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Simulation of adsorption processes performance over supported metal nanoparticles

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ABSTRACT

The statistical lattice model has been proposed which permits one to take into account the change in the shape and surface morphology of the nanoparticle under the influence of the reaction media. The influence of monomolecular and dissociative adsorption on the particles equilibrium shape and surface morphology has been studied. It has been shown that by taking into account attraction "adsorbate-metal" the reshaping of the initial hemispheric particle into the truncated pyramidal one occurs induced by adsorption, similar to the experimentally observed reversible reshaping of active nanoparticles.

1. Introduction

In heterogeneous catalysis, adsorption and reaction processes usually occur on supported metal nanoparticles. To study such processes experimentally, a wide variety of surface science techniques came into the use in the last decades of the 20th century. Besides, considerable progress in manufacturing of model catalysts with well-defined properties like particle size, shape and separation has been achieved. Despite this progress, the cognitive potential of the experimental studies in this field is still limited because the measurements are usually indirect and the information derived demands quantitative interpretation. This can be done only with the use of mathematical models. But the complexity of supported catalytic systems [1–3], coupled with the relatively high pressure of reagents, limits the use of sensitive physical techniques for surface characterization and makes hard the interpretation of reaction kinetics on the supported catalysts compared with a bulk one. Successful interpretation of the results requires constructing mathematical models providing accurate description of systems under consideration. Application of the conventional mean-field models is rather limited here due to the peculiarities of the reaction performance on the nm scale, including the inherent heterogeneity of metal crystallites as well as spontaneous and adsorbate-induced changes of the shape and degree of dispersion of supported catalysts. Despite the potential power of molecular dynamics, the use of this technique for the analysis of the physicochemical processes over supported particles is also limited due to the short length and time scales typical for this approach. Under such circumstances, the use of stochastic simulations based, e.g., on the Monte-Carlo technique, is almost inevitable [1–3]. But the activity in this field is now at the very beginning.

Often as a model of the supported particle a top projection of the truncated pyramid has been considered, i.e., the pyramid is represented by a $N \times N$ square lattice, where the central $M \times M$ array of sites mimics the top facet (active surface of the particle) and the periphery corresponds to the support (or to the side facets with different catalytic properties). Despite the simplicity of such models, both predictable and unexpected results have been obtained by modeling of different peculiarities of the reaction performance over the supported particles. Such factors as reactant supply due to the diffusion over the support (spillover) [4], interplay of the reaction kinetics on the different facets of the supported particle due to the adsorbed species diffusion between the facets [5], the jump-wise reshaping of the active particle under the influence of the adlayer composition [6], oscillations and chaos in the catalytic reactions proceeding on the supported catalysts [7], the influence of geometric parameters of the supported particles on the reactivity and selectivity of the multi-route catalytic reactions [8], reciprocal effect of the surface morphology and adsorption-reaction processes over the catalytic particle [9], were examined in various studies. However, the theoretical models taking into account the dynamic change of the shape and surface morphology of the catalytic particles under the influence of adsorbed species and temperature action are practically lacking.

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The goals of our study are (1) the elaboration of the statistical lattice model of the supported catalyst particle taking into account the change of the shape and surface morphology of the nanoparticles under the influence of the reaction media, and (2) the qualitative description of the peculiarities of the adsorption processes on the supported metal nanoparticles.

2. Model

Recently, the model for the monomolecular and dissociative adsorption on the roughened catalytic surface with dynamically changing morphology has been proposed [10,11]. It was based on the well-known “solid-on-solid” model [12,13] using the «infinite» Kossel crystal. The theoretical analysis of such systems is very complicated even in the case of the infinite surface. Therefore the only possible method for their investigation is modelling based on the Monte-Carlo technique.

Several advantages of this technique should be mentioned: (a) the possibility of independent consideration of the local environment of each active center or adsorbed molecule; (b) simple enough algorithmic realization of almost any concepts describing the occurring physicochemical processes; (c) computer visualization of the simulated surface morphology and the composition of the adsorbed layer. It should be pointed out that it is possible to model the systems under consideration on a real scale: the linear size of nanoparticles is from several to hundreds of atoms.

As a model of the catalytic metal particle we shall consider the Kossel crystal or, more exactly, the SOS (solid-on-solid) model [12,13] located on a neutral support (Fig. 1). The rigid support surface is represented by a square lattice $N \times N$ with periodic boundary conditions. The initial active particle consists of a finite number of elementary cells (metal atoms) situated in the columns of the cubic lattice $N_{\mathrm{in}} \times N_{\mathrm{in}} \times h_{\mathrm{in}}$. Usually, in our simulations $N = 200$, $N_{\mathrm{in}} = 21$, $h_{\mathrm{in}} = 10$ atoms, i.e., in this particular case the base width of the initial particle is N_{in} ~8 nm, and the height h_{in} ~4 nm. The surface morphology of the particle is defined by distribution of heights of the metal atom columns. The metal atoms attract the nearest neighbouring ones and the atoms of the support. The attraction is characterised by energies: J_{mm}, the interaction energy between the nearest neighbour atoms situated at the same level and one on the lower, J_{ms}, the interaction energy between the metal atom and the rigid support underneath. For the sake of simplicity, we do not consider at this stage the diagonal interactions between atoms. The overhangs of atoms in the columns and the appearance of the vacancies in the volume of the crystal are forbidden. The particle surface morphology is changed due to the thermal diffusion of the surface atoms. We consider as a surface atom the upper atom of the Kossel crystal but not a side one; hence, our model is two-dimensional. To model the diffusion of the metal atoms over the metal and support surfaces the Metropolis algorithm [14] has been used. The diffusion proceeds via transfer of the randomly chosen surface atom from any column onto one of the neighbouring ones (for the boundary metal atoms it might be the cell of the support surface). If total energy decreased due to this diffusion transfer, i.e. the transferring atom got a more energetically beneficial position, such an attempt would occur with probability $W = 1$. If the energy increases (the number of the neighbouring metal atoms decreases), the successful attempt happens with probability $W = \exp\{-\Delta E/RT\} < 1$, where ΔE is the difference between the energies of the initial and resulting configurations. Such a procedure ensures the fulfilment of the Boltzmann distribution on the probabilities of the possible configurations and warrants getting to the thermodynamically equilibrium state at an infinite number of Monte-Carlo steps. In this case one MC step consists of N^2 attempts to transfer the surface atom. In reality, however, we are forced to restrict our calculation to a sufficiently great but finite number of MC steps at which the system configuration can be considered to be in equilibrium (within statistical fluctuations). Hereinafter we shall mean by «equilibrium» the shape of the particle in just this «dynamic» sense, taking into account that after each next MC step the shape and the surface morphology of the particle change slightly but the average characteristics keep safe. In our numerical experiments 50,000–70,000 MC steps had been performed usually to establish the equilibrium at fixed temperature. It should be borne in mind that the number of surface atoms (active centres) used for the calculation of surface coverages by adsorbed species can change from one MC step to another as a result of surface atoms diffusion on the support (for the flat initial particle this number equals $21 \times 21 = 441$).

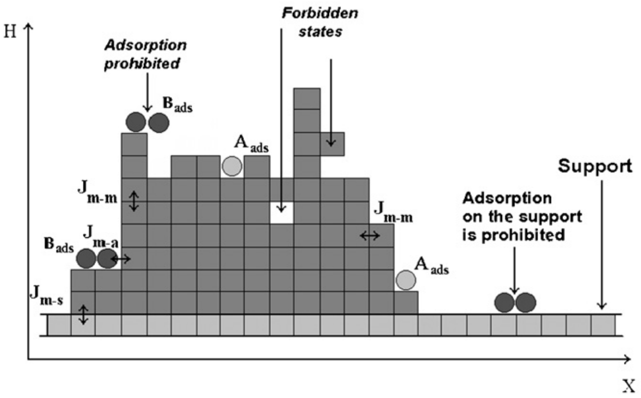

Fig. 1. Scheme of the supported catalytic particle model–cross cut of the Kossel crystal. For explanations to the Figure see the text.

At a sufficiently high temperature the initially cubic shape of the supported crystal begins to change due to increasing of the surface atoms mobility. The particle’s surface becomes rougher: in addition to the increasing number of point defects, collective defects appear, such as steps surrounding relatively planar surface regions (terraces). As a result, some «dynamically» equilibrium shape of the particle arises, depending on the temperature, size of the crystal and the ratio of interaction energies $J_{\mathrm{mm}}/J_{\mathrm{ms}}$ between metal and support atoms.

It is evident that the key factors for our model are the interaction energies J_{mm} and J_{ms}. Owing to the lack of the reliable information about these values (both experimental and theoretical) we shall not consider particular supports, metals and adsorbed species. Our aim is to reveal the common qualitative regularities of the adsorption performance on the supported particles. We estimate the J_{mm} value to be the energy of creation the pair «adatom-vacancy» for the flat (1 0 0) surface, obtained in the frames of effective medium theory. According to ref. [12] and references therein this value equals ~0.115 eV, i.e. −10 kJ/mol. We assume that the attraction «metal–metal» should be stronger than «metal-support», (otherwise it is evident, that the particle will spread over the support surface at any temperature). In our simulations we accept $J_{\mathrm{mm}} = -10$ kJ/mol and $J_{\mathrm{ms}} = -2.5$ kJ/mol (sign «–» correspond to the attraction between the atoms). This ratio between J_{mm} and J_{ms} was chosen from our preliminary simulation experiments: (i) at a lower ratio the particle exhibits a tendency to the spreading even at low temperatures; (ii) at a higher ratio the base of the particle becomes lower and its height grows.

3. Results and discussion

3.1. Equilibrium shapes of the supported particle

In the frames of the proposed statistical lattice model the equilibrium shapes of the supported nanoparticle at different temperatures have been studied. The initial shape and the equilibrium

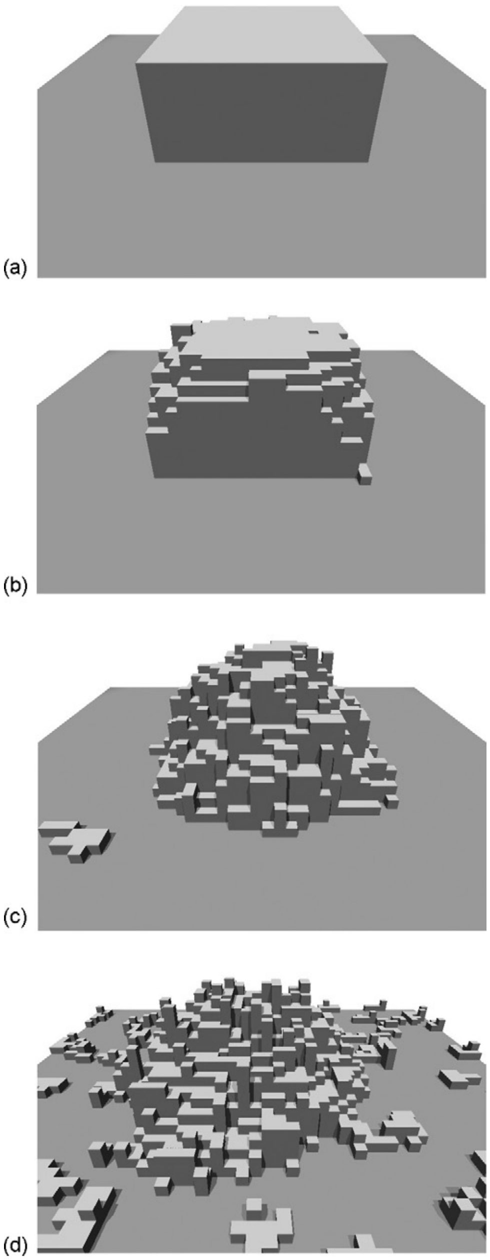

Fig. 2. The initial (a) and equilibrium (b–d) shapes of the active particles simulated at different temperatures: (b) 500 K, (c) 900 K, (d) 1100 K.

shapes of the supported particle simulated at the above-mentioned J_{mm} and J_{ms}, and different temperatures are shown in Fig. 2.

One can see that at the intermediate range of temperatures (T = 500 K) the surface of the particle is flat enough but the corners and edges are partly rounded. The surface of the metal particle becomes extremely rough at the hemispherical shape (T = 900 K). The beginning of the dispersal of metal particle over the support surface in our model (at the above-mentioned values of J_{mm} and J_{ms}) is located between T = 900 K and T = 1100 K. The radius of the dispersal remains unchanged (within statistical fluctuations) during the process of the equilibration. When these radii overlap we can observe the coalescence of closely situated particles at high temperatures (Ostwald ripening). After the reduction of the temperature (from 1100 K to 500 K or from 900 K to 500 K) the particle shape returns to the initial equilibrium characteristic for the given temperature (in that case 500 K). The distribution of the particles sizes after the reduction of the temperature is determined by the procedure of cooling (stepwise or gradual cooling). Obviously, the temperature range of the shape changing depends on the absolute values of interaction energies J_{mm} and J_{ms} – the more are the values of J_{mm} and J_{ms}, the at higher temperatures the corresponding changes of the particle shape and surface roughening should be observed.

3.2. Monomolecular and dissociative bimolecular adsorption on the supported particle

To study the influence of adsorption on the «equilibrium» shape and surface morphology of the catalytically active particle we assume that the adsorption and/or desorption of the diatomic molecule B_2 can occur only on the two neighbouring metal atoms situated at the same level, adsorption and/or desorption of the monoatomic molecule A can occur on any metal atoms and the adsorption on the support surface is prohibited (Fig. 1). The molecules B_2 dissociate immediately after adsorption on atoms B_{ads} which are able to diffuse over the particle's surface. The probability of the successful attempt of adsorption is proportional to the product of adsorption rate coefficient and pressure:

$$W_{\mathrm{ads}}^{\mathrm{A}} = \frac{k_{\mathrm{ads}}^{\mathrm{A}} P_A}{(k_{\mathrm{ads}}^{\mathrm{A}} P_{\mathrm{A}}) + k_{\mathrm{des}}^{\mathrm{A}} \exp(-\Delta E/RT)}, \tag{1}$$

$$W_{\mathrm{ads}}^{\mathrm{B}_2} = \frac{k_{\mathrm{ads}}^{\mathrm{B}_2} P_{\mathrm{B}_2}}{(k_{\mathrm{ads}}^{\mathrm{B}_2} P_{\mathrm{B}_2}) + k_{\mathrm{des}}^{\mathrm{B}_2} \exp(-\Delta E/RT)}, \tag{2}$$

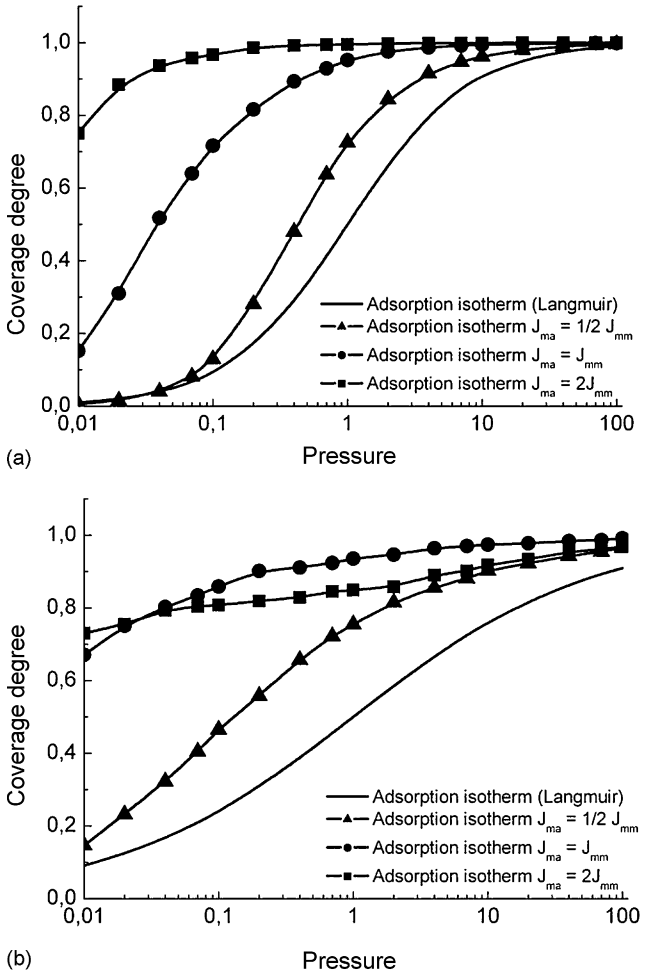

Fig. 3. The isotherms of (a) monomolecular and (b) bimolecular adsorption on the supported metal particle at different interaction energies "metal–adsorbate". The initial equilibrium shape of the particle corresponds to T = 500 K.

where $k^{\mathrm{i}}_{\mathrm{ads}}$ – adsorption rate coefficient of adsorbates, P_{i} – pressure of adsorbates in the gas phase, $k^{\mathrm{i}}_{\mathrm{des}}$ – desorption rate coefficient of adsorbates.

We suppose that the adsorbed molecules interact with neighbouring metal atoms with energy J_{ma}, therefore the probability of desorption is determined by the local surroundings of desorbing molecules:

$$W^{\mathrm{A}}_{\mathrm{des}} = \frac{k^{\mathrm{A}}_{\mathrm{des}} exp(-\Delta E/RT)}{(k^{\mathrm{A}}_{\mathrm{ads}} P_A) + k^{\mathrm{A}}_{\mathrm{des}} \exp(-\Delta E/RT)}, \tag{3}$$

$$W^{\mathrm{B}_2}_{\mathrm{des}} = \frac{k^{\mathrm{B}_2}_{\mathrm{des}} \exp(-\Delta E/RT)}{(k^{\mathrm{B}_2}_{\mathrm{ads}} P_{\mathrm{B}_2}) + k^{B_2}_{\mathrm{des}} \exp(-\Delta E/RT)}, \tag{4}$$

where ΔE – is, as earlier, the difference between the energies of the resulting and initial states, where for the resulting state $E = 0$ (the A and B_2 molecules desorb in the gas phase) and for the initial state $E = \Sigma J_{\mathrm{ma}}$–energy of local surroundings of adsorbed molecule $\mathrm{A}_{\mathrm{ads}}$ or $\mathrm{B}_{\mathrm{ads}}$ (additive interactions). In our simulations $k^{\mathrm{A}}_{\mathrm{ads}} = 1$, $k^{\mathrm{A}}_{\mathrm{des}} = 1$, $k^{\mathrm{B}_2}_{\mathrm{ads}} = 1$ and $k^{\mathrm{B}}_{\mathrm{des}} = 1$.

After each adsorption or desorption attempt several trials of metal and/or adsorbate atom diffusion have been executed (usually 10 trials of diffusion per one adsorption/desorption attempt) to equilibrate both the morphology of particle surface and the adsorbed layer. Increasing the number of these trials up to 100 does not lead to any noticeable changes in qualitative and quantitative characteristics of the simulated process, but essentially increases the simulation time. The adsorbate diffusion over the particle surface takes place in the same manner as of the metal atoms (the Metropolis algorithm [14] has been used too). By simulation of the adsorption isotherms the supported particle was preliminary established in equilibrium at given temperature. Then, step by step rising the pressure of adsorbate, we perform the simulations at each pressure value trying to achieve the equilibrium state both for the adsorbed layer and for the particle surface morphology itself. The values of surface coverages were averaged on last 500 MC steps. In this case one MCS consists of N^2 adsorption/desorption attempts.

The adsorption isotherms, (monomolecular adsorption–Fig. 3a, bimolecular adsorption – Fig. 3b), have been simulated at different ratios of lateral interaction (attraction) between adsorbed species and metal atoms at $T = 500$ K ($J_{\mathrm{ma}} = 0.5J_{\mathrm{mm}}$, $1J_{\mathrm{mm}}$ and $2J_{\mathrm{mm}}$). For a better pictorial view of the low pressure sections of isotherms the P_{A} and P_{B_2} pressures are presented in logarithmic scale. The coverages $\Theta_{\mathrm{A}}(P_{\mathrm{A}})$ and $\Theta_B\left(P_{\mathrm{B}_2}\right)$ simulated at given P and J_{ma} are greater than the corresponding values on the theoretical Langmuir adsorption isotherm $\Theta_{\mathrm{A}} = P_{\mathrm{A}}/(1 + P_{\mathrm{A}})$ and $\Theta_{\mathrm{B}} = \sqrt{P_{\mathrm{B}_2}}/\left(1 + \sqrt{P_{\mathrm{B}_2}}\right)$ (for monomolecular and bimolecular adsorption respectively, $K_{\mathrm{e}} = 1$). This can be explained by the fact that adsorbed species will both stimulate the appearance of the point defect on the surface and stabilize the vacancies filled by adsorbed atoms due to diffusion. As a result, the roughening of the particle surface will increase. On the other hand, the probability of desorption of

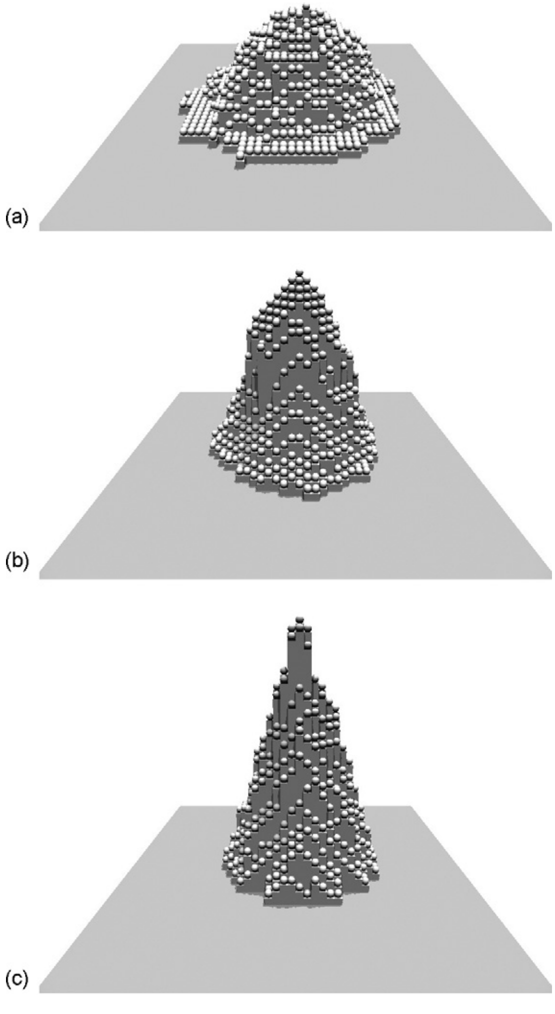

Fig. 4. The surface of the active particle (21 × 21 × 10 atoms in size) at different interaction energies "metal–adsorbate": (a) $J_{\mathrm{ma}} = 1/2J_{\mathrm{mm}}$; (b) $J_{\mathrm{ma}} = J_{\mathrm{mm}}$; (c) $J_{\mathrm{ma}} = 2J_{\mathrm{mm}}$. $T = 500$ K Monomolecular adsorption. The values of coverages Θ_{A} correspond to the pressure $P_{\mathrm{A}} = 100$ (see Fig. 3a). $T = 500$ K.

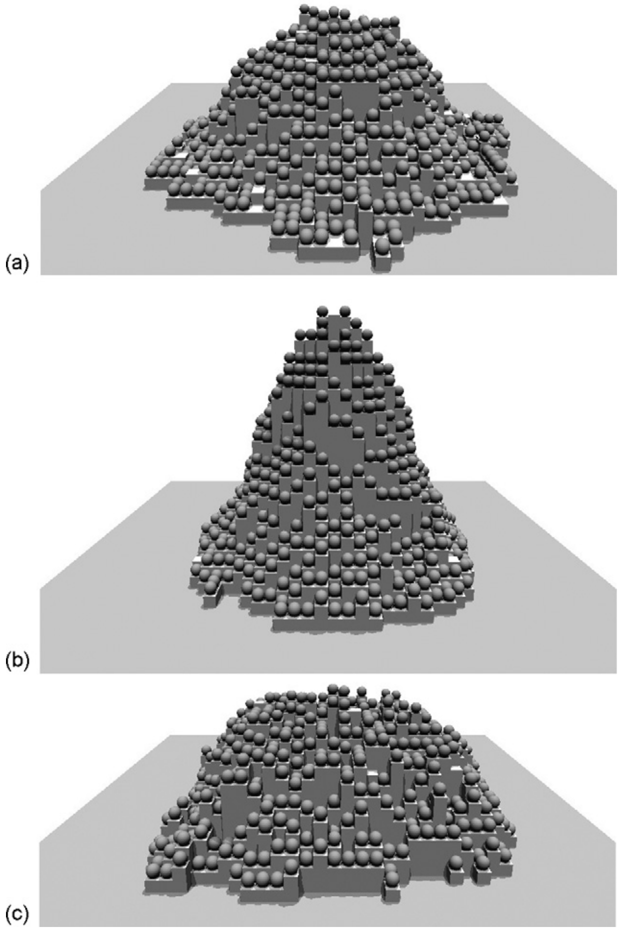

Fig. 5. The surface of the active particle at different interaction energies "metal-adsorbate": (a) $J_{\mathrm{ma}} = 1/2J_{\mathrm{mm}}$; (b) $J_{\mathrm{ma}} = J_{\mathrm{mm}}$; (c) $J_{\mathrm{ma}} = 2J_{\mathrm{mm}}$. Bimolecular adsorption. The values of coverages Θ_{B} correspond to the pressure $P_{\mathrm{B}_2} = 100$ (see Fig. 3b). $T = 500$ K.

the adsorbed species having as neighbours the metal atoms will decrease.

The change of the surface morphology and of the shape of the supported particle induced by the monomolecular and bimolecular dissociative adsorption is presented in Figs. 4 and 5 (respectively), the equilibrium shapes of the particles have been shown at the final point $P = 100$. The increasing of J_{ma} value leads to the transformation of the particle to the pyramidal shape (for the bigger particles–to the truncated pyramidal shape, see below), at that with increasing of the «metal–adsorbate» bond strength the height of the pyramid rises. But at strong interaction «metal–adsorbate» ($J_{ma} = 2J_{mm}$) for bimolecular dissociative adsorption we have instead of the pyramidal shape of the particle the hemispherical one (Fig. 5c) with very rugged surface in comparison with the initial equilibrium particle, and in the high-pressure interval the simulated coverages are lower in comparison with equilibrium values (Fig. 3b). In our opinion, it is due to the fact that the B_2-molecules adsorbed on the surface attract immediately the neighbouring metal atoms at that decreasing the probabilities of their own desorption and diffusion. And what is more, the bare surface metal atoms form the structure that is unfavorable for the adsorption (and desorption) of the diatomic molecule. As a consequence, at each next increasing of the pressure (every time we increase stepwise the pressure conserving the adsorbed layer configuration formed at previous pressure value) the coverage of the surface by B_{ads} increased only slightly (Fig. 3b): the particle surface morphology is positioned on a metastable long-lived state (for more details see [15]). But at $J_{ma} = J_{mm}$ the particle is still pulled to the pyramidal shape as a result of adsorption. In this case the B_{ads} atoms although have the reduced desorption probabilities, but their diffusion probabilities are at least not less than the ones for surface metal atoms diffusion. By monomolecular adsorption (with $J_{ma} = 2J_{mm}$) that drastic change of surface particle morphology does not happen (e.g., [10,11,16]), although in both cases the adsorbed species will stabilize the point defects and vacancies appearing due to the surface metal atoms diffusion, at that the surface roughening increases.

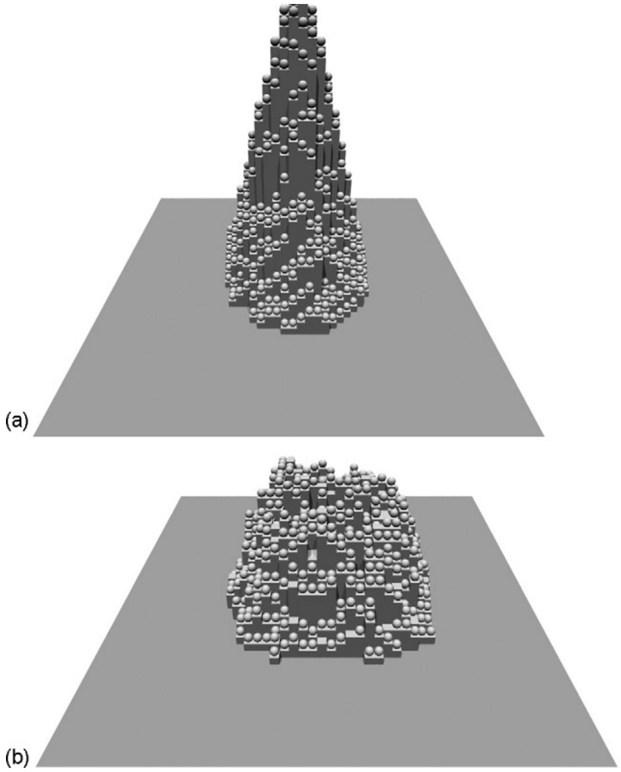

Fig. 6. The surface of the active particle after monomolecular adsorption with $J_{ma} = 2J_{mm}$ and $T = 500$ K: (a) step by step rising pressure from very low ($P_A = 0.01$) to more high ($P_A = 0.1$); (b) single pressure 0.1.

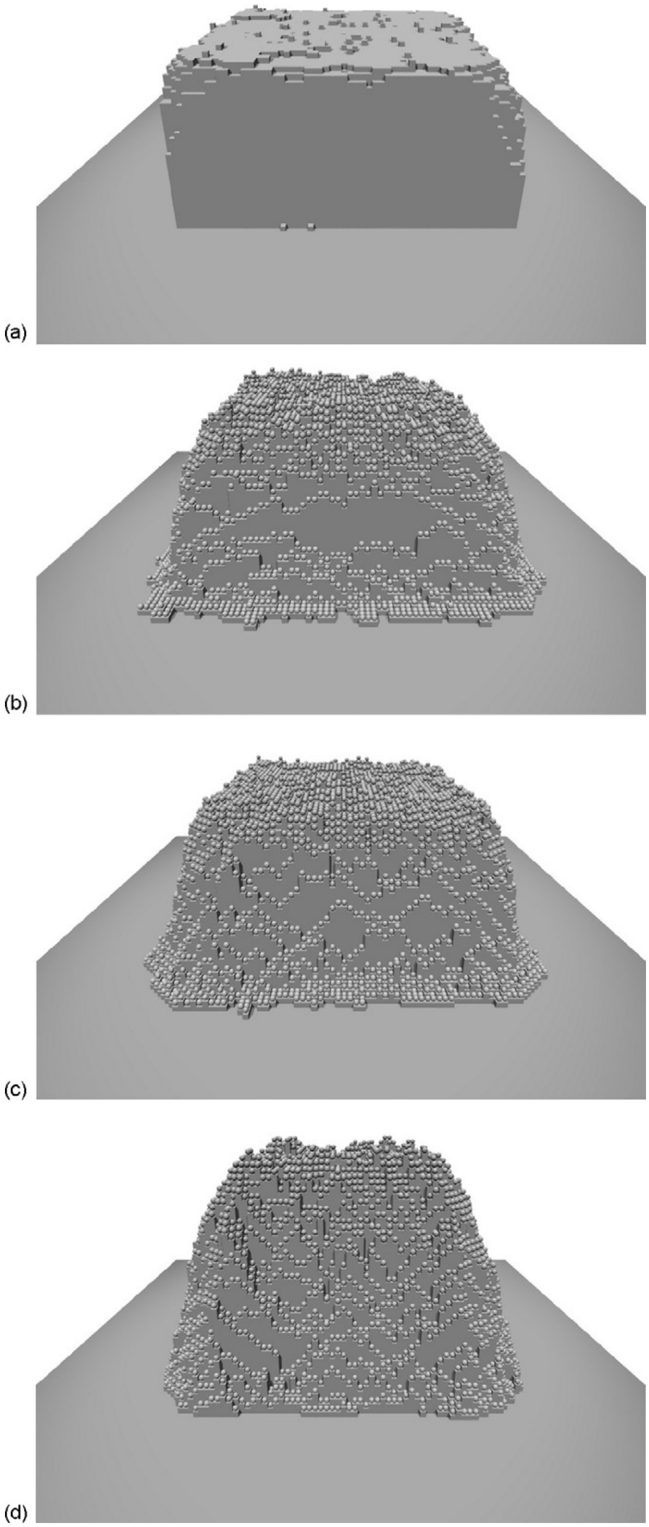

Fig. 7. Influence of size of supported particles on the equilibrium shape and surface morphology at 500 K: (a) Initial particle at $T = 500$ K; (b) $J_{ma} = 1/2\,J_{mm}$; (c) $J_{ma} = 1\,J_{mm}$; (d) $J_{ma} = 2\,J_{mm}$.

When we simulated adsorption beginning with enough high pressure ($P_A = 0.1$), taking into account the interaction between metal and adsorbate, the change of supported particle to pyrami-

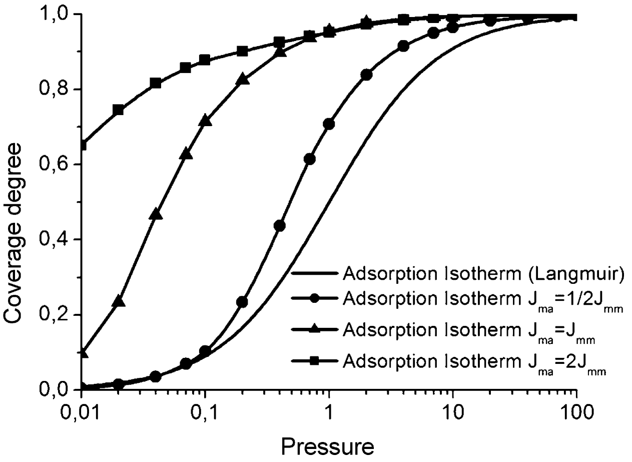

Fig. 8. The isotherms of monomolecular adsorption on the active particle (61 × 61 × 30 atoms in size) at different interaction energies «metal–adsorbate». T = 500 K.

dal shape does not occur as compared with the case when we step by step rising pressure from low ($P_A = 0.01$) to more high ($P_A = 0.1$) value, i.e. gradually increasing the number of adsorbed molecules, (Fig. 6(a)). In the case when we begin with enough high pressure, the high enough coverage of the particle by adsorbed species arises very quickly, (Fig. 6 (b)) and fixes the initial shape and surface morphology of the supported particle. This means that the changes of the shape of the supported particles induced by adsorption can proceed only gradually, beginning from low pressure values.

If we introduce into the model the lateral “adsorbate–adsorbate” interactions (repulsive or attractive, J_{aa}) the change of equilibrium shapes of particle induced by adsorption remains without any significant differences. Adsorption isotherms simulated by taking into account the lateral “adsorbate–adsorbate” interactions agree well with adsorption isotherm without J_{aa}, except for the case with «adsorbate–adsorbate» attraction, in this case adsorption isotherm is situated somewhat higher than one without lateral J_{aa} interaction: the probability of desorption is slightly decreased.

We studied also the influence of the size of supported particles on the equilibrium shape and surface morphology after monomolecular adsorption (Fig. 7). The size of particle in this case is three times as much (61 × 61 × 30 atoms), and the size of support is 200 × 200. We can see from this figure that the changing of such an active particle into a truncated pyramid induced by adsorption is moderate (although surface morphology of active particle becomes very rugged) in comparison with similar changing occurred on smaller nanoparticles (e.g., 21 × 21 × 10 atoms). Nevertheless, it is evident that the shape changing becomes more noticeable with the increasing of J_{ma}, and the adsorption isotherms on “big” particle coincide with isotherms on smaller particles (Fig. 8).

After the removal of the adsorbed layer (e.g., by turning off the adsorption from the gas phase) the shape and the surface morphology of the particle returned to the equilibrium characteristics peculiar to the given temperature. The simulations show that if the «adsorbate–metal» interaction energies become comparable with the «metal–metal» ones the nanoparticle undergoes reversible adsorbate-induced reshaping and that the particles size determines the degree of reshaping as in experiments [17]. In this work the dynamic structure and morphology changes of metallic Cu particles under various gas compositions were studied *in situ* with transmission electron microscopy facility. Authors exposed Cu particles supported on ZnO to more oxidizing conditions by adding H_2O to the hydrogen gas and reducing conditions by adding CO to the hydrogen gas. Upon each change in gas composition, the particles changed their shape. The addition of water to the hydrogen gas transforms the Cu crystals into a more spherical morphology, similar to Fig. 7. If the H_2/H_2O gas mixture is replaced again by pure hydrogen, the Cu crystals revert to their original form. Addition of the reducing gas, carbon monoxide, to the hydrogen gas results in more marked changes [17]. The adsorption-induced reshaping of the nanoparticles could be explained by the joint actions of the following factors: diffusion of the surface atoms of the metal particle, attractive interaction between metal atoms and adsorbed species, metal and support atoms, and possibility of desorption of the adsorbed species. In our simulation experiments, when desorption of the adsorbed species was prohibited, any remarkable change of the particle shape and surface morphology has not been observed. In this case the adsorbed species covered the surface very quickly even at low pressures and this adsorbed layer protects the particle from any changes.

4. Conclusions

The statistical lattice model for the adsorption processes over the supported metal nanoparticle has been elaborated. The model permits one to take into account the change in the shape and surface morphology of the nanoparticle under the influence of the reaction media. Depending on the temperature and the values of the interaction energies “metal–metal” and “metal-support”, different equilibrium shapes of the nanoparticles have been observed. In the case of “adsorbate–metal” interactions adsorption can induce the change of the shape and surface morphology of the supported particle, at that the adsorption isotherms differ noticeably from the ideal Langmuir isotherm.

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