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Computer simulation analysis of conductivity of supported polydisperse systems

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Effects of the support texture and the supported phase distribution on the conductivity of an individual grain or a granulated system have been analyzed theoretically. Experimental criteria are discussed, which allow one to judge the porous structure and sites of localization of a conducting component on the basis of the concentration dependence of the conductivity.

Key words: Monte Carlo simulation, percolation conductivity, supported polydispersed system, surface texture.

At the present time, the urgency of the complex approach to the problem of studying the catalytic surface becomes still more evident. Possible ways for realization of this approach have been considered,[1] and it has been mentioned that the adequate combination of model concepts and experimental studies should qualitatively provide new information about the state of a catalyst. Different spatial scales should be distinguished, each of which requires a specific approach: atomic (adsorption catalytic centers), nanometric (clusters, superclusters, and domains), and macroscopic (grains, samples as a whole). No systematic modelling of the catalyst structure at various levels has been performed up to the present time. Presently it has been actively performed for processes at the atomic level and is only begun for nano- and macroscopic scales.

Previously[2,3] we have begun to analyze the behavior of the electric conductivity of multicomponent dispersed systems, using the numerical modelling method (Monte Carlo). Theoretical models have been suggested[2] and it has been shown how their parameters are related to the character of the component distribution in a mixture. Then[3] these models have been applied for describing the electric conductivity of several real systems. In particular, it turned out to be possible to make a conclusion about the presence or absence of the interaction between initial components on the basis of numerical values of model parameters corresponding to the best accordance with experimental data.

The consideration[2,3] was limited by the case of the same dispersity of all components of mechanical mixtures. At the same time, in the majority of real systems

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different components can be characterized by sizes, which differ more than one order of magnitude. This is observed in mechanical systems, supported catalysts, and systems, in which a finely dispersed phase is obtained by the chemical interaction (partial reduction, oxidation, or formation of surface chemical compounds between components). Peculiarities of the behavior of the electric conductivity of such disperse systems are studied in this work in terms of the Monte Carlo method.

For convenience in the following discussion, a coarsely dispersed phase is arbitrarily called a support, while a finely dispersed phase is called a supported phase. We start from the inequality

$$d_1 >> d_2 >> d_3, \quad (1)$$

where d_1 is the size of the macroscopic sample (containing many grains of dispersed phases), d_2 is the characteristic size of grains of the support, and d_3 is the size characteristic of the supported phase (the diameter of grains or the width of the covering layer). Experimentally observed properties of the system (for example, electric conductivity) depend both on the spatial structure of the support and the character of the supported phase distribution.

The two-stage calculation was caused by the presence of several strongly differed sizes, which is reflected by the double inequality (1). At the first stage, an individual grain of the support phase along with its surroundings occupied by the supported phase (the size ranges from d_2 to d_3) was an object of the modelling. The grain parameters obtained were used as input data at the second stage when the whole sample consisted of many grains was modelled.

Individual grains with different degrees of surface development

General principles

When an individual grain is modelled, the real physical space is presented as a three-dimensional discrete regular lattice. Regions of the space, which are occupied by one of phases or are unoccupied, are compared to elements of the lattice: lattice points and bonds. Depending on the method of filling the lattice with the support phase, some elements turn out to be "internal" (surrounded by the same phase on all sides) or "surface" elements. Surface elements will be used in the future for occupation by the finely dispersed phase.

The totality of surface bonds and points forms an irregular spatial sublattice with the average coordination number Z, and the ratio of the number of surface elements to the number of internal elements is conventionally called the specific surface S. The values of parameters mentioned for the systems modelled with the smooth, moderately developed, and strongly developed surfaces are listed in Table 1.

Table 1. Parameters of the grain surface

Model	S	Z	X_c	$B_c = Z \cdot X_c$
Grain (sphere)	1.2	5.3	0.33	1.75
Grain (polyhedron)	1.0	4.8	0.38	1.82
Half-grain	1.1	5.5	0.32	1.76
Plane		6.0	0.30	1.8
Regular	3.0	7.0	0.20	1.4
Irregular	3.3	7.95	0.18	1.43
Friable	6.0	9.8	0.145	1.42
Three-dimensional lattice (CFC)		12.0	0.12	1.44
Grain with blind pores*	3.0	2.7	0.55	1.5
Grain with blind pores**	3.0	2.5	0.64	1.6

* The size distribution of pores in the form of geometric progression.
** The Poisson size distribution of pores.

When the electric conductivity of the system was modelled, the support phase was considered to be nonconducting, and the specific conductivity of one arbitrary unit was ascribed to the supported phase. Contacting elements form conducting clusters. At a certain relative concentration of the supported phase, the number of conducting elements is sufficient for the formation of the so-called infinite (percolation) cluster, which extends through the whole system considered (from an electrode to an electrode). The whole system becomes conducting due to such clusters.

The concentration corresponding to the formation of a percolation cluster is called the threshold concentration (percolation threshold) and is designated as X_c. In addition to the relative concentration of the conducting phase X (the fraction of surface conducting bonds), it is useful to calculate the values that are fractions of bonds (α_b) and points (α_s) belonging to the percolation cluster. In addition to the parameters mentioned (the specific surface S, the coordination number Z, and the percolation threshold X_c), the value $B_c = Z \cdot X_c$, which is related to the lattice dimension D by a simple correlation[4] and is independent of other properties of the lattice, is also used in the analysis:

$$B_c = D/(D-1). \quad (2)$$

The conductivity σ of the model system obtained was calculated by the standard method of electric potential relaxation.[5] The values calculated were normalized to the conductivity of the completely covered surface for convenience of comparison of different models. The establishment of concentration dependences $\alpha_s(X)$, $\alpha_b(X)$, and $\sigma(X)$ was the final result of the first stage of the model studies.

It is noteworthy that the considered models of an individual grain can also be applied to a bulky catalyst, when the structure of the support is not granulated but

entire (the whole sample can be considered to be one grain). For example, sintered films, sponges, *etc.* are related to such systems.

Results and Discussion

The results of modelling "smooth" grains are presented in the first three rows in Table 1. Grains of the support could have spherical (the model "sphere") or polyhedral (the model "polyhedron") shapes, or could look like two contacting hemispheres (the model "half-grain"). The value of the specific surface of smooth grains was assumed to be equal to one arbitrary unit.

All models of grains with the smooth surface resemble (in all parameters) both to one another and to the planar surface (see Table 1). An insignificant difference of the coordination number from 6 (which is typical of the planar triangular lattice) is related to the final curvature radius of grains. The percolation threshold is slightly shifted. However, the B_c value is almost constant and typical of all two-dimensional systems, although it is decreased compared to the exact value ($B_c = 2$), which is caused by final dimensions of the lattice.

The typical concentration dependences $\alpha_s(X)$, $\alpha_b(X)$, and $\sigma(X)$ are presented in Fig. 1. It should be noted that a sloping run of the conductivity curve does not allow one to determine the percolation threshold with a sufficient accuracy. The consideration of the $\alpha_b(X)$ and especially $\alpha_s(X)$ dependences is considerably more fruitful for this purpose due to their sharp increase in the near-threshold region. The $\alpha_b(X)$ value will be also needed at the second stage of modelling for determining the probability of the intergrain contact.

For the system with a moderately developed surface, the support phase consists of relatively fine overlapping nuclei arranged either in a specified order (the "regular" model) or randomly (the "irregular" model) due to through pores.

In the case of the strongly developed surface (the "friable" model), nuclei of the support are arranged more rarely, which results in an increase in its porosity and in the formation of the branched system of through pores penetrating the modelled grain in all directions. Models describing the moderately developed surface (regular and irregular models, see Table 1) are very similar.

Let us note that the results obtained are insensitive to the degree of regularity of the support structure: the irregular character of the supported phase distribution itself is the determining factor. The existence of the great number of through pores makes it possible to consider the systems considered to be three-dimensional ones. This is also indicated by the B_c, values similar to those inherent in all three-dimensional lattices ($B_c = 1.5$).

The tendency to decrease the percolation threshold as the surface develops due to the formation of through pores is followed on going from smooth grains to grains with a strongly developed surface (Fig. 2, see Table 1). The coordination number Z increases monotonically, while the B_c value is almost unchanged.

The existence of the developed surface can be related both to through and blind pores. In this case, it is assumed in studying the electric conductivity that a pore becomes conducting if it is completely filled with the conducting phase. Two variants of random distributions, Poisson and in the form of geometric progression, were used to describe size scattering of pores. The ratio between the number of pores and their depth was established in such a way to provide a desirable value of the specific surface. It can be seen from Fig. 3 that a considerable decrease in the conductivity and an increase in the percolation threshold are characteristic of systems with blind pores.

The modelling performed makes it possible to follow the effect of the surface texture on the conductivity.

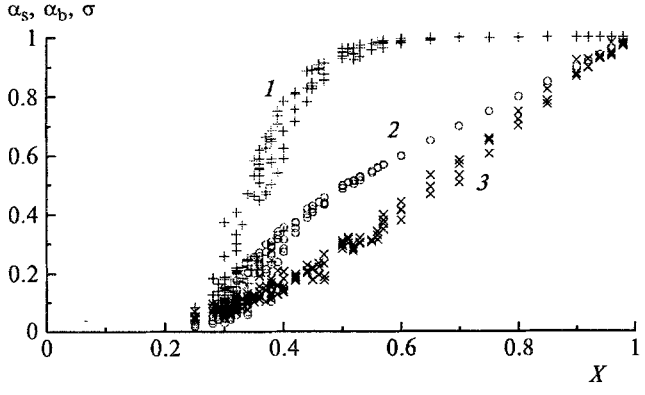

Fig. 1. Concentration dependences of main parameters of the smooth grain model: fraction of surface points in the percolation cluster, α_s (*1*); fraction of surface bonds in the percolation cluster, α_b (*2*); and normalized conductivity, σ (*3*).

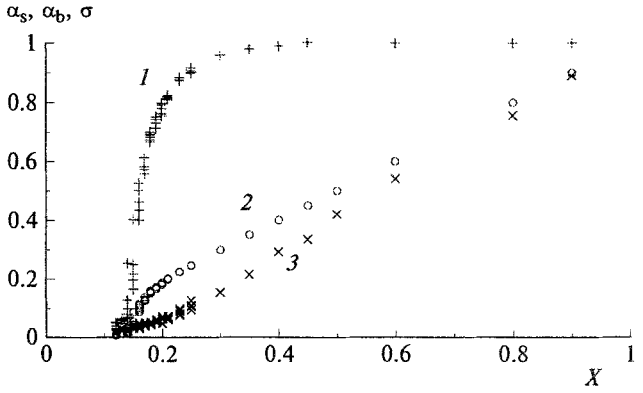

Fig. 2. Concentration dependences of main parameters of the model of the grain with a strongly developed surface due to through pores: fraction of surface points in the percolation cluster, α_s (*1*); fraction of surface bonds in the percolation cluster, α_b (*2*); and normalized conductivity, σ (*3*).

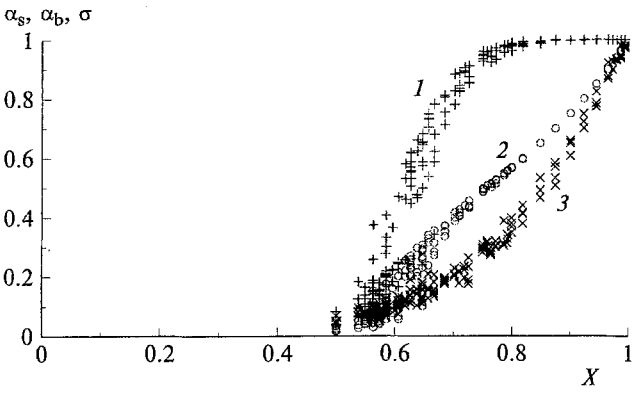

Fig. 3. Concentration parameters of the model of the grain with blind pores: fraction of surface points in the percolation cluster, α_s (*1*); fraction of surface bonds in the percolation cluster, α_b (*2*); and normalized conductivity, σ (*3*).

Depending on the character of the texture, systems with the developed surface can be divided conventionally into three classes: with numerous through pores, with deep folds (like gullies), and with blind pores. It can be easily seen that through pores favor an increase in the conductivity and a decrease in the percolation threshold, because they open parallel routes for the current.

Folds decrease the conductivity, because they lengthen the current path but do not shift the percolation threshold, because the percolation cluster is formed on their slopes at the same concentrations as on the smooth surface. It is also noteworthy that a decrease in the conductivity due to lengthening the current path occurs at all concentrations, including 100 % covering. Therefore, when results are presented in the normalized form (*i.e.*, relative to the conductivity of the entirely covered grain), the effect of the developed surface turns out to be unnoticeable. For this reason, we do not consider such structures in this work.

Finally, blind pores, which almost are not involved in the conductivity but absorb the conducting phase, decrease the total electric conductivity and increase the percolation threshold. The pore distribution in the form of geometric progression results in a weaker effect, because in this case the main porous mass consists of fine pores, which are filled with the conducting phase and begin to participate in the conductivity process more rapidly.

Granulated systems

General principles

In the case of the multigrain system, the real physical space was represented by the three-dimensional lattice, whose points were compared to grains with properties obtained at the first stage of modelling. The difference between conducting properties of a system consisting of many grains and those inherent to an individual grain is caused by the existence of "narrow" sites, intergrain contacts. In fact, the existence of a percolation cluster on the surface of each individual grain does not mean that the whole granulated system is conducting.

The existence or absence of the electric contact between adjacent grains is the determining factor. It is necessary and enough for the appearance of this contact that the contact point of grains belongs to their percolation clusters. Assuming that the position of the contact point is completely random, the probability of this event is equal to $\alpha^2_b(X)$, because $\alpha_b(X)$ is, by definition, the fraction of the grain surface belonging to the percolation cluster. When the granular system on the lattice was modelled, the existence or absence of the contact was specified by the state of lattice bonds. Each bond was considered to be independently "switched-on" (conducting) with a $\alpha_b^2(X)$ probability and "switched-off" with a $1-\alpha_b^2(X)$ probability.

In addition to the described model of the independent conducting phase distribution, another model is also considered, in which the contact point certainly belongs to the region of the conducting covering on each grain, the correlated distribution model. This assumption has a sense with respect to real systems, because the chemical interaction or phase transformation usually begin just in the sites of grain contacts. It is substantial that belonging to the region of conducting covering does not mean belonging to the percolation cluster: a considerable portion of the conducting phase can exist as isolated islands and are not involved in the conductivity. In this case, the probability that the contact point falls in the percolation cluster on an individual grain is equal to $\alpha_b(X)/X$ and the probability of "switching-on" the lattice bond is equal to $[\alpha_b(X)/X]^2$.

Results and Discussion

The results of modelling multigrain systems are presented in Table 2, and the examples of the concentration dependences of the conductivity are given in Fig. 4. In the case of the independent conducting phase distribution, the behavior of the conductivity is the same for nearly all models of an individual grain (except models with blind pores). This result is not surprising, because differences between models mainly appear at $X \leq 0.4$, while percolation in the multigrain system occurs at $X \geq 0.4$, so that these differences are related to the unobserved region before percolation.

The presented value of the threshold is related to the $\alpha_b(X)$ value: it is established in the classic three-dimensional problem of bonds that the percolation appears at $\alpha_b^2(X) \geq 0.15$, which means $X \geq 0.4$, if the character of the $\alpha_b(X)$ dependence (see Figs. 1 and 2) is taken into account. The concentration curve of the conductivity of

Table 2. Percolation threshold X_c in granulated systems depending on the type of the conducting phase distribution on the surface

Model	Distribution	
	Independent	Correlated
Grain (sphere)	0.42	0.36
Grain (polyhedron)	0.45	0.38
Half-grain	0.45	0.33
Regular	0.43	0.25
Irregular	0.43	0.22
Friable	0.43	0.16
Grain with blind pores*	0.70	0.65
Grain with blind pores**	0.75	0.70

* The size distribution of pores in the form of geometric progression.
** The Poisson size distribution of pores.

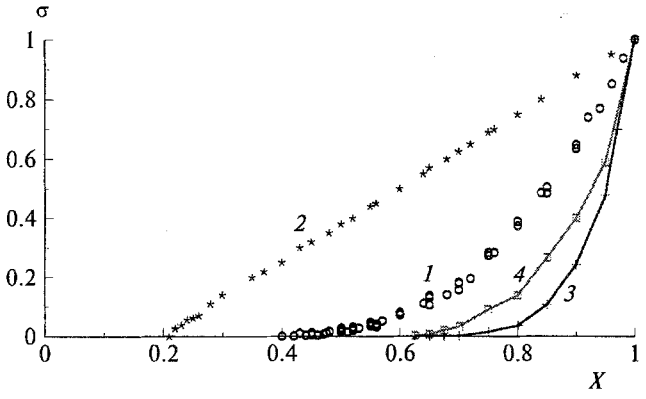

Fig. 4. Concentration dependences in granulated systems: smooth grains and grains with through pores, the independent conducting phase distribution (*1*); grains with through pores, the correlated conducting phase distribution (*2*); grains with blind pores, the independent (*3*) and correlated (*4*) conducting phase distribution.

the multigrain system with the independent conducting phase distribution is presented in Fig. 4 (curve *1*).

In the case of the correlated conducting phase distribution, the percolation begins at substantially lower values of the fraction of the surface covering (see Table 2). Unlike the independent distribution model, the effect of the surface texture of individual grains on the conductivity also appears in the scale of the multigrain system. In addition to positions of the percolation threshold, the shapes of the concentration dependences $\sigma(X)$ change as well (see Fig. 4, curve *2*), and the difference between them can serve as a rather distinct experimental criterion for establishing the type of the conducting phase distribution in each particular case. The exception is granulated systems with blind pores characterized by an extremely high threshold X_c and similar concentration dependences $\sigma(X)$ at independent and correlated types of the conducting phase distribution (see Fig. 4, curves *3* and *4*).

Thus, differences in the behavior of the conductivity of granulated systems can be rather large, while differences in specific surfaces are relatively small; in real disperse samples (in catalysts) the range of changes in the surface is rather large and reaches one to two orders of magnitude. Such a high sensitivity of the theoretical results obtained to the value of the specific surface is related to the fact that ideal cases, when the whole modelled surface is caused by pores of one type, have been considered. Nevertheless, in real samples with pores of all types, the predomination of one of the types should result in the appearance of the regularities mentioned.

The existence of these regularities makes it possible to use them in the empirical analysis of real systems. Measurements of the concentration dependence of the electric conductivity can provide information about peculiarities of a supported system. The absence of the conductivity up to very high concentrations indicates unambiguously that blind pores exist. In systems, in which blind pores do not dominate, the shape of the concentration dependence of the conductivity indicates a certain type of the conducting phase distribution. When the conducting phase is predominantly arranged in sites of intergrain contacts, even a small amount of this phase is enough for the appearance of the conductivity, which changes linearly as the concentration of the phase increases. Since the chemical interaction or phase transformation usually begin just in sites of intergrain contacts, many important processes of the catalyst genesis (reduction of oxides, formation of chemical compounds during preparation or exploitation, *etc.*) can be found at the earliest stages.

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