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Two simple lattice models of the equilibrium shape and the surface morphology of supported 3D crystallites

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Abstract. Two statistical lattice models of a 3D crystal are proposed, which allow us to take into account a change in the shape and in the surface morphology of a nanoparticle under the influence of the temperature. It has been shown that consecutive diffusion of atoms does not give reasonable simulation results, therefore the consideration of "mathematical" diffusion, where the atom is allowed to diffuse at any point of a lattice but not only in the nearest neighbor, or many atoms to diffuse simultaneously, has been included in the algorithm.

1. Introduction

As has been experimentally shown, the structure of a catalytic surface is not fixed and can undergo significant morphological changes not only in the course of catalytic reactions, but also under the action of temperature factors [1–5]. As experimental data testify, various defects of a surface (terraces, steps, ridges of adsorbed atoms and vacancies) arising during the reaction and under the action of temperature, have rather an essential influence on the course of catalytic transformations. Also, it is well known, that properties of the supported catalysts essentially differ from those of massive ones. In particular, it is important that the shape of supported nanoparticles can change in a reasonable time [6]. Recently, a number of studies have been published, concerning modeling catalytic reactions accounting for a change in the morphology of the supported catalyst surface [7, 8]. In their greater part, actually two-dimensional models are considered, while the surface of a real catalyst is not two-dimensional. Models that include dynamic changes in the shape and in the surface morphology of three-dimensional catalytic particles under the action of temperature are not numerous. Thus, an actual problem is the creation of theoretical models of catalytic reactions with allowance for a dynamic change of morphology of the supported three-dimensional nanoparticle not only in the course of a reaction, but also under the action of temperature.

2. A physical model

In this paper, we consider a statistical lattice model of a supported catalyst particle developed with allowance for changes in the shape and in the surface

morphology of an active particle under the action of temperature. Our observations demonstrate that the inclusion of these factors into the model leads to a dramatic change in the surface morphology. In [9], a substrate is comprised of unit cells positioned in columns of the cubic lattice. This lattice is based on the 2D $N \times N$ plane with periodic boundary conditions.

We propose a more realistic model supposing that vacancies and overhanging of a crystal above the support surface may be formed. We used a crystal with a simple cubic lattice with the initial size of $20 \times 20 \times 10$ atoms, located in the center of an immobile support represented by a square 128×128 lattice with periodic boundary conditions. The periods of the crystal lattice and that of the support have been chosen to be equal. The metal atoms attract the nearest neighboring ones and the atoms of the support. The attraction strengths are characterized by energies of the interaction of the nearest neighbor atoms, and of the interaction between the metal atom and the rigid support underneath. The crystal breaking and separation of metal atoms from a crystal as well as separation of the crystal from the support are not considered in the model.

3. The algorithm and simulation results

3.1. Model 1. After forming the initial crystal, a change in the shape of this crystal is simulated using the Metropolis algorithm [10] that is realized in the following form:

1. Coordinates of a surface atom and of one of its nearest neighboring sites were randomly chosen.

2 The possibility of the chosen atom transition into the chosen site is checked (transition is possible if a chosen site is free, the atom does not get off a crystal, as well as a substrate and remains coherent). If the energy of the system as a result of such a transition decreases or remains constant, such an attempt is realized with probability $W = 1$. If the energy of the system increases, transition can be realized with probability

$$W = \exp \frac{dE}{kT} < 1, \tag{1}$$

where dE is a difference between the energies of the final and the initial states of the system, T is temperature, k is the Boltzmann constant. The energy of the initial and the final states of the system is calculated as the sum of the interactions energies of all pairs of the neighboring atoms (additive interactions). This procedure provides the fulfilment of the Maxwell–Boltzmann distribution over the probabilities of possible configurations of the system and assures the thermodynamic equilibrium within an infinite number of Monte Carlo steps. In our case, one Monte Carlo step consists of $20 \times 20 \times 10$ trials of the diffusion transfer of surface atoms on the crystal. In real calculations, a finite but rather a large number of MC steps are

performed, after which the configuration is assumed to be at equilibrium (within statistical fluctuations).

It is clear that the defining factor in our model are the energies of the interaction of the metal atoms with each other and with atoms of the support. As a matter of fact, there is no reliable information about these energies. In our work, we used the values taken from [9], which are actually estimations. The created model has been used for carrying out the experiments with the following values of parameters:

- Temperature: from 300K up to 1200K.
- Energy of interaction "metal-support": from -650 up to $+650$ Calories per mole.
- Energy of interaction "metal-metal": from -1000 up to -2600 Calories per mole.
- The initial size of a crystal $20 \times 20 \times 10$ atoms.

The results of modeling were visually estimated. Figure 1 shows the process of changing a crystal shape at temperature 900 K, the energy of interaction "metal–support" -650 Calories per mole, the energy of interaction "metal–metal" -2600 Calories per mole.

The simulation experiment has revealed the following mechanism of changing the crystal shape. First, tops and edges of an initial parallelepiped "become swollen", thus "swelling" of an initial particle occurs that is associated with the formation of vacancies in the crystal body (see Figure 1, MCS = 100). At the same time (especially at greater temperatures) the roughness of sides of a crystal considerably increases, in particular the formation of "ridges" occurs, that is seen in Figure 1. As distinct from the Kossel crystal, except for the formation of vacancies, the mechanism "dulling" the bases of a crystal also varies. In the beginning, a single-layered film of

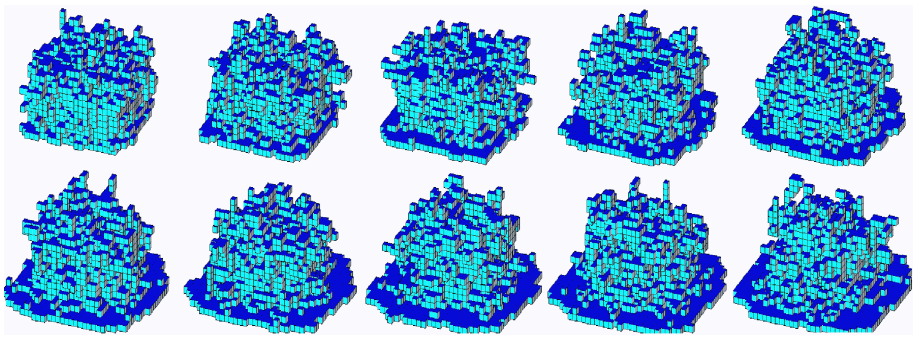

Figure 1. The process of nanoparticle relaxation. MCS 100, 400, 700, 1000, 1300, 1600, 1900, 2200, 2500, 2800, respectively

3–5 atoms wide is formed in the basis of a crystal on the support, then the second layer starts to appear on it with a simultaneous increase of the first layer width, etc. (see Figure 1, MCS from 400 to 2800). It is necessary to note that in the proposed model, the dependence of the character of a change in crystal morphology from the energies of interactions "metal–support" and "metal–metal" has not been revealed. So, with positive energy of interactions "metal–support", a crystal continued to spread beyond all bounds on a substrate in spite of the fact that the movement of an atom to the support in these conditions is not efficient from the energy standpoint. Such a behavior may be apparently explained by the too strong restrictions on atoms movements. We attempted to improve the given model by introducing a threefold non-additive interactions of atoms as follows. Each three of the neighboring atoms brought into the total energy of a crystal the one twelfth of interaction "metal–metal" energy. Such an account of non-additive interactions of atoms has not significantly changed the results. Crystals obtained with allowance for such interactions turned out to have a smoother surface (in particular, the "ridges" disappeared), but still continued to spread beyond all bounds on the support. Introduction into the model of fictitious energy of interaction with vacuum (each pair "metal–vacancy" brings some positive additive in the general energy of the system) has also not led to an essential change in the character of crystal relaxation.

3.2. Model 2. After the formation of an initial crystal, the following algorithm was carried out:

1. From the obtained crystal a certain number of new crystals (up to 100) is created by a random movement of a certain quantity of atoms (up to 50). Breaking of a single atom from the crystal was not allowed.
2. For each created crystal its full energy was calculated, taking into consideration the interactions of atoms between themselves, interactions with vacancies and with atoms of a substrate.
3. In a random way a crystal was chosen, whose energy is assumed to be zero, and a difference of energies between those of the chosen one and each other crystal was calculated.
4. According to formula (1), for each crystal the probability of its existence was calculated.
5. A new crystal was chosen randomly, considering its probability.
6. Transition to the first item of the algorithm.

In this model, like in the first one, the MCS was accepted to be a single realization of Steps 1–6. Such a definition of the MSC differs from the standard one, but this is not an important drawback when the purpose of the study is to obtain the equilibrium properties of a certain system.

As well, the results were visually estimated. For Model 2, a strict dependence of the equilibrium shape of a crystal on the energies of the interactions "metal–metal", "metal–support" is obtained as is seen in Figures 2–4.

At the same time, in another our model, where a different algorithm of the atoms diffusion was used, more realistic equilibrium forms of crystals were obtained. And what is important, they are associated with the interaction energies.

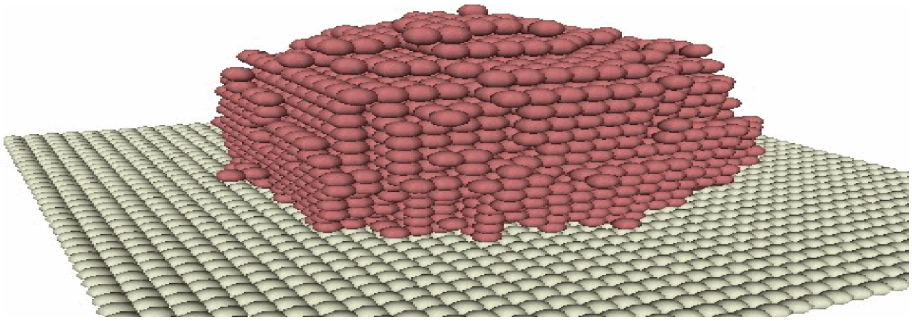

Figure 2. Temperature 1200 K, energy of the interaction "metal–support" −650 Calories per mole, energy of the interaction "metal–metal" −2600 Calories per mole

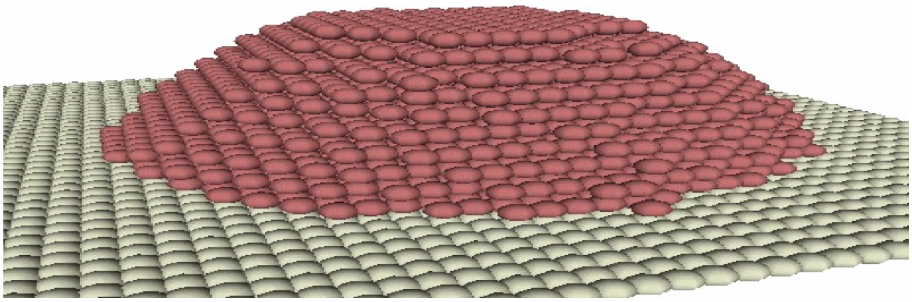

Figure 3. Temperature 1200 K, energy of the interaction "metal–support" −2000 Calories per mole, energy of the interaction "metal–metal" −2600 Calories per mole

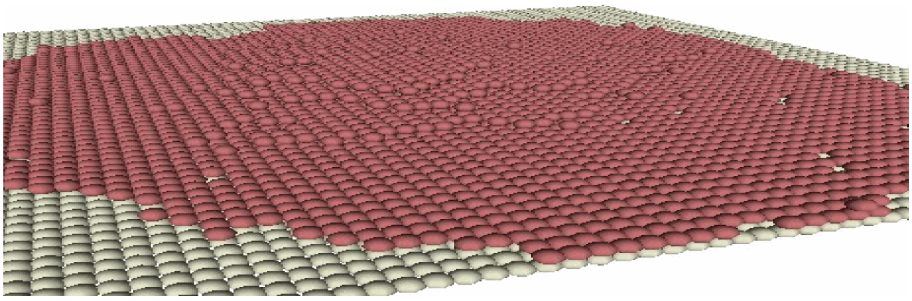

Figure 4. Temperature 1200K, energy of the interaction "metal–support" −2900 Calories per mole, energy of the interaction "metal–metal" −2600 Calories per mole

4. Conclusion

1. Two lattice models of the 3D Kossel crystal formation allowing vacancies and overhanging of metal atoms above the surface of a support are proposed. The "swelling" of an initial particle that is connected with the formation of vacancies in the crystal volume, is observed. The proposed models of the supported metal particle correctly describe some experimentally observable features of a change in the crystal shape. It is necessary to note that we have an opportunity to simulate the supported particles in the real scale: the size of the supported particles usually $\sim$ 1–100 nanometers, i.e., the "cube" section is $\sim$ 3–300 atoms.

2. The model, in which a strict dependence of the equilibrium shape of nanocrystal on a ratio of the interactions energies of "metal–metal" and "metal–support" has been constructed.

3. The consecutive diffusion of atoms does not give reasonable simulation results, therefore considerations of the "mathematical" diffusion, where the atom is allowed to diffuse at any point of a lattice, has been included into the algorithm.

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