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The influence of the medium on the mechanical properties of catalysts

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Abstract. The phenomena involving a decrease in the mechanical strength and durability of catalysts during their use, which can be explained in the light of ideas concerning the mutual influence of the solid phase and the medium during catalysis, are examined. Analysis of the mechanism and the set of conditions inducing these phenomena makes it possible to develop methods for a significant improvement of the quality of a catalyst. It is shown that the appearance on the catalyst surface of a multiplicity of mobile adsorbed atoms on dissociation of chemical bonds during the catalytic reaction can give rise to the acceleration of the surface self-diffusion by a large factor, which promotes a significant decrease in the temperature of the sintering of powdered materials. The bibliography includes 105 references.

I. Introduction

In the study of the mechanisms of catalytic reactions, allowance for the interaction of catalysts with the reaction medium and also for the nature of the surface and the bulk phase of the solid catalyst is extremely important.

In order to ensure a prolonged operation of the catalyst, it is essential to create conditions preventing its disintegration and to increase its mechanical strength. The porous solids of different chemical nature employed in catalysis usually disintegrate under the influence of the reaction medium, the chemical processes occurring on their surfaces, and thermal and internal stresses.[1–5]

Many examples of the effect of the catalytic process on the mechanical and structural characteristics of catalysts are known: the disruption of contacts between corundum grains,[6] the detachment and removal of quartz glass macroparticles in the pyrolysis of benzene,[7] the sputtering of an aluminosilicate catalyst,[7] and the disintegration of the nickel catalyst in the decomposition of n-hexyl alcohol.[8] The disintegration of catalysts (the detachment of solid macroparticles and other types of dispersion of the porous structure) may be associated with the adsorption-induced decrease in mechanical strength (ADS). This question was first formulated as early as the 1960s.[9,10] It was postulated that there is an analogy between the ADS of catalyst under the real conditions of their operation and the phenomenon which is observed when metals and other solids (ionic and covalent compounds, molecular crystals, amorphous materials, etc.) come into contact with surfactants.[11] This phenomenon is due to the decrease in the free surface energy of the grains of the solid material under the influence of the surrounding medium, which must contain adsorption-active components (such are the catalytic conditions).

Such phenomena may (or may not) be accompanied by corrosion, dissolution, the condensation of a new phase, and the formation of films or other phase and chemical transformations (including the reconstruction of the surface, the rearrangement of the lattice, and the formation of a wide variety of structural defects), which influence the mechanical strength of the catalyst. Thus there is the phenomenon of 'catalytic corrosion'[12] expressed by a change in the topography of the surface of platinum, palladium, or nickel under the influence of catalytic hydrogen and ammonia oxidation reactions at comparatively low temperatures. The dynamics of catalytic corrosion and the intensity and mechanism of the rearrangement of the surface of the platinum catalyst have been investigated.[13] Various aspects of the mutual influence of the reaction medium and the chemical (phase) composition, the structure of the surface, and the activity and selectivity of catalysts have been examined.[14–16] Numerous data concerning the migration atoms and ions on the surfaces of heterogeneous catalysts during catalysis and the formation and growth of interacting clusters which represent the nuclei of phase formations and structural reconstruction, have been published.[17–32]

Catalysis and the decrease in the mechanical strength of a solid represent different aspects of the same phenomenon, namely the interaction of the solid with the reaction medium, which induces a change in the bonds within both the solid and the reactant. The catalytic reactions of the initial materials and the changes in the structure of the catalyst, occurring simultaneously, may lead to disintegration of the latter.

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Shchukin and coworkers[9,10] showed for the first time that the mechanical strength and durability of catalysts † depend to a large extent on the number, distribution, and strength of individual contacts between the catalyst particles and on the magnitude of the residual internal stresses arising under the conditions in the formation of structures. The kinetics of the ADS in disperse porous structures with an open porosity have their specific features: the pores are readily accessible to the reactive medium and the rate of permeation of the latter into the bond rupture zone is not the limiting factor, as in the propagation of a macrocrack in a continuous material. Therefore the influence of the medium on the parameters of a porous catalyst should be manifested relatively rapidly and should be determined by thermodynamic factors.

The studies of Shchukin and coworkers[9,10] and subsequent systematic theoretical and experimental investigations[33-88] served as a basis for the creation of a physicochemical theory of the mechanical strength of disperse porous structures. The thermodynamic nature of the ADS (partial compensation of the energy of the ruptured bonds by the interaction with the corresponding 'related' medium) at a macroscopic level is manifested by a decrease in the work of formation of new surfaces, i.e. the work of fracture, and hence by a decrease in mechanical strength. Under conditions close to equilibrium, the effect of the ADS may be expressed quantitatively by the decrease in the free surface energy. It has been observed experimentally that the relation between the decrease in surface energy (σ) and in the mechanical strength (P) of any solids in the corresponding medium is described by the well known Griffith relation

$$\frac{P_0}{P_c} = \sqrt{\frac{\sigma_0}{\sigma}},$$

where the quantities P_0 and σ_0 refer to an inert medium, whilst P_c and σ refer to an adsorption-active medium.

At the same time a definite micromechanism of the facilitation of the rearrangement and rupture of the bonds in the solid corresponds to each specific case of a real decrease in mechanical strength. Either the van der Waals pair potential for spherically symmetrical molecules (noble gas atoms) or the ideas concerning donor–acceptor interactions and the changes in the structure of near-surface zones are used for its description.[78-80] The outcome of all these investigations has been the establishment of the characteristics and the mechanism of the disintegration of catalysts' structures in adsorption and catalytic processes and the creation of the scientific foundations for the regulation of the mechanical strength of disperse porous bodies and for the control of cohesion and structure-formation processes.[1-5,64,66] A set of methods and several series of instruments for a comprehensive estimation of the mechanical properties of materials in different stressed states (under static and dynamic conditions) and also in the processes associated with wear (in various media) have been developed.[34,35] There have also been other approaches. For example, it has been suggested that the deformation and level of disintegrating stresses can be estimated with the aid of acoustic emission.‡ The choice of the method for estimating the mechanical strength under the conditions of a catalytic reaction is determined by the type of reactor in which the process takes place (reactors with stationary, fluidised or moving catalyst beds).[36] Novel methods for the determination of the mechanical strength of the catalyst directly under the conditions of catalysis[37] and also for the determination of the internal microstresses in porous structures before and after catalysis have been devised.[38,39] A series of publications have been devoted to the mechanical strength and durability of catalysts. For example, Fenelonov[81] proposed a texture-geometrical model of the mechanical strength of porous bodies, which differs from the model of Rebinder, Shchukin, and Margolis[9] (RSM) by the allowance for the real statistical packing of the particles. He also obtained an equation for the calculation of the specific strength of a single contact when different methods are employed in tests of mechanical strength, which was checked by employing the results of different investigations.[82]

The applicability of the postulates of the statistical theory to data on the mechanical strength of catalysts and sorbents [the 'weak link' and 'fibre bunch' (rope) models] has been examined.[87] The results of tests on porous materials in different stressed states are presented in the same communication and the validity of the equation PV = const (P = stress, V = deformation) was checked and confirmed.

The influence of the porosity (including the porosity in the 'critical' cross-section) of the catalyst grains and of the conditions in their preparation (temperature and duration of heat treatment) on their mechanical strength have been studied.[88,89] The dependence of the mechanical properties of catalysts (and the possibility of using these properties for a form of monitoring of the mechanical strength testing methods arising from it) on a series of technological factors (for example on the duration of dry-curing, hydrothermal synthesis in hot water, and drying) has been investigated.[90] The change in phase composition (during heat treatment) and the rearrangement of the structures of catalysts under the influence of the reaction medium increase the mechanical strength of the grains of cement-containing systems used in organochlorine synthesis,[91] which indicates the occurrence of crystallisation contacts at the interface. The reason for fracture during the employment of copper-containing catalytic systems designed for the oxidation of hydrocarbons and CO to CO_2 is believed to be the extensive reduction of CuO to zerovalent copper accompanied by the formation of highly crystalline phases which leads to the breakdown of interparticle contacts (point and phase contacts).[92]

The need for the creation of a theoretical basis for the development of a technology for the preparation of industrial catalysts and its implementation has now appeared.[93,94] The problem of the mechanical strength of the catalyst again arises in this connection. The strength properties of specific catalysts may be determined by extremely diverse factors.

The mechanical properties of solids and materials have been the subject of numerous fundamental and applied sciences.The concept of the thermofluctuation nature of fracture has arised from solid state physics. In this case, the dependence of durability under load (t) on the applied stress and temperature is described by the familiar Zhurkov equation

$$t = t_0 \exp\frac{U_0 - \gamma P}{kT},$$

where γ is a constant of the material, t_0 the period of the vibrations, and U_0 the dissociation energy of the interatomic bonds.

In the mechanics of granular media, elastic behaviour is considered from the standpoint of the packing of the particles in monodisperse and polydisperse systems and the nature of the contacts. In the statistical theory of mechanical strength, schematised ideas concerning the parameters of the statistical distribution of defects in the bulk of the material are employed for the description of the macroscopic behaviour of bodies under load. Rheology which studies the viscoelastic, viscoplastic, etc. mechanical behaviour of bodies (usually without taking into account their internal structure) describes the changes occurring during their deformations.

† Mechanical strength is a characteristic of the resistance of solids to disintegration at a constant rate of deformation. It depends on the type and method of application of an external mechanical load. Durability or long-term mechanical strength is characterised by the time required for the disintegration of the material subjected to a constant load.

‡ B I Malyshev, O V Dmitrik, R V Fishkin, in *Nauchnye Osnovy Prigotovleniya Katalizatorov* (Scientific Foundations of the Preparation of Catalysts) (Novosibirsk: Nauka, 1984) p. 249.

In the physicochemical mechanics of solids and disperse materials,[5,11] the strength and mechanical fracture of the material are considered from the standpoint of surface physicochemical interactions, because the rupture of interatomic (chemical) bonds actually leads to the formation of new surfaces and at the instant of their appearance (*in statu nascendi*) they are accessible to the physicochemical influence of the medium, which affects the nature of the deformation and rupture. The rupture of interatomic bonds can be achieved in three ways (in various proportions):

(1) as a result of the work performed by mechanical forces (external and internal stresses) given by

$$Pb^2b\sqrt{\frac{L}{b}} = P\gamma,$$

where b is the lattice period (b is the path traversed and b^2 the area of application of the force), L the characteristic linear parameter describing the defective structure of the body, and $\sqrt{L/b}$ the stress concentration factor;

(2) as a result of the thermal fluctuations

$$kT \ln \frac{t}{t_0},$$

where t is the residence time under load and t_0 the period of the vibrations, whilst the quantity $\ln (t/t_0)$ characterises the increase in the probability of the manifestation of fairly large fluctuations in the course of time;

(3) as a result of the work of adsorption ΔU (which includes the work of reversible physical adsorption, chemisorption, and the chemical reaction),[11] which reduces U_0 to $U = U_0 - \Delta U$ and increases the activation volume (i.e. the path leading to the overcoming of the bonding force) to $\gamma' = \gamma + \Delta\gamma$; in this case

$$P\gamma' + kT\ln\frac{t}{t_0} = U.$$

The universal Zhurkov equation, mentioned above, follows from the last equation.

Studies by the method of molecular dynamics, i.e. numerical experiment of a dynamic type (NEDT) of the long-term strength of an individual bond subjected to a constant load have shown[67] that the logarithm of the average lifetime of an atomic (molecular) bond diminishes linearly with increase in the applied load strictly in accordance with the Zhurkov equation.

The deformation and fracture of a two-dimensional crystal with a concentrator-cavity, the adsorption of a surface-active component on the walls of this cavity, the initiation and growth of a crack when a crystal is subjected to a load in the presence of a second component, and the permeation into the growing crack of foreign atoms which promote its development have been investigated by the NEDT method.[68] The results agree with the ideas concerning the molecular nature of the Rebinder effect.

II. The influence of adsorption on the mechanical strength of catalysts

One of the first pieces of direct evidence concerning the influence of adsorption on the mechanical strength of porous structures has been the results of a study of porous magnesium hydroxide specimens in the presence of the vapours of various liquids: water, sulfuric acid solutions at different concentrations (the presence of H_2SO_4 ensured a change in the partial pressure of water vapour), ethyl alcohol, benzene, cyclohexane, etc.[40,41] It was established that the coverage of the surface by 1–4 adsorbate monolayers induces an appreciable decrease in the strength of the magnesium hydroxide specimens (Fig. 1). The principal contribution to the decrease in mechanical strength (by a factor of 1.5–2) corresponds to the range with increasing moisture content up to 1%–1.5%, which corresponds to the formation of a saturated monolayer of the molecules of the medium on the external and internal surfaces of the porous specimen. The decrease in the

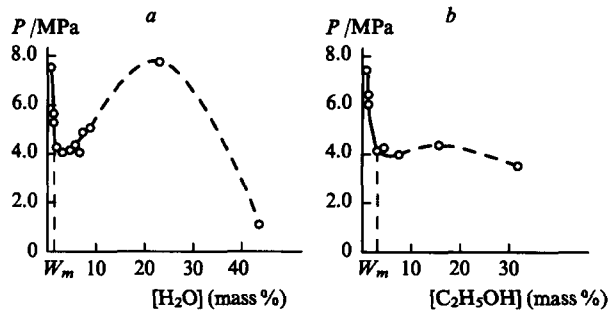


Figure 1. Variation of the compressive strength of magnesium hydroxide specimens during the adsorption of water (*a*) and ethyl alcohol (*b*).[40,41]

mechanical strength of the specimens is not a consequence of the condensation of the adsorbent molecules in contacts between the particles of the solid. The absence of water as an individual phase in magnesium hydroxide (within the limits of monolayer adsorption) has been demonstrated by the NMR method. The true cause is the decrease in the surface energy of the solid on adsorption, i.e. the weakening of the bonds between the atoms (ions) at the surface. The maximum decrease in mechanical strength, attained for a 3%–4% moisture content, is associated with a further decrease in the free surface energy on multilayer adsorption. The subsequent increase in mechanical strength and then its resumed decrease in the presence of high contents of the adsorbate has been explained by the fact that in contrast to continuous media, in disperse porous media the decrease in mechanical strength may be reduced by capillary contracting forces which arise on condensation of the vapour of a liquid in pores.

In the presence of ethyl alcohol, the rise in the curve is not quite so pronounced as in the presence of water owing to the weakening of the capillary contraction forces as a consequence of the smaller surface tension of the boundary with air than for water. The adsorption nature of the decrease in the mechanical strength of magnesium hydroxide specimens in the presence of water is also indicated by the correlation between the relative decrease in the strength of the porous structure and the decrease in the free surface energy of this material ($\Delta\sigma$), which were measured in the presence of water by independent methods (Fig. 2).[42,43] The quantity $\Delta\sigma$ by which the surface energy decreases, i.e.

$$\Delta\sigma = \sigma_0 - \sigma = RT\int_0^P \Gamma \ln p,$$

(p is the water vapour pressure at which the specimens were moistened) was found from the adsorption (Γ) isotherm for water vapour.

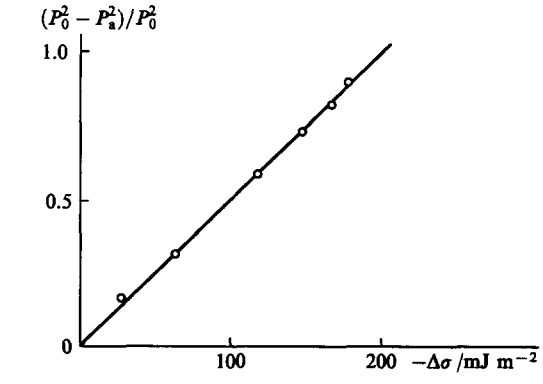


Figure 2. Relation between the decrease in mechanical strength and the decrease in the surface energy of highly disperse porous magnesium hydroxide specimens[42] in terms of the variables of the Griffith equation.

The relation obtained confirms the validity of the Griffith relation, i.e. a proportionality between the relative decrease in mechanical strength $(P_0^2 - P_a^2)/P_0^2$ (P_0 and P_a are the mechanical strengths of the dry specimen and the specimen moistened under equilibrium conditions respectively) and the decrease in surface energy holds for these structures. Hence it follows that $P \sim \sigma^{1/2}$. The quantity $\sigma_0 = 300$ mJ m^{-2}, found from the slope of the straight line, has an acceptable value. The same correlation has been observed in the adsorption of water vapour on silica gel.[95] A relation between the decrease in surface energy and the decrease in the mechanical strength of porous bodies has been indicated.[44] The values of σ for cement were found from the Griffith equation; for a water : solid (WS) ratio of 0.45, we have $\sigma = 1370$ erg cm^{-2}, whilst for WS = 0.60 we have $\sigma = 657$ erg cm^{-2}.

The ADS effect for the monomolecular surface coverage by the adsorbate has been observed in experiments with ionic polycrystalline KCl and NaCl immersed in water–dioxane mixtures of different composition.[45] The decrease in mechanical strength under these conditions was not associated with the impregnation of the grains between the crystals by the liquid.

In the study of the influence of the polarity of the adsorbate on the mechanical strength of porous structures in relation to magnesium hydroxide as an example, it was shown that, in contrast to the polar water and ethanol molecules, the nonpolar benzene and cyclohexane molecules hardly influence the mechanical strength of the hydroxide.[41] Similar features were observed in the study of the decrease in the mechanical strength of pressed calcium carbonate, zinc oxide, sodium chloride, charcoal and silica gel specimens in the presence of water, benzene, and carbon tetrachloride vapours, carbon dioxide, and nitrogen.[95–97] The specimens on the surfaces of which a saturated monolayer of the molecules of the medium had been adsorbed were found to be the least strong. The effect involving a decrease in mechanical strength was greater the closer were the polarities of the adsorbent and the medium (water on silica gel, benzene on charcoal). This indicates a decrease in mechanical strength with decrease in the free surface energy on adsorption. In all the systems indicated, the decrease in mechanical strength was not accompanied by the occurrence of dissolution and chemical interaction processes. The mechanical strength of ionic polycrystalline sodium and potassium halides in heptane, water, and dioxane decreased to a greater extent the greater was the polarity of the medium.[45] Thus in water it amounted to 0.2 of the initial value.

The dispersity of the structure-forming particles, the degree of porosity of the medium, and the nature of the individual contacts did not affect the decrease in mechanical strength in adsorption on magnesium hydroxide specimens.[41] It was observed by X-ray diffraction that, in physical and chemical adsorption (for example, of isopropyl alcohol on magnesium oxide[46] and of water and ethyl alcohol on magnesium hydroxide,[47]) the microdeformations (internal stresses) increase with the consequent adsorption-induced decrease in the strength of the structure. The appearance of internal stresses has been explained by the change in the relation between the resistance of the rigid framework comprising interlinked particles and the Laplace pressure compressing the particles (as a consequence of the decrease in free surface energy on adsorption).

The transition of silica gel to a complex stressed state occurred when it was moistened and dried.[98] When silica gel was fully immersed in water, air was trapped in the structure and was compressed by the capillary pressure due to the gradually permeating water. As a result, high counterpressures arose in the structure, reaching limiting disruptive values.

The ADS phenomenon was observed also on chemically more complex porous structures: specimens of clays of different mineralogical composition (kaolinite, bentonite), NaA and NaX zeolites,[48,49] and an aluminosilicate zeolite-containing cracking catalyst.[50] The mechanical strength of these materials diminished sharply following the adsorption of various substances. The adsorption and especially chemisorption of isopropyl alcohol induces an appreciable comminution of the block structure of magnesium oxide crystals (an increase in the density of dislocations).[46] The possible cause of this is the nonuniformity of the adsorption combined with the mechanical anisotropy of the crystals. The relaxation processes occurring after the catalytic reaction again lead to an increase in the size of the blocks and a decrease in the density of dislocations.

Among the multiplicity of the elementary mechanisms for the formation of the texture of catalysts under various conditions, two most common mechanisms of the increase in surface are distinguished. The characteristics of the thermodynamics of highly disperse systems, which determine the direction and driving force of the process, are manifested in these mechanisms.[91] One of the mechanisms involves the growth of the surface in phase transformations, where the decrease in the phase potential compensates for the increase in the surface potential, which is appropriately reflected in the radius of the critical nucleus of the new phase.[3,91] The second mechanism is associated with the change in entropy. If the interfacial energy is small, the increase in entropy may compensate for the increase in surface energy.[3] On the basis of these mechanisms, it is possible to estimate the minimum size of the nucleus or the 'maximum area which can then only decrease in the absence of phase transformations or a sharp decrease in the interfacial energy'.[81]

The driving forces and the principal mechanisms of the decrease in the surface (for example, as a result of coagulation) can also be related to the local (in the contact zones) decrease in the interfacial energy.[4] On the other hand, the specific mechanisms of the processes, including the mechanisms of the change in porosity, may be extremely varied.[81]

Examination of the ADS phenomena helps us to understand the mechanisms of certain intermediate stages in the new processes involving the formation of a wide variety of aluminium oxide carriers and catalysts using thermochemical (TCA) and mechanochemical (MCA) methods for the activation of solids (see, for example, Refs 84 and 99–101). Thus it has been shown that, in the transformation of the products of the MCA and TCA of technical hydrated alumina, as a result of hydration, from the amorphous to the pseudoboehmite state (which can be readily converted into various aluminium oxide carriers or binders for catalysts), bonds between the elements of the layered structure (plates) are disturbed by the ADS and by the presence of the disjoining pressure of the liquid phase on the surfaces bounding it.[84] This results in the cleavage of the highly disperse particles of the products of the TCA into finely disperse (2–5 nm thick) plates and their subsequent hydration. This phenomenon as well as others have been used in creating a low-waste technology for the manufacture of aluminium oxides used as carriers, adsorbents and catalysts.[84] The formation of surface compounds, which occurs, for example, in the interaction of methanol with magnesium oxide,[85] is accompanied by the dissociation of the bonds in the alcohol molecule and the liberation of energy. In the chemisorption of ethanol on Al_2O_3,[86] the bonds between the aluminium and oxygen ions are 75%–90% weakened according to quantum-chemical calculations and IR spectroscopic data. The clusters formed and their varieties, participating in the formation of surface compounds, also play a definite role in this process.

Comparison of the behaviour of adsorbates having molecules of different size (water, benzene) made it possible to observe that the filling of the inner cavities of the zeolite crystals (within the limits of sorption capacity) with adsorbate molecules prevents a decrease in mechanical strength of granules.[48,49] If there is steric hindrance to the permeation of the adsorbate molecules into the cavities, the mechanical strength of the zeolite grains diminishes already for low degrees of adsorption (of the order of monolayer coverage of the surface of the clay binder). A similar 'protective' effect has been observed in the dispersion of brown coal in the presence of water and heptane.[51]

The data presented referred to physical adsorption, but in catalytic processes the chemical adsorption of the reactants and reaction products plays the main role.

The influence of chemisorption on the short-term and long-term mechanical strength of disperse porous structures has been investigated in detail in relation to the behaviour of the cobalt–molybdenum catalyst under conditions involving a change in the temperature and pressure of the vapours of the products of the incomplete oxidation of propene (carbon dioxide, acetaldehyde, and especially acrolein).[52–54, 102, 103] It was established that the degree of disintegration of the catalyst depends on the degree of surface coverage by chemisorbed molecules and on the strength of the chemisorption bond, i.e. on the decrease in free surface energy on chemisorption (Fig. 3).

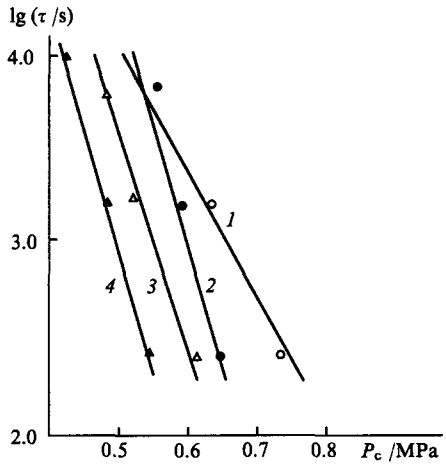


Figure 3. Dependence of the time to fracture of a cobalt–molybdenum catalyst on the applied load in various media at 483 K: (*1*) nitrogen; (*2*) carbon dioxide (partial pressure 350 mm Hg); (*3*) acetaldehyde (60 mm Hg); (*4*) acrolein (60 mm Hg).[49]

The disintegration of a catalyst as a consequence of chemisorption has been observed also under the conditions where the grains of an alumina–chromium oxide–potassium oxide catalyst were ground up in a stream of n-butane and butenes at elevated temperatures.[55]

III. The effect of the catalytic reaction on the mechanical strength of catalysts

The phenomenon of the accelerated disintegration of the structures of catalysts under the reaction conditions has long been known. Shchukin and coworkers[9, 10] showed for the first time that the surface phenomena at the interfaces in the porous structures should be regarded as the main causes of the decrease in the mechanical strength and durability of catalysts. A similar view has been expressed in a study of the surface phenomena accompanying a heterogeneous chemical reaction using methods based on the thermodynamics of irreversible processes.[104] If intermediate compounds or a series of states which possess a higher surface activity than the initial and final compounds are formed in a chemical reaction,§ then their adsorption at the interface reduces the interfacial energy and increases the area of the interface. Consequently, the surface energy of the catalyst should diminish during the catalytic process. A decrease in the hardness of amalgamated zinc and brass catalysts in the decomposition of aqueous solutions of hydrogen peroxide has been observed experimentally and explained by a decrease in the surface tension of mercury during catalysis.[105] According to the data of Shchukin and Margolis,[64] the active intermediate complex interacts more strongly with the catalyst surface than the initial reactants and chemisorption appreciably weakens the metal–metal bond. As a result, surface metal atoms are frequently detached on formation of a bond with active adsorbates.

The mechanical strength of sulfur dioxide oxidation catalysts under the reaction conditions differs appreciably from their strength outside the reactor.[77]

The influence of catalysis on the mechanical strength and durability of porous magnesium oxide catalysts in the endothermic isopropyl alcohol dehydrogenation reaction has been studied systematically.[37, 40, 46, 52, 56, 66, 67] Already 20–30 s after the start of the reactions, even before the establishment of stationary conditions, the compressive strength of the catalyst diminished by a factor of 1.5–2 (the tests were carried out after the cessation of the catalytic reaction and the drying of the grains).[46, 56] A further increase in the duration of the use of the catalyst induced only a slight decrease in its mechanical strength. It was demonstrated by X-ray diffraction that the internal stresses in the catalyst diminish during the reaction owing to the irreversible rupture of the bonds (contacts between the particles).

Numerous experiments have shown that the mechanical strength of the catalyst decreases with increase in the internal stresses associated both with the genesis of the structure (for example, on pressing a magnesium oxide powder or on dehydration of magnesium hydroxide) and with the catalytic reaction conditions (thermoelastic stresses due to the cyclic changes in temperature during catalysis). The mechanical strength of the catalyst, measured directly during catalysis with the aid of a dynamometric device mounted in a specially constructed reactor,[57] proved to be lower than after the cessation of the reaction for the same exposure time. It may be that the decrease in the interfacial energy is influenced by the nonequilibrium adsorption of intermediate compounds during catalysis. If the conditions of the catalysis promote the appearance of internal stresses (for example, as a consequence of cyclic changes in temperature), then the mechanical strength decreases significantly not only at the beginning of the process but also throughout it. The decrease in mechanical strength may be accompanied by a change in the specific surfaces of the specimens, but a direct relation between the decrease in mechanical strength and dispersity was not observed.

The decrease in mechanical strength was independent of the change in the specific surface of the porous structure as was confirmed in experiments on the dehydrogenation of isopropyl alcohol on aluminium oxide specimens.[58]

During the catalytic reaction, not only the mechanical strength but also the durability of the catalyst under load decrease. Thus the disintegration time of a magnesium oxide catalyst subjected to a 0.8 MPa load decreases dramatically in the reaction medium (the disintegration time was determined from the projections of the corresponding points on the relations illustrated in Fig. 4 onto the ordinate axis). A decrease in durability under the conditions of catalysis has been observed also for the cobalt–molybdenum catalyst of the incomplete oxidation of propene.[52]

There are data on the disintegration of sulfate catalysts in stationary and fluidised beds used in the synthesis of sulfuric acid.[59, 60]

In order to test the hypothesis that the bonds are weakened in the solid under the reaction conditions, CO was oxidised on disperse porous iron and nickel specimens.[61] An increase in the area of contact between the metal particles was observed with an electron microscope.

The migration of crystallites as well as the disappearance of small particles and the appearance of large ones with formation of irregular shapes have been observed also in a study of the

§ The possibility of the appearance of intermediate forms of the interaction in catalytic processes was already noted by D I Mendeleev [see D I Mendeleev *Osnovy Khimii* (Fundamentals of Chemistry) Vol. 1 (Moscow, Leningrad: Goskhimizdat, 1947) pp. 523, 524].

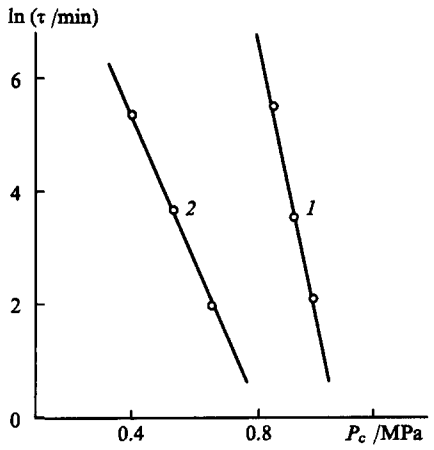


Figure 4. Dependence of the time to fracture of a magnesium oxide catalyst on the applied load at 668 K in nitrogen (line *1*) and in the reaction medium during the dehydrogenation of isopropyl alcohol (line *2*).

behaviour of the Ag/Al_2O_3 catalyst in the ethene oxidation reaction.[103]

These results as well as the data mentioned above concerning the decrease in the durability of the cobalt–molybdenum catalyst in the chemisorption of the reaction products[52,53] confirm the hypothesis of Shchukin and coworkers,[9,10] according to which the decrease in the mechanical strength of the specimens under the conditions of catalysis is caused by the simultaneous effect of the internal stresses in the catalyst and of the weakening of the bonds between the atoms (ions) on the surface of the solid as a result of the adsorption of the reacting components, including the effect resulting from the nonequilibrium adsorption of intermediate compounds.

The rate of the surface diffusion (self-diffusion) in iron under the conditions of catalysis and in the absence of the reaction medium has been investigated.[62] The method involving the 'healing' of a scratched groove was employed: for a specified observation time, the decrease in the depth of the groove δ is proportional to the surface diffusion coefficient D raised to the power 1/4. It was established that, under the conditions of the synthesis of ammonia at 800 K, the diffusion coefficient of iron atoms on the surface of the catalyst increases by a factor of 10^5 compared with the value of D at the same temperature in the absence of catalysis. This effect is due to the sharp increase in the number of mobile adsorbed atoms as a result of the implementation of the reaction steps (in this case, an exothermic reaction). Similar phenomena have been observed in the hydrogenation of benzene on nickel.[54] The similarity in the behaviour of these metals in the reaction described above is due to the fact that molecular hydrogen dissociates on these catalysts and atomic hydrogen induces their embrittlement.

It is noteworthy that, under the conditions of experiments[54] involving the 'healing' of a scratch, the migration mechanism is known to be determined by the surface mass transfer on nickel, since the mechanism involving transfer through the gas phase is impossible owing to the low vapour pressure of nickel, while the bulk diffusion mechanism cannot be achieved because of the considerable predominance of surface self-diffusion over the bulk-phase diffusion at the experimental temperature. The exothermic reaction in which benzene is hydrogenated to cyclohexane at 100 °C and the endothermic cyclohexane dehydrogenation reaction at 350 °C have been investigated.[54] In control experiments, nickel specimens with scratches were annealed in a stream of hydrogen at 100 °C and in a stream of helium at 350 °C. The smoothing of the scratch was estimated from the decrease in its initial depth. This occurred only under the conditions of the exothermic reaction involving the hydrogenation of benzene to cyclohexane. As in the synthesis of ammonia on iron, the nickel diffusion coefficient was greater by a factor of 10^4-10^5 than the value of D in the absence of catalysis. Since the coefficient D increased only in the presence of an exothermic reaction, it is evident that the energy of the chemical reaction is necessary for the acceleration of the mass transfer.

It has been suggested that this effect is possible also in an endothermic reaction, provided that an intermediate stage proceeds with evolution of energy. The role of catalysis in the rearrangement of the surface consists precisely in facilitating a single nickel adatom formation due to an elementary catalytic step and not in facilitating the subsequent migration of the adsorbed atom over thousands of interatomic distances. In other words, since the scratch is not 'healed' in an endothermic reaction, the increase in D during catalysis may be attributed to the heat of reaction: the energy evolved in each catalytic step is consumed predominantly (or completely) not on heating the catalyst but on the local rupture of the bonds of individual atoms (ions) in the surface layer of the solid (on which or in the vicinity of which the catalytic step occurs), on the 'abstraction' of atoms from the defective region of the crystal lattice (for example, from kinks in the steps on the surface), and on their transition to the state of adsorbed atoms. Since the absolute heat of the reactions investigated calculated per mole exceeds by a factor of 2–3 the energy required for the formation of 1 mole of adsorbed atoms, it was postulated[54] that 2–3 additional adsorbed atoms, which participate in the diffusional surface mass transfer, arise in each step.

IV. Contacts between the particles and internal stresses

According to the ideas of physicochemical mechanics, the mechanical strength of a solid depends on the nature of the contacts between the particles. The strength of the crystallisation contacts is relatively high, amounting to 10^{-6} N and more. Depending on the conditions in the preparation of the catalysts and on their chemical properties, the number and strength of the individual contacts may vary and hence the mechanical strength also varies. The characteristics of the structure of the solid (defects, dislocations, etc.) are superimposed on the properties of the porous structures of the catalyst.

It has been shown[37,63] that, in contrast to the decrease in mechanical strength during adsorption, in many cases the adsorption-induced decrease in mechanical strength during catalysis may be sharply weakened with increase in the strength of the contacts in the porous structure. These results have been obtained on specimens of a magnesium oxide catalyst with the same fine and overall porosities, on which the catalytic reaction proceeds at the same rate. Specimens with 'low strength' contacts were formed from a magnesium oxide powder obtained by heating magnesium hydroxide at 1173 K. After moulding, they were annealed at 723 K. Specimens with 'strong' contacts were obtained from hydrated magnesium oxide, by dehydration of magnesium hydroxide specimens at 723 K and following calcination at 1173 K. In both cases the heat treatment conditions were the same and only the sequence of the operations was altered.

Figure 5 presents data on the relative decrease in the compressive strength (along the axis of a cylinder) of magnesium oxide specimens, obtained under the conditions of the dehydrogenation of isopropyl alcohol at 653 K, as function of their porosity (*II*). These relations have been attributed[37,63] to the lower mobility of the chemisorbed molecules ('kinetic difficulties') compared with the mobility of the molecules in the state of physical adsorption. In the latter case, the molecules have sufficient time to migrate, following the tip of the crack opening as a result of the applied stress.

The increase in the durability of the magnesium oxide catalyst containing 15 mass % of added silica, known as white soot, has also been explained by the kinetic difficulties arising following an increase in the strength (area) of the contacts.[56,62] In the presence of white soot, the longterm strength of this catalyst falls to an

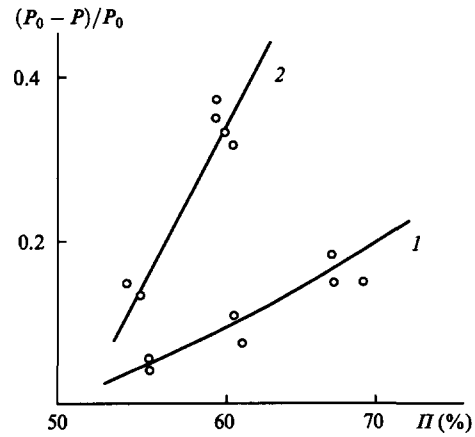


Figure 5. Dependence of the relative decrease in the strength of the samples with 'weak' (line *1*) and 'strong' (line *2*) contacts on the porosity of a magnesium oxide catalyst under the conditions of the dehydrogenation of isopropyl alcohol at 653 K. P = mechanical strength of the specimen 1 h after the start of the reaction; P_0 = mechanical strength of the initial specimen kept in the reactor at the temperature of the catalytic reaction in a stream of dry nitrogen.

appreciably lesser extent 50 min after the start of the catalytic reaction than in its absence. The specimen with the additive possesses the same and in certain cases a higher catalytic activity. The strengthening of the contacts has been attributed to the improvement in the sintering of the magnesium oxide particles as a result of the chemical interaction with silicon oxide.

The possibility of the reconstruction of the catalyst surface under the conditions of adsorption and the catalytic reaction has been demonstrated.[7,8] The driving force for the reconstruction of the lattice of the solid is the decrease in the free surface energy. The kinetics of the mass transfer accompanying this phenomenon indicate [54,62] that, in the course of exothermic catalytic reactions, there is a sharp (by 4–5 orders of magnitude) increase in the coefficient of the surface self-diffusion of the metal atoms on the catalyst surface (the heat of chemisorption, which is always positive, is insufficient for an appreciable acceleration of the surface diffusion). Experiments with porous nickel and iron catalysts have shown that this increases by a factor of 4–6 the strength of the porous structures under the conditions of catalysis by virtue of the increase in the number of adsorbed atoms and their directed diffusion to sites with a changed chemical potential, including contact regions. The same mechanical strength under an inert gas atmosphere as in catalysis may be attained only at an appreciably higher (by 300 °C) temperature. Under the conditions of catalysis, where the self-diffusion coefficient increases by a factor of 10^5, the calculated sintering temperatures of a series of substances (iron, nickel, magnesium oxide, iron oxide) decrease by several hundreds of degrees; a decrease in the sintering temperature is promoted by a decrease in the activation energy for self-diffusion.[62]

The relation between the elementary catalytic events and the adsorption mechanisms of the decrease in mechanical strength was established by comparing the processes involving the synthesis of ammonia on an iron catalyst, one of the stages of which is the dissociative chemisorption of hydrogen, and the hydrogen-induced embrittlement of iron.[64–66] The weakening of the interatomic bonds in molecular hydrogen and in iron are two aspects of a single process: the iron catalyst promotes the dissociation of the bond in the H_2 molecule, while atomic hydrogen facilitates in its turn the rupture of the Fe–Fe bonds in the iron lattice. Nickel, which is a catalyst for exothermic hydrogenation reactions and is also susceptible to hydrogen-induced embrittlement, behaves similarly.

In other words, together with the 'direct' effect of the surface of the solid phase on the reaction kinetics, there is a 'reverse' effect of the medium on the structure of the solid — the catalyst.

The appearance and decomposition of contacts as a result of fluctuating oscillations, the mechanisms of the elementary steps in the deformation and disintegration, and the influence of the medium on these processes have been examined at the atomic-molecular level with the aid of the method of molecular dynamics (numerical experiment of a dynamic type).[67,68] Analysis of the long-term strength of an individual bond subjected to a constant load showed that the logarithm of the average lifetime of the bond decreases linearly with increase in the applied load, which is strictly consistent with the universal Zhurkov equation.

This approach made it possible to confirm also the idea of the molecular nature of the Rebinder effect. The deformation and fracture of a two-dimensional crystal havig a concentrator-cavity during the adsorption of a surface-active component on the walls of the cavity have been explained by the fact that when a crystal is subjected to a load, a crack is initiated, which is followed by its growth and the permeation into the growing crack of surface-active atoms, which promote its propagation.

The principle of the interrelation between the elementary catalytic steps and the adsorption-induced decrease in mechanical strength,[64–66] i.e. the analogy between the rupture of the interatomic bonds induced by mechanical disintegration and the chemical reaction, has been confirmed in a theoretical analysis of the catalytic cracking of hydrocarbons.[69] Acid catalysts are used in cracking processes and the reaction proceeds via a stage involving the formation of a carbonium ion. In this connection, it was postulated that the acid agents must facilitate also the mechanical disintegration of the hydrocarbon chain. In order to establish the mechanism of the Rebinder effect and to determine the quantitative characteristics of the adsorption-dependent influence of the medium, a direct quantum-mechanical calculation of the force and energy parameters of single and double C–C bonds during their mechanical rupture was carried out and the influence of the hydrogen cation — the active principle in acid catalysts of the cracking of hydrocarbons — on this process was estimated. The calculation showed that the addition of a proton diminishes the strength of the C–C bond and that the magnitude of the effect depends significantly on the nature of the carbonium ion formed. The interrelation principle has been confirmed also in numerous experimental observations of the rearrangement of the surfaces of catalysts under the conditions of a catalytic reaction.

It was established that the stresses in solids arising during the formation of the structure can both decrease and increase their mechanical strength.[2] The increase in the mechanical strength of solids has been observed on pressing powders, whereupon phase contacts were produced as a result of the plastic deformation in the contact zone. On the other hand, the presence of residual internal stresses in the solid always induces a decrease in mechanical strength, especially in the study of catalytically active media which accelerate the relaxation of stresses due to the weakening, as a result, of chemisorption of the bonds between the atoms (ions) of the surface.[2,3] One of the most important conditions governing the increase in the durability of heterogeneous catalysts, sorbents, and carriers is therefore a decrease in the residual internal stresses by the optimisation of structure formation.

Among the procedures for decreasing the residual internal stresses one may name, for example, the regulation of the dispersity of the initial binding substance in the structures arising as a result of the hydration-induced hardening of calcium and magnesium oxides, the introduction of seeds in crystallisation processes, and the addition of some electrolytes (i.e. the creation of conditions promoting a decrease in the supersaturation of suspensions in the aqueous phase during the preparation of the catalyst).[2,70] An increase in porosity and a decrease in the rigidity of the crystallisation structures are also used to eliminate internal stresses, for example by introducing small amounts of a highly

disperse inert filler, which hinders the formation of phase contacts in the bulk of the material in the initial stages.

Catalysts based on silica and alumina gels having an amorphous matrix constitute a separate group. They acquire special functional (catalytic, adsorption, etc.) properties following the introduction of a crystalline filler, for example, a zeolite. As in crystallisation structures, in these composite structures the internal stresses reach magnitudes close to the mechanical strength of the material itself ($\sim 10^7$ N m^{-2}).[4,71] An increase in the dispersity of the filler crystals and the introduction of anisometric particles are procedures for reducing the residual stresses in such materials.[2] Thus the introduction into an amorphous aluminosilicate xerogel (a cracking catalyst) of fluorite crystals with a lower dispersity as a filler reduces the internal stresses by a factor greater than two, while small amounts of added ($\sim 2\%$) asbestos fibres diminish microdistortions by a factor of two.[2]

The internal stresses in catalysts and sorbents become smaller when vibration-induced compaction is used instead of static pressing.[72,73] In this case, the decrease in the internal stress is accompanied by the simultaneous increase in the density of the structure, increasing its strength,[1,10] which depends on the number of particles per unit cross-section (the granulometric composition is the same under the conditions of static and vibration-induced compaction). A decrease in the fraction of large pores, which under the conditions of catalysis in the presence of residual stress may play the role of the nuclei of cracks, has an extremely positive effect on the increase in density. It has been shown for the bismuth–molybdenum catalyst of the oxidative ammonolysis of propene that a denser structure with smaller internal stresses obtained by vibrocompaction is also more durable.[73] Its catalytic properties remain unchanged under these conditions.

V. The sintering and strengthening of catalysts

Since the coefficient D increases during the catalytic reaction,[62] a decrease in the sintering (presintering) temperature and hence an increase in the strength of the porous structure of the powdered pressed catalysts compared with similar specimens heat-treated at the temperature of the catalytic reaction but in an inert medium might have been expected. A heterogeneous catalytic reaction proceeds only on the outer or inner surface of the solid catalyst and therefore one should expect that the cause of such strengthening is an increase in the area of the true contact between the particles for an unchanged porosity of the specimens.

Naturally the postulated effect involving the strengthening of catalysts in exothermic reactions may be observed only if it surpasses the effect involving the adsorption-induced decrease in the strength of the porous structure.

The oxidation of CO has been investigated in through-put apparatus at atmospheric pressure under isothermal conditions, where the temperature of the catalyst (carbonyl iron) increase during the reaction by not more than 0.2 °C.[61,75,76] The reacting gases — oxygen and carbon monoxide in stoichiometric proportions — were supplied to the reactor in a mixture with helium. The influence of the reaction mixture and of its individual components — CO (in a mixture with helium) and O_2 (in a stream of air) as well as H_2 — on the mechanical strength of the catalyst was elucidated. 'Mild' conditions in the preparation of the specimens promoted a decrease in the residual internal stresses and the adsorption-induced decrease in mechanical strength.

Table 1 presents the results of the measurement of the mechanical strengths of carbonyl iron specimens after their annealing in various media. During the reaction at 573 and 623 K, there is a sharp (by a factor of 4–5) increase in the mechanical strength of the catalyst compared with the initial specimen and the specimens annealed in the presence of one of the reaction components. It was demonstrated by means of an electron microscope that the catalyst particles form contact chords, produced during the annealing of the specimen under the reaction conditions. In the absence of the reaction medium at the same temperature, the effect is much weaker.

Table 1. The influence of the carbon monoxide oxidation reaction and of the components of the reaction medium on the mechanical strength of the porous structure of the catalyst — carbonyl iron.[54]

Composition of medium (vol. %)	Strength (in MPa) at	
	573 K	623 K
8% CO + 4% O_2 + 88% He	6.4	7.46
21% O_2 + 78% N_2 (air)	2.40	2.88
100% Ar	1.37	1.46
8% CO + 92% He	0.31	0.36

Note. The porosity of the specimens was 57.5±0.2% before and after catalysis and the mechanical strength was 1.27 MPa.[54]

The increase in mechanical strength is due to the increase in the area of contact between the particles as a result of the surface self-diffusion. A sharp increase in the strength of the catalyst for a constant porosity was achieved in this reaction also on specimens of electrolytic nickel.

A decrease in the sintering temperatures of iron and nickel during the catalytic reaction was established experimentally. The strength of the porous structures of iron and nickel in an inert medium increased only at higher temperatures (by 300–350 °C).

Thus the sintering temperatures of metallic powders decrease appreciably under the conditions of an exothermic catalytic reaction. A significant strengthening of the porous structures is then attained as a result of the development of contacts between the particles with retention of the initial porosity, which is important for both catalysts and adsorbents and for membranes. Qualitatively similar results have been obtained on the MgO and V_2O_5 oxide catalysts in exothermic oxidation reactions,[74,75] but the strengthening effect proved to be smaller in this case than on porous metallic catalysts. This is apparently due to the greater defectiveness (metastability) of the oxides obtained by the decomposition of hydroxides and salts at relatively low temperatures, appreciably those lower than the melting points of the corresponding oxides.

VI. Conclusion

The interaction between the catalyst surface and the molecules of the medium induces certain changes both in the adsorbed molecules and in the catalyst itself. For example, the mechanical strength and durability of the MgO, Co–Mo, Al–Cr–K, etc. catalysts may decrease significantly in the course of the catalytic reaction. Iron may serve as yet another striking example: as a catalyst of the synthesis of ammonia, iron participates in the cleavage (dissociative adsorption) of the hydrogen molecule and is in its turn subjected to hydrogen-induced embrittlement.

The influence of the catalytic reaction on the mechanical properties of the catalyst must be regarded as one of the manifestations of the Rebinder effect — a decrease in the mechanical strength of a solid under the influence of the adsorption active components of the medium, which reduce the surface energy (and the work of disintegration), and of the mechanical stresses induced by the weight of the catalyst layer, collisions, and thermal gradients. The residual internal stresses, arising at different stages in the preparation of the grains, also make their own contribution. The catalyst is therefore, as it were, doomed to accelerated wear precisely by virtue of its purpose.

However, comprehensive analysis made it possible to also discover ways whereby these undesirable effects can be significantly weakened. The strengthening and increase in the stability of granules in an active medium are achieved by the optimisation of the entire technological chain in the preparation of the catalyst by selecting pressing and hydration conditions, by the use of inert carriers, by employing modifying agents during sintering, by

introducing mineral binders, by modifying the contacts themselves, which promotes a decrease in their sensitivity to the medium, by combining finely disperse and coarsely disperse fractions, by adding anisometric (fibrous), including inert, fillers, etc. All this makes it possible to increase drastically the useful life of the catalyst.

At the same time, the weakening of the bonds between the atoms on the surface of the catalyst leads to a sharp increase in the number of mobile atoms and intensification of the surface self-diffusion. Direct observations by the method involving the 'healing' of a scratch indicate an enormous (by 4–5 orders of magnitude) increase in the coefficient of surface self-diffusion. This effect has been observed on iron during the synthesis of ammonia and on nickel during the hydrogenation of benzene.

The intensification of self-diffusion may in its turn intensify the sintering process, making it possible to carry it out at reduced temperatures. The sintering temperatures of iron and nickel powders under the conditions of the oxidation of CO may be reduced by 300 °C without affecting the mechanical strength of the specimens, i.e. it ensures the development of strong contacts between the particles. Similar effects have been observed on the MgO, V_2O_5, and Al_2O_3 catalysts under the conditions of the corresponding reactions.

The approach described leads to new possibilities for the selection of catalysts and the optimisation of the technology of their preparation, the improvement of the processes involving the sintering of high-temperature components, and in general the development of new principles of the treatment of materials.

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References

1. E D Shchukin, in *Fiziko-khimicheskaya Teoriya Prochnosti Dispersnykh Struktur i Materialov. Fiziko-khimicheskaya Mekhanika Prirodnykh Dispersnykh Sistem* (Physicochemical Theory of the Strength of Disperse Structures and Materials. Physicochemical Mechanics of Natural Disperse Systems) (Ed. E D Shchukin) (Moscow: Izd. Moskovsk. Gos. Univ., 1985) p. 72
2. E D Shchukin, S I Kontorovich, E A Amelina *Zh. Vses. Khim. O-va im D I Mendeleeva* **34** (2) 23 (1989)
3. E D Shchukin (Ed.) *Uspekhi Kolloidnoi Khimii i Fiziko-khimicheskoi Mekhaniki* (Advances in Colloid Chemistry and Physicochemical Mechanics) (Moscow: Nauka, 1992)
4. E D Shchukin, A V Pertsov, E A Amelina *Kolloidnaya Khimiya* (Colloid Chemistry) (Moscow: Vysshaya Shkola, 1992)
5. E D Shchukin, in *Fiziko-khimicheskaya Mekhanika i Liofil'nost' Dispersnykh Sistem* (Physicochemical Mechanics and Lyophilicity of Disperse Systems) (Kiev: Naukova Dumka, 1981) Vol. 13, p. 46
6. A G Leibush, in *Khimicheskaya Pererabotka Neftyanykh Uglevodorodov* (Chemical Processing of Petroleum Hydrocarbons) (Moscow: Izd. Akad. Nauk SSSR, 1956) p. 121
7. A P Rudenko, in *Sovremennye Problemy Fizicheskoi Khimii. Voprosy Kataliza, Adsorbtsii i Fiziko-khimicheskoi Mekhaniki* (Current Problems in Physical Chemistry. Problems of Catalysis, Adsorption, and Physicochemical Mechanics) (Eds Ya I Gerasimov, P A Akishin) (Moscow: Izd. Moskovsk. Gos. Univ., 1968) Vol. 3, p. 263
8. A A Balandin, A P Rudenko, G Stegner *Izv. Akad. Nauk SSSR, Ser. Khim.* 762 (1961)
9. P A Rebinder, E D Shchukin, L Ya Margolis *Dokl. Akad. Nauk SSSR* **154** 695 (1964)
10. E D Shchukin *Kinet. Katal.* **6** 641 (1965)
11. V I Likhtman, E D Shchukin, P A Rebinder *Fiziko-khimicheskaya Mekhanika Metallov* (Physicochemical Mechanics of Metals) (Moscow: Izd. Akad. Nauk SSSR, 1962)
12. S Z Roginskii, I I Tret'yakov, A B Shekhter *Dokl. Akad. Nauk SSSR* **91** 881 (1953)
13. M R Lyubovskii, V V Barelko *Kinet. Katal.* **35** 412 (1994)
14. G K Boreskov *Kataliz. Voprosy Teorii i Praktiki* (Catalysis. Problems of Theory and Practice) (Eds K I Zamaraev, G I Panov) (Novosibirsk: Nauka, 1987)
15. G K Boreskov *Kinet. Katal.* **21** 5 (1980)
16. A Ya Rozovskii *Katalizator i Reaktsionnaya Sreda* (The Catalyst and the Reaction Medium) (Moscow: Nauka, 1988)
17. K N Spiridonov, O V Krylov, in *Problemy Kinetiki i Kataliza* (Problems of Kinetics and Catalysis) (Moscow: Nauka, 1975) Vol. 16, p. 7
18. V A Khalif, B V Rozentuller, A M Frolov, E L Aptekar', K N Spiridonov, O V Krylov *Kinet. Katal.* **19** 1231 (1978)
19. V P Zhdanov *Elementarnye Fiziko-khimicheskie Protsessy na Poverkhnosti* (Elementary Physicochemical Surface Processes) (Ed. K I Zamaraev) (Novosibirsk: Nauka, 1988)
20. L Ya Margolis *Okislenie Uglevodorodov na Geterogennykh Katalizatorakh* (Oxidation of Hydrocarbons on Heterogeneous Catalysts) (Moscow: Khimiya, 1977) p. 327
21. I V Berestetskaya, P Yu Butyagin *Dokl. Akad. Nauk SSSR* **260** 361 (1981)
22. A D Berman, O V Krylov, in *Problemy Kinetiki i Kataliza* (Problems of Kinetics and Catalysis) (Moscow: Nauka, 1978) Vol. 17, p. 112
23. P A Rebinder, E D Shchukin, L Ya Margolis *Dokl. Akad. Nauk SSSR* **154** 695 (1964)
24. F E Massoth *J. Catal.* **30** 204 (1973)
25. J Iwasawa *Adv. Catal.* **35** 187 (1987)
26. G A Somarjai, M A Vantive *Surf. Sci.* **299/300** 487 (1994)
27. C N R Rao, S R S Gopolakrishnan *New Directions in Solid State Chemistry* (London: Cambrige University Press, 1986)
28. J Johansen, A G Andersen (Eds) *Selected Topics in High Temperature Chemistry* (*Chemical Defects in Solids*) (Amsterdam: Elsevier, 1989)
29. C K D Tomlinson, J H Catlow *J. Phys. Chem. Solids* **51** 477 (1990)
30. R A Buyanov *Kinet. Katal.* **28** 157 (1987)
31. O V Krylov *Kinet. Katal.* **22** 1391 (1982)
32. Sh K Shaikhudinov, V I Kochubei *Usp. Khim.* **62** 443 (1993) [*Russ. Chem. Rev.* **62** 409 (1993)]
33. E D Shchukin *Izv. Akad. Nauk SSSR, Ser. Khim.* 2424 (1990)
34. E D Shchukin, A I Bessonov, S A Paranskii *Mekhanicheskie Ispytaniya Katalizatorov i Sorbentov* (Mechanical Tests on Catalysts and Sorbents) (Moscow: Nauka, 1971)
35. E D Shchukin, A I Bessonov, in *Standartizatsiya Metodov, Priborov i Ustanovok Kontrolya Kachestva Promyshlennykh Katalizatorov* (Standardisation of the Methods, Instruments, and Equipment for the Quality Control of Industrial Catalysts) (Eds R A Buyanov, N N Bobrov) (Novosibirsk: Institute of Catalysis, Siberian Division of Academy of Sciences of the USSR, 1991) p. 12
36. L F Mel'gunova, A A Samakhov, in *Standartizatsiya Metodov, Priborov i Ustanovok Kontrolya Kachestva Promyshlennykh Katalizatorov* (Standardisation of the Methods, Instruments, and Equipment for the Quality Control of Industrial Catalysts) (Eds R A Buyanov, N N Bobrov) (Novosibirsk: Institute of Catalysis, Siberian Division of Academy of Sciences of the USSR, 1991) p. 36
37. S F Suzdal'tseva, S I Kontorovich, E D Shchukin *Kolloid. Zh.* **39** 814 (1967)
38. E D Shchukin *Dokl. Akad. Nauk SSSR* **173** 139 (1967)
39. S I Kontorovich, E D Shchukin, in *Nauchnye Osnovy Tekhnologii Katalizatorov* (Scientific Foundations of the Technology of Catalysts) (Ed. G K Boreskov) (Novosibirsk: Nauka, 1976) p. 131
40. E D Shchukin, M V Dukarevich, S I Kontorovich, P A Rebinder *Dokl. Akad. Nauk SSSR* **167** 1109 (1966)
41. M V Dukarevich, S I Kontorovich, E D Shchukin, in *Tr. Vsesoyuz. Nauchnogo Seminara po Vzaimodeistviyu Materialov Vysokotemperaturnogo Naznacheniya so Sredoi, Kiev, 1968* (Proceedings of the All-Union Scientific Seminar on Interaction of High-Temperature Materials with the Environment, Kiev, 1968) p. 201
42. V S Yushchenko, M V Dukarevich, V F Chuvaev, E D Shchukin *Zh. Fiz. Khim.* **53** 1556 (1969)
43. E D Shchukin, S I Kontorovich, in *Razrushenie Katalizatorov — Sledstvie Vzaimnogo Vliyaniya Tverdoi Fazy i Reaktsionnoi Sredy. Problemy Dezaktivatsii Katalizatorov* (Disintegration of Catalysts — A Result of the Mutual Influence of the Solid Phase and the Reaction Medium. Problems of the Deactivation of Catalysts) (Novosibirsk: Nauka, 1985) Part 1, p. 3

44. F Wittman *Z. Angew. Phys.* **25** 160 (1968)
45. V Yu Traskin, N V Pertsov, Z N Skvortsova, E D Shchukin, P A Rebinder *Dokl. Akad. Nauk SSSR* **191** 147 (1970)
46. L M Shishlyannikova, S F Suzdal'tseva, S I Kontorovich, E D Shchukin *Kolloid. Zh.* **36** 612 (1974)
47. S F Suzdal'tseva, L M Shishlyannikova, E D Shchukin *Kolloid. Zh.* **48** 1031 (1986)
48. A T Slepneva, B A Lipkind, M V Dukarevich, S I Kontorovich, E D Shchukin *Kolloid. Zh.* **32** 251 (1970)
49. A T Slepneva, S I Kontorovich, B A Lipkind, E A Amelina, E D Shchukin *Kolloid. Zh.* **31** 281 (1969)
50. L V Koval'skaya, Ya V Mirskii, in *Tseolitnye Katalizatory i Adsorbenty* (Zeolite Catalysts and Adsorbents) (Ed. A Z Dorogochinskii) (Moscow: TsNIITE Neftekhim, 1978) p. 78
51. S I Kontorovich, L I Bogomolova, L N Sokolova, E D Shchukin *Khim. Tv. Topliva* 97 (1985)
52. S F Suzdal'tseva, E I Skvortsova, L Ya Margolis, E D Shchukin *Dokl. Akad. Nauk SSSR* **201** 415 (1971)
53. S I Kontorovich, M V Dukarevich, S F Suzdal'tseva, E D Shchukin, in *Materialy V Vsesoyuz. Konf. po Fiziko-khimicheskoi Mekhanike, Ufa, 1971* (Proceedings of the Fifth All-Union Conference on Physicochemical Mechanics, Ufa, 1971) p. 144
54. S I Kontorovich, T P Ponomareva, Ya E Geguzin, Yu S Kaganovskii, E D Shchukin *Poverkhnost'* (1) 111 (1983)
55. S A Paranskii, V N Medvedev, A I Veden'eva, A I Bessonov, O D Sterligov, E D Shchukin *Kinet. Katal.* **12** 473 (1971)
56. E D Shchukin, S I Kontorovich, M V Dukarevich *Dokl. Akad. Nauk SSSR* **175** 882 (1967)
57. S F Suzdal'tseva, S I Kontorovich, E D Shchukin *Kolloid. Zh.* **39** 814 (1977)
58. M V Dukarevich, Candidate Thesis in Chemical Sciences, Institute of Physical Chemistry, Academy of Sciences of the USSR, Moscow, 1968
59. L N Mamaeva, E I Dobkina, I P Mukhlenov, V I Malkiman *Kinet. Katal.* **21** 805 (1980)
60. G R Kotel'nikov, V A Potanov, E D Shchukin, L N Kozina *Kolloid. Zh.* **37** N5 875 (1975)
61. E D Shchukin, S I Kontorovich, N I Girenkova, V K Yatsimirskii, Yu S Kaganovskii, L N Sokolova *Dokl. Akad. Nauk SSSR* **318** 1417 (1991)
62. Ya E Geguzin, N I Girenkova, Yu S Kaganovskii, S I Kontorovich, T P Ponomareva, M V Tovbin, E D Shchukin, in *Nestatsionarnye Protsessy v Katalize* (Nonstationary Processes in Catalysis) (Novosibirsk: Institute of Catalysis, Siberian Division of the Academy of Sciences of the USSR, 1979) Part 1, p. 138
63. USSR P. 554 883; *Byul. Izobret.* (15) 57 (1977)
64. E D Shchukin, L Ya Margolis *Poverkhnost'* (8) 1 (1982)
65. E D Shchukin, in *Atomistics of Fracture* (Eds R M Latanision, J R Pickens) (New York: Plenum, 1983) p. 421
66. E D Shchukin, in *Metody Issledovaniya Kataliticheskikh Reaktsii* (Methods for the Investigation of Catalytic Reactions) (Eds G K Boreskov, T V Andrushkevich) (Novosibirsk: Nauka, 1984) p. 142
67. V S Yushchenko, E D Shchukin *Dokl. Akad. Nauk SSSR* **242** 653 (1978)
68. V S Yushchenko, A G Grivtsov, E D Shchukin *Dokl. Akad. Nauk SSSR* **219** 162 (1974)
69. E D Shchukin, V S Yushchenko, T P Ponomareva *Kolloid. Zh.* **53** 319 (1991)
70. S I Kontorovich, Zh G Malikova, E D Shchukin *Kolloid. Zh.* **32** 224 (1970)
71. S I Kontorovich, K A Lavrova, E D Shchukin *Kolloid. Zh.* **37** 57 (1975)
72. I G Shatalova, N S Gorbunov, V I Likhtman *Fiziko-khimicheskie Osnovy Vibratsionnogo Uplotneniya Poroshkovykh Materialov* (Physicochemical Foundations of the Vibration-Induced Compaction of Powdered Materials) (Moscow: Nauka, 1965)
73. Z M Polukarova, I G Shatalova, R K Yusupov, I K Kolchin, L Ya Margolis, E D Shchukin *Neftekhimiya* **8** 899 (1968)
74. E D Shchukin, S I Kontorovich, B V Romanovsky *Abstracts of Reports of the 13th European Conference on Chemistry of Interference, Kiev, 1994* p. 46
75. E D Shchukin, S I Kontorovich, B V Romanovsky *J. Mater. Sci.* **28** 1937 (1993)
76. E D Shchukin, S I Kontorovich, N I Girenkova, V K Yatsimirskii, Yu S Kaganovskii, L N Sokolova *Mendeleev Commun.* 136 (1991)
77. I P Mukhlenov, E I Dobkina, V I Deryuzhkina, V E Soroko *Tekhnologiya Katalizatorov* (Technology of Catalysts) (Khimiya: Leningrad, 1989) p. 114
78. E D Shchukin *Fiz-Khim. Mekh. Mater.* **12** (1) 3 (1976)
79. V S Yushchenko, E D Shchukin *Fiz-Khim. Mekh. Mater.* **4** (10) 46 (1981)
80. ARC Westwood, J S Ahearn, J J Mills *Colloid Surf.* **2** 1 (1971)
81. V B Fenelonov, in *Nauchnye Osnovy Prigotovleniya Katalizatorov* (Scientific Foundations of the Preparation of Catalysts) (Novosibirsk Institute of Catalysis, Siberian Division of Academy of Sciences of the USSR, 1984) p. 130
82. L V Koval'skaya, Author's Abstract of Candidate Thesis in Chemical Sciences, Lensovet Leningrad Technological Institute, Leningrad, 1983
83. V A Dzis'ko *Osnovy Metodov Prigotovleniya Katalizatorov* (Foundations of the Methods of Preparation of Catalysts) (Novosibirsk: Nauka, 1983) p. 264
84. B P Zolotovskii, R A Buyanov, V A Balashov, O P Krivoruchko, A Ya Bakaev, V E Loiko, A A Samakhov, V I Bashin, in *Nauchnye Osnovy Prigotovleniya i Tekhnologii Katalizatorov (Sbornik Nauchnych Trudov)* [Scientific Foundations of the Preparation and Technology of Catalysts (Collection of Scientific Reports)] (Novosibirsk: Institute of Catalysis, Siberian Division of Academy of Sciences of the USSR, 1990) p. 108
85. R O Kagel, R G Greenlar *J. Chem. Phys.* **49** 1648 (1968)
86. V A Korsunov, I Ya Chuvylkin, G M Zhidomirov, V V Kazanskii *Kinet. Katal.* **22** 938 (1981)
87. L I Titel'man *Obzorn. Informatsiya, Ser. Azotnaya Promyshlennost'* (Review Information, Nitrogen Industry Ser.) (Moscow: NIITEKhIM, 1986) p. 30
88. L I Titel'man, in *Nauchnye Osnovy Prigotovleniya i Tekhnologii Katalizatorov (Sbornik Nauchnych Trudov)* [Scientific Foundations of the Preparation and Technology of Catalysts (Collection of Scientific Reports)] (Novosibirsk: Institute of Catalysis, Siberian Division of Academy of Sciences of the USSR, 1990) p. 61
89. M A Kipnis, in *Tezisy Dokladov III Konferentsii po Nauchnym Osnovam Prigotovleniya i Tekhnologii Katalizatorov, Yaroslavl',* (Abstracts of Reports at the Third Conference on the Scientific Foundations of the Preparation and Technology of Catalysts, Yaroslavl') (Novosibirsk: Institute of Catalysis, Siberian Division of Russian Academy of Sciences, 1996) p. 123
90. N A Levitskaya, L I Titel'man, G V Makrushina, A I Nechugovskii, E Z Golosman, in *Tezisy Dokladov III Konferentsii po Nauchnym Osnovam Prigotovleniya i Tekhnologii Katalizatorov, Yaroslavl',* (Abstracts of Reports at the Third Conference on the Scientific Foundations of the Preparation and Technology of Catalysts, Yaroslavl') (Novosibirsk: Institute of Catalysis, Siberian Division of Russian Academy of Sciences, 1996) p. 142
91. I I Kurlyandskaya, I G Solomonik, E D Glazunova, Yu A Treger, E A Boevskaya, E Z Golosman, V I Yakerson, in *Tezisy Dokladov III Konferentsii po Nauchnym Osnovam Prigotovleniya i Tekhnologii Katalizatorov, Yaroslavl',* (Abstracts of Reports at the Third Conference on the Scientific Foundations of the Preparation and Technology of Catalysts, Yaroslavl') (Novosibirsk: Institute of Catalysis, Siberian Division of Russian Academy of Sciences, 1996) p. 139
92. E Z Golosman, L L Klinova, G I Solomatin, A I Nechugovskii, E A Boevskaya, I A Mamaeva, G V Kozyreva, in *Tezisy Dokladov III Konferentsii po Nauchnym Osnovam Prigotovleniya i Tekhnologii Katalizatorov, Yaroslavl',* (Abstracts of Reports at the Third Conference on the Scientific Foundations of the Preparation and Technology of Catalysts, Yaroslavl') (Novosibirsk: Institute of Catalysis, Siberian Division of Russian Academy of Sciences, 1996) p. 99
93. R A Buyanov, in "Nauchnye Osnovy Prigotovleniya i Tekhnologii Katalizatorov (Sbornik Nauchnych Trudov) [Scientific Foundations of the Preparation and Technology of Catalysts (Collection of Scientific Reports)] (Novosibirsk: Institute of Catalysis, Siberian Division of Russian Academy of Sciences, 1996) p. 3

94. V K Duplyakin, in *Tezisy Dokladov III Konferentsii po Nauchnym Osnovam Prigotovleniya i Tekhnologii Katalizatorov, Yaroslavl'*, (Abstracts of Reports at the Third Conference on the Scientific Foundations of the Preparation and Technology of Catalysts, Yaroslavl') (Novosibirsk: Institute of Catalysis, Siberian Division of Russian Academy of Sciences, 1996) p. 5
95. D Dollimore, G R Heal *J. App. Chem.* **11** 459 (1961)
96. D Dollimore, S Y Gregg *Trans. Br. Ceram. Soc.* **54** 261 (1955)
97. P S Bonsall, D Dollimore, Y Dollimore *Proc. Br. Ceram. Soc.* **6** 61 (1966)
98. G D Dibrov, in *Fiziko-Khimich. Mekhanika Dispersnykh Struktur* (Physicochemical Mechanics of Disperse Structures) (Moscow: Nauka, 1966) p. 32
99. M I Volkov, N V Dvoretskii, M I Ogil'ko, E G Stepanov, G R Kotel'nikov, in *Tezisy Dokladov III Konferentsii po Nauchnym Osnovam Prigotovleniya i Tekhnologii Katalizatorov, Yaroslavl'*, (Abstracts of Reports at the Third Conference on the Scientific Foundations of the Preparation and Technology of Catalysts, Yaroslavl') (Novosibirsk: Institute of Catalysis, Siberian Division of Russian Academy of Sciences, 1996) p. 89; P Yu Butyagin *Usp. Khim.* **53** 1769 (1984) [*Russ. Chem. Rev.* **53** 1025 (1984)]
100. V V Boldyrev *Izv. Akad. Nauk SSSR, Ser. Khim.* 2228 (1990)
101. A Kapoor, R T Yang, C Wong *Catal. Rev. Sci. Eng.* **31** 43 (1989)
102. E Ruckenstein, S H Lee *J. Catal.* **109** 100 (1988)
103. A A Zhukhovitskii, V A Grigoryan, E Mikhalik *Poverkhnostnye Yavleniya v Rasplavakh i Voznikayushchikh iz Nikh Tverdykh Fazakh* (Surface Effects in Melts and in the Solid Phases Originating from Them) (Nal'chik: Kab.-Balkarsk. Kn. Izd., 1965)
104. V A Grigoryan, A A Zhukhovitskii, L S Shvindlerman, M I Chikonosova *Zh. Fiz. Khim.* **40** 1144 (1966)
105. F C Tompkins, in *Surface Science. Recent Progress and Perspectives* (Eds T S Jayadevian, R Vandselow (Boca Raton. FL: CRC Press, 1974) p. 235