Russian Journal of General Chemistry, Vol. 72, No. 4, 2002, pp. 590–606. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 4, 2002, pp. 633–650.

Nanoscaled Structuring as a Way to Constructing New Solid Substances and Materials

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Received November 1, 2001

Abstract—State of the art and prospects of research in the field of the precise solid-phase chemical synthesis of highly organized nanostructured solid substances with various level of structural organization are discussed. The notion of topology is introduced for solid chemical compounds to describe the spatial atomic distribution in a substance synthesized. The processes of superordering of a solid, i.e. the formation (synthesis) of ordered distributions of matter of a certain (nanometric) size, as well as the interrelation between the spatial atomic distribution in a structure synthesized and its properties are studied.

INTRODUCTION

The current tendency of development of chemistry includes increasing complexity of structures to be synthesized and investigated. Correspondingly, the structural organization of substance becomes the question of the day. This is one of the key problems of natural science, since physics, chemistry, and biology just study organization of matter on various levels.

In chemistry, the problem is solved on the basis of the composition–properties functional interrelation. However, the progress in organic chemistry, supramolecular chemistry, and the chemistry of clusters proves once more that the synthesis of new chemical compounds always was and currently remains the main driving force of development of chemical science. At the present time, most attention should be evidently paid to studying the specificity of substance organization on different levels of complexity (from a molecule and a monocrystal, on one side, to highly organized supramolecular and solid compounds, on the other).

It is of note that the structural organization of matter, i.e. the ordering of mutual spatial locations of structural units, proceeds either spontaneously or under force.

Currently, together with traditional ways of finding new solid substances and materials (synthesis of solids with an equilibrium (crystalline) structure), more and more attention is paid to the synthesis of solid chemical compounds and materials on the ground of their metastable states. In addition, we note that the chemical possibilities for forming properties of solids can be utilized most completely when using nonequilibrium states [1]. Such approach is most perspective for creating new solid substances and materials. The macroscopic organization of crystalline (including biological) structures is built on the basis of self-organization and proceeds, which is of note, on the atomic-molecular level of natural ordering processes.

The problems of synthesis (construction) of solid substances and materials with various levels of structural organization are discussed in this article. Some questions related to description and classification of highly organized compounds are debatable.

1. NATURAL ORDER AND ARTIFICIAL “SUPERORDERING” IN A SOLID

In spite of the current extensive and manifold knowledge of the structure of condensed matter [2–7], the the chemical aspect of the problem continues to attract researchers’ attention. There is no a commonly accepted notion of the nature of solid substances, that would allow description of a real solid chemical compound and embrace the chemical properties of the compound.

The specific features of the chemical behavior of simple substances and compounds are manifested when a chemical individuum is in the molecular state. Transition to the solid state amplifies the contribution of purely physical factors [6]. As follows from [8–12], physical laws differentiate between the behavior of disordered amorphous solids and ideal crystals. Possessing a less ordered internal structure, amorphous bodies have higher (than crystals) entropy and internal energy. The behavior of unstable equilibrium systems is more interesting and surprising than that of stable ones: the instability often leads not simply to a loss of equilibrium, but also gives rise to new physical effects, such as spontaneous ordering in a chaotic system. Synergetics, a new field of science, investigates and describes self-organization processes [12]. Synergetics studies systems able to abruptly change their characteristics, and their response to external action is not proportional to the action.

The metastable state is realized in nature almost with the same frequency as stable. However, there is no true stability, both internal and with respect to the surrounding medium, in the metastable state. Prigogine [13] showed that open system under strongly nonequilibrium conditions can undergo self-organization, i.e. formation of ordered structures which were named dissipative structures. The examples of self-organization of nonbiological systems, given in [9, 10], show the following. Within certain limits, animate (biological) systems themselves predetermine the character of interaction with the surrounding medium and, in this way, determine the entropy flux caused by exchange with the surrounding medium. By contrast, in the case of a nonbiological system, the character of interaction between the system and the surrounding medium is determined by experimentalist. They usually say about the atomic-molecular structure in chemical investigations on low-molecular and solid substances. We assume the chemical structure of a substance to be a finite set of chemically bound atoms.

1.1. Natural Order in a Solid

The notion of structure is usually introduced when regarding the order in a system. Therewith, a certain location (configuration) of particles (atoms, molecules, or ions), for example, in a crystal, is assumed. In fact, we can say that the notion of structure is equivalent to the notion of ordering (coherence), when the particles are organized in a strictly determined configuration. It is of note that the progress in the chemistry of solids related to the synthesis and investigation of crystals, made some scientists to conclude hastily that the solid state is a crystalline state only [14], since only crystals are in a thermodynamically stable state and have the phase-transition (melting) point. Glasses were referred to as supercooled liquids not possessing the elasticity limit. Actually, thermodynamic equilibrium determines neither the category of state of aggregation, nor the stability of a given system. By the present time, a large number of substances are known never undergoing crystallization and, therefore, being completely stable [fossil resins (amber) maintaining their amorphous structure for a dozen millions years, can serve as the most representative example].

Only the presence of potential barriers is evident to block up transition from one state to another and to secure the enduring existence of various forms of the outworld. If the barrier is high enough, the system can be very stable, and the probability of phase transition becomes smaller than the probability of accidental destruction. For this reason, it was just to conclude [2, 15] that not the crystal lattice, but the frame, a continuous system (chain, network, skeleton) of interatomic bonds, is the most general characteristic of a solid substance.

Thus, the type, structure, and properties of a substance are determined by the frame structure and frame dimensionality. It is now clear that crystallization is only one and, probably, not the principal way of solidification of matter. So it is important to study other structure-formation processes, especially those leading to the synthesis of complex substances of aperiodic but regular structure [2].

Crystallization is the main type of natural ordering processes (self-organization on the atomic-molecular level). Highly organized structures are objects of a more complex structural organization as compared with products of natural ordering processes with the same number of atoms and chemical composition. From this point of view, molecules and monocrystals correspond to the lowest (although different) stages of structural organization.

For the sake of comparison, let us take two, close in chemical composition, systems: the monocrystal of a complex oxide (for example, spinel) and an artificially synthesized complex oxide composed of two or several (even many) spatially separated parts of different chemical composition, the parts adjoining with internal interfaces. Such parts are usually called “superlattice” in the physics of semiconductors and the electronics of solids, but, from the chemical viewpoint, they are spatially separated solid chemical substances [16]. So what of a superlattice? It is implied that one can prepare a solid composed of alternant layers of any thickness (including monolayers) and chemical composition. As a result, we obtain a solid in which, together with an ordinary lattice formed by periodically located atoms, there is a superlattice of alternant layers. We can make to order energetic zones in a solid by regulating the chemical composition, location, and thickness of the layers.

The crystal structure of a solid is characterized by two main parameters: structural units (from a single atom to big molecular objects) and ordering degree (from the amorphous state to monocrystal). Auxiliary parameters are needed for describing artificially synthesized highly organized structures and for characterizing these complex systems.

As a rule, the task of any solid-phase synthesis is creation of a certain structure. There are several aspects of understanding the term “synthesis of a solid chemical compound” or its physicochemical analog “synthesis of a certain structure”:

(1) The physicochemical aspect includes consideration of composition and crystal (sometimes amorphous) structure.

(2) The topological aspect includes consideration of the spatial distribution of the composition and structure (actually, the spatial distribution of structural units of an object).

(3) The electronic aspect concerns electronic states of a solid substance under consideration.

The notion of topology implies a complex structure of matter. Therefore, we consider in more detail the notion of topology for highly organized solid compounds. This notion is related to the possibility of various spatial atomic distributions in an artificially synthesized substance [17–19].

1.2. Artificial “Superordering” in a Solid

From the viewpoint of topology, the limiting states are, on one side, a substance uniform in composition and structure (for example, monocrystal, glass, etc.) and, on the other side, multielement (not in a chemical, but in a structural meaning) structure where each structural unit can be arbitrarily connected with others (for example, biological objects). Artificial structures of the simplest topological organization (uniformly laminated structures, Fig. 1*A*), for example, with thin oxide layers ($L \geq 30$ nm), has long been prepared [20]. A more complex topological organization includes nonuniform distribution of composition and structure (layered structure) along one of the spatial coordinates both of periodic (*A*) and of aperiodic (*B*, *C*) character. The synthesis of such structures is well-run. However, certain difficulties arises if it is necessary to obtain a small nanostructure period (L) of order 1 nm.

Further complication of topological organization is possible on organizing atoms also in the monolayer plane (for one or several monolayers) (Fig. 1*D*). Still higher levels of organization of matter imply formation of spatial nonuniformity in a structure synthesized and differ in the degree of internal symmetry (Fig. 1*E*).

In fact, we discuss the possibility of realizing the processes of superordering in a solid, i.e. formation (synthesis) of ordered distributions of matter of a certain size. Let us compare the realization of natural ordering and artificial superordering in a solid. It is of note that macroscopically ordered distributions are sufficiently widespread in nature. As examples, macroscopic ordered distributions in plumeous clouds, in the radial structure of volcanoes, in ordered eutectics, and in sea sandbanks can be enumerated.

Since these examples are related to the structure of matter, the processes under consideration involve mass transfer (diffusion) and may follow the only direction to a uniform state of the system. The origin of such processes lies in that they are caused by thermodynamic driving forces and directed to extreme values of thermodynamic parameters, including the entropy maximum at equilibrium.

The closer a system to equilibrium, the more pronounced are internal self-ordering processes in the system, the easier is maintaining physicochemical conditions, and the more difficult is changing them by external action. Hence, as we approach equilibrium, the range of allowed nonuniform structures becomes narrower, while uniform structures become simpler to synthesize. The reverse situation takes place far from equilibrium: a very precise external control is needed, but almost all structures are allowed. The choice of an optimal synthetic strategy is one of the most intricate problems. Thus, the only way to creating an aperiodic order consists in changing the ordering processes described by equilibrium thermodynamics and directed to securing system stability by a synthetic program directed to obtaining highly organized solid-phase structures in the metastable state.

Because of the low mobility of atoms in a solid, a certain thermodynamically unfavorable structure (for example, diamond) can exist for any long time. Figure 2 shows the conditions of structural stability. As seen, a system can maintain its structure for a long time in the following cases: (a) the system is in the state of stable (Fig. 2a) or metastable (Fig. 2b) equilibrium; these states are practically equivalent at a sufficiently high activation barrier E/kT (for example, graphite and diamond at room temperature); (b) the relaxation of the system to the equilibrium state is kinetically hindered (Fig. 2c); and (c) the energy exchange with the surrounding medium retains the system in a given state (Fig. 2d). Such a system is called dissipative, since its existence is associated with continuous dissipation of energy.

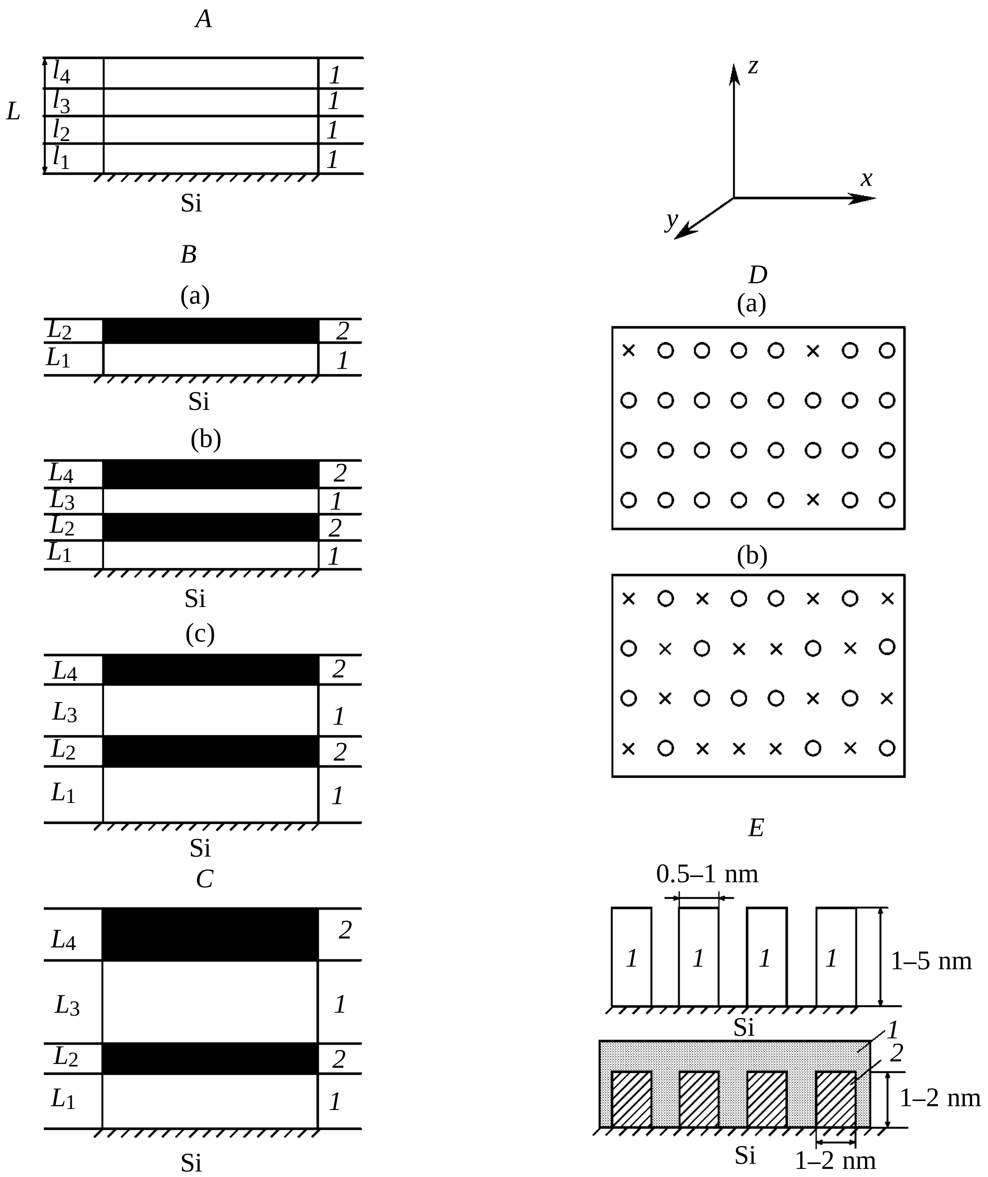


Fig. 1. Scheme of two-dimensional nanostructures at silica surface. (*A*) Uniform distribution of chemical composition and structure, for example, monolayers of element-oxygen groups of a given composition: (*l*) monolayer thickness; (*L*) total layer thickness, $l_1 = l_2 = l_3 = l_4$; and (*1*) Ti–O monolayers. (*B*) Periodical distribution along the *z* axis of element–oxygen layers containing a certain number of monolayers: (*1*) Fe–O groups and (*2*) Ti–O groups [(a) two-layer structure, $l_1 = l_2$ and (b) four-layer structure, $l_1 = l_3$ and $l_2 = l_4$]. (*C*) Aperiodic distribution of element–oxygen layers along the *z* axis (four-layer structure with $l_1 \neq l_2 \neq l_3 \neq l_4$). (*D*) Aperiodic atomic distribution in the surface monolayer plane (top view): (crosses) Fe–O groups and (circles) Ti–O groups [(a, b) different Fe–O/Ti–O ratios]. (*E*) Aperiodic distribution of “zero-dimensional” structures in the substrate plane: (*1*) Fe and (*2*) Si.

2. PECULIARITIES OF STRUCTURING ON THE NANOLEVEL

It is now firmly established that the synthesis of solid chemical compounds by crystallization can result in formation, from the same structural units, of a number of equivalent variants of composition and structure with close energies (actually, this is an unseparable mixture of variable composition). This occurs since the solidification process always proceeds at a certain supersaturation [7]. In the case of the solid-phase synthesis of highly organized structures, a solid compound to be obtained should possess the following characteristics [23]: (a) any topology

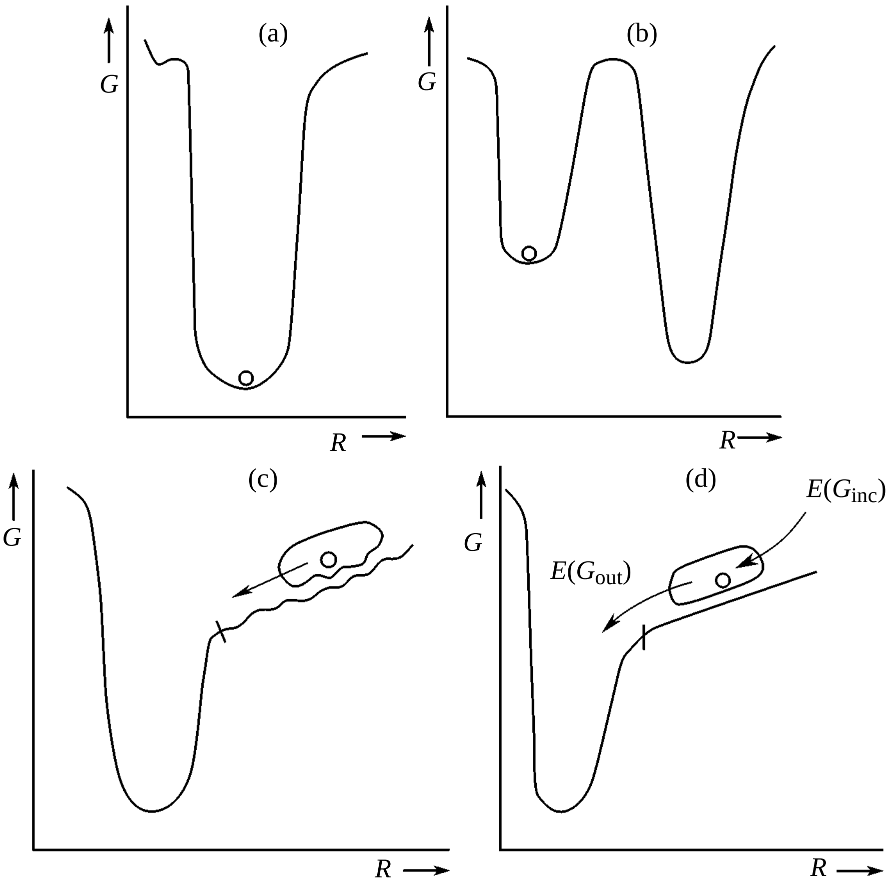


Fig. 2. Energetic and kinetic nature of stability of solid substances: (a) stable state, (b) metastable state, (c) kinetic retardation of system movement to the stable state, and (d) dissipative state of a system maintaining its stability at the expense of the energy influx from an external source. (*G*) Thermodynamic potential of a system and (*R*) process coordinate.

including uniform and nonuniform distribution of composition and structure should be attainable; (b) aperiodic structure (periodicity is possible as a particular case); and (c) thermodynamic nonequilibrium state. We imply that the chemical potentials in the existing homogeneity regions are different under conditions chosen temperature, pressure, etc.), and this does not lead to destruction of the resulting structure.

It is of note that chemical processes on the atomic-molecular level should play the main role in the synthesis of nanostructures with a small period and a given topology. Then all the processes are reduced to a certain sequence of surface chemical reactions between functional groups of the solid and molecules of necessary chemical nature [21]. Herewith, the only way for creating highly organized structures (of aperiodic order) is replacing crystallization by the synthesis of solid-phase structures in the metastable state. In fact, to accomplish such synthesis, one should control the activity of some chemical bonds and prevent reaction of other chemical bonds.

As noted in [23], the Glansdorff–Prigogine criterion that a new structure is always the result of instability and arises from fluctuations, needs a principal improvement when applied to controlled syntheses. One should ensure selective instability with respect to a desirable direction of ordering and, simultaneously, the maximum stability with respect to spontaneous processes. Thus, the problem of controlled synthesis splits into two problems: creation of a non-equilibrium but sufficiently stable initial state and control of relaxation processes.

Let us remember that a monocrystal seed in the form of a microcrystal plays the role of a giant fluctuation that drives the process along a given direction. This synthesis principle is schematized in Fig. 3. The initial state is energetically localized by a sufficiently high barrier. Our process control means are reduced to creating artificial fluctuations (seeds, heterogeneity, etc.), which allows the system to behave as if it undergoes barrier tunneling in a given direction. The higher the ratio of the probability of tunnelling to the pro-

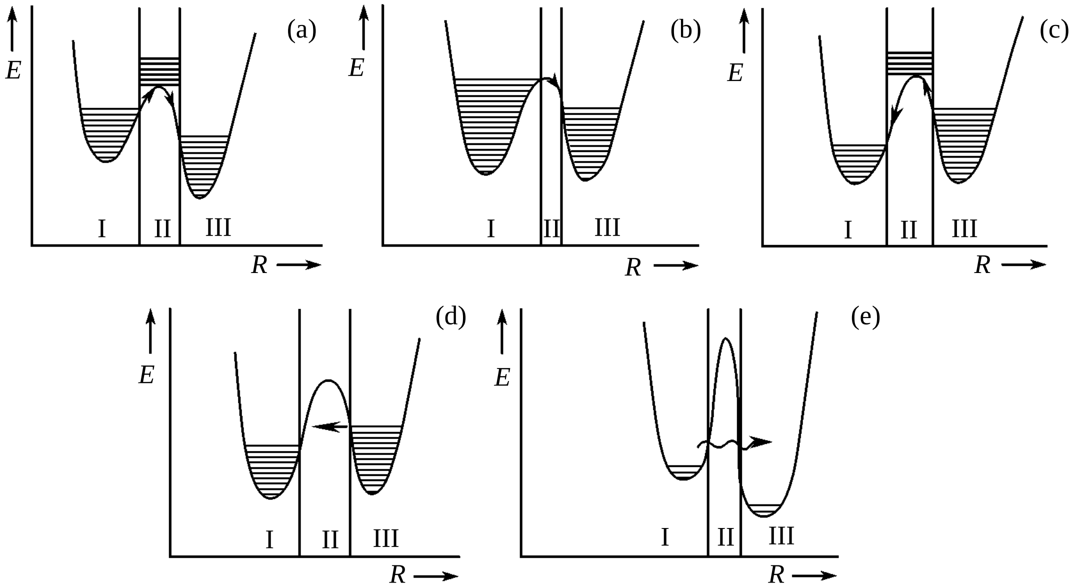


Fig. 3. Energy diagrams of syntheses: (a) chemical reactions and first-order phase transitions, (b) melting, (c) crystallization, (d) seed crystllization, and (e) tunneling. (I) Initial, (II) intermediate, and (III) final states. (*E*) System energy and (*R*) process coordinate.

bability of over-barrier processes, the higher is the controllability of the process.

There is an important aspect to be used at realizing the solid-phase matrix synthesis. With microcrystal seeds, the main role is played by the surface of a solid, since physicochemical processes just develop at the surface. It is of note that thermodynamic and kinetic barriers are not eliminated but only diminished by introduction of a seed (substrate) in a system. Separate relative equilibrium is established for each substrate under given conditions. Traditional methods of epitaxial synthesis (deposition) are controllable processes. However, it is hard to speak about obtaining a nanometric substance layer of a given thickness by the epitaxial deposition method, because epitaxial layers are formed by way of appearance and integration of crystal nuclei whose dimensions certainly exceed the monolayer thickness.

Additional difficulties in realizing the synthesis of solid substances arise from the fact that the overwhelming majority of reactions used in chemical science and technology belong to the type of “unorganized” reactions. We mean the reactions with particles (atoms, molecules, ions, or radicals) reacting at accidental meetings both in time and in space and by mutual orientation. In other words, there is no spatiotemporal molecular and solid-phase organization of chemical interaction in such reactions. At the same time, the possibility of such an organization is known from molecular biology, e.g., the biosynthesis process [24]. For example, Merrifield has realized the solid-phase (matrix) synthesis of polypeptides [25, 26] by successive extension of the polypeptide chain on an inert polymeric substrate.

The problem of a standard solid surface remains actual in synthesis of nanostructures. Let us consider the principles of synthesis of solid substances of reproducible composition [7, 15]. They are the process irreversibility conditions, the availability of a matrix, and the program of production and accumulation of information.

When performing controlled solid-phase synthesis, a researcher actually carries out a number of operations to obtain a solid chemical substance possessing (a) a certain excess of free energy contained in the system of interatomic bonds, as compared with the initial reagents, and (b) a higher degree of ordering of interatomic bonds as compared with the initial reagent mixture at equilibrium.

Thus, to construct necessary nonequilibrium systems, one has to do some work using external sources of energy. This energy typically acts as chemical energy, the energy of highly active reagents used in the synthesis. Let us consider Fig. 4. From the thermodynamic standpoint, one can say that the synthesis results in a solid product **C** which higher in energy compared with the initial substance. We note that, firstly, to synthesize product **C** from a solid chemical compound **A**, one should endow the system

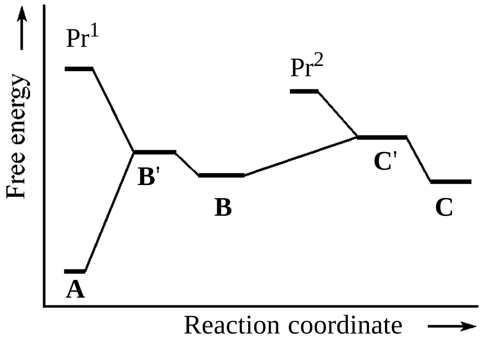


Fig. 4. Energy diagram of a hypothetical multistage synthesis **A** → **B** → **C** (**B**' and **C**' are intermediate transition states and Pr^1 and Pr^2 are reagents).

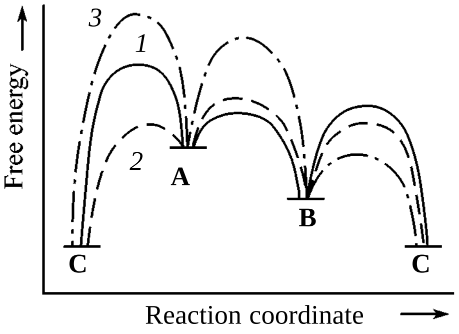


Fig. 5. Energy diagram of a reaction with kinetic and thermodynamic control: (*1*) reaction **A** → **B** dominates, product **B** is kinetically stable; (*2*) side reaction **A** → **C** dominates; (*3*) reaction **A** → **B** dominates but product **B** is kinetically unstable and fast transforms into **C**.

with additional energy (in a given order) at the expence of sufficiently active reagents. Secondly, in the course of the synthesis, highly reactive intermediates **B** and **C** may form (surface complexes in our case) which possess excess free energy and tend to various chemical transformations, including undesirable ones.

Let us use the example of chlorination of an inorganic substrate, silica [reaction (1)], to discuss the problem of the thermodynamic and kinetic stability of the **A** → **B** system, with account for the possibility of formation of a thermodynamically more stable product **C** 10:32:30(Fig. 5).

$$\underset{\mathbf{A}}{[SiO_2]_{m-1}O_{1.5}SiOH} + Cl_2$$

$$\longrightarrow \underset{\mathbf{B}}{[SiO_2]_{m-1}O_{1.5}SiCl} \longrightarrow \underset{\mathbf{C}}{SiCl_4}. \qquad (1)$$

The most favorable case for the synthesis of **B** is represented by curve *1*. The initial system **A** can react in two directions with formation of the target (for our synthesis) product **B** and by-product **C**. The barrier is considerably lower for the reaction **A** → **B** than for the reaction **A** → **C**. Therefore, the rate of the main reaction **A** → **B** is much higher that the rate of the side reaction. As a result, the initial substances are consumed in the main reaction, while the side reaction falls behind. It is of note that the reaction product **B** (≡SiCl surface groups) can transform into the more stable product $SiCl_4$. However, this requires a significant barrier to be overcome, so that compound **B** turns to be sufficiently stable, and its synthesis from **A** becomes realizable. The stability of **B** here is in essence metastability, since the possibility of formation of the thermodynamically more stable product **C** is preserved, but the system exists due to potential barriers.

Practically, the reproducible synthesis of nanostructured solid substances is realized via chemical assembling of structural units on appropriate matrices. The monolayer-by-monolayer chemical assembling of solid substances involves a number of preprogrammed surface reactions with at least bifunctional molecules of either one substance or another.

The principal significance of this method of synthesis of solid matter is "that, instead of spontaneous packing structural units in the crystallization process, their forced packing in a preset order is performed, i.e. preset composition and structure of the solid substance are realized" [7]. By varying temperature and other conditions of chemical assembling, one can change the density of packing of structural units. Apart from crystalline structures, one can create other, significantly more complex structures whose number has no limit.

We now turn to chemical reactions performed in the process of synthesis. The progress in the field of precise inorganic synthesis is associated with the rapid development of surface chemistry. This branch of the inorganic chemistry of solid substances studies chemical reactions in the surface atomic layer of a solid substance and also studies the ways controlling these reactions [22]. Such reactions open the unique possibility for controlling, on the atomic level, the synthesis of new substances of reproducible composition and structure by means of reactions between functional groups of a solid substance and molecules of necessary chemical nature. Such surface reactions result in formation of surface chemical compounds.

About 80 years ago, such compounds were first observed by Langmuir in chemisorption studies and

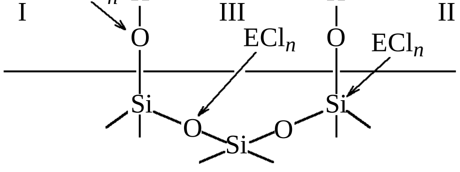
Table 1. Stoichiometry of reaction of silica $[SiO_2]_{k-1}0_{1.5}SiOH$ with low-molecular reagents

No.	Surface chemical reaction	Hal/E[a]	E/OH$_{react}$[b]	$N_{chem} : N_{surf}$[c]
1	$2[SiO_2]_{4.1}O_{1.5}SiOH + AlCl_3 \xrightarrow{\text{gas phase, 200°C}} [SiO_2]_{8.2}(O_{1.5}SiO)_2AlCl + 2HCl$	1.54/1.57	1.57/3.10	1:2
2	$[SiO_2]_{22}O_{1.5}SiOH + AlCl_3 \xrightarrow{\text{gas phase, 200°C}} [SiO_2]_{2.2}O_{1.5}SiOAlCl_2 + HCl$	0.74/0.38	0.38/0.39	1:1
3	$[SiO_2]_{29}O_{1.5}SiOH + FeCl_3 \xrightarrow{\text{vacuum, 250°C}} [SiO_2]_{29}O_{1.5}Si–O–Fe–Cl_2 + HCl$	1.10/0.54	0.54/0.53	1:1
4[d]	$[SiO_2]_{29}O_{1.5}SiOH + FeCl_3 \xrightarrow{\text{vacuum, 250°C}} [SiO_2]_{29}(O_{1.5}SiOH)_{0.63}(O_{1.5}Si–O–Fe_3Cl_2)_{0.37}$	0.431/0.205	0.205/0.204	1:1
5	$[SiO_2]_{4.1}O_{1.5}SiOH + CH_3I \xrightarrow{\text{gas phase, 160°C}} [SiO_2]_{4.1}O_{1.5}SiOCH_3 + HI$	–/3.09	3.09/3.12	1:1
6	$[SiO_2]_{3.5}O_{1.5}SiOH + BBr_3 \xrightarrow{\text{gas phase, 160°C}} [SiO_2]_7[(O_{1.5}SiO)_2BBr_2]_{0.76}[(O_{1.5}SiO)_2]_{0.24}$	1.49/1.50	1.50/3.01	1:2
7	$[SiO_2]_{23.6}O_{1.5}SiOH + Cu(NO_3)_2 \xrightarrow{\text{vacuum, 120°C}} [SiO_2]_{23.6}O_{1.5}Si–O–Cu–NO3 + HNO_3$	0.57/0.55	0.55/0.54	1:1

[a] Ratio of halide to element E in added group of atoms (values in mmol/g SiO_2). [b] Ratio of added ion of element E to reacted amount of functional groups (OH$_{react}$) (values in mmol/g SiO_2). [c] N_{chem}/N_{surf} = E/OH$_{react}$. [d] Synthesis in the presence of gaseous HCl (*P* 1.1 kPa).

later on were repeatedly studied. Nevertheless, they remained, up to the present time, a poorly explored class of solid compounds, as judged from the fact that there is no generally accepted formulation of the term “surface chemical compound” [19, 22, 27, 28]. They mostly use the term “chemisorption” and “chemical modification of surface” when describing surface reactions. Groundlessly, it was presumed that chemical reactions of low-molecular substances with solid substances scarcely go in chemical systematics because of the diversity of chemisorption bonds. However, studies on surface reactions of silica with low-molecular substances [29–34] revealed stable stoichiometric relations between the number of reacted surface atoms (functional groups) of a solid substance and the number of molecules bound. In other words, the surface chemical reactions studied obey the stoichiometry laws.

Scheme 1.



This is confirmed by the results of the reactions with anhydrous chlorides of macroporous silica with a specific surface area of 275 m^2/g and containing various amounts of OH groups according to scheme (2) (Tables 1 and 2).

$$m(\equiv Si–OH) + ECl_n \longrightarrow (\equiv Si–O–)_mECl_{n-m} + mHCl. \quad (2)$$

The reactivity of surface Si–O bonds can be different. Scheme 1 shows variants I–III of reactions of halide molecules with ≡SiOH groups. Under certain conditions, strong electrophilic and nucleophilic reagents react, besides OH groups, also with siloxane bonds of the silica frame (type III). For example, the composition of products of silica surface reactions with methanol is temperature-dependent.

At temperatures above 220°C, reaction (3) occurs.

$$[SiO_2]_{3.5}O_{1.5}SiOH + CH_3OH \rightleftarrows [SiO_2]_{3.5}(O_{1.5}SiOH)_{1-x}(O_{1.5}SiOCH_3)_x + H_2O. \quad (3)$$

When 300°C are attained, reaction (3) gives way to reaction (4).

$$[SiO_2]_{3.5}(O_{1.5}SiOH)_{1-x}(O_{1.5}SiO–)_x + CH_3OH \rightleftarrows [SiO_2]_{3.5}(O_{1.5}SiOCH_3)_{1-xy}(O_{1.5}SiOH)_y(O_{1.5}SiO–)_x + H_2O. \quad (4)$$

Table 2. Stoichiometry of reaction of silica OH groups with $FeCl_3$ at temperatures above 200°C

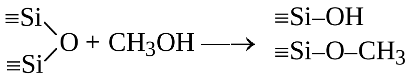
Sample no.	Initial substance, reaction conditions	OH_{init}[a], mmol/g SiO_2	Fe, mmol/g SiO_2	Cl, mmol/g SiO_2	Cl/Fe	N_{chem}/N_{surf}[b]	Surface reactions, %
1	Silica gel, argon, 280°C	2.70	1.45	1.60	1.1	1.45/1.00 = 1:1.9	(7) 90; (8) 10
2a[c]	Aerosilogel, vacuum, 220–300°C	0.55	0.54	1.10	2.03	0.54/0.55 = 1:1	(8) 100
2b[c]	Vacuum, 350°C	0.54	0.63	1.40	2.22	0.54/0.63 = 1:1.2	(8) 85; (9) 15
3	Aerosil, argon, 280°C	1.80	1.66	3.10	1.87	1.66/1.80 = 1:1.1	(8) 82; (7) 18

[a] Initial content of OH groups. [b] N_{chem}/N_{surf} = Fe/OH_{react}. [c] The surfaces of sample nos. 2a and 2b were standardized by thermal treatment at 723 K for 8 h, followed by vacuum thermal treatment at 623 K for 20 h (p 8×10^{-6} Pa).

At 330°C, the reaction becomes still more complicated:

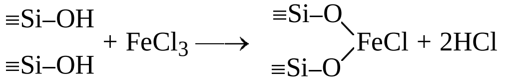
$$[SiO_2]_{3.5}(O_{1.5}SiOH)_{1-x}(O_{1.5}SiO–)_x + CH_3OH$$
$$\rightleftarrows [SiO_2]_{3.5}(O_{1.5}SiOCH_3)_{1-3x/4-y}(O_{1.5}SiOH)_{x/4} \cdot$$
$$(O_{1.5}SiO–)_{x/2} + H_2O. \qquad (5)$$

Thus, the temperature 330°C is a minimum temperature when ≡Si–O–Si≡ bonds react with CH_3OH:

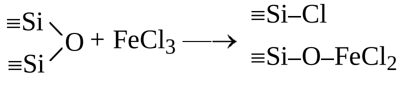

(6)

The possibility of concurrent frame (heterogeneous) reactions with frame destruction is a specific feature of the above surface chemical reactions.

As is seen from Table 1, the surface reactions studied obey stoichiometry, i.e. there are stable stoichiometric ratios between the number of molecules bound and the number of surface atoms (functional groups) of the solid substance (N_{chem}/N_{surf}). The stoichiometry of surface reactions is strongly dependent on sample preparation and reaction conditions. The N_{chem}/N_{surf} ratio changes from 1/2 for an exhaustively hydroxylated silica to 1/1 for an dehydroxylated sample (nos. 1 and 2). It was shown that an even slight change of conditions of surface chemical reactions can induce concurrent surface reactions. This is to be taken into account when calculating real stoichiometric ratios. For example, $FeCl_3$ reacts with silica (Table 2) by reactions (7)–(9):


(7)

$$≡Si–OH + FeCl_3 \longrightarrow ≡Si–O–FeCl_2 + HCl, \qquad (8)$$


(9)

With sample 2b, the reaction occurs by 85% by scheme (8) and by 15% by scheme (9). With sample 1, the contributions of reactions (7) and (8) are 90 and 10%, respectively.

The resulting experimental evidence shows that the majority of surface reactions of silicon polydioxide with chlorides at temperatures above 200°C possess a complex stoichiometry reflecting the possibility of participation of functional groups of the silica frame in various chemical reactions.

By repeating the cycle of molecular layering [35, 36], for instance, by treatment with chlorides and water in preparing oxides [reactions (10) and (11)] and with chlorides and hydrogen sulfide in preparing sulfides, one can synthesize solid substances consisting of a certain number of corresponding monolayers.

$$m(≡Si–OH) + MCl_n \longrightarrow (≡Si–O–)_mMCl_{n-m} + mHCl, \qquad (10)$$

$$m(≡Si–O–)_mMCl_{n-m} + (n - m)\ H_2O$$
$$\longrightarrow (≡Si–O–)_mM(OH)_{n-m} + (n - m)\ HCl. \qquad (11)$$

The monolayers can be of the same composition (Fig. 1*A*, four monolayers) or of a given composition in a certain sequence with a given number of monolayers of element–oxygen groups of another chemical nature (Figs. 1*B* and 1*C*). It is of note that, in the case of alternation of the chemical composition of element–oxygen monolayers deposited, it is possible to obtain not naturally occurring solid compounds of a more complex composition and structure. They can be synthesized only artificially. We will term such compounds as spatially separated.

Let us consider the structure of surface and spatially separated compounds (Fig. 6). The monolayer of silicon–oxygen groups is formed by reaction of an oxide with silicon tetrachloride and then with water vapor. Since the monolayer of surface atoms is inseparable from the solid substance, the substance as a whole should be named a surface compound. Its formation gives rise to surface electronic states characteristic of the new solid substance. After 3 to 4

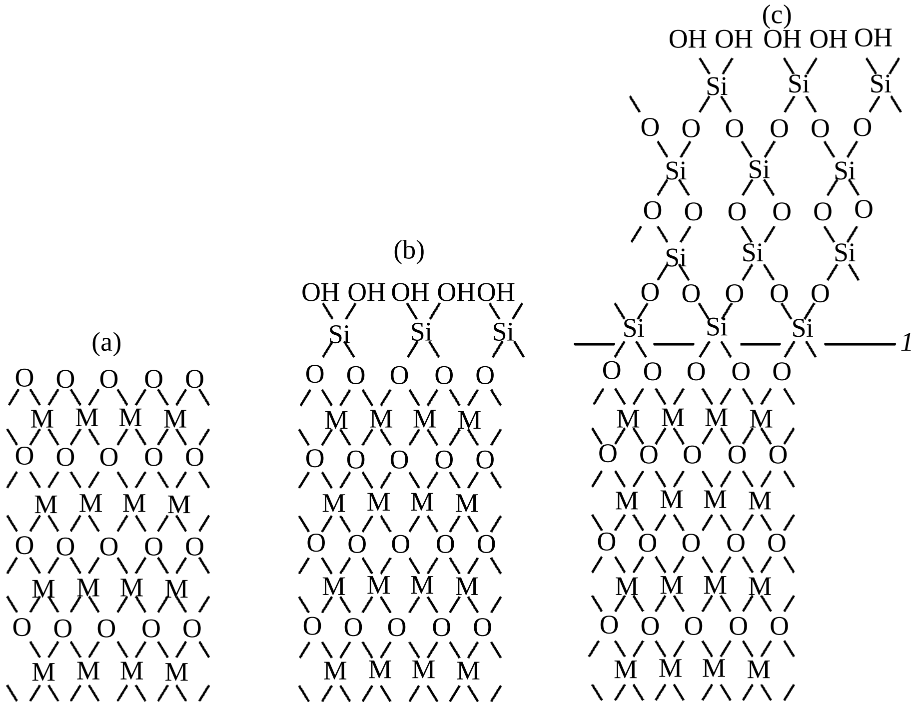


Fig. 6. Structure of solid chemical compounds: (a) initial metal oxide (MO_n), (b) surface chemical compound $[MO]_{n-1} \cdot (M–O)_2Si(OH)_2$, and (c) spacially separated compound $[MO_n]–[SiO_2]$. (*1*) Conditional (internal) boundary.

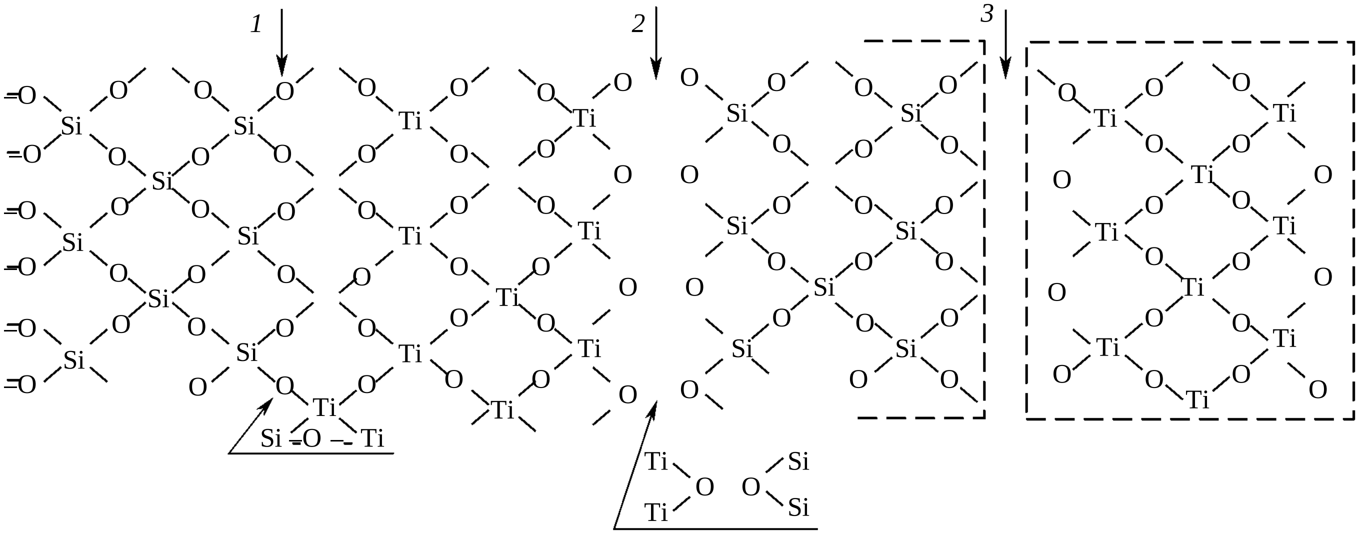


Fig. 7. Fragment of the chemical structure of a solid comprising parts of different chemical composition (Si–O and Ti–O groups) combined in three different ways [37]: (*1*) spatially separated compound, (*2*) spatially separated adduct, and (*3*) mechanical mixture of SiO_2 and TiO_2 particles.

monolayers have been deposited, an oxide silica layer arises, the synthesis product being a spatially separated compound. The question arises: what is the difference between these structures and those obtained by chemical vapor deposition (epitaxy)?

Figure 7 represents the spatially separated compound that, according to Aleskovskii [37], has an interatomic Si–O–Ti bond (case 1). In the case, for example, of chemical vapor deposition, a product with intermolecular bonds is obtained (case 2), which facilitates phase-formation processes. Thus, with the aid of the synthesis of two-dimensional nanostructures (nanolayers) one can avoid (in a certain temperature range) phase-formation processes and obtain artificial chemical compounds not occurring in nature.

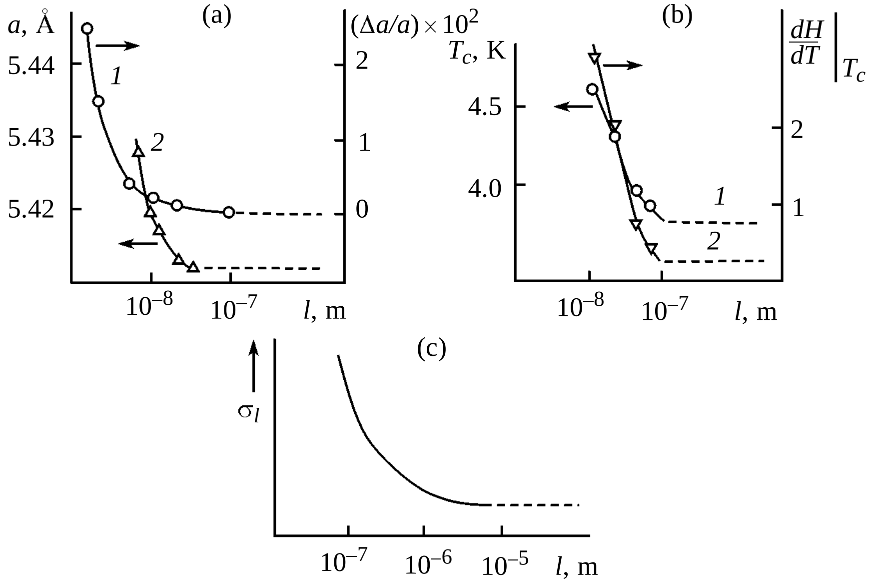


Fig. 8. Size dependence of properties for solid substances [39]: (a) crystal lattice parameter for (*1*) silicon and (*2*) cerium dioxide; (b) (*1*) critical superconductivity temperature T_c and (*2*) derivative of critical magnetic field for tin films on glass; and (c) crystal breaking strength σ_l. (*l*) Sample size.

3. PROPERTIES OF HIGHLY ORGANIZED NANOSTRUCTURES

The progress in the physical and chemical investigation of solid substances for two last decades discovered many new facts concerning their properties. In particular, abundant evidence is available concerning the dimensional effect, i.e. the dependence of the physical and chemical properties of solid samples on their size [38, 39]. Since we are interested in nanosize objects, let us consider the dimensional effect in detail. The dimensional effect is observed when the sample size is comparable with one of characteristic lengths: the electron mean free path length (*l*), the mean de Broglie wavelength (λ), etc. We put two cases first. The first case is when the sample size is comparable with the electron mean free path length (classical dimensional effect). The electron mean free path length usually is about hundreds angstroms at room temperature, so sufficiently thin films are needed for measuring the dimensional effect. This effect was most frequently observed for the conductance of thin metal or semiconductor films and wires (one-dimensional systems) whose thickness *d* was compared with *l*. Resistivity increases with decreasing *d*, which is related to additional electron scattering at the surface. The second case is when the sample size (nanolayer thickness, whiskers diameter, etc.) is comparable with the mean de Broglie wavelength of electron (λ is of order tens angstroms). This is a quantum dimensional effect.

The dimensional effects of that type are discovered, as a rule, in semiconductor or semimetal films and whiskers with smooth surface (for massive substrates) and with charge carriers having a relatively large de Broglie wavelength. Generally, the quantum dimensional effects arise as a consequence of quantization of the electron quasi-momentum [38]. By the present time, the experimental evidence for the dimensional effect in crystals has grown significantly, and its quality and reliability increased. Let us consider on particular examples [40] how the properties of various substances change with decreasing crystal size. The dependence of lattice parameter on crystallite size is shown in Fig. 8a for silicon and zirconium dioxide. Deviations from the bulk parameter are seen to occur within the range 1000–100 Å. Similar dependences are known for tin, magnesia, and some other substances.

Figure 8b displays the dependence of the critical temperature of superconducting transition and the dependence of the temperature derivative of the critical magnetic field on crystallite size for tin films. Deviations from the corresponding bulk values are observed beginning within 1000–100 Å. Such dependences are typical enough for superconductors in the state of fine particles.

Figure 8c shows the size dependence of the breaking strength of various crystalline samples: whiskers of metals and salts, thin flat monocrystals of alkali

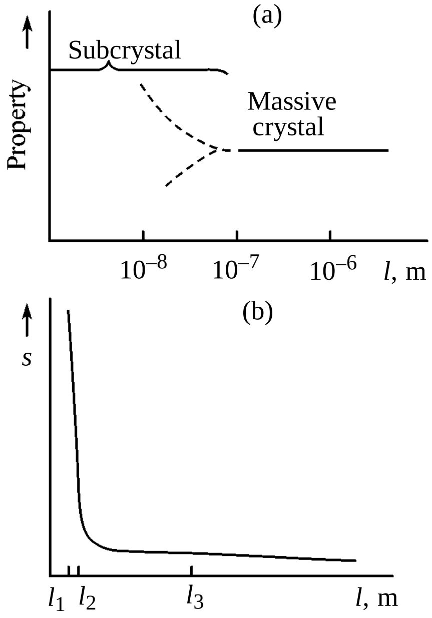


Fig. 9. Generalized shape of size dependence of properties for (a) a solid chemical substance. (b) Size dependence of specific surface area S. (l) Body size: (l_1, l_2, l_3) nano-, micro-, and macrosizes of a solid object.

halides, polycrystalline metallic films, and wire samples. Strength growth with respect to bulk values begins here close to 10^4 Å, i.e. at a larger sample thickness than in the preceding cases.

Similar size dependences of structural transformations are known for thin films of various substances. Together with transformations between crystal modifications of a given substance, the amorphous-to-crystal phase transition is often observed in thin films. Size dependence of the latter was repeatedly studied for various substances. The amorphous phase is often realized in the small thickness region at room temperature. Spontaneous crystallization occurs when a certain critical film thickness is attained in the deposition process. The critical thickness usually lies within the range 1000–100 Å. Such data are known for antimony, bismuth, germanium telluride, ytterbium, and other films.

As is seen from Fig. 9a, with decreasing crystal size, the value of a property is almost invariable until a critical size l_{cr} (1000–100 Å) is attained. This dependence is similar to the hyperbolic size dependence of specific surface area S, found by Aleskovskii *et al.* [7] (Fig. 9b).

The above properties of particles (crystals in most cases) allow estimation of the sample size (minimum amount of crystalline solid), when normal properties characteristic of bulk substance are still maintained. A crystal of a smaller size loses (or essentially changes) these properties. The size limits for various substances lie within 1000–100 Å.

3.1. Physicochemical Properties of Highly Organized Two-Dimensional Oxide Nanostructures

3.1.1. Uniform layer structure. Investigation of the properties of uniform layer structures, the simplest topological type (Fig. 1*A*), on an example of oxide structures revealed a number of interesting facts. We turn to the composition–structure–property dependence for two-dimensional oxide nanostructures. A number of physicochemical properties (catalytic activity, wetting heat, solubility, potential contact difference, acidity) were studied to show that the surface of an oxide nanostructure synthesized acquires the properties characteristic of the corresponding bulk oxide after depositing four and more element–oxygen monolayers [19, 21, 31].

The transition from the properties of an initial surface to those of bulk oxides can be traced by the dependence of electrokinetic potential ζ on pH. Nanostructures on silica, containing Ti–O and Al–O monolayers, were investigated in [41]. Electrophoretic mobility was measured and then the isoelectric point was determined (pH at $\zeta = 0$). From the results obtained, the following conclusions could be reached:

(a) If the isoelectric points of the initial surface and of an oxide deposited differ only slightly (SiO_2 and TiO_2), already one–two element–oxygen mono-

Table 3. Activity of two-component oxide nanostructures in the catalytic gas-phase hydrolysis of carbon tetrachloride at 240°C

Sample	Element content in monolayer, mmol/g SiO_2		S, m^2/g	$K_s \times 10^4$, mmol m^{-2} min^{-1}
	internal	external		
$[SiO_2]OH$			246	0.2
$[SiO_2]Ti$		1.09	218	65.0
$[SiO_2]P$		1.07	225	0.3
$[SiO_2]Si$		1.05	230	0.3
$[SiO_2]PTi$	1.07	1.16	197	20.0
$[SiO_2]TiTi$	1.09	0.73	204	22.0
$[SiO_2]AlTi$	1.57	0.89	197	20.3
$[SiO_2]FeTi$	2.00	0.71	201	19.4
$[SiO_2]Cr^{+3}Ti$	1.05	1.21	207	53.0
$[SiO_2]PP$	1.07	0.80	197	0.3
$[SiO_2]TiP$	1.09	0.51	194	0.7
$[SiO_2]SiSi$	1.05	0.91	214	0.4
$[SiO_2]TiSi$	1.09	0.73	203	4.5

layers deposited will suffice to pass to bulk oxide properties.

(b) If the isoelectric points are sharply different (SiO_2 and Al_2O_3), complete transition to bulk oxide parameters occurs after depositing four monolayers. One can also mention the peculiar behavior of oxide nanolayers in the model catalytic gas-phase hydrolysis of CCl_4. The activity of samples with deposited element–oxygen monolayers was compared with the activity of samples of the same chemical composition but obtained by impregnation and deposition. The higher catalytic activity of the nanolayer samples was shown to be caused by the higher content of surface element–oxygen groups. As for the samples obtained by impregnation, part of their active matter does not participate in reaction: only surface atoms of microcrystals do work [19].

3.1.2. Nonuniform layer structures. Precise synthesis also includes covering the substrate surface with monolayers of element–oxygen groups of different chemical nature. This makes possible investigation of nanostructures containing a multicomponent oxide layer of a certain composition with monolayers alternating in the direction from the substrate to the new sample surface, for example, as in Scheme 2.

Scheme 2.

▌‖–O–A–O–B–OH	(AB sample)
▌‖–O–B–O–A–OH	(BA sample)
▌‖–O–A–O–A–O–B–OH	(2AB sample)

With such samples, one can experimentally test (a) the effect of activating or passivating atom A on the activity of surface atom B, (b) the activity of atom B covered with inert (catalytically inactive) atom A, and (c) the activity of atom B (sample 2AB) as a function of the thickness (number) of intermediate monolayers of atom A.

Table 3 represents the chemical composition and catalytic activity (K_s is the specific rate constant) of the samples studied. As seen from Table 3, activity of oxide catalytic systems can be controlled. The activity of the samples with an almost the same specific surface area (ca. 200 m^2/g) is determined mostly by the chemical composition of the monolayer that forms the surface of the oxide layer synthesized. Samples containing nTi and nPTi layers were studied to trace the effect of substrate Si atoms on the activity of the Ti atoms of the surface monolayer, both through titanium–oxygen and phosphorus–oxygen monolayers. Phosphorus ions are catalytically inactive and, being in the surface monolayer, completely depress the activity of subjacent titanium–oxygen layers. Table 4 exhibits the activity of samples differing from each other in the number n of the phosphorus–oxygen and titanium–oxygen monolayers intervening the silica frame and the surface titanium–oxygen monolayer. It follows from Table 4 that the effect of silicon atoms on the activity of titanium atoms in the surface layer of a catalyst is inversely proportional to the distance d between them: $K_s = l/bd$, where l is the intermediate monolayer thickness and b is a constant. The resulting

Table 4. Activity of nanostructures a titanium–oxygen surface monolayer and various number of intermediate monolayers (*n*) in the gas-phase catalytic hydrolysis of carbon tetrachloride at 240°C

Sample	*n*	Conent of titanium in surface monolayer, mmol/g SiO_2	$K_s \times 10^4$, mmol m^{-2} min^{-1}
$[SiO_2]T$	0	1.09	65
$[SiO_2]PT$	1	1.16	20
$[SiO_2]PPT$	2	1.08	12
$[SiO_2]PPPT$	3	0.94	9
$[SiO_2]TT$	1	0.71	22
$[SiO_2]TTT$	3	0.94	13
$[SiO_2]TTTT$	3	0.91	6

Table 5. Activity of nanostructured aluminosilicate systems in cumene cracking at 500°C

Sample	$K_s \times 10^{10}$, mmol m^{-2} min^{-1}	E_{app}[a], kJ/mol	α_{surf}[b], atom Al/m^2
Silica gel (SG)	0.17	71	
Alumina (A)	0.10	54	1.5×10^{18}
Aluminosilicate (AS)	2.6	58	1.0×10^{12}
SG–1Al	0.25	88	3.6×10^{18}
SG–2Al	1.25	104	2.0×10^{18}
SG–4Al	0.4	79	1.8×10^{18}
SG–AlSi	0.19	82	3.6×10^{18}
SG–AlSiAl	0.9	96	1.4×10^{18}
A–1Si	0.1	67	
A–2Si	0.2	75	
A–SiAl	1.47	125	6.0×10^{18}
A–SiAlSi	3.3	67	
A–2SiAl	3.48	104	8.0×10^{19}
AS–1Al	3.23	54	8.4×10^{17}
AS–2Al	3.93	58	7.0×10^{17}
AS–AlSi	1.93	71	1.0×10^{12}
AS–1Si	9.8	58	1.0×10^{12}
AS–SiAl	4.3	63	7.0×10^{17}

[a] Apparent activation energy. [b] Content of surface atoms.

data show that the silicon atoms located at a distance of about 0.8 nm from surface titanium atoms, still effect their properties. The effect is transmitted along the chain $\equiv Si–O–(E–O)_n–TiOH$, where (E–O) is the intermediate element–oxygen monolayer.

The activity of aluminosilicate systems was studied in the cumene cracking reaction (Table 5). The microcatalytic pulse-operated reaction was performed at 250–550°C on the samples obtained on the basis of silica gel (SG), alumina (A), and aluminosilicate (AS) as substrates. It was shown that the activity of the aluminosilicate systems synthesized on substrates can be increased by controlled variation of the chemical composition of the surface. The activity of A–Si–Al, A–Si–Si, and A–2Si–Al samples are an-order-of-magnitude more active than the initial alumina and compare in activity with the initial aluminosilicate. Therefore, we can conclude that samples, either comparable or exceeding in catalytic activity the industrial aluminosilicate catalyst, can be synthesized by alternating several aluminium– and silicon–oxygen monolayers on alumina surface. It is of note that chemical modification of the surface of the initial aluminosilicate also improves its catalytic properties.

The existence of surface magnetism was confirmed experimentally [32, 42], and an idea was forwarded that ordered spin systems can be created with the aid of chemical design of a given atomic topology. We

Table 6. Magnetic susceptibility of one- and two-component nanostructures

No.	Sample	n^a	$\theta \times 10^6$, rel. units
	Series I		
1	Ti	1	–0.4
2	Sn	1	–0.33
3	Zn	1	–0.47
4	Cu	1	0.1
5	Fe	1	20
6^b	0.22Fe + 0.78Ti	1	4.5
7^b	0.53Fe + 0.47Ti	1	18.6
8^b	0.71Fe + 0.29Ti	1	17.9
	Series II		
9	FeSn	2	–0.12
10	SnFe	2	0.63
11	FeCu	2	–0.38
12	CuFe	2	–0.12
13	FeTi	2	18.8
14	TiFe	2	19.3
15	FeZn	2	48.3
16	ZnFe	2	42.1
17	TiTiFe	3	19.5
18	ZnZnFe	3	62.1

[a] Number of element–oxygen monolayers. [b] Two-component monolayer.

Table 7. Sorption properties of nanostructures materials

No.	Sample	S, m^2/g	Total dynamic exchange capacity	
			mmol/g	mg/g
1	SiO_2 (Aerosil)	300	Traces	Traces
2	Titanogel	100	0.1	
3^a	$[SiO_2]\cdot 2Ti–O$	230	8.31	1978
4^b	$[SiO_2]\cdot Fe^{+3}/Fe^{+2}\cdot 2Ti–O$	215	8.34	1981
5	Organic sorbent		1.2	285.6

[a] Sample with two Ti–O monolayer. [b] Ferromagnetic sample with Fe–O monolayers and two Ti–O monolayers.

synthesized samples containing a multicomponent oxide nanolayer, similar to those in Scheme 2. Magnetic ordering was assumed to be secured both by mutual location of atoms of adjacent element–oxygen monolayers and by an optimal interatomic distance between the Fe–O monolayer and the E–O monolayer of necessary chemical nature. The the possibility of creating oxide systems with different magnetic ordering due to alternating element–oxygen monolayers of a certain chemical composition (Fe^{3+} and Sn^{4+}, Fe^{3+} and Cu^{2+}, Fe^{3+} and Ti^{4+}, Fe^{3+} and Zn^{2+}) was studied. The magnetic susceptibility of samples χ was measured using the Faraday method within the temperature range 90–293 K at four magnetic field strengths H: 4100, 5820, 7120, and 8280 Oe. The accuracy of the measurements was 2%. The initial silica substrate is a diamagnetic material ($\chi_{gram} = –0.277 \times 10^{-6}$ emu/g). There were synthesized structures containing two or three oxide monolayers of a certain chemical composition (Fe^{3+} and Sn^{4+}, Sn^{4+} and Fe^{3+}, Fe^{3+} and Cu^{2+}, Cu^{2+} and Fe^{3+}, Fe^{3+} and Ti^{4+}, Ti^{4+} and Fe^{3+}, Fe^{3+} and Zn^{2+}, Zn^{2+} and Fe^{3+}) with various alternations of the monolayers.

We first turn to the magnetic characteristics of one-component monolayers, the knowledge of which is important for analysis of the magnetic properties of samples with two-component alternant element–oxygen monolayers. As is seen from Table 6, the element–oxygen monolayers containing Ti^{4+}, Sn^{4+}, and Zn^{2+} exhibit diamagnetic properties, whereas the monolayers containing Cu^{2+} and Fe^{3+} are paramagnetic. Monolayer Fe^{3+}–O groups characteristically exhibit uncompensated antiferromagnetic interaction. We earlier obtained experimental evidence showing that at certain amount of Fe^{3+}–O groups in the monolayer on the diamagnetic matrix surface, there is a two-dimensional magnetization region where the local surrounding of Fe^{3+}–O groups does not prevent spin parallel orientation [32].

The magnetic properties of samples containing alternant element–oxygen monolayers of various chemical nature (Table 6) give evidence for the diverse effect of an element–oxygen monolayer deposited on the orientation of spins of iron ions. Let us consider individual systems.

System Fe–O–Ti. As follows from Table 6, the χ value for the sample with the surface monolayer of Fe–O groups containing Ti–O groups in the sublayer, is practically equal to the χ value for the sample with the monolayer of Fe–O groups. Thus, inclusion of an additional diamagnetic Ti–O monolayer does not change the spin parallel orientation, and the ferromagnetic ordering is maintained.

System Fe–O–Zn. As seen from Table 6, inclusion of a Zn–O monolayer to the structure synthesized increases the χ value, and the magnetic susceptibility, as with the sample containing Ti–O monolayer, is almost independent of the order of deposition of different-in-composition monolayers. One can say that introduction of diamagnetic monolayers containing d-metal ions does not effect the location of iron spins. At the same time, the presence of a completely filled

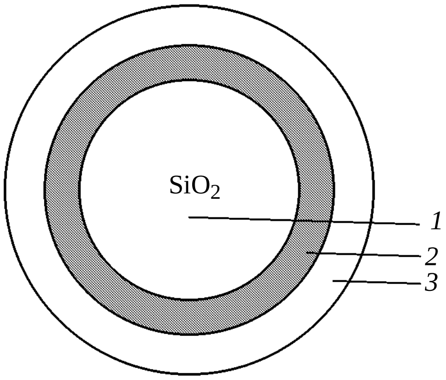


Fig. 10. Scheme of a ferromagnetic nanostructural sorbent: (*1*) SiO_2 particle (Aerosil), (*2*) Fe_3O_4 layer (thickness 10–15 Å), and (*3*) TiO_2 layer (thickness 6–10 Å).

d shell in Zn^{2+} ($3d^{10}$) probably enhances the orienting effect of the substrate due to electron density redistribution along the Si–O–Zn–O–Fe–$(OH)_2$ chain. Such process is impossible in Ti^{4+} ($3d^0$). The above regularity holds for systems with increased number of Ti–O and Zn–O monolayers deposited (Table 6).

System Fe–O–Sn. The χ value abruptly decreases (Table 6) in this case, where the structure synthesized contains an Sn^{4+}–O monolayer (i.e. *p*-element–oxygen). In the first approximation, one can say about the registration, in magnetic measurements, of the different effects of a nontransition element and of a *d*-element on formation of covalent bonds binding element–oxygen groups with a substrate.

System Fe–O–Cu. The presence of a Cu–O monolayer, too, decreases χ. But here this effect can be related to the appearance of an antiferromagnetic contribution to magnetic susceptibility due to additional interaction Cu–O–Fe via oxygen atoms.

As a whole, the data obtained show that by alternating element–oxygen nanolayers, i.e. by controlling the spatial location of atoms in a structure synthesized, one can affect the character of magnetic ordering.

Finally, we put the case of obtaining a nanostructural material. In view of the actuality of elaboration of new sorbents and separation technologies, the sorption properties of a nanostructural sorbent for uranium was studied. Sorption of uranium ions from a see water imitator was studied on samples containing Ti–O groups. As is seen from Table 7, the total dynamic exchange capacity of oxide nanostructures containing Ti–O groups is more than an order of magnitude higher that the exchange capacity of titanium dioxide. By including a Fe–O monolayer (one or several) as a sublayer and subsequently varying the Fe^{2+}/Fe^{3+} ratio we could obtain a ferromagnetic layer 12 Å thick (Fig. 10), with optimal ferromagnetic properties. The good magnetic properties of the sorbent make it possible to avoid the ineffective filtration stage of the sorption process and to procceed to magnetic separation.

Thus, one can conclude that, by the present time, there has been created the scientific basis for solving complex synthetic problems, including constructing highly organized nanostructural solid substances and materials.

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project no. 99-03-32010) and the *Nauchnye Shkoly* Program (project no. 00-15-97356).

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