Kinetics and Catalysis, Vol. 44, No. 1, 2003, pp. 141–147. Translated from Kinetika i Kataliz, Vol. 44, No. 1, 2003, pp. 152–158.
Original Russian Text Copyright © 2003 by Zeigarnik, Abramova, Baranov.

Monte Carlo and UBI–QEP Modeling of the Coverage-Dependent Binding Energy for Atomic Adsorbates on the (111) and (100) Transition Metal Surfaces

A. V. Zeigarnik*, L. A. Abramova*, and S. P. Baranov**

** Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia*
*** Lebedev Physical Institute, Russian Academy of Sciences, Moscow, 119991 Russia*

Received June 21, 2002

Abstract—Using the unity bond index–quadratic exponential potential (UBI–QEP) formalism and the Monte Carlo method, functions are obtained that describe the dependence of the binding energies of atomic adsorbates on the single crystal surface coverage for the models of random adsorption, models with a site choice and site preference, models with neighbor exclusion, and models with diffusion assistance.

INTRODUCTION

Over the last few years, many processes on transition metal surfaces have been successfully modeled using the unity bond index–quadratic exponential potential (UBI–QEP) method [1–3]. This method has been applied to calculations of various heterogeneous catalytic reactions: methanol synthesis [4–6], carbon dioxide reforming of methane [7], ethane hydrogenolysis [8, 9], acetylene hydrogenation [10], methanol oxidation to formaldehyde [11], CO hydrogenation [12], Fischer–Tropsch synthesis [13, 14], decomposition of NO and its reduction [15], ammonia synthesis [16], N_2O decomposition [17], and many other processes. The UBI–QEP makes use of the atomic binding energies of adsorbates on metal surfaces as input. These energies are obtained in the experiment or by reliable theoretical methods and often refer to different surface coverages, so in order to use them one has to know the dependence of the binding energy on the coverages. Several publications have been devoted to this problem [2, 3, 18, 19], since the coverage dependence of the binding energy is one of the key questions in the theory of adsorption and kinetic modeling of catalytic reactions.

The UBI–QEP method makes it possible to calculate the binding energy of an atomic adsorbate depending on its local environment with lateral adsorbate–adsorbate interactions. However, based on the local effects of lateral interactions, it has only been possible to predict the global behavior of the system for specific cases when adsorbates form regular overlayer structures on metal surfaces. In these cases, if interpreted correctly, local adsorption patterns model the global pattern. To obtain a theoretical function that describes the coverage dependence of the binding energy, we used the Monte Carlo method. This method has been applied earlier together with UBI–QEP and DFT to describe pairwise lateral interactions in the O/Rh(100) system [20], to model the temperature-programmed desorption of oxygen from the Rh(100) surface [21], and to model a number of heterogeneous catalytic processes [22]. In this work, we consider the simplest models of coverage dependence of adsorption energies; trace the effects associated with the surface structure, site preference, and adsorbate mobility; and explore various assumption related to the adsorption behavior.

FORMALISM OF THE UBI–QEP METHOD

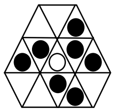
It is known that the adsorbate binding energies depend on the surface coverage due to the lateral interactions between adsorbates. These may be direct and indirect (mediated by the metal). Although the UBI–QEP method provides a quantitative description of both, we will consider only indirect interactions, which lead to a decrease in the adsorbate binding energy. This decrease in the binding energy is due to the fact that metal atoms bind more than one adsorbate. According to the principle of bond index conservation, which underlies the UBI–QEP method, a metal atom cannot interact with each of the coadsorbed species as strongly as it would in the absence of other coadsorbates. At low and moderate coverages, atomic adsorbates usually prefer sites with the highest coordination (hollow sites): $n = 3$ for the (111) surface and $n = 4$ for the (100), and we will proceed from this assumption. Note, however, that at a certain critical coverage θ_{crit} adsorption on bridging sites becomes preferable. Thus, it has been proposed that at $\theta_{crit} = 1/2$ atomic adsorption on the bridging sites of the (111) surface becomes preferable [19–21, 23]. This factor, which substantially affects the behavior of the coverage-dependent function $Q(\theta)$ (see below), will be considered in more detail in our future papers.

In the framework of the UBI–QEP method, the following formula has been obtained [2, 19] for the ratio between the binding energy in the case of neighboring atomic coadsorbates $Q(\theta)$ and the binding energy in the zero-coverage limit Q_0:

$$\sigma = Q(\theta)/Q_0 = \frac{1}{n}\sum_i \frac{k_i}{m_i}\left(2 - \frac{1}{m_i}\right), \qquad (1)$$

where k_i is the number of metal atoms in the unit mesh bound to the same number of adsorbates, the subscript i refers to the ith equivalence class, m_i is the number of bonds formed by any metal atom from the ith equivalence class with the adsorbates.

To illustrate the use of this formula, consider a fragment of the (111) surface:



The central adsorbate (open circle) is surrounded by three metal atoms (lattice nodes) and $n = 3$. The upper and left metal atoms of the central triangular unit mesh are bound to four adsorbates each; the right metal atom is bound to five adsorbates. Therefore, according to formula (1), we have

$$\sigma = \frac{1}{n}\sum_i \frac{k_i}{m_i}\left(2 - \frac{1}{m_i}\right)$$

$$= \frac{1}{3}\left(\left(\frac{2}{4}\left(2 - \frac{1}{4}\right)\right) + \left(\frac{1}{5}\left(2 - \frac{1}{5}\right)\right)\right) = 0.41167.$$

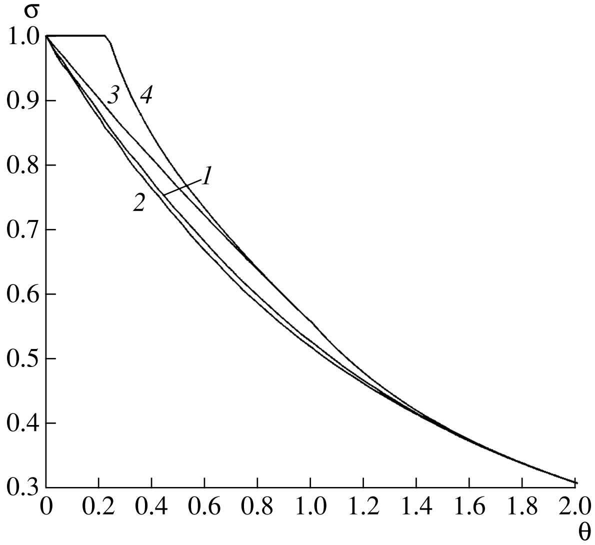


Fig. 1. Coverage dependence of σ for the (111) surface: (*1*) random adsorption without constraints; (*2*) site-choice model (see text); (*3*) fcc site preference model; (*4*) neighbor-exclusion model. The lattice size is 100 × 100.

The inconvenience of this formula is due to the fact that the value $Q(\theta)$ characterizes the local situation, whereas kinetic and adsorption modeling requires knowledge of the average value for the whole surface. This problem can be solved if we apply the Monte Carlo method: for each value of the surface coverage the adsorption sites of the lattice are populated with adsorbates according to the chosen model algorithm and the binding energy is calculated for each adsorbate. The arithmetic mean over all adsorbates is the target value.

MONTE CARLO MODELING

The metal surface was modeled by a two-dimensional regular lattice. The lattice size was chosen high enough to make the results insensitive to statistical fluctuations. The lattice size changed from one task to another, but it was always at least 100 × 100. We used periodical boundary conditions to avoid incorrect σ values at the lattice boundaries. The lattice geometry reproduced the arrangement of metal atoms on the corresponding single crystalline planes: the (111) surface was modeled by a triangulated lattice, and the (100) surface was modeled by a square lattice. According to our initial assumption, the sites for population were the centers of triangles and squares for the (111) and (100) surfaces, respectively. The number of sites was equal to the number of nodes in the case of the (100) lattice and was double the number of nodes in the case of the (111) lattice. At the initial moment, all adsorption sites were considered vacant, and the change in their state with time was determined according to the models described below. Adsorbates populated the lattice one after another, and the values of σ were recorded at 0.02-monolayer intervals.

In the most general case (when a model that takes into account diffusion was applied), the following elementary events may occur on a randomly chosen site at any given moment of time: the population of this site with a new adsorbate, a hop of an adsorbate to a neighboring hollow site through a bridge, and an empty event in which case nothing happens. The model involves two free parameters (expressed in units of reciprocal time): the f_{pop} parameter is the frequency of collisions of potential adsorbates with the surface and the f_{diff} parameter is the frequency of hops from the occupied to a free neighboring hollow site. Changes in the state of the system occur at random with the probabilities proportional to the above parameters. In our simulations described below we always set f_{pop} equal to unity to define the scale of time and eliminate one of the free parameters.

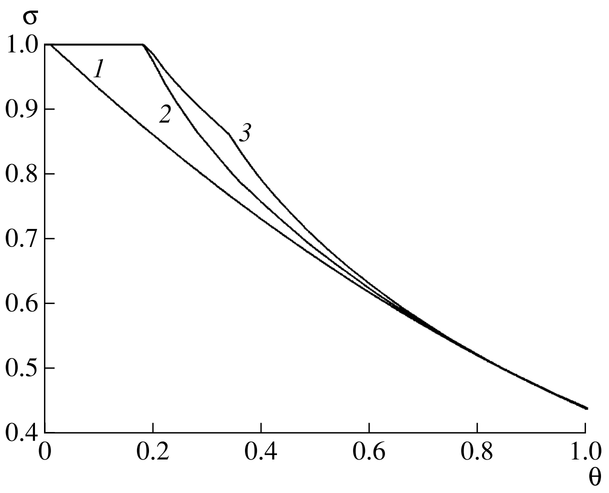


Fig. 2. Coverage dependence of σ for the (100) surface: (*1*) random adsorption without constraints; (*2*) neighbor-exclusion model; (*3*) complex variant of neighbor-exclusion model (see text). The lattice size is 100 × 100.

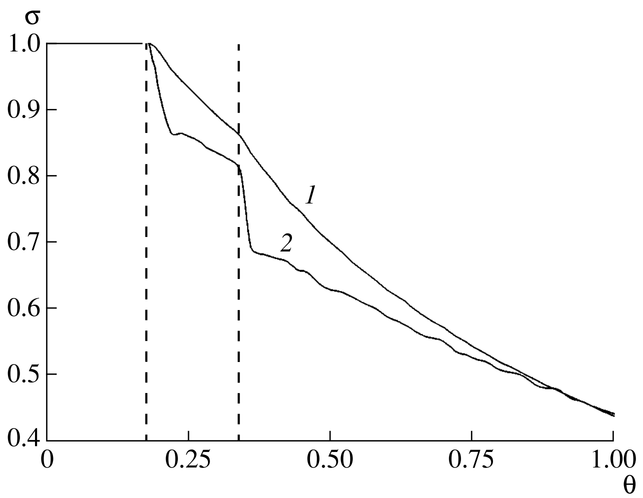


Fig. 3. Coverage dependence of σ for the (100) surface: (*1*) neighbor-exclusion model, the same as curve *3* in Fig. 2, averaging over all adsorbates; (*2*) the same model but averaging is over newly arrived adsorbates.

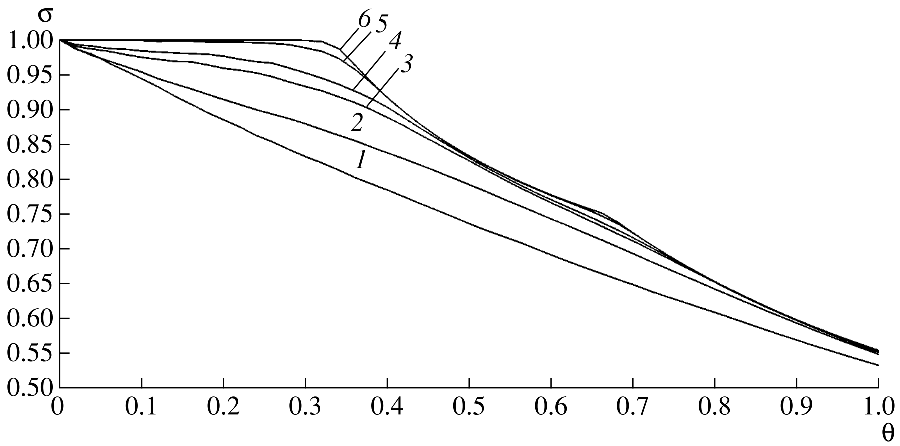


Fig. 4. Coverage dependence of σ for the (111) surface at different values of f_{diff}: (*1*) 1 and 0 (curves for these values coincide); (*2*) 10, (*3*) 50, (*4*) 100, (*5*) 1000, and (*6*) 10000. The lattice size is 200 × 200.

Populating the occupied site was considered impossible, and the respective event was treated as an empty event. The diffusion of atoms along the surface was also constrained. Thus, a hop to a site was considered impossible if this site was occupied by another adsorbate or if this hop led to an increase in the total energy of the system (taking into account changes in bond energies of all neighboring adsorbate atoms). The corresponding hopping attempt was considered empty in these cases.

Note that unlike dynamic Monte Carlo models developed for the description of adsorption dynamics and reaction kinetics (see, for instance, [24, 25] and literature cited therein), we explored equilibrium models. These models consider the population of atomic adsorbates and their diffusion without taking into account the real physics behind these processes. Of course, in most cases real adsorption processes (unlike site population) occur via more complex mechanisms, which may involve (with various probabilities) the formation of weakly adsorbed precursors of chemisorption, the dissociation of molecular adsorbates, desorption, the recombination of atomic adsorbates, adsorption-assisted desorption, diffusion, and many other processes. In our models diffusion is introduced to approach the equilibrium dependence of the parameter σ on θ, and the population of adsorption sites is used to obtain patterns at different surface coverages.

RESULTS AND DISCUSSION

When discussing the results, we will proceed from simpler models to more complex ones to trace the

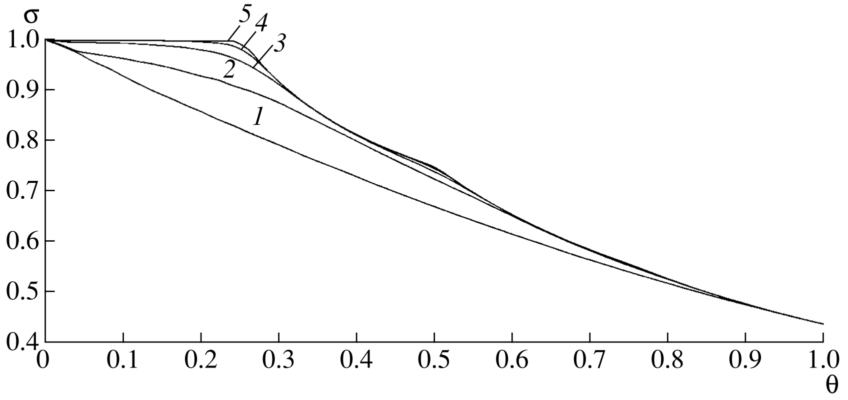


Fig. 5. Coverage dependence of σ for the (100) surface at different values of f_{diff}: (*1*) 0, (*2*) 10, (*3*) 100, (*4*) 1000, and (*5*) 10000. The lattice size is 200 × 200.

effects of various factors on the behavior of the scaling parameter σ.

Random adsorption. According to this model, adsorption sites are populated in a random fashion and adsorbates remain at their initial positions. No constrains are applied. This is the simplest model of immobile adsorbates. The results of Monte Carlo simulations for this model are shown in Fig. 1 (curve *1*) for the (111) surface and Fig. 2 (curve *1*) for the (100) surface.

Site-preference model. For the fcc (111) surface, the sites are not identical and differ in energies of atomic adsorption. Quantum mechanical calculations do not always provide unambiguous results, but most researchers agree that fcc sites are preferable over hcp sites. The models with site preference take this into account. For instance, the model may imply that fcc sites are randomly populated first and hcp population begins (also at random) when all fcc sites are exhausted. Figure 1 (curve *3*) shows the results of Monte Carlo simulations for this model.

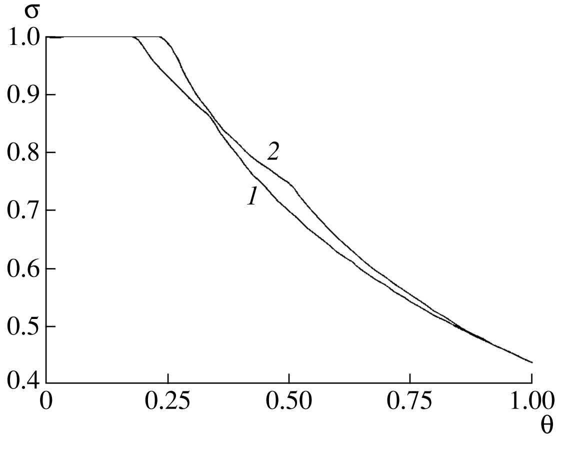


Fig. 6. Comparison of (*1*) the neighbor-exclusion model (complex variant) and (2) the model with fast diffusion (f_{diff} = 10000) for the (100) surface.

Neighbor-exclusion model. Obviously, sites adjacent to the populated ones are less energetically favorable for adsorption than distant sites. This follows from formula (1). Therefore, we can constrain the model as follows. First, adsorbates populate the sites at random so that all sites around the populated site are temporarily blocked. When all accessible sites are exhausted, the population of sites with neighbors becomes allowed. Figure 1 (curve *4*) and Fig. 2 (curve *2*) show the results of Monte Carlo simulations for the (111) and (100) surfaces respectively. A more complex variant of this model is as follows. Sites without neighbors are populated first. When they are exhausted, sites without nearest neighbors (which share two metal atoms) are populated. Then, the rest of the sites become accessible for population (Fig. 2, curve *3*). Models with the exclusion of nearest neighbors are the closest to the models that take into account surface diffusion (see below). An obvious drawback of the neighbor-exclusion models is the fact that the decision on the possibility of populating a site depends on the global rather than local situation.

An interesting picture is observed when one varies the method of σ averaging. Two variants are possible: (a) averaging over all adsorbed atoms on a lattice and (b) averaging over a portion of newly arrived adsorbates for a certain interval of Δθ (in our case, Δθ = 0.02). Figure 3 illustrates the difference between the two variants. As can be seen, the second method gives a staircase-like curve and the transitions associated with site exhaustion are seen more distinctly. Such a shape of the curve is due to the stochastic character of the process and the discreteness of an interval chosen for averaging. Even when a lattice is large, the curve does not become smooth. The physical meaning of the σ parameter depends on the method of averaging.

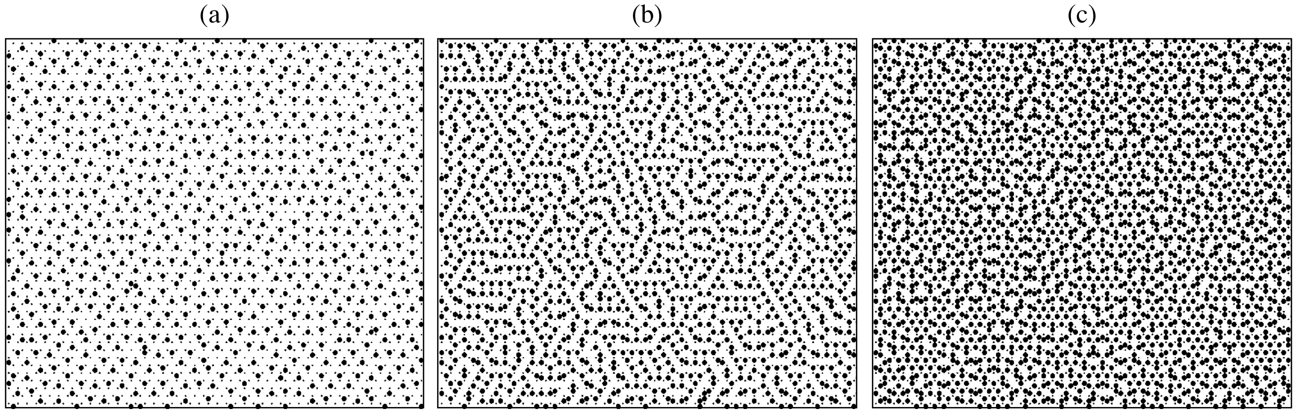


Fig. 7. Overlayer structures on the (111) surface at θ = 1/3 (a), 2/3 (b), and 1 (c).

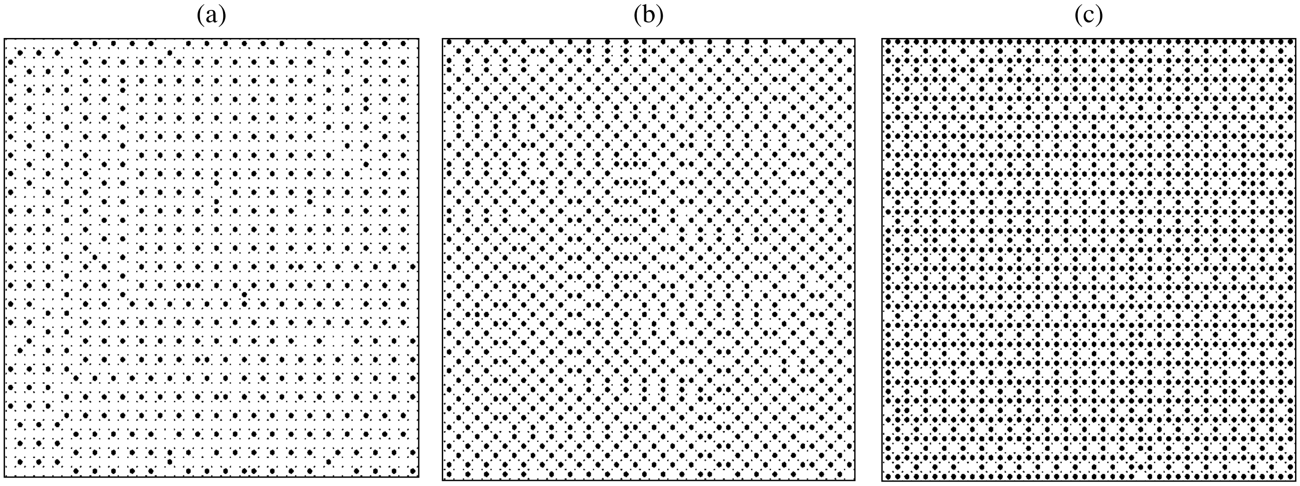


Fig. 8. Overlayer structures on the (100) surface at θ = 1/4 (a), 1/2 (b), and 3/4 (c).

When the scaling factor is averaged over all nodes of the lattice we obtain the value

$$\sigma = \left[\frac{1}{NQ_0}\sum_{i=1}^{N} Q_i(\theta)\right],$$

where N is the number of nodes and Q_0 is the binding energy in the zero-coverage limit. This value of σ corresponds to the integral heat of adsorption obtained in the microcalorimetric experiments: $\sigma = q_{\text{int}}/Q_0$. When averaging is over newly arrived adsorbates, we obtain the σ value, corresponding to the differential heat of adsorption: $\sigma = q_{\text{diff}}/Q_0$. The differential and integral heats of adsorption are related by the formula

$$q_{\text{int}} = \frac{1}{\theta}\int_0^{\theta} q_{\text{diff}} \mathrm{d}\theta.$$

Model with a site choice. In this model, a site is populated so that an adsorbate chooses between two adjacent sites that have a common edge in the (111) lattice. In this model adsorbates arrive at the edge and then one of the following events happens: if an fcc site is vacant, it is populated; if not, the adjacent hcp site is populated; if both sites are occupied, then an empty event takes place. This model implies the preference of fcc sites, but this preference is artificial rather than based on energetics. Monte Carlo simulations for this model are illustrated by Fig. 1 (curve *2*). The results obtained for this model are very close to those obtained for the unconstrained random adsorption. The concavity of the curve is somewhat more pronounced.

Diffusion-assisted models. The inclusion of diffusion in the model does not itself lead to any qualitative change in the description of the coverage-dependent binding energy if an additional constraint is not introduced that local migration of adatoms along the surface should not worsen the overall energy situation in the system. In this case, if diffusion is efficient, it scatters adatoms over the surface to minimize the number of adatoms in the neighboring sites, maximize the average

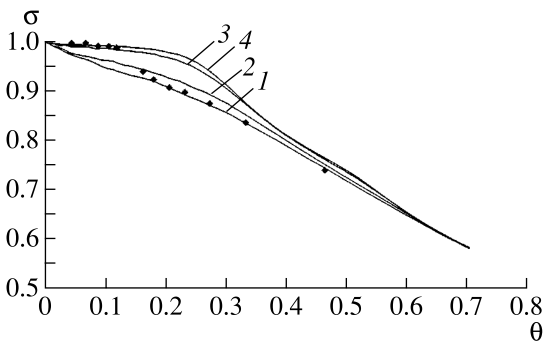


Fig. 9. Coverage dependence of σ for the atomic oxygen on the Ni(100) surface: points refer to experimental data [26], lines refer to the calculation according to the model with diffusion assistance at $f_{\rm diff}$ equal to (*1*) 5, (*2*) 10, (*3*) 50, and (*4*) 100. The lattice size is 200 × 200.

value of the binding energy, and minimize the total energy of the system.

Figure 4 shows various dependences of σ on the global values of θ at different values of $f_{\rm diff}$ for the (111) surface. Figure 5 shows analogous dependences for the (100) surface. These patterns qualitatively agree with those obtained by analyzing possible local situations [19].

Figure 6 shows a curve for the models of site exclusion (complex variant) and the diffusion-assisted model with $f_{\rm diff} = 10000$. As can be seen, the model of site exclusion correctly describes the initial portion of the curve where the energy does not change. However, this portion ends at $\theta = 0.2$ rather than at $\theta = 1/n = 0.25$. The second transition is observed at $\theta = 0.34$, when the sites without nearest neighbors are exhausted, which is earlier than in the model with infinitely fast diffusion ($\theta = 1/2$). The reason for these differences is that the former model implies nonoptimal site population due to the randomness of population, whereas the latter model corrects this nonoptimal population by the diffusion process.

It is interesting to trace the structures formed at coverages when the function of σ vs. θ changes its behavior in the case of the model with fast diffusion (Figs. 7 and 8; points are the nodes of a lattice and solid circles are adatoms). For the (111) surface, a decrease in σ begins at $\theta = 1/3$. At this moment (Fig. 7a), disordered structures are formed on the surface, which are characterized by the absence of neighbors. Each metal atom (with the exception of some local defects) coordinates only one adsorbate. The next bend on the curve σ(θ) is observed at $\theta = 1/3$. At this point an adatom has either three neighbors that have a common node in the crystal lattice or two neighbors, one of which is on the opposite site from the edge. Each metal atom coordinates two adatoms. Finally, at $\theta = 1$, each metal atom in the lattice node coordinates three adsorbates, and each adsorbate has four or five neighbors.

In the case of the (100) surface ordered overlayer structures are formed at $\theta = 1/4$, 1/2, and 3/4 in which every metal atom coordinates one, two, or three adsorbates, respectively.

COMPARISON WITH EXPERIMENTAL DATA

As mentioned above, models discussed in this work are not dynamic. They consider limiting cases of the system in equilibria. In real situations, the dynamics may impose its own constraints. Let us consider the experimental dependence of σ on θ borrowed from the literature [26]. Figure 9 shows experimental data calculated from the integral heat of oxygen adsorption on the Ni(100) surface. It can be seen that at low coverages, the experiment is described well by a model with fast diffusion, whereas at $\theta > 0.2$ the model with slow diffusion provides a better description. Thus, for the correct description of the experiment in this case, one has to take into account the dynamics of diffusion deceleration with an increase in the surface coverage. Moreover, the experimental curve is affected by constraints associated with the formation of atomic oxygen from O_2 molecules, which adsorb and dissociate only if certain clusters of vacant sites are available on the surface. All these factors were taken into account in the dynamic model proposed in [26]. To verify our data one has to carry out an experiment in which atoms are directed to the surface and stick with 100% probability if they hit vacant sites or an experiment in which they are readily formed on the surface by any other method.

CONCLUSION

Earlier, formulas describing the dependence of the atomic binding energy on the local adsorption environment on the single-crystal metal surfaces were obtained [19]. However, for the purpose of microkinetic modeling one has to know the continuous function describing the coverage dependence of the binding energy that averages all possible local situations on the surface. In this work, we obtained such functions to describe equilibrium coverage dependences using various approximations.

ACKNOWLEDGMENTS

We thank Professor E. Shustorovich for helpful discussions.

REFERENCES

1. Shustorovich, E., *Adv. Catal.*, 1990, vol. 37, p. 101.
2. Shustorovich, E. and Sellers, H., *Surf. Sci. Rep.*, 1998, vol. 31, p. 1.
3. Sellers, H. and Shustorovich, E., *Surf. Sci.*, 2002, vol. 504, p. 167.
4. Shustorovich, E. and Bell, A., *Surf. Sci.*, 1991, vol. 253, p. 386.

5. Paredes Olivera, P., Patrito, E.M., and Sellers, H., *Surf. Sci.*, 1995, vol. 327, p. 330.
6. Wang, G., Zhao, Y., Cai, Z., Pan, Y., Zhao, X., Li, Y., San, Y., and Zong, B., *Surf. Sci.*, 2000, vol. 465, p. 51.
7. Hei, M.J., Chen, H.B., Yi, J., Lin, Y.J., Lin, Y.Z., Wei, G., and Liao, D.W., *Surf. Sci.*, 1998, vol. 417, p. 82.
8. Zeigarnik, A.V., Valdés-Pérez, R.E., and Myatkovskaya, O.N., *J. Phys. Chem. B*, 2000, vol. 104, p. 10578.
9. Zeigarnik, A.V. and Myatkovskaya, O.N., *Kinet. Katal.*, 2001, vol. 42, p. 464.
10. Gislason, J., Xia, W., and Sellers, H., *J. Phys. Chem. A*, 2002, vol. 106, p. 767.
11. Shen, B., Chen, X., Fan, K., and Deng, J.-F., *Surf. Sci.*, 1998, vol. 408, p. 128.
12. Bell, A. and Shustorovich, E., *J. Catal.*, 1990, vol. 121, p. 1.
13. Shustorovich, E. and Bell, A., *Surf. Sci.*, 1991, vol. 248, p. 359.
14. Shustorovich, E., *Catal. Lett.*, 1990, vol. 7, p. 107.
15. Shustorovich, E. and Bell, A., *Surf. Sci.*, 1993, vol. 289, p. 127.
16. Shustorovich, E. and Bell, A., *Surf. Sci.*, 1991, vol. 259, p. 791.
17. Zeigarnik, A., *Kinet. Katal.*, (in press).
18. Shustorovich, E., *Surf. Sci.*, 1985, vol. 163, p. 645.
19. Shustorovich, E., *Surf. Sci. Rep.*, 1986, vol. 6, p. 1.
20. Hansen, E. and Neurock, M., *Surf. Sci.*, 1999, vol. 441, p. 410.
21. Hansen, E. and Neurock, M., *Surf. Sci.*, 2000, vol. 464, p. 91.
22. Hansen, E. and Neurock, M., *Chem. Eng. Sci.*, 1999, vol. 54, p. 3411.
23. Ge, Q., Hu, P., and King, D.A., *J. Chem. Phys.*, 1997, vol. 108, p. 6447.
24. Brown, W.A., Kose, R., and King, D.A., *Chem. Rev.*, 1998, vol. 98, p. 797.
25. Zhdanov, V.P., *Surf. Sci.*, 2002, vol. 500, p. 966.
26. Vattuone, L., Yeo, Y.Y., and King, D.A., *J. Chem. Phys.*, 1996, vol. 104, p. 8096.