 vs. Θ_{tot} plot for O_2 adsorption in the case when the bonding energies of adsorbed particles on terraces are higher than those on steps (kJ/mol): (*1*) $E_t = 78$, $E_s = 74$; (*2*) $E_t = 82$, $E_s = 78$; (*3*) $E_t = 86$, $E_s = 82$. The data are given for $N_{dif} = 100$.

is subsequently scattered over the entire surface, plays the role of a precursor state.

Let us try to imagine the situation when the adsorption rate on steps is much higher than the adsorption rate on terraces, whereas the coupling energy of adsorbed particles on steps is lower than that on terraces. According to the well-known Sachtler model of a surface [14], we can propose that "upright" orbitals of low-coordinated atoms of steps provide a high rate of dissociation of adsorbed O_2 molecules ($s \sim 1.0$). These orbitals are absent from the "smooth" surface of the terraces (111). Thus, the adsorption rate on terraces from a gas phase is negligibly small. On the other hand, the heat of adsorption at single atoms of steps (onefold) can be lower than on threefold terraces (111). These suppositions are evidently allowable, although it is difficult to unambiguously state that this hypothesis is valid.

It is believed that the model can be used for describing the kinetics of hydrogen and nitrogen adsorption on metals.

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