Mechanochemical Activation for Resolving the Problems of Catalysis[†]

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Abstract

The role of structure-energy properties of the mechanically induced defects of the crystal structure of heterogeneous catalysts is considered here. The main concepts of the effect of mechanochemical activation on the activity and selectivity of catalysts are theoretically stated. The most promising research trends are presented.

Keywords: mechanochemistry, catalysis, catalysis preparation change of activity and selectivity

1. Introduction and Definition of the Problem

The development of mechanochemical activation (MCA) of solids and the appearance of high-energy tense mills have shown the considerable promise of this method. In the last years, the possibilities of MCA have drawn the attention of specialists in catalysis.

During MCA, a solid (a catalyst in our case) accumulates excess potential energy as elastic and plastic deformations and a great variety of defects, which is accompanied by an increase in its reactivity. The reactivity of a system is universal in that a simultaneous decrease in its thermodynamic potential tend to a simultaneous decrease. This tendency can involve different relaxation channels, which allow synthesis of catalysts with new properties, reduction of the number of stages in its production, and also acceleration of the catalytic reactions.

In the present work we make an attempt to consider peculiarities of the synthesis process and the preparation of catalysts using MCA, the nature of its effect on catalytic activity and selectivity and thus to define the problem in detail.

2. Plausible MCA Applications in Catalysis

The Principle Sections of Catalysis are as Follows:

2.1. Development of the scientific basis of catalyst preparation.

The content of this division/section is determined by its main problem, i.e. development of the methods of preparation of catalysts with the desired properties. These are: specific surface area, porous structure, phase composition, crystallization degree, morphological properties of crystals, defectiveness, dispersion, thermal stability, structural and mechanical properties, component distributions on the supports, etc.

To solve the problem, one should investigate the physicochemical regularities which determine the features of synthesis and the action of materials during all stages of the method chosen for the preparation of separate families of similar materials, catalysts in our case¹⁾.

2.2. Development of the scientific basis for prediction of catalytic action

This section includes the most complicated and important problems, such as:

- Chemical nature, structure and mechanism of action of active sites during operation on the catalyst surface;
- Nature and relationships between the main and side reactions of catalytically active sites, the means and methods of influencing the above in order to increase selectivity towards the desired product;

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- Nature of the effect and input of physical characteristics of the catalyst surface. The role of defects and energy-non-equilibrium states in the chemical nature and efficiency of active sites;
- Stability, resistance, lifetime of the active sites and reasons for their deactivation.

Let us consider specific features and potentialities of MCA in catalysis.

3. Preparation of Catalysts using MCA.

3.1. Brief review of the theoretical and practical backgrounds of the MCA application for catalyst preparations.

Traditional preparations of heterogeneous catalysts include, as a rule, several stages and exhibit a number of serious disadvantages. Thus, reactivity is usually increased by performing processes in solutions or high-temperature treatments. As a result, the known methods do not meet the present-day ecological and energetic requirements.

The development of high-efficiency mechanical activators made it possible to use MCA as an independent and in some cases as the main stage for increasing the reactivity of the solids involved in the catalyst preparation.

A considerable body of articles, reviews and monographs^{2,9)} is devoted to the theory and practical applications of MCA in the preparation of multicomponent solid systems. In this application field, the emphasis is placed on the processes occurring in the bulk mass. Phenomena occurring on the solid surface are of secondary importance and only assume critical importance if one considers the nature of catalytic actions.

Catalysts are specific products. For this reason, their synthesis by the interaction of solids should take into account the requirements imposed on the characteristics of such a product. Nevertheless, the main and already stated theoretical basis remains. The concepts described in the above works are as follows.

The MCA-based preparation technologies of two- and multi-component solid systems involve chemical and other interactions between solid ingredients. The rate of interactions is limited by such parameters as contact area, mass transfer processes and activation barriers.

Dispergation of solid phases increases a ratio between particle surfaces and their volumes and thus

increases the total contact area between the solid phases.

It was established²⁾ that MCA reactions in the solid mixtures follow two regimes. At a low intensity of MCA, solids undergo crushing. In this case, the reaction rate depends on the number and area of contacts between the reacting particles. At a high intensity of MCA, we observed the regime of plastic deformation, at least of one reacting component. This results in a contact throughout the whole surface of a hard-to-grind material. Note that in the initial period, the chemical interaction of components is a limiting process stage. As the formed product layer begins to isolate the reacting products from each other, the diffusion mass transfer regime begins to define the reaction rate.

Under conditions of plastic deformation, the solid phase takes on the properties of «a quasi-liquid». This state is associated with the formation of dislocations, linear and point defects, anion and cation vacancies and the appearance of external and internal interfaces, i.e. total disorder of crystals. Available data³⁾ suggest that for the vacancy mechanism of material transfer, the diffusion coefficient is proportional to the vacancies concentration. As the intensity of MCA is sufficiently high, the saturation with defects reaches the point where a solid transforms into «a cold melting» state.

The tension gradient noticeably affects mass transfer in such dissipative systems. The non-equilibrium system is responsible for the formation of a broad structure, energy, chemical and physical variety depending on the MCA intensity. This extends the area of objects and potentialities which may be of interest for catalysis and catalysts.

Allied mixtures (ionic salts, metals) subjected to MCA may be mixed at the atomic level via a dislocation-diffusion mechanism. Thus, mass transfer of substance occurs due to plastic yielding and diffusions resulting from moving of linear and point defects.

It was shown³⁾ that under conditions of elastic crystal deformation, the excess energy of MCA is distributed throughout the volume of dislocations and defects. Such energy distribution is thermodynamically more efficient than the uniform distribution through all interatomic bonds. This peculiarity of the substance crystalline state defines the nature of MCA conversions.

Synthesis of multicomponent systems under MCA conditions should be considered with regard to the thermodynamics of the processes. During MCA, the reacting solid phases increase the free energy store

(isobaric potential) $\Delta G = \Delta U - T \Delta S$, which is associated with equilibrium constant K by equation $\Delta G = -RT \ln K$. Such a relationship permits a seemingly paradox conclusion that it is possible to create super-equilibrium systems. However, this paradox can be explained from the standpoint of thermodynamics. Under MCA conditions, the energy of the reacting phases significantly differs from the reference data corresponding to the standard conditions. For this reason, non-equilibrium systems can appear under such conditions. As the energy stops dissipating, such energy-intensive systems undergo an extinction relaxation process towards standard characteristics. This is an activation process. Owing to internal friction and retardation of atoms, relaxation decays and complete equilibrium is not attained. A metastable non-equilibrium system appears^{7,9)}.

It is pertinent to note that some individual crystal materials, which were treated by MCA but did not experience chemical conversion, change their structure and properties to an extent that they could be taken as new substances having the composition of the initial substance.

This brief description of the present-day concepts of the mechanism, regularities and peculiar features of MCA is aimed at promoting an interest in this promising method and its application in the development of a scientific basis of the preparation technologies of catalysts¹⁾.

Let us mention some areas where significant results have been already obtained:

1. Changes of the technology stages employing solutions by the mechanically activated homogenization of systems or mechanical alloying, which permits one to obtain new structures and prevent ecologically harmful waste. The performance of direct synthesis of catalysts under MCA conditions (mechanochemical synthesis).
2. Syntheses of new solid materials (catalysts) due to an increase in the reactivity of the reacting solid phases under MCA conditions.
3. Preparations of non-equilibrium solid systems that cannot be prepared by traditional methods, including solid solutions whose concentrations are significantly higher than the equilibrium one.
4. A decrease in temperature and provision of an easy interaction of phases during further treatments as calcination, hydration, sorption, reduction, etc.
5. A decrease in the temperature of the synthesis of binary and more complex systems owing to MCA, resulting in improved structural and other characteristics.

6. Modifications of operation properties (formability, strength, texture, etc.).
7. Preparations of highly dispersed and nano-sized systems.
8. Simplifications of technologies by reducing the number of stages and aggregate costs.

3.2. Some results of MCA applications for catalyst preparations

We want to present several examples and researches to illustrate the potentialities of MCA in the preparation of catalysts.

Thus, by exposing the powder mixtures of metallic magnesium and iron group metals to MCA, it is possible to obtain a number of mechanical alloys that after subsequent hydrogenation in a hydrogen medium at 10-17 atm, permit the synthesis of new intermetallic hydrides Mg_2MH_x (where $M = Co, Fe$ and $x = 5 \div 6$). These hydrides are unique catalysts of the hydrogenation of acetylene and diene hydrocarbons to mono olefins, the process selectivity being about 100%¹⁰⁾. The mechanism of hydrogenation has been established. Hydrogenation follows the stage mechanism in the low-temperature region and the heterogeneous-homogeneous radical mechanism at relatively high temperatures¹¹⁾.

The mechanochemical activation of the metal powders at a hydrogen pressure of 100 atm permitted the synthesis of two formerly unknown intermetallic hydrides as Mg_2NiH_6 and $MgCuH_2$ exhibiting hydrogenating abilities¹²⁾.

It was established that MCA strongly affects the properties of supports as well as nickel chlorides and nickel metals supported on them.

For Al_2O_3 , TiO_2 , ZnO , and $ZnAl_2O_4$, the following phenomena were observed: (1) an increase in the sorption ability of the supports regarding the metal; (2) a decrease in the temperature of reduction of nickel chloride with hydrogen by 200-300°, and (3) an increase in the activity of the supported metals in a number of catalytic reactions. MCA of $\gamma-Al_2O_3$ makes it possible to increase coke resistance, dispersion of the supported metals and catalytic activity of the supported catalysts^{13, 14)}.

We suggest a new synthesis method of heteropoly acids from molybdenum, tungsten and vanadium oxides. The method is very efficient for the synthesis of phosphorous-vanadium-molybdenum and phosphomolybdic acids. In contrast to the traditional syntheses including 6-8 stages, our method involves only 2-3 stages: MCA of oxides or their mixtures and the interaction with an aqueous phosphoric acid. We

synthesized a number of heteropoly acids described by the following formulae:

and $\text{H}_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$, where $M=\text{Mo}$ or W , and $m = 0 \div 4$. These HPA are efficient catalysts in a series of commercial processes¹⁵⁾.

We have developed an absolutely new catalytic system based on the metal particles that are definitely incorporated into carbon filaments via the catalytic decomposition of hydrocarbons on such particles. The as-prepared catalysts make it possible to perform a number of catalytic processes.

Dispersed particles of the iron group metals and their alloys with some other metals were prepared by mechanical grinding of the corresponding metal oxides in high-power activators with subsequent reduction. To prevent sintering of the metal particles, the substances with a layer-type structure, i.e. magnesium or aluminum hydroxides, were introduced into the activated mixture¹⁶⁾.

MCA enabled the synthesis of new alumina forms such as $\pi\text{-Al}_2\text{O}_3$. This crystal modification results from dehydration of the mechanically activated gibbsite. The modification is characterized by a layer structure similar to that of gibbsite and the presence of four, five and six coordinated ions. Two neighboring ions Al(III) , that are five-coordinated towards oxygen, are paired Lewis centers exhibiting catalytic activity^{17, 18)}.

It was established that the preliminary activation of gibbsite, boehmite and bayerite reduces the temperature of their phase transfer into corundum by 200-300°¹⁸⁾.

For the analysis of some components polluting an environment, the conducting composites possessing catalytic properties are required. One of such systems is the composite nano-sized platinum and conducting carbon. Works on the synthesis of such systems by a mechanochemical activation method have been started.

The sample of conducting carbon black of mark E-245 was impregnated with a water solution of H_2PtCl_6 , dried at 1200 C and then exposed to mechanochemical activation in a planetary mill AGO-2 at a rotational speed of the barrels of 10 s⁻¹. The analysis of products was carried out by XRD. Mechanical activation of a mix of carbon black and H_2PtCl_6 results in a reduction of the last up to metal platinum. The particle size of platinum determined by XRD is 5 nm. Catalytic activity was determined in a modeling reaction of hydrogenation of butadiene in a flowing installation at speeds of hydrogen - 7 l/hour and bu-

tadiene - 1.4 l/hour. The temperatures of reaction were 80-1800 C. A shot of the catalyst - 0.5 g. Before definition of catalytic activity, samples of catalysts were reduced in a current of hydrogen at temperatures between 250 and 3500C. The obtained sample displays catalytic activity in reaction of hydrogenation of butadiene. After the reduction of a sample at 350 °C, conversion of butadiene makes 78%, selectivity on butenes of 68%, on butane - 32%.

4. Development of Concepts of the MCA Effect on the Activity and Selectivity of Catalysts

4.1. The problem description

In section 2.2, we presented the main problems whose solution will make it possible to develop a theory for predicting the catalytic actions. However, the task is complicated by the fact that a traditional problem definition also involves phenomena of the MCA system.

In this context, we suggest two possible applications of MCA for increasing catalytic action¹⁹⁾:

1. Effect on the catalytic properties of the preliminary MCA treatment of a catalyst. In this case, the action of MCA manifests itself in as much as a partially relaxed catalyst system preserves some part of its defectiveness and the excess free energy associated with it.
2. Effect on the catalytic properties of MCA during the catalytic process. In this case, manifestation of the MCA action depends on the power density of MCA, i.e. on the level of energy dissipation and properties of the catalyst dissipation state.

Catalysis occurs on the surface of heterogeneous catalysts. The properties of the atoms on the solid surface differ from those in the solid bulk. Their reactivity is affected by steric and power properties of the defects on the surface. For this reason we are primarily interested in the phenomena and processes occurring on the surface under MCA action^{5, 8)}.

In some reports, defects in the crystal structure are given with a catalytic action, whereas the chemical nature of the catalytic action is not mentioned at all. Meanwhile, catalytic action is based on the formation of a chemical intermediary (active complex) on the surface. In other words, catalysis is a chemical phenomenon. The question now arises: What are the relations and the input of chemical and structure-energy components into the nature and properties of catalytically active centers? This question can be subdivided into a number of specific questions as:

1. What is the nature of the MCA effect on the activ-

- ity of the catalysis centers?
2. Are there individual active centers of the target and side reactions?
 3. Can MCA destroy active centers or initiate generation of alternative active centers?
 4. If 100% conversion of the initial product is composed of selectivity of the desired and by-products, can we use MCA to control selectivity of the desired product, etc.?

At present, definition of the above questions is still underway and there are no unambiguous answers to the above questions. We have just indicated the problems as guidelines to assist in the performance of future researches.

4.2. Brief review of the information concerning the MCA effect on the activity and selectivity of catalysts

The nature of chemical bonds in the crystal lattice defines physicochemical properties of solids, including reactivity. This nature varies over a wide range: ionic, covalent, metallic, molecular, hydrogen. MCA affects chemical bonds in different ways. These are responsible for anisotropy of the properties of crystals and distinctions between different crystal faces in surface energy and reactivity.

Catalytic action in heterogeneous catalysis begins with adsorption or chemisorption of the reacting molecules. The processes rely on the chemical nature of bonds. The solid surface of catalysts is energetically and chemically inhomogeneous. As a consequence of chemical inhomogeneity in the composition and bonds saturation, the interaction with the molecule surface results in complexes with different binding energies. The catalytic action itself significantly depends on the energy properties of the adsorbed complexes, i.e. on the properties of the surface where the reacting molecules are adsorbed.

During MCA, the range of inhomogeneity of the catalyst surface properties sharply increases, which extends the variety of active centers.

In our case, the question of the nature and mechanisms of MCA's effect on the efficiency of active centers is reduced to the explanation of a relationship between structure-energy properties of an active center and its reactivity. Furthermore, one should assume that different defects (i.e. carriers of excess energy in the solid) have a different effect on the chemical, catalytic and other properties of catalysts.

Relaxation in a heterogeneous catalyst structure can proceed through several channels of different natures. However, the main reason of increasing

catalytic activity is that a feature of the defects in the crystal structure. The system tends to minimize its free energy by localizing it on the defects³⁾. Such distribution of free energy is thermodynamically more efficient than the uniform distribution of elastic stresses throughout the crystal lattice bonds. As follows from ref. ⁸⁾, the chemical activity of the catalytic centers is increased by extended defects such as interblock boundaries formed by dislocation array and shift defects resulting from shifts and turns of the layers. Such areas are characterized by maximal concentrations of the surface atoms with unsaturated bonds and increased reactivity. An increase in free energy of the above areas reduces a potential barrier of activation of the catalytic reactions.

One would expect the highest effect of MCA on the catalytic activity from a combination of a catalytic action and MCA. In this case, a catalytic system can be approximately treated as a dissipative one²⁰⁾. The system state will depend on the intensity of energy dissipation. On each dissipation level, the corresponding dynamic order and a non-equilibrium stationary structure will appear. Thus, as the process of catalysis and MCA action are used at the same time, one may speak about a statistically defined set of the system dynamic states with its own potentials. These states appear only in the area of impact action, but not in the whole bulk of particles. For this reason, the observed increase in catalytic activity should be attributed to the input of this area alone.

Pulse action of MCA on the catalyst is responsible for two counter processes, occurring in the system at each instant of time, i.e. deformation accompanied by increasing free energy and relaxation. For each constant regime of MCA, the processes come to equilibrium. Owing to self-organization, the structure of the system assumes both spatial order and specific properties, including catalytic ones.

A dynamic equilibrium between all defects depends on the intensity of dissipation (MCA)⁹⁾. After MCA, the process of relaxation occurs accompanied by condensation of the dispersed defects in linear and planar formations. Note that a possibility to obtain states with different defect saturations depends on the MCA intensity and the type of chemical bonds in a solid. As the MCA action decreases, the main part is played by the rate of "hardening" in the relaxation process. One can suggest that after MCA, the rate of relaxation is described by equations as one of radio-active elements half-life.

Relaxation energy can be rather high due to the conversion of elastic energy into vibration energy.

For this reason, an excited bond can initiate a chemical reaction. Annihilation of the structural defects is accompanied by release of the energy sufficient for the electron excitation and bonds destruction, which also increases activity of the catalytic centers^{3, 4)}. In any case, the as-activated catalytic complex acquires some excess energy providing a penetration of the potential barrier of a catalytic reaction. This is a manner in which a specific channel of energy relaxation (here it is a catalytic reaction) acts. Qualitative analysis of the varying thermodynamic and kinetic parameters of the catalytic processes under MCA conditions¹⁹⁾ has shown that catalyst activity should increase if the nature of active centers does not change. In this case, selectivity can vary with the relation between the rates of main and side reactions. Some information on the nature of selectivity can be received by studying correlations between the rates of separate reactions and the presence of the corresponding structural defects.

As MCA is combined with a catalytic process, a special channel for the process performance appears. Under these conditions, fresh surfaces with broken and distorted bonds, where active centers have a radical character, are continuously generated. The appearance of excited atoms on the above surface determines their reactivity. The lifetime of these atoms is comparable with the rate of chain breaking. In this case, the reaction with gas proceeds without activation²⁾. Radical reactions are defined by the rate of formation and spending of active centers that is proportional to the rate of reproduction of fresh surfaces. The centers are destroyed via: spontaneous annihilation and interaction with gases during the catalytic act²⁾.

4.3. MCA as a means of affecting both the activity and selectivity of catalysts

In ref.⁸⁾ we presented a detailed analysis of the publications that consider the effect of MCA on the activity and selectivity of catalysts. The present article considers a number of new examples.

Thus, the performance of catalytic reactions under

MCA conditions permits an increase in activity and selectivity and an essential extension of the range of plausible processes. Of particular interest are new potentialities of the MCA performance under reaction medium pressure: synthesis of new compounds, selective performance of catalytic reactions in the solid phase, new efficient ways of reactions performance. Thus, the hydrogenation in the solid phase of a number of organic compounds promotes a selective reduction of functional groups and unsaturated bonds. The most illustrative example is the hydrogenation of caryophyllene- α -oxide (**Scheme 1**). The activation of caryophyllene- α -oxide (I) for 10 min at the barrels' rotational frequency of 10 s⁻¹ in the presence of the hydride Mg₂NiH₄ at hydrogen pressure 5 atm leads to hydrogenation of the double bond and the quantitative transformation into dihydrocaryophyllene- α -oxide (II). An increase of MCA time to 90 min under the same conditions leads to the reduction of the epoxy group to form a hydroxyl group at a selectivity of 90%. Fourteen isomers of alcohols (III) are formed. Finally, at a barrel speed of 17 s⁻¹, the complete removal of hydroxyl groups occurs within 20 min resulting in the formation of dihydrocaryophyllene (IV). According to the data of X-ray phase analysis, no changes in the composition of hydride occur. Hence we may suppose that catalytic hydrogenation of caryophyllene- α -oxide takes place.

The MCA of 2-methylnaphtalene for 30 min at a hydrogen pressure of 20 atm (barrels' rotational frequency 17 s⁻¹) in the presence of hydride Mg₂NiH₄ results in hydrogenation of one of the benzene rings with the formation of a mixture of tetralines (**Schematic 2**).

Quantitative transformation of benzamide into benzamine observed on the hydride Mg₂NiH₄ after MCA for 30 min at barrels' rotational frequency of 17 s⁻¹ and hydrogen pressure of 15 atm (**Schematic 3**).

The high efficiency this method demonstrate for the hydrogenation of. The MCA of a number of nitroaromatic compounds for 30 min at hydrogen pressure of 50-100 atm (barrels' rotational frequency 17 s⁻¹) in the presence of hydride Mg₂NiH₄ results in

Schematic 1.

Schematic 2.

Schematic 3.

hydrogenation of nitro groups with the formation of corresponding amines (**Schematic 4**).

This method also demonstrates a high efficiency for the reaction of catalytic oxidation. The MCA of organic solids at pure oxygen pressure 30-80 atm in the presence of transition metal oxides results in full oxidation. This phenomenon may be used for the sterilization of toxic substances including poisonous gases. The hexamethylphosphoramide was used as a model poisonous gas (**Schematic 5**). The oxides of iron and manganese were used as catalysts.

The reactions of partial oxidation take place if the high pressure in the barrels is created by the mix-

ture of oxygen and inert gases (argon, nitrogen). The following reactions of partial oxidation were realized (**Schematic 6**):

Ursolic acid was oxidized at elevated oxygen pressure²¹. The structure of ursolic acid (**Schematic 7**) allows the synthesis of biologically active substances.

Practically all the known derivatives of ursolic acid exhibit physiological activity. Possible syntheses are hindered because of the low reactivity of ursolic acid. The development of methods to integrate ursolic acid into chemical processes will open the way for new large-scale sources of raw materials for the chemical industry, because this acid is present in a series of

Schematic 4.

Schematic 5.

Schematic 6.

plants in large amounts. Investigation of the catalytic oxidation of ursolic acid was carried out under MCA, increased oxygen pressure and the use of traditional metal oxides as catalysts (MnO_2 , Fe_2O_3 , WO_3). Four compounds are the major oxidation products after the reaction under MCA, increased oxygen pressure

and MnO_2 as the catalyst. Fragments of the structural formula of ursolic acid that undergo transformation during oxidation are shown in **Schematic 7**.

Ursolic acid amide was obtained at elevated ammonium pressure. Cooper salts were used as catalysts. Without solvents, the amide yield was no higher

Ursolic acid

Schematic 7.

than 8-10%. Amination in the presence of methanol or acetic acid as the solvent made it possible to obtain amide of ursolic acid at a yield of 65% (Schematic 9).

Under the same conditions but without the catalysts, ammonia salt of ursolic acid was obtained.

The phthalimide was obtained (Schematic 10) by amination of phthalic anhydride at ammonia pressure 10 atm.

The reactions of hydro-dechlorination of toxic chlorine aromatic compounds, including complete destruction of 1,2,3,4-tetrachlordibenze-p-dioxin (Schematic 11), were performed²¹.

Of particular interest is the catalytic action of ammonia observed in the synthesis of intermetallic compound hydrides performed during mechanochemical activation of the reacting metals at the gas-phase pressure ($H_2 + 5\% NH_3$). Adding ammonia into the hydrogen medium made it possible to change the mechanism and the rate of formation of nickel-magnesium intermetallide hydrides. Ammonia was adsorbed on the solid activated particles (reaction

Schematic 8.

Schematic 9.

Schematic 10.

Schematic 11.

participants), was activated by them and provided the stage mechanism for the transfer of hydrogen atoms²³⁾.

It was established²⁴⁾ that the specific rate of oxidation of CO on TiO₂ linearly depends on the concentration of crystal shear planes which was measured by ESR of Ti₂⁷⁺ dimers (**Fig. 1**). This dependence can be considered as unambiguous proof of the role of extensive defects.

MCA tripled the specific catalytic activity of zinc oxide in the reaction of CO oxidation. This was accompanied by an essential decrease of activation energy, which indicated the generation of alternative active centers. This observation was associated with the formation of low-angle interblock boundaries and the appearance of exits of dislocations and packing defects onto the surface. The linear dependence of the specific rate of oxidation of CO and the quantity of microstrange was established (**Fig. 2**). The ions of Zn²⁺ involved in the defects are the centers of chemisorption of oxygen, which is a catalytically active cen-

ter providing the stage mechanism of CO oxidation. It was also established that point defects do not affect the activity of ZnO in this reaction²⁵⁾.

Experimental evidence was obtained that the stacking fault generated during MCA of zinc ferrite is responsible for increasing the specific rate of CO oxidation. The linear relationship of the specific rate of CO oxidation is observed from the concentration of defects determined by Moessbauer spectroscopy (**Fig. 3**) and X-ray diffraction (**Fig. 4**) methods.

Of special interest are our recent results (unpublished) concerning the changes in catalyst selectivity towards desired and by-products caused by MCA action. The results prove the possibility of generating one active center and the annihilation of other centers. It was established that MCA affects the selectivity of vanadium oxide in the oxidation of formaldehyde into formic acid and by-products. In addition, the selectivity of zinc oxide changes in the conversion of isopropyl alcohol, which follows two routes such as

Fig.1 Dependence of the specific rate of CO oxidation vs. concentration of shear plane.

Fig.2 Dependence of the specific rate CO oxidation on the quantity of microstrange.

Fig.3 Dependence of the specific rate CO oxidation vs. the concentration of stacking fault measured by Moessbauer spectroscopy.

dehydrogenation yielding acetone, and dehydration resulting in propylene.

In both cases, the selectivity was changed by the formation of aprotonic acid centers under MCA action and a decrease in the number of protonic acid centers.

The comparison of the effect of MCA on properties of solids indicates that the same mechanically induced defects of the crystal structure exhibit a higher activity in the three chemical processes differing by their nature and mechanisms: simple chemical transformations, sorption and catalysis (**Table 1**).

Fig.4 Dependence of the specific rate CO oxidation vs. the concentration of stacking fault measured by X-ray diffraction.

Table 1 Influence of defects in the catalyst structure on chemical processes

Catalyst	Chemical transformation	Sorption	Catalytic reaction
ZnO	Oxidation-reduction	O ₂ , H ₂ Se, Ni ²⁺	Oxidation of CO
TiO ₂	Oxidation, dissolution in acids	Ni ²⁺	The same
ZnAl ₂ O ₄ , ZnFe ₂ O ₄	Leaching	Ni ²⁺ , H ₂ S	The same
Fe ₂ O ₃	Dissolution in acids	H ₂ S	The same
V ₂ O ₅	Dissolution in hydrogen peroxide	NH ₃	Oxidation formaldehyde to formic acid

In the literature there are not so many works on the application of MCA in catalysis. We summarized these works in tables. In **Table 2**, works on the preparation of catalysts using MCA are given. In **Table 3**, works on the influence of MCA on catalytic properties are given.

5. Conclusions

Our review considers the role of structure-energy properties of the mechanically induced defects in the crystal structure of the heterogeneous catalysts. The main theoretical concepts of the effect of MCA on the activity and selectivity of catalysts are stated. We considered the most promising trends in the research activities in this field. The use of literary and our own data on high-performance MCA in three areas makes it is possible to judge:

- Preparation of catalysts with decreasing power

consumption, less time for synthesis and the absence of a harmful drain

- Increase of the activity and change of the selectivity of catalysts after MCA
- Performance of catalytic reactions using MCA with the quantitative yields and high selectivity

The increasing interest in MCA applications in catalysis reflects the tendencies in this field. There is good reason to believe that the basic researches of the nature and mechanisms of MCA actions performed in all divisions of the science of catalysis and catalysts will promote general progress in the practical realization of the method.

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Table 2 Results of the MCA application for the preparation of catalysts

Initial product	Final product or derived result	Apparatus for MCA	Additional effects	Reference
α -TiCl ₃ , γ -TiCl ₃	δ -TiCl ₃	BM	Increased activity in the reaction of propylene polymerization	26, 27
TiCl ₃ +AlCl ₃ +R ₃ Al	δ -TiCl ₃	BM	–	28
TiCl ₃ +AlCl ₃	Solid solution with δ -TiCl ₃ structure	BM	Increased activity in the reaction of ethylene polymerization	29-31
TiCl ₄ +MgCl ₂	Fixation of TiCl ₄ on the MgCl ₂ surface	BM	ditto	32-34
α -Fe ₂ O ₃ or α -Al ₂ O ₃ +H ₂ CrO ₄ , Catalysts of vapor conversion of CO		–	Increased activity, enhanced strength	35, 36
Fe ₂ O ₃ +H ₂ CrO ₄				
ZnO+H ₂ CrO ₄	Catalyst of methanol synthesis		Increased activity	37, 42
MgO+Cu ²⁺ in ACS	Catalysts of vapor conversion of CO	BM	Increased activity	38
H ₂ CrO ₄ +Al(OH) ₃ +ZnO+CuCO ₃ × Cu(OH) ₂	Catalyst of vapor conversion of CO		Increased activity	39
CuAl ₂ O ₄ +ethanol or acetone solution	Improved quality of binding agent	–	Enhanced strength	40
ZnO+Al ₂ O ₃ in ACS	Sulfur adsorbent	–	Enhanced strength, increased sulfur capacity	41
ZnO	The same	VM, PM	The same	43, 44
Cu(OH) ₂ CuCO ₃ + ZnO	Solid solution Zn-Cu-O	PM		45
Cu(OH) ₂ CuCO ₃ + Ni(OH) ₂ NiCO ₃	Solid solution Ni-Cu-O	PM		46
Al(OH) ₃ +CuO, MgO, ZnO, CaO, Cu(OH) ₂ CuCO ₃	Amorphization of aluminum hydroxide	PM	Substitution of the wet method of aluminum hydroxide preparation	47
CoO+CuO	Catalyst of after-burning	PM		48, 49
CuO, Co ₃ O ₄	Improved capacity for founding by extrusion	PM	Increased activity in CO oxidation, resistance to poisoning with SO ₂	50
La ₂ O ₃ +Co ₃ O ₄ , La ₂ (CO ₃) ₂ +CoCO ₃ × Co(OH) ₃	LaCoO ₃ (catalyst of after-burning of gas emissions)	PM	Increased CuO activity in butane oxidation	51
La ₂ O ₃ +Mn ₂ O ₃ (or MnO ₂ or Mn ₃ O ₄)	LaMnO ₃ (catalyst of after-burning of gas emissions)	PM	–	52
Al-Ni (alloy)	Raney Ni	VM		53
Ni+Al	Alloys, precursors of Ra/Ni	PM	Increased activity in cyclohexene hydrogenation, Pr ⁱ OH dehydrogenation	54-57
Ni+Al+M (M = V, Cr, Mn, Fe, Co, Mo, W)	Modified Raney nickel	PM	Increased activity in reactions of hydrogenation	58
Ra/Ni (used)+Al	Ra/Ni		ditto	59
M ₂ CO ₃ +Fe ₂ O ₃ (M = K, Rb, Cs)	Catalyst of ethylbenzene dehydrogenation	DS	ditto	60,61
Aluminum hydroxides+SiO ₂	Aluminosilicates, zeolites	PM	Increased activity, enhanced strength	62,63
Ca-Cr-Ni-phosphate catalyst IM-22O ₄	Regulation of the processes of crystallization and baking	PM	–	64
			Enhanced strength	

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

Table 3 Influence of MCA on catalytic properties of various compounds

Catalyst	Reaction	Active centre	Reference
Cu	Dehydrogenation of ethanol	Dislocations	65
Ni	Hydrogenation of cinnamic acid, dehydrogenation of ethanol, decomposition of H ₂ O ₂ , <i>ortho-para</i> conversion of hydrogen	Vacancies, dislocations	66, 67
Ag	Decomposition of formic acid, decomposition of H ₂ O ₂ , oxidation of ethanol	Dislocations	68
Au	Decomposition of H ₂ O ₂	ditto	69
Pt	Decomposition of formic acid, hydrogenation of cinnamic acid	Point defects, dislocations	70
Co	Decomposition of H ₂ O ₂ , hydrogenation of benzene	Defects and distortions of the structure	71, 72
Ni	Hydrogenation of benzene	Distortions of the lattice	73, 74
Ni	Hydrogenation of phenol and mixtures of higher unsaturated alcohols	ditto	75
Ni	Hydrogenation of fats, <i>ortho-para</i> conversion of hydrogen	Dislocations	76, 77
V ₂ O ₅	Oxidation of SO ₂ to SO ₃	Distortions of the lattice	78
Fe ₂ O ₃ , Fe ₃ O ₄	The same	ditto	79
Fe ₂ O ₃ , Fe ₃ O ₄	Oxidation of CO	–	80
Fe ₂ O ₃ , Fe ₃ O ₄	Vapor conversion of CO	Distortions of the lattice	81
CuO	Decomposition of N ₂ O, <i>ortho-para</i> conversion of hydrogen	Defects of the lattice	82, 83
CaO	Decomposition of N ₂ O	ditto	84
NiO	Decomposition of H ₂ O ₂	Distortions of the lattice	85
KHSO ₄	Polymerization of acetaldehyde	New acidic centers	86
H ₂ WO ₄	Hydration of propylene	New proton centers	87
Cr ₂ O ₃ + CuO or ZnO	Dehydrogenation of PriOH	Distortions of the lattice	88, 89
TiO ₂ , ZnO, BaTiO ₃ , NiO	Oxidation of CO	Anionic vacancies	90
TiO ₂ + WO ₃ , TiO ₂ + Fe ₂ O ₃ , TiO ₂	ditto	Distortions of the lattice	91
CaF ₂	Dehydrogenation and dehydration of PriOH	–	92
V ₂ O ₅ + SiO ₂	Oxidation of methane to formaldehyde	–	93
CuO	Oxidation of butane	Surface Cu ⁺ ions	94
Co ₃ O ₄	ditto	Excess oxygen	95
Fe ₂ O ₃	Oxidation of CO	Defects with a local symmetry of spinel	95, 96
MnO ₂ , MnO, Mn ₃ O ₄ , Mn ₂ O ₃	ditto	Extended defects, steps	95

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