Russian Chemical Reviews **69** (5) 435 – 450 (2000) © 2000 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2000v069n05ABEH000555

Mechanochemistry of catalysts

V V Molchanov, R A Buyanov

Contents

I.	Introduction	435
II.	Synthesis of catalytic systems	436
III.	Effect of mechanochemical activation on catalytic properties of compounds	441
IV.	The role of defects as active centres for chemical processes	445
V.	Catalytic reactions under conditions of mechanochemical activation	445
VI.	The nature of the effect of mechanochemical activation on the reactivity of solids	446

Abstract. Data on the use of mechanochemical activation for the preparation of catalysts and supports are generalised. The effect of mechanochemical activation on the catalytic properties of various systems is noted. Catalytic reactions occurring under conditions of mechanochemical activation are discussed. The hypotheses concerning the nature of the effect of mechanochemical activation on the reactivity (including catalytic properties) are considered. The bibliography includes 197 references.

I. Introduction

An interesting, though, in our view, insufficiently studied problem is the application of mechanochemistry to heterogeneous catalysis. In both these fields, investigators are still on the way to creating general theories which would allow prediction of the behaviour of solids in various chemical and catalytic processes. In mechanochemistry as well as in catalysis, much is dependent on the solution of the problem of revealing catalytically active and reactive centres. For this reason, studies carried out at the borderline of the two sciences can favour to a considerable extent their mutual enrichment.

The development of mechanochemistry has begun with studies of grinding processes. It was found that grinding changes not only the sizes of particles of a material, but also their physicochemical properties. This provided the ground for introducing the term 'mechanochemical activation' (MCA). Grinding of substances is widely used in the chemical industry, including preparation of catalysts. The processes occurring under mechanical treatment of solids are described in sufficient detail in a number of monographs and reviews,[1–5] and we will not dwell upon them. Let us only note the consequences of mechanochemical treatment on catalytic properties of solids or on the synthesis of catalytic systems.

Physicochemical changes resulting from MCA are the consequence of relaxation of the field of stresses in a solid after mechanical impact on it. In all cases, irrespective of the relaxation mode, changes in the thermodynamic potentials of compounds under activation occur. The physicochemical properties of substances are related to the free energy G, for example,

$$\Delta G = -RT\ln\frac{k_2}{k_1},$$

$$\Delta G = RT\ln\frac{c}{c_\infty},$$

$$\Delta G = RT\ln\frac{p}{p_\infty},$$

$$\Delta G = \frac{-\lambda\Delta T}{T_\mathrm{p}},$$

where k_1 and k_2 are the rate constants of forward and reverse reactions, c and c_∞ are the current and equilibrium solubilities, p and p_∞ are the current and equilibrium vapour pressures, λ and T_p are the heat and temperature of a phase transition, respectively. The free energy in turn depends on the sizes of particles of a compound and the presence of defects in it.

$$\Delta G = 2\sigma V\left(\frac{1}{r_1}-\frac{1}{r_2}\right),$$

where σ is the surface tension, V is the molar volume, r_1 and r_2 are the radii of the particles of fine and coarse fractions, respectively;

$$\Delta G = -kT\ln W,$$

where k is the Boltzmann constant, W is the thermodynamic probability equal to the possible modes of the distribution of defects in the lattice. It should be noted that the symbols r_1 and r_2 refer not only to the real physical size of particles but also to the sizes of ordered areas between the extended defects.[5]

The relaxation channel of the stress field related to the formation of fresh surface was studied most thoroughly. Many studies were devoted to the investigation of the kinetics of this process. Both the simplest regularities of coarse grinding (see Khodakov's monograph[6]) and more advanced models of fine grinding were considered which take into account the pulsed character of the mechanical impact and the effect of mechanical activation on the formation of fresh surface.[7–11] These models have a formal character and are far from being capable of describing all experimental results, particularly those derived from studies of compounds with anisotropic properties. Detailed investigation of the chemical properties of the fresh surface

V V Molchanov, R A Buyanov G K Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, ul. Akad. Lavrent'eva 5, 630090 Novosibirsk, Russian Federation.
Fax (7-383) 234 30 56. Tel. (7-383) 234 45 53 (V V Molchanov),
Tel. (7-383) 234 27 57. E-mail: buyanov@catalysis.nsk.su (R A Buyanov)

Received 5 October 1999
Uspekhi Khimii **69** (5) 476 – 493 (2000); translated by V D Gorokhov

showed [2,5,12] that MCA of silicon, germanium, tin and magnesium oxides leads to the formation of different centres on their surfaces which have predominantly a radical nature. Interactions of these centres with various gases were described. The data obtained may be used for the prediction of processes occurring in the synthesis of catalytic systems and modification of their surfaces.

Yet another general channel of relaxation of the stress field is the formation of defects of the crystal structure and the exit of these defects onto the surface of crystallites. Numerous studies systematised in monographs [1,3,4] showed that it was the formation of defects rather than fresh surface, that was the cause of higher, MCA-induced reactivities and catalytic activities of compounds. There is a suggestion (based on indirect data) that it is the defects of the crystal structure that are the catalytically active centres. In our opinion, in order to elucidate the effect of MCA on the catalytic activity, it is necessary to relate physicochemical features of defects to the nature of the catalysis considered as a sequence of chemical transformations of the catalyst and reagents.

The process of formation of defects has a thermodynamic nature: the system tends to minimise its free energy, while the localisation of the excess energy on defects is thermodynamically more advantageous than the regular distribution of elastic stresses over all the bonds of the crystal lattice. The appearance of defects is, as a rule, accompanied by changes in the electronic properties of activated compounds. For example, electronic levels are formed in the forbidden bands, the forbidden bands become narrower, the conductivity electrons appear in semiconductors, and the electron-donor properties are enhanced in semiconductors and dielectrics. The electronic theory of catalysis considers the influence of all these changes on the catalytic properties.

These are the basic channels of relaxation of the field of stresses arising upon mechanical impact on solids. Other emissive phenomena also take place; however, their influence on the catalytic properties and peculiarities of the synthesis of catalysts is not very obvious, and we will consider them henceforth only where necessary.

Studies devoted to the investigation of the effect of mechanical treatment on catalysts may be divided into three groups. In the first group the MCA effect is used for the synthesis of catalytic systems: in the second group the effect of MCA on the catalytic properties of compounds is dealt with and in the third group catalytic reactions under MCA conditions are considered.

II. Synthesis of catalytic systems

The methods of mechanochemistry can be used for both synthesis of catalysts, supports and sorbents and control of their performance.

One of the first examples of the systematic and purposeful use of MCA for the preparation of catalysts is the preparation of a polymerisation catalyst based on titanium and aluminium chlorides. It was found that grinding of titanium(III) chloride in a ball mill increases its catalytic activity in the propylene polymerisation.[13] It turned out that in this case the α- and γ-$TiCl_3$ phases pass to the δ-modification, which is more active in this reaction.[14] Aluminium–titanium chloride catalysts are prepared by joint grinding of either metallic aluminium and $TiCl_4$ [15] phases or titanium and aluminium chlorides,[16,17] or the chlorides with the addition of trialkylaluminium.[18] In all probability, this technological technique was discovered purely empirically, and its scientific substantiation was started only after the publication of the corresponding patents.[15–18] The processes occurring during mechanical treatment of catalysts were described in Refs 19–21. Somewhat later, an analogous study of titanium–magnesium chloride catalysts was carried out.[22–24] Summing up the results obtained, one can state that upon MCA of mixtures of $TiCl_3$ with $AlCl_3$ and $TiCl_4$ with $MgCl_2$ an interaction between the components takes place. In the former case, this leads to the formation of solid solutions with the structure of δ-$TiCl_3$, while in the latter case titanium chloride is fixed on the surface of magnesium chloride. Discrepancy between some results should be noted: the catalyst prepared by joint activation of titanium and magnesium chlorides possesses high activity according to Kashiwa,[22] while Zakharov *et al.*[24] found that it is not very active, although the conditions and duration of activation were similar in both studies.

Systematic studies on the application of MCA for the preparation of catalysts were carried out at the Ivanovo Institute of Chemical Technology. These studies were aimed at solving the problem of intensification of the interaction between solids and solutions containing other components of the catalysts. Mechanical treatment accelerated the interaction of iron, zinc and aluminium oxides with a solution of chromic acid.[25–27] Upon treatment of aluminium oxide in an ammonium-carbonate solution of zinc,[28] of α- and γ-aluminium oxides [29] and of magnesium oxide [30] in an ammonium-carbonate solution of copper, sorption of ions from the solution onto the surface of the solid component was observed. This technological approach both favoured the interaction of components and allowed regulation of some operational properties of the catalysts: their catalytic activities, strength and mouldabilities. The activities of chromium catalyst in the methanol synthesis,[27] of complex oxide and magnesium–copper catalysts in the vapour conversion of CO,[29,30] of aluminium–nickel catalyst in the vapour conversion of hydrocarbons [31] increased. The enhancement of the strength of iron–chromium,[26] aluminium–copper–zinc–chromium [29] and aluminium–nickel [31] catalysts, zinc–aluminium spinel and aluminium oxide used as supports [28,29] was also observed. In addition, α-aluminium oxide acquired mouldability by the extrusion method, which allowed the preparation of granules of complex shape.[32]

Studies aimed at the development of a sulfur sorbent were carried out at the same Institute. Dispersion of zinc oxide in solutions of carboxymethylcellulose and poly(vinyl alcohol) enhanced its mouldability by the extrusion method, increased its specific surface and sorption capacity with respect to sulfur-containing compounds.[33] An analogous effect was achieved upon dispersion of zinc oxide with aluminium oxide in an ammonium-carbonate solution.[34] According to Shirokov and Il'in,[28] the enhancement of the sorbent strength results from the hydration of the surface of aluminium oxide and formation of zinc aluminate, which plays the role of a binding agent. Treatment of zinc oxide in a planetary or vibratory mill led to an increase in its static and dynamic sulfur sorption capacity and enhancement of its cleavage strength and abrasion resistance.[35,36] Based on these studies, a technology of production of a sulfur absorbent was developed.[37]

The method of MCA was applied for the preparation of catalysts of deep oxidation used for the after-burning of flue gases. Studies by Bulgarian investigators were aimed at the enrichment of the surface of cobalt oxide with copper oxide owing to local overheating arising during MCA.[38,39] Upon treatment of a mixture of cobalt and copper oxides, the copper oxide phase disappeared as a result of formation of a mixed oxide compound on the surface.[38] Comparison of different techniques of grinding of a mixture of oxides (in a planetary or vibratory mill, in a mechanical mortar) showed that the use of the vibratory mill is the most efficient.[39] Presumably, the copper ions are incorporated into the voids in the layer of the cobalt cations. An attempt was made to perform the mechanochemical synthesis of analogous systems using magnesium, zinc and manganese oxides [40] instead of copper oxide; however, these oxides did not interact in a vibratory mill. The cobalt–copper oxide catalysts prepared using MCA possessed higher activities in the CO oxidation and were more resistant to poisoning with sulfur dioxide [38,39] than the catalysts obtained by conventional methods.

Massive copper and cobalt oxides are efficient catalysts of deep oxidation. However, practical application of these oxides is problematic because it is difficult to mould them. This problem may be solved by subjecting the oxides to a short-time MCA in a planetary mill before moulding.[41–43] The authors relate the

positive effect to hydration of the surface of copper oxide upon interaction of a mechanically activated oxide with water [41, 43] and to changes in the morphology of cobalt oxide particles.[41]

The use of MCA for the synthesis of lanthanum cobaltites and manganites proved to be successful.[44, 45] Activation of mixtures of oxides and carbonates made it possible to reduce the temperature of formation of the corresponding perovskites by 250–300 K; the interaction at lower temperatures was more complete when the initial components were in the form of carbonates. As regards the specific surface and catalytic activity, the catalysts prepared using MCA were superior to the analogous systems obtained by traditional ceramic technology and were close to the catalysts prepared by the co-precipitation method; the advantage of the MCA consists in the absence of deleterious wastes.

The preparation of skeletal catalysts is very energy-consuming since the initial alloys of the corresponding metals with aluminium are obtained by the pyrometallurgical method. Besides, definite difficulties are associated with the completeness and rate of aluminium leaching. The use of MCA solves both these problems.

The beneficial influence of MCA on the properties of skeletal nickel was reported for the first time over four decades ago.[46] Treatment of an aluminium–nickel alloy in a vibratory mill increased the activity of the catalyst obtained after leaching in the reactions of cyclohexene hydrogenation and propan-2-ol dehydrogenation. Comparatively recently, methods were developed for the preparation of nickel–aluminium alloys by the so-called 'mechanical alloying', *i.e.* by mechanochemical activation of a mixture of powders of nickel and aluminium metals.[47, 48] The use of 'mechanical alloys' makes it possible to increase the degree of aluminium leaching and to prepare Raney catalysts which are more active in the reactions of hydrogenation of phenylacetylene, potassium maleate and nitrobenzene.[47, 49, 50] The skeletal catalysts prepared from the alloys obtained by the 'mechanical alloying' method may have a more complex composition and contain modifying additives.[51] It should be noted that not any composition of the 'mechanical alloys' makes them advantageous. Thus the pyrometallurgical alloys containing >80% of aluminium are better leached and ensure higher catalytic activity. The advantages of MCA are most clearly manifested in the regeneration of worked-out skeletal catalysts: its use for the preparation of 'mechanical alloys' makes it possible not only to restore the properties of skeletal nickel but also to achieve the activity several times higher than that before regeneration.[52] The higher activity of the catalysts prepared from 'mechanical alloys' is possibly explained by the fact that after leaching nickel passes to a metastable state with the structure NiAl, whereas leaching of pyrometallurgical alloys leads to the formation of the face-centred cubic lattice.[53]

The 'mechanical alloying' method was also used for the preparation of hydrides of intermetallic magnesium compounds.[54] The 'mechanical alloys' are hydrogenated more easily than the pyrometallurgical ones, and hydrogen present in the hydrides obtained is more mobile. Hydrides of magnesium intermetallides proved to be efficient hydrogenation catalysts.[55] Compared to conventional catalysts, their advantage is particularly noticeably manifested in the reactions of selective hydrogenation of alkynes and dienes to alkenes. Thus the hydride with composition Mg_2FeH_6 provides a nearly 100% selectivity of hydrogenation of butadiene to butenes,[56] while Mg_2CoH_5 ensures the 100% selectivity of hydrogenation of acetylene to ethylene.[57] It should be noted that such a high selectivity in these reactions is reached on none of the known traditional catalysts. Preparation of hydrides through the 'mechanical alloying' stage is a waste-free energy-saving method which was used for the synthesis of new catalytic systems, *e.g.*, Mg_2FeH_6, Mg_2CoH_5 and Mg_3CoH_5.

The application of MCA for the preparation of iron–potassium dehydrogenation catalysts is described in sufficient detail in the literature. These catalysts are traditionally obtained by mixing iron oxide with potassium carbonate and potassium silicate. Thermal treatment of the paste obtained in water vapour leads to the formation of the active component, *viz.*, potassium ferrite. Pretreatment of iron oxide in a disintegrator makes it possible to reduce the temperature of its reaction with alkali metal carbonates, to increase the yields of the corresponding ferrites and the rates of their formation. Higher degrees of conversion of ethylbenzene to styrene and a higher selectivity of styrene formation are reached [58] on the catalysts obtained from iron oxide treated in a disintegrator. Both these parameters are improved as the specific energy of treatment is increased.[59, 60] In addition, such catalysts are better mouldable and possess higher strength.[59] Upon treatment of a mixture of iron oxide and potassium carbonate in a planetary mill, potassium ferrite is formed directly in the drum.[61] If dehydrogenation is performed with the catalyst obtained after thermal treatment of a mixture activated in water vapour, the process begins at 670 K, whereas on the initial catalysts it starts only at 800 K. The mechanically activated catalyst exhibits an increased activity until 880 K at which it drops to the activity level of the initial specimen, which is associated with the annealing of defects in the crystal structure.[61]

Numerous studies were devoted to the use of MCA for the preparation of alumina-based catalysts and supports. Shirasaki *et al.*[62] showed that grinding of corundum in water facilitates its formation; analogous data were obtained later by Il'in *et al.*[32] The mouldability of alumina increases after MCA of the initial aluminium hydroxide.[63] In this case the resulting alumina is not inferior in its strength and sorption properties to the oxide formed from precipitated aluminium hydroxide the production of which provides large volumes of wastes. The possibility of regulation of some operational properties of catalysts with the aid of MCA was noted.[32, 62, 63]

The possibilities of the use of MCA for the preparation of alumina-based catalysts and supports based on aluminium oxide are described in more detail in a series of papers from the Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences. Transformations of aluminium hydroxide in the course of MCA and during subsequent treatments were studied in detail. Upon activation of hydrargillite, grinding of crystals, shift of hydroxylic packs, cleavage of crystals into plates and dehydration with formation of molecular water which remains in the bulk among activation products occur.[64–66] Analogous processes also take place upon MCA of bayerite.[67] The maximum quantity of excess energy accumulated in hydrargillite is 33 kJ mol^{-1}. This value is reached at the thickness of plates commensurable with the size of the unit cell of hydrargillite;[68] in this state hydrargillite manifests its maximum chemical activity. In studies of thermal transformations of activated hydrargillite, a new state of alumina was revealed and denoted as π-Al_2O_3.[69, 70] This is characterised by the presence of aluminium cations in the pentacoordinated state. The structure of this oxide was established, and it was found that π-Al_2O_3 is capable of dissociative chemisorption of ammonia.[71] Thermal transformations of all aluminium hydroxides subjected to MCA proceed in the same manner:[72]

$$\text{GG, BE, BA} \xrightarrow{423-873\ \text{K}} \pi\text{-}Al_2O_3 \xrightarrow{1023-1123\ \text{K}} \longrightarrow M_\eta \xrightarrow{1173-1273\ \text{K}} \alpha\text{-}Al_2O_3,$$

where GG, BE and BA are hydrargillite, bochmite and bayerite, respectively; M_η is the spinel-like phase of alumina.

On the other hand, non-activated aluminium hydroxides are transformed into corundum each in its own mode which is more complex than that considered above. It should be noted that the temperature of phase transition of activated hydroxides into corundum is 200 K lower than that of non-activated ones.[72]

Detailed investigation of the processes which occur during MCA of aluminium hydroxides has allowed the development of techniques for the preparation a wide range of alumina-based catalysts, supports and sorbents. Thus depending on conditions, hydration of activated hydrargillite and π-Al_2O_3 leads to the formation of bayerite or pseudobochmite from which different

aluminas are formed after thermal treatment.[73] The mechanism of hydration of the hydrargillite and π-Al_2O_3 MCA products has been established.[74, 75]

Methods for the preparation of hydroxyaluminates of a number of divalent metals on the basis of the products of MCA of aluminium hydroxides were developed. Interaction of activated hydroxides with solutions of magnesium and zinc salts or with zinc oxide leads to the formation of the corresponding hydroxyaluminates.[76–78] Under the same conditions, π-Al_2O_3 also enters into analogous interactions.[77] Presumably, hydroxyaluminates are formed through the stage of intercalation of salts.[77, 78]

Yet another field of application of activated aluminium hydroxides is the synthesis of various aluminosilicates. In the MCA of kaolinite, processes analogous to those revealed in the activation of hydrargillite occur, *viz*., shift and turn of layers as well as dehydration with the formation of molecular water remaining within the compound's structure.[79] In contrast to MCA of hydrargillite, mechanical activation of kaolinite does not alter the pathways of its thermal transformations.[80] The initial stage of thermal treatment includes formation of metakaolinite containing pentacoordinated aluminium cations.[70, 80]

Upon MCA of a mixture of hydrargillite and silica gel, hydrated aluminosilicate is formed [81, 82] from which an aluminosilicate spinel is formed first upon heating and then mullite. A non-activated mixture undergoes transformations which differ in many aspects. By varying conditions of hydration and thermal treatment of activated mixtures of hydrargillite and silica gel, it is possible to obtain amorphous aluminosilicates, kaolinite, montmorillonite, aluminosilicate spinel of high purity and mullite with large specific surface and without admixtures of corundum and cristobalite.[73] Furthermore, zeolites of types A, X, Y were obtained,[73, 83] and the possibility of synthesis of over 100 other zeolites is predicted,[84] *i.e*., good prospects are open for the development of little-waste methods for the preparation of zeolites.

Some aluminosilicates were synthesised using the so-called 'soft mechanochemical synthesis',[85] which involves MCA of hydrated or moist mixtures. It is suggested that in this case conditions are close to hydrothermal ones. The use of this method allows preparation of mullite without admixtures of other phases, a number of other aluminosilicates, as well as aluminates, titanates, zirconates, tungstates and vanadates of alkaline-earth metals. According to Avvakumov,[85] the method of 'soft mechanochemical synthesis' may be used for performing acid–base reactions proceeding with liberation of water.

New methods, including MCA, were developed for the synthesis of heteropolyacids (HPA) and catalysts based on them. A broad spectrum of HPA was obtained using mechanical activation of molybdenum and tungsten oxides and their mixtures with vanadium, silicon, aluminium and iron oxides. The most successful proved to be the use of MCA for the preparation of phosphomolybdic and phosphomolybdenovanadic HPA,[86–89] in particular high-purity $H_6P_2Mo_{18}O_{62}$ and $H_{3+n}PMo_{12-n}V_nO_{40}$ with $n = 0–4$. The process is characterised by the total absence of deleterious wastes and flue gases, the time of synthesis is substantially reduced, energy consumption is decreased, losses of expensive raw materials are precluded, fire-hazard stages are absent, while the yield of HPA reaches the quantitative level.

When developing methods for the preparation of HPA, we revealed new oxide compounds of molybdenum and vanadium in the system V_2O_5–$nMoO_3$.[90] It is their formation that is the reason for such a smooth synthesis of HPA. Reactions of compounds of the system V_2O_5–$nMoO_3$ with phosphoric acid and its salts under conditions of MCA lead to the formation of HPA with composition $H_{3+n}PMo_{12-n}V_nO_{40}$, where $n \geqslant 3$, or their salts.[87] Apparently, an important role in these reactions is played by water of crystallisation since activation under the same conditions of a mixture containing anhydrous phosphates does not lead to the formation of HPA salts.

A waste-free method for the preparation of a catalyst for L-sorbose acetonation (one of the stages in the synthesis of vitamin C) was developed.[89] The catalyst is a mixture of phosphomolybdic heteropolyacids and provides higher yields of isopropylidene-L-sorbose than does oleum, which is normally used for this purpose, and precludes harmful acidic wastes. Mechanochemical activation is also used for the regeneration of the catalyst after isolation of the target product.[89]

The application of MCA for the synthesis of nickel catalysts of decomposition of hydrocarbons proved to be rather effective. The reaction proceeds with the elimination of hydrogen and formation of filamentous carbon which is a material possessing specific, and in a number of cases, unique, physicochemical properties. Catalysts for these reactions are traditionally obtained by co-precipitation from solutions of nickel, copper and aluminium salts. MCA of nickel oxide or its mixtures with other oxides together with compounds of lamellar structure (magnesium and aluminium hydroxides, graphite) produces more efficient catalysts of decomposition of hydrocarbons than those obtained by co-precipitation.[91–93] They operate for a long time without loosing their activities, which provides higher degrees of transformation, *e.g*., of methane. This makes cost-effective the production of hydrogen from hydrocarbons. The carbonaceous material formed can be used as a sorbent, a support for catalysts and as a catalyst.

Besides synthetic purposes, MCA is also used for improving certain operational characteristics of catalysts and supports. Thus treatment of a suspension of zeolite in a bead mill in the presence of surfactants made it possible to increase its strength.[94] Treatment of aluminium hydroxide in a vibratory mill facilitates its moulding and enhances the strength of granules of the final product.[63] As noted above, analogous results were obtained upon treatment of iron–chromium [26] and aluminium–zinc [28] catalysts, catalyst of vapour conversion of CO,[29] aluminium, zinc, copper and cobalt oxides.[34, 35, 41–45] The reasons for the increase in the strength of a phosphate catalyst of dehydrogenation resulting from the application of MCA were considered by Molchanov and Goidin. In the non-activated catalyst processes of baking, phase transition and recrystallisation of calcium phosphate occur [95] at virtually the same temperature. The last two processes induce mechanical stresses in the catalyst pellets which decrease their strength. Prior MCA reduces the phase transition temperature by 300–350 K and favours the completion of recrystallisation before the beginning of baking, which enhances substantially the strength of pellets.

Modification can also occur as a result of changes in sorption properties of a specimen due to grafting of various groups, formation of fresh surface and outcrops of defects to the surface. Mechanochemical grafting is used for the preparation of fillers for rubbers and plastics (see, *e.g*., Ref. 96). We failed to find in the literature any examples of this kind of modification of surfaces of catalysts, supports or sorbents, though, in our opinion, this method is promising. However, the effect of formation of fresh surface upon MCA is used for the preparation of catalysts.[25–30] The influence of defects in the crystal structure on properties of the surface was also revealed.[97, 98] Mechanochemical activation of a number of oxide supports leads not only to the increase in their sorption capacity but also to a substantial decrease in the temperature of reduction of supported salts to metals and also to a higher catalytic activity of supported nickel in the ethylene hydrogenation. Data on the use of MCA for the preparation of catalysts are presented in Table 1.

We made an attempt to generalise the regularities of mechanochemical synthesis, *i.e*., the interaction of compounds directly in the mill without any additional treatment. The mechanochemical synthesis occurs in the cases where the reagents have similar crystal structures; in the acid–base interaction, where one of the reagents is a strong acid or base (such a process is considered in sufficient detail by Avvakumov [85]); in the formation of pseudomelts where an intense mechanical stirring can increase the

Table 1. Application of MCA for the preparation of catalysts.

Initial products	Final product obtained or the result	Apparatus for MCA	Additional effects	Ref.
α-$TiCl_3$, γ-$TiCl_3$	δ-$TiCl_3$	BM	increased activity in the propylene polymerisation	13, 14
$TiCl_3 + AlCl_3 + R_3Al$	δ-$TiCl_3$	"	–	18
$TiCl_3 + AlCl_3$	solid solution with δ-$TiCl_3$ structure	"	increased activity in the ethylene polymerisation	19–21
$TiCl_4 + MgCl_2$	fixation of $TiCl_4$ on the $MgCl_2$ surface	"	the same	22–24
α-Fe_2O_3 or α-$Al_2O_3 + H_2CrO_4$, $Fe_2O_3 + H_2CrO_4$	catalysts of vapour conversion of CO	BdM	increased activity, enhanced strength	25, 26
$ZnO + H_2CrO_4$	catalyst of methanol synthesis	–	increased activity	27
$Al_2O_3 + Zn^{2+}$ in ACS	sorption of Zn^{2+}, formation of $ZnAl_2O_4$	BdM	increased strength of the catalyst for desulfurisation	28
$H_2CrO_4 + Al(OH)_3 + ZnO +$ $+ CuCO_3 \cdot Cu(OH)_2$	catalyst of vapour conversion of CO	–	increased activity	29
$MgO + Cu^{2+}$ in ACS	the same	–	the same	30
$CuAl_2O_4$ + ethanol or acetone solution	improved quality of binding agent	–	Enhanced strength	31
α-Al_2O_3	possibility of moulding by extrusion	BM, VM	–	32
ZnO + CMC (or PVA or PEG)	sulfur adsorbent	USD	improved capability for moulding, increased sulfur capacity	33, 37
$ZnO + Al_2O_3$ in ACS	the same	–	enhanced strength, increased sulfur capacity	34, 35
ZnO	"	VM, PM	the same	36
CoO + CuO	catalyst of after-burning	the same	increased activity in CO oxidation, resistance to poisoning with SO_2	38, 39
CuO, Co_3O_4	improved capacity for moulding by extrusion	PM	increased CuO activity in butane oxidation	41–43
$La_2O_3 + Co_3O_4$, $La_2(CO_3)_3 + CoCO_3 \cdot Co(OH)_2$	$LaCoO_3$ (catalyst of after-burning of flue gases)	"	–	44
$La_2O_3 + Mn_2O_3$ (or MnO_2 or Mn_3O_4)	$LaMnO_3$ (catalyst of after-burning of flue gases)	"	–	45
Al–Ni (alloy)	Ra/Ni	VM	increased activity in cyclohexene hydrogenation Pr^iOH dehydrogenation	46
Ni + Al	alloys, precursors of Ra/Ni	PM	increased activity in hydrogenation reaction	47–50
Ni + Al + M (M = V, Cr, Mn, Fe, Co, Mo, W)	modified Raney nickel	"	the same	51
Ra/Ni (used) + Al	Ra/Ni	"	"	52
Mg + Ni (or Fe or Co)	alloys, precursors of intermetallic hydrides	"	high selectivity of hydrogenation of dienes and acetylenes to alkenes	55–57
$M_2CO_3 + Fe_2O_3$ (M = K, Rb, Cs)	catalyst of ethylbenzene dehydrogenation	DS	Increased activity, enhanced strength	58–60
Aluminium hydroxides	various crystalline modifications of Al_2O_3	PM	–	64–75
	formation of hydroxyaluminates through intercalation of Mg and Zn salts	"	–	76–78
Aluminium hydroxides + SiO_2	aluminosilicates, zeolites	"		73, 81–85
MoO_3 or its mixture with V_2O_5	heteropolyacids	"	total absence of waste	86–89
NiO + $Al(OH)_3$ or CuO + $Mg(OH)_2$	catalysts of decomposition of hydrocarbons to C and H_2	"	high activity and stability	91–93
Ca–Cr–Ni-phosphate catalyst IM-2204	regulation of the processes of crystallisation and baking	"	enhanced strengthd	95
ZnO, TiO_2, Al_2O_3, $ZnAl_2O_4$	changes in sorption properties	"	decrease of the temperature of reduction of deposited salts, increased activity of supported metals	97, 98

Note. Abbreviations: ACS, ammonium-carbonate solution; CMC, carboxymethylcellulose; PVA, poly(vinyl alcohol); PEG, poly(ethylene glycol); Ra/Ni, Raney nickel; BM, ball mill; BdM, bead mill; UD, ultrasonic disintegrator; VM, vibratory mill; PM, planetary mill; DS, disintegrator.

mobilities of molecules of at least one of the reagents to the level of their mobilities in a melt.

But even if no reactions occur in the mill, MCA all the same facilitates substantially other stages of the catalyst's preparation. This is determined by changes in the thermodynamic potentials due to the formation of defects, changes in electronic properties, appearance of fresh surface, *etc*. The most substantial effect is observed for high degrees of homogenisation of mixtures of reagents, which facilitates appreciably mutual diffusion.

The interaction of components in the MCA is determined by different properties of solids, such as chemical compositions and reactivities, hardness and fragility, crystal structure and bond strength, melting temperatures and others. For this reason, there is no integral theory or any versatile reference points so far which

would make it possible to predict the result of joint MCA of at least binary systems. So far one can be satisfied solely with some specific speculations.

In our opinion, a kind of activated state arises in the MCA of mixtures of compounds. Relaxation after discontinuing of load results either in the formation of new compounds or in the return to the initial compounds which are however characterised by higher dispersion and excess energy. Naturally, the former is only possible in the absence of thermodynamic restrictions for the reaction of components. But even if the formation of new compounds is possible in principle, one cannot be sure that this possibility is realised under the MCA conditions. A substantial importance has the transition of at least one of the compounds subjected to activation to the viscous-fluid state. Here, it is possible to draw an analogy with the processes of adhesion of liquids or melts or mixing of liquids where several interacting components pass to the viscous-fluid state. In this state, the number and area of contacts between reagents increase substantially, and in the case of chemical affinity, interaction between them becomes possible. If we continue to draw an analogy with the processes of adhesion, then the phase passing to the viscous-fluid state should be called adhesive, while the other phases should be termed substrates. Correct methods for the calculation or determination of thermodynamic potentials in the adhesion or mixing of melts could also be used for predicting the possibility of the occurrence of mechanochemical synthesis. In particular, one can use the known expressions for the adhesion and cohesion works (W_{ad} and W_c, respectively), *i.e.*, the energies that should be spent for the separation of the adhesive and substrate over the interface or for the separation of components of the adhesive to an infinite distance.

$$W_{ad} = \gamma(1 + \cos\theta),$$

$$W_k = 2\gamma,$$

where γ is the surface energy of adhesive (in our case, for the phase which passed to the viscous-fluid state), θ is the angle of wetting.

In the mechanochemical synthesis, the following processes presumably take place successively. First, one or several components pass to the viscous-fluid state. As this process is not momentary, grinding and activation of other components occur simultaneously. After formation of the viscous-fluid phase its adhesion on the surface of other components occurs. If $W_{ad} > W_c$, total wetting takes place. This condition is always fulfilled in the case of formation of chemical bonds between the adhesive and substrate. As a rule, the adhesion forces are stronger than the cohesion forces, *i.e.*, than the forces of intermolecular attachment in the viscous-fluid phase. Because of this, relaxation of stresses in repeated loading of substrate–adhesive particles is manifested in the cleavage of bonds inside the viscous-fluid phase rather than in the separation over the interface. The separated part of the adhesive wets the free surface of the substrate which is formed as a result of grinding. Mechanical loading of the substrate phase with the fixed adhesive should lead to phenomena analogous to the effect of adsorption-induced dispersion since the surface energy of the interface (an analogue of the surface tension for solids) tends to a minimum upon complete wetting. Intensification of the dispersion processes leads to an increase in the surface of wetting. Atoms and molecules belonging to the interface possess high mobilities due to both the viscous-fluid state and the external mechanical impact. This favours an increase in the rates of mutual diffusion. All the above-mentioned factors result in the formation in MCA of lamellar structures either at the molecular level, as in the system $V_2O_5-MoO_3$, or at the microlevel, as in the mechanical alloying of metals [99] or upon application of metals onto solid supports by means of MCA of their mixtures [100, 101] (see below).

If complete wetting does not occur, *i.e.*, none of the interacting phases passes to the viscous-fluid state, the phases undergone activation are dispersed and their particles several nanometres in size prove to be homogeneously mixed, which facilitates substantially the diffusive transfer which is necessary for the interaction of components during subsequent treatments of activated mixtures. Owing to the changes in thermodynamic potentials, the reactivities of components increase in both cases.

Thus, MCA can successfully be used for the direct synthesis of catalytic systems, for facilitating the interaction of components during further treatments (calcination, hydration, sorption, *etc.*) and for the improvement of performances of the products obtained (their mouldability, strength, sorption and catalytic properties). The most important advantage of the mechanochemical methods is the possibility to develop wasteless technologies of the production of catalysts based on them. The importance of the development of wasteless methods is determined by the fact that at present the world production of catalysts is estimated at hundreds of thousands of tons. A considerable part of catalysts is obtained using precipitation methods, which are accompanied by large volumes of wastes. Over half the elements of the Periodic system, including highly toxic ones, are used in the production of catalysts and supports. It may be said without exaggeration that the preparation of catalysts, supports for them and adsorbents are environmentally most deleterious industries. The application of wasteless methods can not only improve the environmental situation in areas of production of catalysts but also decrease their cost owing to lower expenses for neutralisation of wastes. Examples of successful replacement of precipitation methods by wasteless methods based on the use of MCA are the preparation of supports and catalysts based of alumina [64–84] and the synthesis of catalysts of decomposition of hydrocarbons.[91–93] The use of wasteless methods of HPA synthesis is environmentally friendly.[86–89]

Yet another advantage of mechanochemical methods is the decrease in energy consumption. This is achieved owing to the reduction of temperature and time of interaction of components. Thus the preparation of aluminides of several metals, which are precursors of skeletal catalysts, by pyrometallurgical methods requires heating to melting temperatures and in some cases multiple alternations of fusion and grinding are needed. Alloying under the MCA conditions is completed within a few minutes, and in this case the possibilities of variation of the composition of alloys are substantially extended.[47–53] The same advantages are realised in the preparation of hydrides of intermetallic compounds from 'mechanical alloys'.[54–57] Heteropolyacids are formed by reactions of metal oxides with phosphoric acid at its boiling temperature ($\sim$ 373 K) for several hours, whereas the application of MCA makes it possible to decrease the temperature to 323–343 K and the reaction time to a few minutes (some HPA can be prepared at room temperature within a few seconds).[86–89] There are numerous other examples of a substantial decrease in the temperatures of interaction of components and phase transitions. The reduction of energy consumption improves indirectly the environmental situation since energy production is one of the most deleterious for the environment.

With the use of MCA novel catalysts have been synthesised, including those never isolated earlier in the form of individual chemical compounds. Often such systems possessing unique catalytic and chemical properties cannot be synthesised by other methods. This is exemplified in the preparation of alumina π-Al_2O_3 [69, 70] and Raney nickel with the structure of the type NiAl,[53] as well as in the synthesis of hitherto unknown hydrides of magnesium intermetallides [99] and new compounds in the system $V_2O_5-MoO_3$.[90] The application of new catalytic systems prepared using MCA makes it possible to increase the efficiency of catalytic processes, which is often difficult or impossible to achieve by conventional methods.

Broad possibilities are opened by the use of MCA for the regulation of processes which occur in the course of formation of catalytic systems (crystallisation, baking, phase transitions, *etc.*). The temperatures of all these processes and their rates can be varied with the aid of MCA. This makes it possible to govern the

strength, parameters of a porous structure and the specific surface area of catalysts.

Mechanochemical modification of catalysts and supports is not described in sufficient detail in the literature. It is, however, clear that MCA increases the strength of specimens, improves their mouldability and regulates sorption properties. It should be noted that structures formed upon mechanochemical synthesis are non-equilibrium and possess increased reactivities, including those in the target reactions. This phenomenon will be considered in more detail below.

However, a broad range of issues has not been duly described as yet. Thus the possibilities of the use of short-living active sites for the modification of catalytic and sorption systems were not virtually studied. Few studies were devoted to the methods of mechanochemical grafting of various functional groups onto the surface of solids to be used in processes of sorption and catalysis. Potential possibilities of the methods of mechanochemistry are tremendous, as regards the search for novel catalytic systems hitherto unknown as chemical compounds. The list of similar topics could be continued but even those cited above are sufficient for becoming aware of the advisability of intensification of studies in this field.

III. Effect of mechanochemical activation on catalytic properties of compounds

1. Metal catalysts

Apparently, the effect of mechanical impact on catalytic properties of compounds was first revealed by Eckell[102] who has compared the activity of nickel foil in the ethylene hydrogenation before and after rolling. The rolling led to a substantial increase in the nickel activity which decreased after annealing the foil at 473–573 K. Analogous results were obtained in studies of formic acid decomposition.[103, 104] Correlation of the catalytic activities of the specimens studied[102, 103] with the physical properties of mechanically treated metals made it possible to suggest that the catalytically active centres are dislocations.[105] This suggestion was confirmed later in numerous examples by Japanese investigators. It was shown[106–112] that cold treatment of metals (twisting, rolling, moulding) increased the catalytic activity of copper, nickel, silver, gold and platinum in decomposition reactions of diazonium chloride, formic acid and hydrogen peroxide, dehydrogenation of ethanol, hydrogenation of cinnamic acid, oxidation of ethanol and *ortho–para* conversion of hydrogen. It was concluded that both dislocations and point defects are responsible for the increase in catalytic activity. Thermal annealing led in all cases to a decrease in activity to the level of activity of untreated metals; and properties of catalysts such as hardness, electroconductivity and thermo-EMF changed simultaneously. Many investigators[106–112] relate this to the disappearance of defects.

The reasons for the increase in the catalytic activity of metals resulting from mechanical impact were elucidated in more detail in studies of the effect of treatment of nickel and cobalt powders in ball and vibratory mills on their activities in the hydrogenation of benzene and fats. An extreme dependence of cobalt activity on the time of treatment was revealed and the transition of the cubic form of metal to the hexagonal one was established.[113, 114] Examination of a cobalt powder subjected to treatment in mills with subsequent heating, using a set of physicochemical methods, showed that the increase in the catalytic activity of the metal in benzene hydrogenation is determined by the presence of defects and a distorted crystal lattice, as well as by the density of defects.[115–118] Deactivation of catalysts upon heating was associated with dislocation and annihilation of vacancies.[118]

A nickel powder treated in a ball mill increased its activity in the hydrogenation of benzene,[113, 119] phenol and higher alcohols[120] and fats.[121] Correlation of the nickel activity in the above-mentioned reactions with changes in its physicochemical properties suggests that the increase in activity is to a larger extent associated with disordering of the crystal lattice than to the surface area increase.[120, 121] In their completing study, the authors attempted to relate changes in the catalytic properties of mechanically activated nickel to changes in its crystal structure.[122] Specific rate constants of hydrogenation of fats and *ortho–para* conversion of hydrogen were found to be linearly dependent on the number of distortions of the crystal lattice and the density and energy of dislocations. The activation energy of reactions was inversely proportional to the energy of dislocations.[122] The data obtained would seem to provide an unambiguous proof that dislocations in metals are catalytically active centres. However, the method of determination of specific activities of catalysts used by the authors cannot unfortunately be regarded as correct. The rates of reactions were estimated from the degree of conversion referred to a unit surface. But the degree of conversion is an integral (as regards time and concentrations) magnitude and cannot serve as a measure of the catalytic activity. The models used for the determination of the number and density of dislocations were far from being perfect. Analogous drawbacks are also inherent in the above-cited studies by Japanese researchers.[116–122] Nonetheless, all these publications made a substantial contribution to the understanding of the nature of the effect of mechanical impact on the catalytic activities of metals.

2. Oxide catalysts

The effect of mechanical treatment on the catalytic properties of oxide systems was revealed for the first time in studies of the catalytic activity of lead oxide in the decomposition of hydrogen peroxide as a function of time of treatment in a ball mill.[123] The effect of mechanical treatment on the activity of V_2O_5, Fe_3O_4 and Fe_2O_3 in the oxidation of sulfur dioxide was studied more than two decades later.[124, 125] The dependence of the catalytic activity of vanadium oxide on the time of treatment has two maxima,[124] while the activities of both iron oxides pass through one maximum.[125] The increase in catalytic activity is presumed to be related to distortions of the crystal lattice rather than to a larger surface area. Mechanical activation of iron oxides was also used in the oxidation and vapour conversion of CO.[126, 127] The dependences of the Fe_2O_3 activity on the treatment time has an extremal character in both reactions, whereas the same dependence for Fe_3O_4 is described by a curve with saturation. Fe_3O_4 subjected to mechanical treatment is more active than the industrial catalyst of vapour conversion of CO;[127] however, no satisfactory explanation of this effect has been given so far.

Mechanical treatment of vanadium and iron oxides leads to an increase in their adsorption capacity with respect to sulfur dioxide and hydrogen sulfide;[124, 128, 129] the positions of the maxima of the catalytic activities and adsorption capacities virtually coincide on the time dependence curves.

An attempt was made to elucidate the reasons for the effect of mechanical activation on the catalytic properties of calcium and copper oxides in the decomposition of N_2O and *ortho–para* conversion of hydrogen.[130–132] There is a quantitative dependence between the catalytic activity of calcium oxide in the decomposition of N_2O and the concentration of defects in the crystal lattice. This is evidenced by the same degree of decrease, resulting from thermal treatment, of both the catalytic activity and some parameters (determined by the X-ray diffraction method) which characterise the defectiveness of activated samples. The increase in the copper oxide activity is rationalised within the framework of the electronic theory of catalysis. It is presumed that as a result of mechanical treatment the conductivity of *n*-type passes to the conductivity of *p*-type, while the activity of the catalyst in the decomposition of N_2O is determined by the ease of electron transfer in elementary stages.[132] Changes in the catalytic properties of copper oxide in the *ortho–para* conversion of hydrogen are related to magnetic properties,[131] while no mention is made about electronic properties.

Mechanical treatment can not only increase, but also decrease catalytic activity. Examples of this type, though not numerous, are the decrease in the zinc oxide activity in the decomposition of

hydrogen peroxide and photooxidation of propan-2-ol after treatment in a ball mill.[133–135] The activity of zinc oxide drops linearly as the degree of disorderliness of the crystal lattice increases. The activation energy of hydrogen peroxide decomposition on mechanically treated zinc oxide decreases with the increase in the number of paramagnetic centres which are edge dislocations.[136]

The increase in the activity of zinc oxide, treated under analogous conditions, in the decomposition of hydrogen peroxide is related to a distortion of the crystal lattice.[137–139] A comparative study of the effect of nickel and zinc grinding in a ball mill on the activation energy of hydrogen peroxide decomposition[139] made it possible to conclude that the differences observed are determined by the type of conductivity of these semiconductors possessing the *p*-type and *n*-type conductivities, respectively.

Changes in catalytic properties occur not only upon treatment in a mill, but also under other types of mechanical impact. Thus the effect of compacting pressure on the properties of a number of catalysts was reported.[140–150] The accompanying changes in acidic properties of potassium hydrogensulfate and tungstic acid induce an increase in their activities in the acetylene polymerisation and propylene hydration, respectively.[140–141] The activities of chromium-containing oxide catalysts in the dehydrogenation of alcohols[142–148] and of an aluminium–cobalt–molybdenum catalyst in hydrogenolysis of thiophene[149,150] show extremal dependences on the compacting pressure. The changes in catalytic activities are rationalised with the use of data on porous structures and variation of the interplanar distances. However, it should be noted that the methods used for the determination of the activity of catalysts in the studies cited are incorrect.[140–150]

Yet another type of mechanical impact is the treatment of materials with shock waves. The activity of numerous simple and complex oxides as well as their mixtures in the CO oxidation increases after the application of shock waves.[151] This is related to the appearance of anionic vacancies and other perturbations of the crystal structure. The increase in the titanium dioxide activity is not associated with the presence of paramagnetic centres Ti^{3+} and paramagnetic defects.[152] It should be noted that upon application of shock waves appreciable admixtures of the reactor construction material are introduced into catalysts, and these admixtures can affect their catalytic properties.[151] Therefore, it is not excluded that high activity of titanium dioxide observed by Golden *et al.*[152] is explained by the presence of copper oxide compounds of which the reactor was made. By varying conditions of shock load one can regulate catalytic properties of fluorite;[153] not only an increase in the degree of transformation on this catalyst was observed, but also wide-range changes in the ratio of propan-2-ol dehydrogenation and dehydration rates.

Activation of supported catalysts is of definite interest. Thus treatment of a mixture of metallic nickel and quartz in a vibratory mill results in coating of quartz with nickel, and this makes it possible to reach a high rate of benzene hydrogenation.[100] The increase in catalytic activity is explained by distortions of the crystal lattice of nickel. Schulz *et al.*[101] treated a mixture of nickel–ruthenium alloy and aluminium oxide in a similar manner. The system obtained was studied in detail by physicochemical methods; however, no data on its catalytic properties were reported. Of some interest is the preparation of alloys with non-equilibrium composition which preserve their thermal stabilities up to 673–773 K. Chromium, vanadium and molybdenum oxides supported on silica gel were also subject to mechanical treatment.[154–156] Their catalytic activities in ethylene polymerisation,[154] propylene metathesis[155] and methane oxidation to formaldehyde[156] increased after activation in a vibratory mill in different media. Possible mechanisms of formation of active centres of these catalysts involving radical centres of silica were considered. Though, the authors do not provide any conclusive evidence of these mechanisms. A possible mechanism of the catalytic oxidation of methane is also discussed.[156] Of interest is the fact of an increase in the selectivity of formaldehyde formation resulting from a virtually complete suppression of the reactions of deep oxidation of methane on activated catalysts; however, this effect is observed only at low degrees of methane conversion (1%–2%).[156] Unfortunately, in all studies the activity of deposited catalysts was determined without due account for the specific surface of the active component. In a number of cases, indeed, there are no corresponding methods, but they do exist for supported metals. Without knowledge of the specific surface of active component, it is impossible to establish the reason for the effect of mechanical activation on catalytic properties; furthermore, there is a risk of reaching conclusions which are opposite to the real situation.

Analysis of a large body of available experimental data allows one to avoid mistakes made in some works and to continue studies of the effect of mechanical treatment on catalytic properties of compounds at a more perfect level using modern methods. This concerns primarily the methods for the determination of catalytic activity. In the studies discussed below, the catalytic activity was determined, in our opinion, in the most correct manner, *viz.*, in the gradient-free (with regard to temperature and concentrations) conditions, while the reaction rates were referred to a catalysts unit surface. In addition, a set of modern research methods were used in these studies in order to determine the nature and concentration of defects formed in the MCA.

Oxides which are effective catalysts of deep oxidation were the subjects of studies. Activation of copper oxide in a planetary mill even for a few seconds increased 2–5-fold the specific rate of butane oxidation.[43,157] Presumably, the reasons for this are structural perturbations in the subsurface layer and the increase in the surface concentration of Cu^+ ions, which are the centres of chemisorption.[157] On the contrary, cobalt oxide decreases its activity in the oxidation of butane,[158] and this is explained by the removal of excess oxygen in the course of mechanical treatment. A decrease in activity was also observed upon mechanical treatment of iron(III) oxide[159] having a defective structure. It is presumed that the treatment results in the disappearance of surface and subsurface defects with a local spinel symmetry. It was reported[159] that specific catalytic activity of α-Fe_2O_3 depended almost linearly on the concentration of extended defects determined by the method of small-angle X-ray scattering. The graph which we plotted on the basis of these data (Fig. 1) confirms the conclusion made by the authors. Activation of manganese oxides induced a 2–5-fold increase in the specific rate of CO oxidation depending on the chemical composition of the oxide.[160] An increase in the activity of Mn_2O_3 is explained, as for Mn_3O_4, by the appearance of extended defects. In this case, an increase in the oxygen content is also observed. The authors relate the appearance of active centres of Mn_2O_3 to the formation of steps on the faces $\langle 120 \rangle$, whereas the activity of MnO is believed to be associated with the formation of γ-Mn_2O_3 on the surface. Sadykov *et al.*[161] have generalised and analysed the data on the effect of MCA on the defectiveness and reactivity of oxide catalysts of deep oxidation.

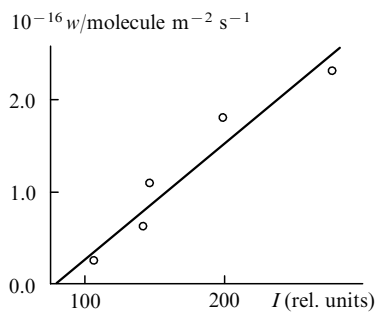


Figure 1. Dependence of the specific rate of CO oxidation on α-Fe_2O_3 (w) on the integral intensity of small-angle scattering (I) (according to the data of Ref. 159).

In the MCA of zinc oxide the following three processes occur successively, *viz*., accumulation of shear defects, relaxation of the structure resulting from grinding and agglomeration of particles formed upon grinding.[162] Accumulation of defects is accompanied by the increase in the specific activity of the catalyst for the oxidation of CO; upon fissuring or breaking of crystallites over shear defects the activity returns to the preactivation level.[163, 164] A catalytic act is supposed to involve oxygen chemisorbed at sites of the exit of shear defects onto the surface.[164] Accumulation of defects occurs in a very narrow range of activation times; apparently, it is due to the fact that the effect of activation was not revealed in the above-cited studies.[133–136]

An unambiguous evidence of the role of defects as the centres responsible for the increase in catalytic activity was obtained in studies of titanium dioxide. Figure 2 shows the linear dependence of the specific rate of CO oxidation on TiO_2 on the concentration of planes of crystallographic shear.[165] To our knowledge, there are only three studies which revealed experimentally the quantitative dependence of the specific catalytic activity on the concentration of defects.[122, 159, 165] Only this dependence may be regarded as a strict proof that defects are the active centres of catalysis. However, Schrader *et al.*[122] used an incorrect method for the determination of specific catalytic activity, and in this case such a conclusion cannot be regarded as correct. The data on the effect of mechanical impact on the activity of catalysts of different nature are presented in Table 2.

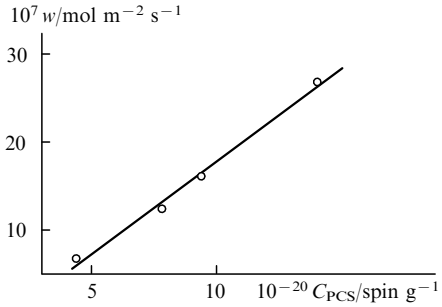


Figure 2. Dependence of the specific rate of CO oxidation on TiO_2 on the concentration of planes of crystallographic shear (C_{PCS}).

Table 2. The effect of MCA on catalytic properties of various compounds.

Catalyst	Reaction	Active centre	Ref.
Ni	hydrogenation of ethylene	–	102
	decomposition of formic acid	dislocations	103–105
Cu	decomposition of diazonium chloride	the same	106, 107
	dehydrogenation of ethanol	"	107
Ni	hydrogenation of cinnamic acid, dehydrogenation of ethanol, decomposition of H_2O_2, *ortho–para* conversion of hydrogen	vacancies, dislocations	108, 109
Ag	decomposition of formic acid, decomposition of H_2O_2, oxidation of ethanol	dislocations	110
Au	decomposition of H_2O_2	the same	111
Pt	decomposition of formic acid, hydrogenation of cinnamic acid	point defects, dislocations	112
Co	decomposition of H_2O_2, hydrogenation of benzene	defects and distortions of the structure	113–118
Ni	hydrogenation of benzene	distortions of the lattice	113, 119
	hydrogenation of phenol and mixtures of higher unsaturated alcohols	the same	120
	hydrogenation of fats, *ortho–para* conversion of hydrogen	dislocations	121, 122
PbO	decomposition of H_2O_2	–	123
V_2O_5	oxidation of SO_2 to SO_3	distortions of the lattice	124
Fe_2O_3, Fe_3O_4	the same	the same	125
	oxidation of CO	–	126
	vapour conversion of CO	distortions of the lattice	127
CuO	decomposition of N_2O, *ortho–para* conversion of hydrogen	defects of the lattice	130, 131
CaO	decomposition of N_2O	the same	132
NiO	decomposition of H_2O_2	distortions of the lattice	137–139
$KHSO_4$	polymerisation of acetaldehyde	new acidic centres	140
H_2WO_4	hydration of propylene	new proton centres	141
Cr_2O_3 + CuO or/and ZnO	dehydrogenation of Pr^iOH	distortions of the lattice	142–148
TiO_2, ZnO, $BaTiO_3$, NiO, $TiO_2 + WO_3$, $TiO_2 + Fe_2O_3$	oxidation of CO	anionic vacancies	151
TiO_2	the same	distortions of the lattice	152
CaF_2	dehydrogenation and dehydration of Pr^iOH	–	153
$Ni + SiO_2$	hydrogenation of benzene	distortions of the lattice	100
$CrO_3 + SiO_2$	polymerisation of ethylene	$\equiv SiO^{\bullet} + Cr^{n+}$ ($n < 6$)	154
$MoO_3 + SiO_2$	metathesis of propylene	$\equiv SiO^{\bullet} + Mo^{4+}$	155
$V_2O_5 + SiO_2$	oxidation of methane to formaldehyde	–	156
CuO	oxidation of butane	surface Cu^+ ions	43, 157, 161
Co_3O_4	the same	excess oxygen	158, 161
Fe_2O_3	oxidation of CO	defects with a local symmetry of spinel	159, 161
MnO_2, MnO, Mn_3O_4, Mn_2O_3	the same	extended defects, steps	160, 161
ZnO	"	shear defects	162–164
TiO_2	"	planes of crystallographic shift	165

3. Annihilation of defects as a factor of deactivation of catalysts

In the process of operation, catalysts are known to loose gradually their activity and selectivity, to degrade, *etc*. The reason for deterioration of properties of catalysts, which can also be differently manifested in the use of systems subjected to MCA, were examined in detail.[166] The problem of the lifetime of systems with increased reactivities resulting from MCA has an independent significance and is fairly topical.

In a number of instances, the mechanism of the disappearance of defects resembles in many respects mutual annihilation of particles and antiparticles. For example, this seems to be the case of the interaction of dislocations with the counter-directed Bürgers vectors of the same magnitude or the interaction of vacancies with the internodal ion. In virtually all of the studies cited in this section, a decrease in catalytic activity resulting from the disappearance of defects was noted. Most often, the annihilation of defects is induced by thermal annealing. This concerns both metal [106–122] and some oxide [123, 130, 138] catalysts.

The activity of mechanically activated copper oxide in the butane oxidation decreases when a specimen is stored for a long time and as a result of catalytic reaction.[157] In our opinion, this occurs due to processes which are analogous to those taking place in the course of annealing, although the rate of the disappearance of defects is substantially lower due to a decreased temperature. Sometimes, other factors are also found to play a role. Thus the degradation of crystallites of zinc oxide over shear defects leads to relaxation of the crystal structure.[162] For iron oxide, a mechanism was proposed for the disappearance of defects due to the shear of layers.[159] The recovery of the initial stoichiometry of compounds can be yet another reason for deactivation. For instance, the removal of excess oxygen from cobalt oxide in the process of MCA leads to a decrease in its activity in the butane oxidation,[158] while the disappearance of the planes of crystallographic shear in titanium dioxide in oxidative media makes it less active in the oxidation of CO.[165] All these facts altogether gave us ground for supplementing the existing list of reasons for deactivation of catalysts [166] with one more factor, *i.e*., annihilation of defects of the crystal structure.[163, 167]

In some cases, mechanical treatment can lead to a complete and irreversible inactivation of catalysts. Thus mechanical treatment of zeolite FeZSM-5 destroys its crystal structure and leads to the total loss of activity in the phenol oxidation by dinitrogen oxide.[168] For the same reason, aluminium oxide looses its ability for coke formation after mechanical treatment,[169] which is a positive factor under the condition of preservation of useful properties by this material, *e.g*., high sorptional capacity.[97]

It is commonly assumed that the defects disappear at sufficiently low temperatures, so the effect of increase in activity upon MCA cannot be used for practical purposes. However, there are many well known chemical processes which occur at temperatures substantially lower than the temperatures of annealing of defects. For example, skeletal catalysts prepared with the use of mechanical melting are effective in the hydrogenation reactions at temperatures of 373 K and below. The catalysts of deep oxidation preserve their elevated activities acquired upon MCA for at least tens of hours.[157] In a number of cases, annealing of defects requires unusually high temperatures. For example, the activity of iron–potassium catalyst in the dehydrogenation of n-butenes is decreased only upon heating to temperatures above 903 K,[61] which is the operation conditions of an industrial reactor. Thus, the increase in the catalytic activity by MCA may be used for practical purposes, too.

4. Effect of mechanochemical activation on the selectivities of catalysts

Very few studies have been devoted to the investigation of the effect of MCA on the selectivities of catalysts. Treatment of molybdenum disulfide in a vibratory mill changes its selectivity in the thiophene hydrodesulfuration, the direction of this change being dependent on the composition of the medium in which this treatment is carried out.[170] This is attributed to changes in the ratio of crystallographic facets possessing different catalytic properties. Upon grinding in heptane, the ratio of the surfaces of basal and lateral facets of molybdenum disulfide is 72 : 28, whereas upon grinding in air it is 5 : 95. At close degrees of thiophene conversion the ratios of concentrations of butane and butenes formed on these samples reach 0.7 and 3.0, respectively. In addition, the sample with a larger proportion of lateral facets is capable of sorbing a larger amount of hydrogen, chemisorption beginning at substantially lower temperatures. The use of fluorite subjected to MCA increases the selectivity of acetone formation from propan-2-ol.[151] Treatment of a suspension of $VOHPO_4$ in ethanol in a planetary mill leads to the increase of the portion of the surface formed by the facets $\langle 001 \rangle$ of vanadium hydrogenphosphate, which are transformed into the facets $\langle 100 \rangle$ of vanadyl pyrophosphate upon thermal treatment.[171] The elevated content of the latter favours an increase in the selectivity of maleic anhydride formation upon oxidation of n-butane. We observed a decrease in the selectivity of butadiene formation upon dehydrogenation of n-butenes on a mechanically activated iron–potassium catalyst.[61] Iron carbide Fe_3C subjected to MCA increases the selectivity of formation of hydrocarbons C_n, where $n \geqslant 2$, and decreases the alkene : alkane ratio in the reaction of CO_2 hydrogenation. Analogous effects are observed with a carbide catalyst synthesised by mechanochemical interaction of metallic iron with carbon.[172] The authors do not discuss the nature of this phenomenon.

In virtually all the cases, changes in selectivity are related to the changes in the nature of the crystallographic facets upon grinding, while the influence of defects is not considered in any of the cited studies. In our opinion, it is necessary to take into account that the selectivity of multiroute reactions is determined by the ratio of several reactions, one of which yields the target product. Each reaction occurs on its own active centres, and by varying their ratio one can regulate selectivity. MCA can be a possible way of regulating the selectivity of catalysts. The increase in the selectivity of formation of target products is favoured by higher activity and a larger number of active centres responsible for the occurrence of major reactions and by a lower activity or a lower concentration of centres on which side reactions take place. By studying the dependence of the yield of various products on structural changes, one can establish the relationship between the occurrence of specific reactions and the presence of the corresponding structures, and this will contribute to the development of the theory of prediction of catalytic action.

Thus, the relevant, sufficiently numerous literature data point to a substantial influence of mechanical impact on the activities and selectivities of catalysts. Despite the long-standing opinion that it is impossible to use this effect for practical purposes because of the metastability of defects, some studies revealed high thermal stability of active states resulting from MCA and a substantial increase in the activities of catalysts of a number of industrially important low-temperature reactions. This is promising for the development of industrial technologies for increasing the activities of catalysts by MCA.

The reasons for the effect of MCA on the catalytic properties of compounds cannot nowadays be regarded as elucidated. The overwhelming majority of studies only state the facts of changes in catalytic properties resulting from mechanical impacts. The catalytically active centres are usually denoted with general terms, *viz*., defects, distortions of the crystal lattice, *etc*., without definition of their structures. Sometimes, changes in the activity (as a rule, its increase) are attributed to the appearance of specifie defects: dislocations in the structure of various metals,[105–112, 122] planes of crystallographic shear in the lattice of titanium dioxide,[165] steps on the facets $\langle 120 \rangle$ of Mn_2O_3,[160] dislocations with the known Bürgers vectors in some oxides.[161] We know only three studies [122, 159, 165] which provided direct experimental evidence of the participation of defects of definite type in the increase in the

catalytic activity. The results of these studies allow description of the structure of active centres at the atomic level. In our view, the best successes in the investigation of the influence of defects on the activity of catalysts were achieved in the study of N_2O decomposition on copper oxide (the electronic theory of catalysis [132] was used for its description) and in the investigation of the nature of the chemisorbed or surface oxygen involved in elementary catalytic acts.[157–161, 164]

IV. The role of defects as active centres for chemical processes

Analysis of the literature data shows that compounds subjected to MCA exhibit increased reactivities in various chemical processes, *viz*., simple chemical transformations, sorption processes and catalytic reactions. This indicates that defects are the active centres of all above-mentioned transformations. Let us consider a few examples of the versatile character of MCA action. Thus MCA of iron oxides increases both their catalytic activities in the CO oxidation and vapour conversion of CO [125–127] and the sorption capacity with respect to hydrogen sulfide.[128, 129] Mechanochemical activation of vanadium(V) oxide induces symbatic modification of its sorption capacities with respect to sulfur dioxide and its activity in the SO_2 oxidation to SO_3.[124] In addition, vanadium oxide manifests an increased activity in the reactions with hydrogen peroxide and alkalis after MCA.[173] Zinc and titanium oxides the structure of which contains shear defects, exhibit an increased activity in the CO oxidation [162–165] and at the same time increased sorption capacities with respect to nickel and copper salts.[97, 98] In addition, MCA increases the sorption capacity of zinc oxide with respect to hydrogen sulfide,[36] while titanium dioxide becomes more reactive in reactions involving oxygen [165] and sulfuric acid.[3] The increase in reactivity is manifested also in a lower temperature of reduction, by hydrogen, of nickel chloride deposited on oxide supports subjected to MCA.[97, 98] After activation of zinc ferrite with the structure of spinel, the rate of its dissolution in hydrochloric acid is substantially increased [174] together with the sorption capacity of zinc ferrite with respect to hydrogen sulfide.[175] In this state, zinc ferrite exhibits higher catalytic activity in the oxidation of CO.

Thus, if the sites of the exit of defects on the surface are catalytically active centres, they play simultaneously the role of sorption centres for salts from solutions and chemisorption of various gases, as well as of the reaction centres where simple chemical reactions take place. This refers not only to those defects which result from MCA but also to other defects. Thus the appearance of planes of twinning in the particles of metallic nickel in the formation of filamentous carbon leads to the increase in the specific rate of butadiene hydrogenation.[176] The reactivity of such nickel in the reaction with molecular bromine is also increased. As a result of interaction of silver supported on corundum with the reaction medium, one observes formation of interblock boundaries. These defects are the active centres of ethylene oxidation to ethylene oxide.[177] In the above-mentioned systems the character of oxygen chemisorption on silver and of hydrogen on nickel is changed.[178] Among uranium nitrides used as catalysts in the synthesis of ammonia, the maximum activity is characteristic of the sample with composition $UN_{1.7}$ with an ordered structure, *i.e*., it has defects in the crystal structure of a definite type.[179] This nitride is also distinguished by a special character of chemisorption of nitrogen and a higher reactivity in the reaction with hydrogen.

These data show that the mechanically induced defects of the crystal structure exhibit higher activity in the three chemical processes differing in their nature and mechanisms: simple chemical transformations, sorption and catalysis (Table 3).

The increase in the sorption capacity of different oxides with respect to gases and the concomitant increase in their catalytic activities in the CO oxidation with formation of the same active centres is well explicable since chemisorption is an elementary stage of a catalytic reaction. But the fact that the increase in the activities of oxides in chemical reactions and stronger sorption of ions from solutions on them correlates with these two effects is surprising. Taking into account the versatility of active centres, one may suggest that the increase in chemical activity is explained not by changes in the mechanism of processes, but has a more common origin. It is changes in the thermodynamic potentials of compounds as a result of MCA that can be such a reason.

Table 3. Chemical processes depending on defects in the catalyst's structure.

Catalyst	Chemical transformation	Sorption	Catalytic reaction
ZnO	oxidation – reduction	O_2, H_2Se, Ni^{2+}	oxidation of CO
TiO_2	oxidation, dissolution in acids	Ni^{2+}	the same
$ZnAl_2O_4$, $ZnFe_2O_4$	leaching	Ni^{2+}, H_2S	"
Fe_2O_3	dissolution in acids	H_2S	"

V. Catalytic reactions under conditions of mechanochemical activation

Scarce data on catalytic reactions occurring under MCA conditions may be divided into two groups: some of them are regarded as pseudocatalytic (the term proposed by P Yu Butyagin) and all other as really catalytic reactions. The so-called pseudocatalytic reactions represent a recurrent sequence of simple chemical transformations of reagents involving a solid. Each of these transformations may be regarded as an analogue of an elementary act in the stepwise mechanism of a catalytic reaction. Their motive forces are continuous induction of active centres as a result of mechanical impacts. For the reaction to continue after the interaction of reagents with the centre, the latter should be regenerated due to the supply of mechanical energy. In contrast to this, in the catalytic reactions the active centres are regenerated in subsequent elementary acts as a result of chemical transformations. Oxidation of carbon, hydrogen and CO under the conditions of mechanical activation of quartz [180–182] represents examples of pseudocatalytic reactions. The mechanism of CO oxidation was described by Butyagin.[5] Apparently reactions of polymerisation occurring upon mechanical activation of various materials in the medium of the corresponding monomers belong to the same type.[183–185] Radical or charged centres of freshly formed surface act as initiators of the growth of polymeric chains.

The truly catalytic reactions include, *e.g*., the synthesis of ammonia which takes place upon treatment of the catalyst with carborundum particles [186] in a jet mill [186] and in a ball mill,[187] hydrogenation of benzene on nickel in a vibratory mill,[188–190] and of ethylene on iron,[190] and oxidation of SO_2 on vanadium(V) oxide.[124] All the above-listed reactions, except for the last mentioned one, proceed with high conversion degrees at room temperature. To accelerate the reactions of hydrogenation, solids possessing high hardness, *e.g*. corundum, were introduced into the reaction volume; these reactions can proceed even in the presence of catalytic poisons (thiophene).[188] The activation energy of sulfur dioxide oxidation in the temperature range 623–773 K under conditions of MCA was 5 kcal mol^{-1}, this energy being much lower than that in the conventional catalysis (32–34 kcal mol^{-1}). Methanation of CO_2 on metal catalysts under mechanical activation is also carried out at elevated temperatures.[191] Catalytic hydrogenation of CO to methane on the inert alloy $Zr_{0.5}Ni_{0.5}$ saturated with hydrogen is believed to follow two pathways.[192] One of them includes the stage of dissociative chemisorption of CO with the liberation of elementary carbon and its subsequent hydrogenation; this is confirmed by studies of individual stages of the process under the MCA conditions. The

occurrence of the reaction through the second pathway is presumably associated with the generation of short-living active states on the catalyst surface.

We undertook systematic studies of catalytic reactions under the MCA conditions. This refers to many reactions: CO oxidation on oxides and metals, synthesis of ammonia on the industrial catalyst CA-1B, pyrolysis of butane on magnesium oxide, hydrogenolysis of butadiene on hydrides of magnesium inermetallides, synthesis of boric acid esters with the use of spherical granules of zeolites as catalysts, grinding bodies and absorbents of water formed in the reaction, as well as numerous reactions of hydrogenation and reduction of functional groups.[163, 193] These reactions do not occur in the absence of catalysts, while the composition of the catalysts themselves is not changed in the course of the process. This indicates that they are indeed the accelerators of the process rather than mere reagents.

The reactions of hydrogenation and reduction of solid organic compounds have been studied in sufficient detail. The most efficient catalysts of such processes proved to be hydrides of intermetallic compounds. The mechanochemical reactions of catalytic hydrogenation or reduction involve only the terminal unsaturated bonds and functional groups; no reactions take place when these bonds and groups occupy internal positions. By varying conditions of mechanical activation, one can regulate the selectivity of reactions which has been clearly exemplified in transformations of caryophyllene α-oxide.[163] Apparently, in many cases, the mechanisms of reactions differ under the MCA conditions from those in traditional catalysis. Thus in the hydrogenation of butadiene under usual conditions on the hydride Mg_2FeH_6 the selectivity of formation of butenes is close to 100%,[56] whereas under the MCA conditions complete hydrogenolysis occurs on this catalyst.[193]

How can MCA affect the course of catalytic reactions? One of the most important advantages of catalysis is the possibility of an easier overcoming the reaction activation barrier or, more precisely, its elementary act. This is as a rule achieved by supplying the catalyst and reagents with external energy, most often in the form of heat. The energy can also be supplied by sonication (sonocatalysis) or as electromagnetic radiation (radiation-induced catalysis or photocatalysis depending on the radiation wavelength).

We took the liberty of introducing a new term 'mechanochemical catalysis', *i.e.*, the catalysis in which the energy is supplied by mechanical impact on catalysts and reagents. As a result of such impact, not only the activities of catalysts are increased, but also the chemical reactivities of solid reagents and, besides, the regularities of activation of catalysts are changed. Since any measurements inside the working chambers of mills are not technically feasible, it may only be suggested what kind of processes occur during mechanical activation.

The simplest way is to suppose that the energy is supplied by means of transformation of the mechanical energy to thermal energy, after which a catalytic reaction occurs in a usual manner. Indeed, some investigators believe that the temperatures up to 1500 – 2000 K are developed at the sites of contact of grinding bodies with the compound under activation (the theory of magmaplasma). However, this view is not corroborated by valid experimental evidence. A conclusion based on calorimetric measurements which states that during grinding the temperature reaches 650 – 900 K seems to be better substantiated. Nonetheless, in this case, too, it is difficult to explain why at these temperatures either ammonium nitrate (published data) or some organic compounds (own results) virtually do not decompose. Apparently, introduction of compounds which can be readily activated changes the friction coefficients, while the temperatures in the working chambers are substantially lower under conditions of mechanochemical catalysis than those mentioned above. Hence, the transformation of the mechanical energy to thermal energy can explain only some of experimental data.

We believe that the most probable way of activation of reagents is the transfer of excess energy concentrated in the short-living centres formed in the course of cleavage of the catalyst's crystallites. Such centres have, as a rule, a radical nature, and the thermodynamic requirement for the reduction of their energy is fulfilled at the expense of bonding. The reactants situated in the immediate proximity of such a centre react with the unsaturated bond and pass to the activated state. In this case, the vibratory and electronic levels are excited, electronic levels appear in the forbidden bands (especially when defects of the crystal lattice are available), and the forbidden band becomes narrower. It is these processes that are the result of energy redistribution according to the scheme: mechanical energy → excess energy of the catalyst → excess energy of a reactant.

In contrast to other types of catalysis, the mechanochemical catalysis induces continuous formation of defects, their migration, interaction and annihilation. It is known that compounds are sorbed predominantly on sites of the exit of defects onto the surface and migrate together with these defects. Even dislocations of molecules into the bulk of solids were detected. Migration of point defects and dislocations is described in sufficient detail in the literature, but there is little information about the migration of planar defects. The planar defects are formed upon shear and turn the layers of cations and anions relative to each other. Apparently, recovery of the normal packing in some places and formation of shear defects in others occur in the MCA. In this situation, the places of exit of such defects migrate over the surface of crystallites. Interaction and annihilation of defects result in release of energy, and since the reactants are localised basically on defects, a part of the released energy is most probably spent in the activation of reactants.

We believe that the three modes of energy transfer mentioned above are the most probable since they are indirectly confirmed experimentally. One should not however rule out other ways of energy transfer to reactants. For example, the acceptor compounds may be activated by capturing the so-called mechanoelectrons. Several reports discuss the problem of participation of high-frequency phonons in the activation processes. Upon mechanical activation of solids, different types of electromagnetic radiation arise which can also induce activation of reactants in the mode similar to that of the radiation-induced catalysis or photocatalysis. Concomitant realisation of several described channels of energy redistribution is not precluded either.

VI. The nature of the effect of mechanochemical activation on the reactivity of solids

Using theoretical concepts, it is possible to predict to some extent, and in a number of cases to make approximate quantitative estimates of the effect of MCA on the properties of catalysts and catalytic reactions. Changes in the thermodynamic potentials of catalysts should induce changes in the equilibrium constants of formation of intermediate products, *e.g.*, chemisorbed compounds, towards their higher concentrations. With correct data on the values of thermodynamic potentials, it is possible to establish how changes in the catalyst's state influence its activity. To this end, use is made of the known expressions which relate the rate of a catalytic reaction to thermodynamic parameters. Such an approach is described, for example, by Boreskov.[194] At the qualitative level, one may say that the shift of equilibrium towards higher concentration of intermediates should lead to an increased reaction rate. It is obvious that both the magnitude of activity and its increment due to MCA have definite limits which are determined by the chemical nature of the compound subject to activation. The maximum of stored excess energy is determined by the type of crystal structure of a compound and by the nature of defects arising during MCA. In addition, if the appearance of defects results in changes in the heat of chemisorption of the

reactants, the activation energy of reaction (E) is also changed in conformity with the equation of Brønsted and Polanyi:

$$E = E_0 \pm \alpha q ,$$

where the activation energy E_0 and the coefficient α depend on the type of reaction and q is the heat of chemisorption. This will also affect the rate of catalytic reactions. Upon formation of fresh surfaces by crystal splitting, localised free valences appear, the number of which may be close to the number of surface atoms. The presence of free valences favours the increase in the adsorption and chemical activities of the catalyst with respect to the gas and liquid phases and also solutes. Within the lifetime of such states, which ranges from 10^{-4} to 10^{-7} s (see Ref. 3), all processes of 'chemical relaxation' have enough time to occur, including chemical reactions with contacting compounds.[4]

The appearance of defects leads to changes in the electronic properties of a solid, which will be discussed below, and to changes in the geometry of the surface due to the appearance on it of sites for the exit of extended defects. Changes in the regular structure affect not only the sites of the exit of defects onto the surface themselves but also considerable areas around them. Relevant calculations indicate that at fairly moderate concentrations of dislocations ($10^{11}-10^{12}$ cm^{-2}) the part of distorted structure amounts to 70%–80% of all the surface.[3] For this reason, the defects of the crystal structure will substantially influence the processes of adsorption and hence the catalytic properties of a substance. This influence is realised through the geometric factor, *i.e.*, the geometric correspondence of the structure of reactants to the surface of catalysts. Apparently, the selectivity of multiroute reactions should vary most substantially. The sorption properties of the surface in the places of the exit of the defects of crystal structure should differ from those of the remaining surface, first, because of changes in the surface geometry and, second, due to the fact that such places serve as traps of electrons and possess special electronic properties.[195] The effect of defects on the catalytic properties of compounds is apparently also manifested in the variation of the energy of bonding between atoms in the lattice of catalysts which is determined by changes in the interatomic distances in the course of formation of extended defects. For example, the strength of the oxygen bond in oxides is well known to correlate with the catalytic activity of oxides in the reactions of oxidation. It is not excluded that the appearance of defects can result in changes in the nature of the chemisorbed reagents. Thus upon MCA of quartz the activated catalyst generates singlet oxygen; an analogous phenomenon is observed with the reduced and hence defective vanadium oxide.[196] This induces changes in the catalytic properties of this oxide in the oxidation reaction of naphthalene to phthalic anhydride.

Changes in the electronic properties of catalysts resulting from MCA can have a substantial effect on the redox and other reactions requiring transfer of electrons. We have already noted above that chemisorption is possibly influenced by changes in the surface properties in the places of the exit of defects where electrons are localised. It may also be expected that during the occurrence of both catalytic and ordinary reactions the conductivity electrons and the electrons belonging to anions with enhanced electron-donor properties will be involved in the elementary acts with electron transfer. According to the literature data, the catalytic properties of compounds can be influenced by the peculiarities of transition of electrons from one electronic level to another, work of electron release, position of the Fermi level, width of the forbidden band, availability of electronic levels in it, *etc*. All these parameters may be influenced by means of MCA.

All the changes listed above favour the increase in the reactivities of components in the synthesis of catalysts, modification of their sorption properties due to the formation of new surface and the appearance of places for the exit of defects onto the surface, as well as changes in the specific catalytic activity. By now, a considerable body of experimental data has been accumulated on the dependence of the catalytic activity on the mechanical impact. However, the authors of the overwhelming majority of works confine themselves either to a trivial statement of such influence or to attempts to explain specific situations that they have observed.

Comparison of different viewpoints would possibly allow interpretation of experimental observations, formulation of general theoretical concepts and creation of the scientific ground for the purposeful control of the processes occurring. Of special interest is the elucidation of the reasons of the effect of MCA on the catalytic activity of compounds and selectivity of reactions of different nature (redox, acidic and other reactions). To this end, physical theory of mechanical impact should be combined with concepts of the chemical nature of the catalytic activity. It is possible that this will not however allow creation of an integral theory, as it is still the case in the heterogeneous catalysis on the whole, but there is a possibility to formulate local theoretical conceptions relevant to individual types of catalysis.

The problem of estimation of the specific activity of a catalyst is of crucial importance. The well known Boreskov's rule on the approximately constant specific activities of catalysts of the same chemical compositions [194] may be regarded only as a statement of the chemical nature of a catalytic act which was formulated by Berthelot as far back as 1877: 'Owing to a chemical impact of contacting substances, intermediate compounds are formed which in turn are degraded as they emerge and eventually vanish in the final metamorphosis.[197] If the catalytic properties of compounds were determined solely by the chemical composition of active centres, then it would be absurd to expect that the same centres could display different activities, and no additional experiments would have been required.

The constancy of specific catalytic activity is approximate in the extent to which the total set of properties of the surface of catalysts is reproduced. The actual level of the development of the scientific bases underlying the preparation of catalysts does not allow high reproducibility. However, from the viewpoint of applied science this is not required in most cases. The term 'approximate constancy' means that the activity of catalysts is also influenced by other factors which were not denied by Boreskov either (see his monograph,[194] p. 47). In his opinion, these factors can induce differences in properties of individual facets of crystals and the non-equilibrium states of the catalyst's surface. But even the catalysts with completely the same chemical, structural and other characteristics would possess an approximate rather than absolute constancy of specific activity.

It is the role of additional factors which influences the specific catalytic activity that was the topic of our review. The activity of a catalyst with defects is somewhat higher than its activity in the equilibrium state. The degree of increase in activity depends on the amount of excess energy which is stored in defects and influences the catalytic properties through the variation of thermodynamic potentials. This amount of energy is determined by the physicochemical nature of the catalytically active sites.

The non-equilibrium structural and phase states of catalysts arising in the process of their preparation should be subject to annealing in the course of reaction, and the catalysts should pass to the steady state. However, there are numerous examples of rather high stability of such states of solid catalysts at elevated temperatures in real reaction media. This is explained by the fact that thermal annealing of defects is an activation process, and if the conditions do not permit overcoming of the activation barrier, some metastable structures of higher reactivity may exist for a rather long time.

Further studies of the nature of the structural factors and of their role in a chemical act will allow a deeper insight into the detailed mechanism of catalysis. The progress in this field can be achieved using novel MCA techniques and modern physical methods of research.

The review was supported by the Russian Foundation for Basic Research (Project No. 00-15-97440).

References

1. V V Boldyrev *Eksperimental'nye Metody v Mekhanokhimii Tverdykh Neorganicheskikh Veshchestv* (Experimental Methods in Mechanochemistry of Solid Inorganic Compounds) (Novosibirsk: Nauka, 1983)
2. P Yu Butyagin *Usp. Khim.* **53** 1769 (1984) [*Russ. Chem. Rev.* **53** 1025 (1984)]
3. E G Avvakumov *Mekhanokhimicheskie Metody Aktivatsii Khimicheskikh Protsessov* (Mechanochemical Methods of Activation of Chemical Processes) (Novosibirsk: Nauka, 1986)
4. G Heinicke *Tribochemistry* (Berlin: Akademie-Verlag, 1984)
5. P Yu Butyagin *Kinet. Katal.* **28** 5 (1987) [a]
6. G S Khodakov *Fizika Izmel'cheniya* (The Physics of Grinding) (Moscow: Nauka, 1972)
7. Yu T Pavlyukhin, Ya Ya Medikov, V V Boldyrev *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk* (2) 3 (1983)
8. S V Vossel', N T Vasenin, E E Pomoshchnikov, V F Anufrienko, V A Mikhailov *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk* (17) 102 (1986)
9. E L Gol'dberg, S V Pavlov *Sib. Khim. Zh.* (4) 147 (1992)
10. S V Pavlov, E L Gol'dberg *Sib. Khim. Zh.* (1) 126 (1993)
11. E L Gol'dberg, S V Pavlov *Sib. Khim. Zh.* (1) 131 (1993)
12. V A Radzig, A A Bobyshev, in *Catalyse et Environment. Techniques d'Analyses Physico-Chimiques Appliquees a la Catalyse. 7 Colloque Franco-Sovietiquee de Catalyse, Strasbourg, 1987* p. 172
13. G Natta, I Pasquon *Adv. Catal.* **11** 2 (1959)
14. G Natta, P Corradini, G Allegra *J. Polym. Sci.* **51** 399 (1961)
15. US P. 3 010 787; *Ref. Zh. Khim.* 4 L 139 (1963)
16. US P. 3 032 509; *Ref. Zh. Khim.* 15 T 39 (1963)
17. US P. 3 032 510; *Ref. Zh. Khim.* 15 T 40 (1963)
18. US P. 3 034 992; *Ref. Zh. Khim.* 20 L 123 (1963)
19. E G M Tornqvist, J T Richardson, Z W Wilchinsky, R W Looney *J. Catal.* **8** 189 (1967)
20. W R Carradine, H F Rase *J. Appl. Polym. Sci.* **15** 889 (1971)
21. Z W Wilchinsky, R W Looney, E G M Tornqvist *J. Catal.* **28** 351 (1973)
22. N Kashiwa *Polym. J.* **12** 603 (1980)
23. V A Zakharov, D V Perkovets, G D Bukatov, S A Sergeev, E M Moroz, S I Makhtarulin *Kinet. Katal.* **29** 903 (1988) [a]
24. V A Zakharov, D V Perkovets, G D Bukatov *Kinet. Katal.* **29** 1202 (1988) [a]
25. Yu G Shirokov, A P Il'in, I P Kirillov *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk* (7) 45 (1979)
26. USSR P. 1 235 523; *Byull. Izobret.* (21) 16 (1986)
27. A P Il'in, N N Smirnov, Yu G Shirokov, D V Afanas'v, in *Nauchnye Osnovy Prigotovleniya i Tekhnologii Katalizatorov (Tez. Dokl. II Vsesoyuz. Soveshch.), Minsk, 1989* [Scientific Foundations of the Preparation and Technology of Catalysts (Abstracts of Reports of the Second All-Union Meeting), Minsk, 1989] p. 91
28. Yu G Shirokov, A P Il'in, in *Nauchnye Osnovy Prigotovleniya Katalizatorov (Tez. Dokl. Vsesoyuz. Soveshch.), Novosibirsk, 1983* [Scientific Foundations of the Preparation of Catalysts (Abstracts of Reports of the All-Union Meeting), Novosibirsk, 1983] p. 56
29. Yu G Shirokov *Vopr. Kinet. Katal.* 3 (1984)
30. N N Smirnov, A P Il'in, E N Novikov, Yu G Shirokov *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* **32** (4) 83 (1989)
31. USSR P. 1 253 661; *Byull. Izobret.* (32) 46 (1986)
32. A P Il'in, A N Trofimov, Yu G Shirokov, in *Nauchnye Osnovy Prigotovleniya i Tekhnologii Katalizatorov (Tez. Dokl. II Vsesoyuz. Soveshch.), Minsk, 1989* [Scientific Foundations of the Preparation and Technology of Catalysts (Abstracts of Reports of the Second All-Union Meeting), Minsk, 1989] p. 93
33. Yu G Shirokov, A P Il'in, I P Kirillov, L I Titel'man, O P Khrutskii, O P Akaev *Zh. Prikl. Khim.* **52** 1228 (1979) [b]
34. A P Il'in, I P Kirillov, Yu G Shirokov *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* **22** 246 (1979)
35. V L Gartman, V G Ikonnikov *Vopr. Kinet. Katal.* 99 (1986)
36. V G Ikonnikov, L I Titel'man, O V Rastegaev, Yu G Shirokov *Vopr. Kinet. Katal.* 93 (1986)
37. URRS P. 1 301 483; *Byull. Izobret.* (13) 31 (1987)
38. S A Angelov, R P Bonchev *Appl. Catal.* **24** 219 (1986)
39. S A Angelov, R P Bonchev *Dokl. Bolg. Akad. Nauk* **40** 63 (1987)
40. S A Angelov, R P Bonchev, in *Heterogeneous Catalysis (Abstracts of Reports of the 6th International Symposium on Heterogeneous Catalysis), Sofia, 1987* Part 1, p. 394
41. L A Isupova, V Yu Aleksandrov, V V Popovskii, G N Kryukova, in *Proceedings of the 2nd Czechoslovakian Conference on Preparation and Properties of Heterogeneous Catalysts (Abstracts of Reports), Bechyne-near-Tabor, 1985* p. 74
42. L A Isupova, V V Popovskii, V Yu Aleksandrov, G N Kryukova, E M Moroz, V A Balashov in *Kataliticheskaya Ochistka Gazov (Tez. Dokl. 4-i Vsesoyuz. Konf.), Alma-Ata, 1985* [Catalytic Purification of Gases (Abstracts of Reports of the Fourth All-Union Conference), Alma-Ata, 1985] Part 1, p. 91
43. L A Isupova, V Yu Aleksandrov, V V Popovskii, E M Moroz *Zh. Prikl. Khim.* **61** 1976 (1988) [b]
44. I A Pauli, E G Avvakumov, L A Isupova, V A Poluboyarov, V A Sadykov *Sib. Khim. Zh.* (3) 133 (1992)
45. L A Isupova, V A Sadykov, L P Solovyova, M P Andrianova, V P Ivanov, G N Kryukova, V N Kolomiichuk, E G Avvakumov, I A Pauli, O V Andryushkova, V A Poluboyarov, A Ya Rozovskii, V F Tretyakov, in *Scientific Bases for the Preparation of Heterogeneous Catalysts (Abstracts of Reports of the 6th International Symposium), Louvian-La-Neuve, 1994* Vol. 2, p. 231
46. S L Kiperman, A A Balandin, I R Davydova *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 1482 (1957) [c]
47. V V Boldyrev, G V Golubkova, T F Grigor'eva, E Yu Ivanov, O T Kalinina, S D Mikhailenko, A B Fasman *Dokl. Akad. Nauk SSSR* **297** 1181 (1987) [d]
48. E Yu Ivanov, T F Grigor'eva, G V Golubkova, V V Boldyrev, A B Fasman, S D Mikhailenko, O T Kalinina *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk* (19) 80 (1988)
49. A B Fasman, S D Mikhailenko, O T Kalinina, E Yu Ivanov, T F Grigor'eva, V V Boldyrev, G V Golubkova *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk* (19) 83 (1988)
50. L G Nishchenkova, V P Gostikin, S V Litvinova, in *Vysokodispersnye Materialy na Osnove Platinovykh Metallov i Ikh Soedinenii v Katalize i Sovremennoi Tekhnike* (Highly Dispersed Materials Based on Platinum Metals and Their Compounds in Catalysis and Modern Technics) (Ivanovo: Ivanovo Chemical Technological Institute, 1991) p. 81
51. L G Nishchenkova, E Yu Ivanov, G V Golubkova, in *Vysokodispersnye Materialy na Osnove Platinovykh Metallov i Ikh Soedinenii v Katalize i Sovremennoi Tekhnike* (Highly Dispersed Materials Based on Platinum Metals and Their Compounds in Catalysis and Modern Technics) (Ivanovo: Ivanovo Chemical Technological Institute, 1991) p. 76
52. L G Nishchenkova, G V Golubkova, in *Vysokodispersnye Materialy na Osnove Platinovykh Metallov i Ikh Soedinenii v Katalize i Sovremennoi Tekhnike* (Highly Dispersed Materials Based on Platinum Metals and Their Compounds in Catalysis and Modern Technics) (Ivanovo: Ivanovo Chemical Technological Institute, 1991) p. 79
53. G V Golubkova, E Yu Ivanov, T F Grigor'eva *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk* (3) 60 (1990)
54. E Yu Ivanov, I G Konstanchuk, A A Stepanov, V V Boldyrev *Dokl. Akad. Nauk SSSR* **286** 385 (1986) [d]
55. V V Molchanov, A A Stepanov, I G Konstanchuk, R A Buyanov, V V Boldyrev, V V Goidin *Dokl. Akad. Nauk SSSR* **305** 1406 (1989) [d]
56. USSR P. 1 638 865; *Byull. Izobret.* (31) 226 (1996)
57. USSR P. 1 638 866; *Byul. Izobret.* (31) 226 (1996)
58. M I Volkov, E G Stepanov, L V Strunnikova, G R Kotel'nikov *Vopr. Kinet. Katal.* 100 (1986)
59. G R Kotel'nikov, L V Strunnikova, A S Okuneva, E G Stepanov, in *Ispol'zovanie Fiziko-Khimicheskikh i Matematicheskikh Metodov v Issledovanii Protsessov Polucheniya Monomerov i Sinteticheskogo Kauchuka* (The use of Physicochemical and Mathematical Methods in Investigation of Processes of the Preparation of Monomers and Synthetic Rubber) (Moscow: TsNIITENeftekhim, 1984) p. 26
60. M I Volkov, E G Stepanov, T N Sudzilovskaya, G R Kotel'nikov *Vopr. Kinet. Katal.* 36 (1984)
61. V V Molchanov *Khim. Promst* (7) 386 (1992)
62. T Shirasaki, Y Ochiai, K Muranaka *Kogyo Kagaku Zasshi* **71** 1363 (1968); *Chem. Abstr.* **70** 41 115 (1969)

63. N V Mal'tseva, G M Belotserkovskii *Zh. Prikl. Khim.* **56** 1009 (1983) [b]
64. S M Paramzin, Yu D Pankrat'ev, E A Paukshtis, O P Krivoruchko, B P Zolotovskii, R A Buyanov *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk* (11) 33 (1984)
65. S M Paramzin, O P Krivoruchko, B P Zolotovskii, R A Buyanov, V V Malakhov, G N Kryukova, N N Boldyreva *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk* (17) 39 (1984)
66. B P Zolotovskii, S M Paramzin, O P Krivoruchko, R A Buyanov *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk* (17) 80 (1987)
67. S M Paramzin, L M Plyasova, O P Krivoruchko, B P Zolotovskii, S V Bogdanov, G N Kryukova, E A Paukshtis, R A Buyanov *Izv. Akad. Nauk SSSR, Ser. Khim.* 1209 (1988) [c]
68. S M Paramzin, Yu D Pankrat'ev, V M Turkov, B P Zolotovskii, O P Krivoruchko, R A Buyanov *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk* (5) 47 (1988)
69. O P Krivoruchko, V M Mastikhin, B P Zolotovskii, S M Paramzin, D P Klevtsov, R A Buyanov *Kinet. Katal.* **26** 763 (1985) [a]
70. D P Klevtsov, O P Krivoruchko, V M Mastikhin, R A Buyanov, B P Zolotovskii, S M Paramzin *Dokl. Akad. Nauk SSSR* **295** 381 (1987) [d]
71. B P Zolotovskii, S M Paramzin, A G Pel'menshchikov, E A Paukshtis, D P Klevtsov, N V Ermolaeva, R A Buyanov, G M Zhidomirov *Kinet. Katal.* **30** 1439 (1989) [a]
72. S M Paramzin, B P Zolotovskii, O P Krivoruchko, V M Mastikhin, G S Litvak, R A Buyanov, L M Plyasova, D P Klevtsov *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk* (1) 33 (1989)
73. 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 (Tez. Dokl.), Novosibirsk, 1990* [Scientific Foundations of the Preparation and Technology of Catalysts (Abstracts of Reports), Novosibirsk, 1990] p. 108
74. B P Zolotovskii, S M Paramzin, V I Zaikovskii, R A Buyanov, L M Plyasova, V E Loiko, G S Litvak *Kinet. Katal.* **31** 751 (1990) [a]
75. S M Paramzin, B P Zolotovskii, V I Zaikovskii, R A Buyanov, V E Loiko, L M Plyasova, G S Litvak, V M Mastikhin *Kinet. Katal.* **32** 234 (1991) [a]
76. O P Krivoruchko, R A Buyanov, S M Paramzin, B P Zolotovskii *Kinet. Katal.* **29** 252 (1988) [a]
77. S M Paramzin, B P Zolotovskii, R A Buyanov, L M Plyasova, O N Novgorodova *Kinet. Katal.* **32** 507 (1991) [a]
78. B P Zolotovskii, R A Buyanov, S M Paramzin, L M Plyasova *Kinet. Katal.* **32** 1248 (1991) [a]
79. D P Klevtsov, V M Mastikhin, O P Krivoruchko, B P Zolotovskii, R A Buyanov, G N Kryukova, E A Paukshtis *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk* (9) 62 (1988)
80. D P Klevtsov, O P Krivoruchko, V M Mastikhin, B P Zolotovskii, R A Buyanov *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk* (2) 75 (1985)
81. D P Klevtsov, O P Krivoruchko, V M Mastikhin, E A Paukshtis, B P Zolotovskii, R A Buyanov *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk* (9) 70 (1988)
82. D P Klevtsov, B P Zolotovskii, O P Krivoruchko, R A Buyanov *Zh. Prikl. Khim.* **61** 914 (1988) [b]
83. D P Klevtsov, O P Krivoruchko, V M Mastikhin, B P Zolotovskii, R A Buyanov *React. Kinet. Catal. Lett.* **36** 319 (1988)
84. B P Zolotovskii, D P Klevtsov, S M Paramzin, R A Buyanov, in *Mekhanokhimicheskii Sintez v Neorganicheskoi Khimi* (Mechanochemical Synthesis in Inorganic Chemistry) (Novosibirsk: Nauka, 1991) p. 125
85. E G Avvakumov *Khim. Inter. Ustoich. Razvitiya* **2** 541 (1994) [e]
86. Russ. P. 2 019 513; *Byull. Izobret.* (17) 81 (1994)
87. Russ. P. 2 076 070; *Byull. Izobret.* (9) 151 (1997)
88. Russ. P. 2 076 071; *Byull. Izobret.* (9) 151 (1997)
89. Russ. P. 2 080 923; *Byull. Izobret.* (16) 78 (1997)
90. V V Molchanov, L M Plyasova, V V Goidin, O B Lapina, V I Zaikovskii *Neorg. Mater.* **31** 1225 (1995) [f]
91. V V Chesnokov, V I Zaikovskii, R A Buyanov, V V Molchanov, L M Plyasova *Kinet. Katal.* **35** 146 (1994) [a]
92. Russ. P. 2 042 425; *Byull. Izobret.* (24) 118 (1995)
93. Russ. P. 2 071 932; *Byull. Izobret.* (2) 162 (1997)
94. B M Pavlikhin, T V Kurchatkina, I A Zelepukhina, O P Greben'kova *Neftepererab. Neftekhim.* (3) 7 (1986)
95. V V Molchanov, V V Goidin *Khim. Promst* (12/13) 613 (1993)
96. E V Terlikovskii, V Yu Tretinnik, in *Fiziko-Khimicheskaya Mekhanika i Liofil'nost' Dispersnykh Sistem* (Physicochemical Mechanics and Lyophilicity of Dispersed Systems) (Kiev: Naukova Dumka, 1988) p. 79
97. R A Buyanov, V V Molchanov *Khim. Promst* (3) 151 (1996)
98. V V Molchanov, R A Buyanov, V V Goidin *Kinet. Katal.* **39** 465 (1998) [a]
99. E Yu Ivanov, Doctoral Thesis in Chemical Sciences, Institute of Problems of Materials Technology, Academy of Sciences, Ukr. SSR, Kiev, 1991
100. R Schrader, P Nobst, G Tetzner, D Petzold *Z. Anorg. Allg. Chem.* **365** 255 (1969)
101. R Schulz, A van Neste, P A Zielinski, S Boily, F Czerwinski, J Szpunar, S Kaliaguine *Catal. Lett.* **35** 89 (1995)
102. J Eckell *Z. Elecktrochem. Angew. Phys. Chem.* **39** 433 (1933)
103. G Rienäcker *Z. Elecktrochem. Angew. Phys. Chem.* **46** 369 (1940)
104. G Rienäcker, J Völter *Z. Anorg. Allg. Chem.* **296** 210 (1958)
105. L E Cratty, A V Granato *J. Chem. Phys.* **26** 96 (1957)
106. I Uhara, S Yanagimoto, K Tani, G Adachi *Nature (London)* **192** 867 (1961)
107. I Uhara, S Yanagimoto, K Tani, G-Y Adachi, S Teratani *J. Phys. Chem.* **66** 2691 (1962)
108. I Uhara, T Hikino, Y Numata, H Hamada, Y Kageyama *J. Phys. Chem.* **66** 1374 (1962)
109. I Uhara, S Kishimoto, T Hikino, Y Kageyama, H Hamada, Y Numata *J. Phys. Chem.* **67** 996 (1963)
110. I Uhara, S Kishimoto, Y Yoshida, T Hikino *J. Phys. Chem.* **69** 880 (1965)
111. S Kishimoto, M Nishioka *J. Phys. Chem.* **76** 1907 (1972)
112. S Kishimoto *J. Phys. Chem.* **67** 1161 (1963)
113. R Schrader, H Grund, G Tetzner *Z. Chem.* **3** 356 (1963)
114. R Schrader, G Tetzner, H Grund *Z. Anorg. Allg. Chem.* **342** 204 (1966)
115. R Schrader, G Tetzner, H Grund *Z. Anorg. Allg. Chem.* **342** 212 (1966)
116. R Schrader, G Tetzner, H Grund *Z. Anorg. Allg. Chem.* **343** 308 (1966)
117. G Tetzner, R Schrader *Z. Anorg. Allg. Chem.* **407** 227 (1974)
118. G Tetzner, R Schrader *Z. Anorg. Allg. Chem.* **409** 77 (1974)
119. R Schrader, H Grund, G Tetzner *Chem. Ing. Techn.* **39** 806 (1967)
120. R Schrader, W Staedter *Acta Chim. Acad. Sci. Hung.* **55** 39 (1968)
121. R Schrader, W Staedter, H Oettel *Chem. Techn.* **23** 363 (1971)
122. R Schrader, W Staedter, H Oettel *Z. Phys. Chem.* **249** 87 (1972)
123. G L Clark, R Rowan *J. Am. Chem. Soc.* **63** 1302 (1941)
124. R Paudert *Chem. Techn.* **17** 449 (1965)
125. R Paudert *Monatsber. Deutschen Akad. Wissenschaft.* **9** 719 (1967)
126. R Schrader, G Jacob *Chem. Techn.* **18** 414 (1966)
127. R Schrader, W Vogelsberger *Z. Anorg. Allg. Chem.* **368** 187 (1969)
128. R Schrader, G Tetzner *Z. Anorg. Allg. Chem.* **309** 55 (1961)
129. R Schrader, Z Kroll, S Seifert *Z. Anorg. Allg. Chem.* **336** 11 (1965)
130. R Schrader, E Thiem *Z. Phys. Chem.* **238** 41 (1968)
131. R Schrader, B Fritsche *Z. Anorg. Allg. Chem.* **379** 17 (1970)
132. R Schrader, J Deren, B Fritsche, J Ziolkowski *Z. Anorg. Allg. Chem.* **379** 25 (1970)
133. H Takahashi, K Tsutsumi *Dechema-Monographien* **57** 475 (1967); *Chem. Abstr.* **67** 76 995 (1967)
134. H Takahashi, K Tsutsumi *J. Chem. Soc. Jpn.* **71** 1345 (1968)
135. H Takahashi, K Tsutsumi *Rep. Inst. Ind. Sci. Univ. Tokyo* **20** 37 (1970); *Ref. Zh. Khim.* 9 B 1072 (1971)
136. Y Sadahiro *J. Soc. Mater. Sci. Jpn.,* **29** 125 (1980); *Ref. Zh. Khim.* 15 B 1297 (1980)
137. Y Sadahiro, K Shimidzu *Hokkaido Kyoku Daigaku Kiyo, Sect. 2A* **18** 26 (1967); *Chem. Abstr.* **70** 41 119 (1969)
138. Y Sadahiro, K Shimidzu *Zairyo* **17** 475 (1968); *Chem. Abstr.* **69** 68 540 (1968)
139. Y Sadahiro, K Shimidzu *J. Chem. Soc. Jpn.* **71** 1374 (1968)
140. Y Ogino, T Kawakami, K Tsurumi *Bull. Chem. Soc. Jpn.* **39** 639 (1966)
141. Y Ogino, T Kawakami, T Matsuoka *Bull. Chem. Soc. Jpn.* **39** 859 (1966)

142. S Nakajima, Y Ogino *Shokubai* **8** 287 (1966). *Chem. Abstr.* **69** 39 052 (1968)
143. Y Ogino, S Nakajima *J. Catal.* **9** 251 (1967)
144. T Ono, Y Ogino *Shokubai* **8** 284 (1966); *Chem. Abstr.* **69** 39 059 (1968)
145. Y Ogino, T Ono *Bull. Chem. Soc. Jpn.* **40** 2223 (1967)
146. A Uda, T Ono, Y Ogino *J. Chem. Soc. Jpn.* **71** 1352 (1968)
147. A Uda, T Ono, Y Ogino *J. Chem. Soc. Jpn.* **71** 1358 (1968)
148. Y Takamidzawa, T Ono, Y Ogino *J. Chem. Soc. Jpn.* **70** 1611 (1967)
149. Y Saito, M Ichimura, Y Ogino *J. Chem. Soc. Jpn.* **73** 266 (1970)
150. H Katsuzawa, H Saito, Y Saito, Y Ogino *Bull. Jpn. Petrol. Inst.* **13** 26 (1971); *Ref. Zh. Khim.* 23 B 1116 (1971)
151. S S Batsanov, G K Boreskov, G V Gridasova, N P Keier, L M Kefeli, V M Kudinov, V I Mali, I S Sazonova *Kinet. Katal.* **8** 1348 (1967) [a]
152. J Golden, F Williams, B Morosin, E L Venturini, R A Graham, in *Shock Waves Condensed Matter (Abstracts of Reports of AIP Conference), Menlo Park, 1981* p. 72; *Ref. Zh. Khim.* 18 B 1104 (1982)
153. S S Batsanov, V P Bokarev, I A Kostenchuk, Yu S Mardashev, I N Temnitskii *React. Kinet. Catal. Lett.* **20** 43 (1982)
154. A A Bobyshev, V B Kazanskii, I R Kibardina, V A Radtsig, B N Shelimov *Kinet. Katal.* **30** 1427 (1989) [a]
155. A A Bobyshev, V B Kazanskii, I R Kibardina, B N Shelimov *Kinet. Katal.* **33** 363 (1992) [a]
156. O V Krylov, A A Firsova, A A Bobyshev, V A Radtsig, D P Shashkin, L Ya Margolis *Catal. Today* **13** 381 (1992)
157. L A Isupova, V Yu Aleksandrov, V V Popovskii, V A Balashov, A A Davydov, A A Budneva, G N Kryukova *React. Kinet. Catal. Lett.* **31** 195 (1986)
158. L A Isupova, V Yu Aleksandrov, V V Popovskii, E M Moroz, G S Litvak, G N Kryukova *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk* (1) 39 (1989)
159. V A Sadykov, L A Isupova, S V Tsybulya, S V Cherepanova, G S Litvak, E B Burgina, G N Kustova, V N Kolomiichuk, V P Ivanov, E A Paukshtis, A V Golovin, E G Avvakumov *J. Solid State Chem.* **123** 191 (1996)
160. L A Isupova, V A Sadykov, I A Pauli, O V Andryushkova, V A Poluboyarov, G S Litvak, G N Kryukova, E V Burgina, L P Solov'eva, V N Kolomiichuk, in *Mekhanokhimiya i Mekhanokhimicheskaya Aktivatsiya (Tez. Dokl. Mezhdunar. Seminar), S.-Peterburg, 1995*[Mechanochemistry and Mechanochemical Activation (Abstracts of Reports of International Seminar), St. Petersburg, 1995] p. 24
161. V A Sadykov, L A Isupova, N N Bulgakov *Khim. Inter. Ustoich. Razvitiya* **6** 215 (1998) [e]
162. E M Moroz, S V Bogdanov, V I Zaikovskii, V V Molchanov, R A Buyanov *Kinet. Katal.* **30** 993 (1989) [a]
163. R A Buyanov, B P Zolotovskii, V V Molchanov *Sib. Khim. Zh.* (2) 5 (1992)
164. V V Molchanov, E G Avvakumov, in *Tez. Dokl. VI Vsesoyuz. Seminara po Dezyntegratornoi Tekhnologii, Tallin, 1989* (Abstracts of Reports of the Sixth All-Union Seminar on Disintegration Technology), Tallin, 1989] p. 61
165. E G Avvakumov, V V Molchanov, R A Buyanov, V V Boldyrev *Dokl. Akad. Nauk SSSR* **306** 367 (1989) [d]
166. R A Buyanov *Kinet. Katal.* **28** 157 (1987) [a]
167. V V Molchanov, R A Buyanov, E G Avvakumov, V V Boldyrev, in *Tez. Dokl. II Vsesoyuz. Soveshch. po Dezaktivatsii Katalizatorov, Ufa, 1989* (Abstracts of Reports of the Second All-Union Meeting on Deactivation of Catalysts, Ufa, 1989) Part 1, p. 3
168. A S Kharitonov, V B Fenelonov, T P Voskresenskaya, N A Rudina, V V Molchanov, L M Plyasova, G I Panov *Zeolites* **15** 253 (1995)
169. V V Chesnokov, V V Molchanov, E A Paukshtis, T A Konovalova *Kinet. Katal.* **36** 759 (1995) [a]
170. G C Stevens, T Edmonds *J. Less-Common Met.* **54** 321 (1977)
171. V A Zazhigalov, J Haber, J Stoch, L V Bogutskaya, I V Bacherikova *Appl. Catal. A, Gen.* **135** 155 (1996)
172. A Trovarelli, P Matteazzi, G Dolcetti, A Lutman, F Miani *Appl. Catal.* **95** L9 (1993)
173. V V Molchanov, G M Maksimov, L M Plyasova, V V Goidin, I V Kozhevnikov *Neorg. Mater.* **29** 555 (1993) [f]
174. Yu T Pavlyukhin *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk* (12) 45 (1987)
175. V Šepelák, K Tkácova, U Steinike, in *Proceedings of the International Conference on Environment and Mineral Processing, Ostrava, 1994* Part 1, p. 125
176. V V Molchanov, V V Chesnokov, R A Buyanov, N A Zaitseva, V I Zaikovskii, L M Plyasova, V I Bukhtiyarov, I P Prosvirin, B N Novgorodov *Kinet. Katal.* **39** 416 (1998) [a]
177. S V Tsybulya, G N Kryukova, S N Goncharova, A N Shmakov, B S Balzhinimaev *J. Catal.* **154** 194 (1995)
178. V I Bukhtiyarov, in *Interfacial Science* (Ed. M W Roberts) (Oxford: Blackwell, 1997) p. 109
179. G I Panov, G K Boreskov, A S Kharitonov, E M Moroz, V I Sobolev *Kinet. Katal.* **25** 123 (1984) [a]
180. R Schrader, G Glock, K Köhnke *Z. Chem.* **9** 156 (1969)
181. A V Bystrikov, A I Streletskii, P Yu Butyagin *Kinet. Katal.* **21** 1148 (1980) [a]
182. I V Kolbanev, I V Berestetskaya, P Yu Butyagin *Kinet. Katal.* **21** 1154 (1980) [a]
183. S Schönner, R Schrader, K-H Steinert *Z. Anorg. Allg. Chem.* **432** 215 (1977)
184. Y Tamai, S Mori *Z. Anorg. Allg. Chem.* **476** 221 (1981)
185. V A Kuznetsov, A G Lipson, D M Sakov, P V Fedenyuk, A M Shapiro, I K Martynov, I A Gagina, Yu P Toporov *Izv. Akad. Nauk SSSR, Ser. Khim.* 2730 (1990) [c]
186. G Heinicke, K Meyer, U Senzky *Z. Anorg. Allg. Chem.* **312** 180 (1961)
187. P A Thießen, G Heinicke, N Bock *Z. Chem.* **14** 76 (1974)
188. G Heinicke *Ropa Uhlie* **4** 150 (1962); *Chem. Abstr.* **57** 11 904 (1962)
189. G Heinicke, I Lischke *Z. Chem.* **3** 355 (1963)
190. G Heinicke, I Lischke *Z. Chem.* **11** 332 (1971)
191. S Mori, W-C Xu, T Ishidzuki, N Ogasavara, J Imai, K Kobayashi *Appl. Catal.* **137** 255 (1996)
192. P Yu Butyagin, A N Streletskii, O S Morozova, I V Berestetskaya, A B Borunova *Dokl. Akad. Nauk* **336** 771 (1994) [d]
193. V V Molchanov, R A Buyanov, V V Gojidin, in *The 2nd International Conference on Mechanochemistry and Mechanical Activation (INCOME-2) (Abstracts of Reports), Novosibirsk, 1997* p. 125
194. G K Boreskov *Geterogennyi Kataliz* (Heterogeneous Catalysis) (Moscow: Nauka, 1986)
195. M I Molotskii *Kristallografiya* **17** 1015 (1972) [g]
196. S A Zav'yalov, I A Myasnikov, L M Zav'yalova *Dokl. Akad. Nauk SSSR* **284** 378 (1985) [d]
197. A Mittasch, E Theis *From Davy and Döbereiner to Deacon. 50 Years of Heterogeneous Catalysis* (Berlin: Verlag Chemie, 1932)

[a] — *Kinet. Catal. (Engl. Transl.)*
[b] — *Russ. J. Appl. Chem. (Engl. Transl.)*
[c] — *Russ. Chem. Bull. (Engl. Transl.)*
[d] — *Dokl. Chem. Technol., Dokl. Chem. (Engl. Transl.)*
[e] — *Chem. Sustainable Devel. (Engl. Transl.)*
[f] — *Inorg. Mater. (Engl. Transl.)*
[g] — *Crystallogr. Rep. (Engl. Transl.)*