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Mechanochemical activation as a tool of increasing catalytic activity

Roman A. Buyanov [a], Victor V. Molchanov [a,*], Vladimir V. Boldyrev [b]

[a] Boreskov Institute of Catalysis, Siberian Branch of Russian Academy of Sciences, Prospekt Akademika Lavrentieva 5, Novosibirsk 630090, Russia
[b] Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of Russian Academy of Sciences, Novosibirsk 630090, Russia

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ABSTRACT

The role of structure–energy properties of mechanically induced defects in the crystal structure of heterogeneous catalysts is considered. The main concepts of the mechanochemical activation effect on the activity and selectivity of catalysts are discussed. The wasteless and energy-saving methods of preparation of some catalysts are presented. Rigorous experimental proofs of the influence of defects in the crystal structure of catalysts on their specific catalytic activity are obtained. High performance of mechanochemical catalysis application for hydrogenation, oxidation, amination and hydroalumination processes is shown. For the first time catalytic reactions under the conditions of mechanochemical activation at elevated temperature and increased pressure of gases are carried out.

1. Introduction and definition of the problem

The development of mechanochemical activation (MCA) of solids has shown its considerable promise for the preparation of catalysts with novel properties and improvement of the catalyst activity and selectivity. During MCA a solid (a catalyst in our case) accumulates an excess potential energy as elastic and plastic deformations and great variety of defects accompanied by an increase in its reactivity. This excess energy can considerably affect both the reactivity and activity of catalysts. The system reactivity is universal in the sense that it appears as a universal tendency for the decrease of its thermodynamic parameters. This tendency can involve different relaxation channels, including catalytic reactions yielding the desired products.

MCA allows creating defects of a fixed type, to form a surface by faces and edges not typical of catalysts in the usual state. All this extends a range of bond energies and properties of the intermediate surface species and is the reason of change in activity and selectivity.

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

2. Possible MCA applications in catalysis

The principle sections of the catalysis science are as follows.

2.1. Development of the scientific basis for catalyst synthesis

The main problem of this division/section is the development of methods to prepare catalysts with 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 study physicochemical regularities determining the features of the synthesis and action of materials during all preparation stages of separate families of similar materials (catalysts in our case) [1].

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

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

- The chemical nature, structure and action mechanism of the active sites during operation on the catalyst surface.
- The nature and relations between catalytically active sites of the main and side reactions, means and methods of affecting the above in order to increase the selectivity towards the desired product.
- The effect 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 of their deactivation.

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[*] Corresponding author. Tel.: +7 383 3309553; fax: +7 383 3308056.
E-mail address: molchanov@catalysis.ru (V.V. Molchanov).

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

3. Preparation of catalysts using MCA

3.1. Brief review of the theoretical and practical background of the MCA application for catalyst synthesis

Traditional methods used for synthesis of heterogeneous catalysts include, as a rule, several stages and have a number of significant disadvantages. For instance, the reactivity is usually increased by performing processes in solution or at high temperatures. As a result, the known methods do not meet the present-day ecological and energetic requirements.

The development of highly efficient 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 number of articles, reviews and monographs [2–9] are devoted to the theory and practical applications of MCA in the preparation of multi-component solid systems. In this application field, the emphasis is placed on the processes occurring in the bulk. Various phenomena occurring on the solid surface are of secondary importance and become critical only if one considers the nature of the catalytic action.

The preparation of two and multi-component solid systems by MCA involves chemical as well as other types of interaction between solid ingredients. Their rate is limited by such parameters as contact area, mass transfer processes and activation barriers.

Dispersion of solid phases increases the ratio between the particle surfaces areas and their volumes, and thus increases the total contact area between the solid phases.

It was established [2] that MCA reactions in solid mixtures follow two regimes. For low intensity MCA, solids undergo crushing. In this case, the reaction rate depends on the number and area of contacts between the reacting particles. At high intensity MCA, we observed the plastic deformation regime, at least for one reacting component. This results in a contact throughout the whole surface of a hard-to-grind material. Note that at the initial period, the chemical interaction of the components is a rate-limiting process stage. As the formed product layer begins to isolate the reacting products from each other, the diffusion mass transfer begins to define the reaction rate.

Under plastic deformation conditions, the solid phase acquires 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, that is, total disorder of crystals. Available data [3] suggest that for the vacancy mechanism of material transfer, the diffusion coefficient is proportional to the vacancy concentration. As the MCA intensity is sufficiently high, the saturation with defects reaches a point where a solid transforms into a “cold melting” state.

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

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

It was shown [3] that under elastic crystal deformation conditions, the excess energy of MCA is distributed throughout the volume of dislocations and defects. Such energy distribution is thermodynamically more efficient than uniform distribution through all bonds. This feature of the substance crystalline state defines the nature of MCA conversions.

Synthesis of multi-component systems under MCA conditions should be considered with regards to the process thermodynamics. During MCA, the reacting solid phases increase Gibbs energy $\Delta G = \Delta U - T\Delta S$, which is related with the equilibrium constant K by equation $\Delta G = -RT \ln K$. Such relation leads to a seemingly paradox conclusion that it is possible to create metastable systems. However, this paradox can be explained from the thermodynamic viewpoint. Under MCA conditions the energies of reacting phases significantly differ from the reference data corresponding to the standard conditions. For this reason, non-equilibrium systems can appear under such conditions. As the energy stops to dissipate, such energy-intensive systems undergo an extinction relaxation process towards standard characteristics. This is an activated process. Owing to internal friction and retardation of atoms, relaxation decays and complete equilibrium is not attained. This results in a metastable non-equilibrium system [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 such an extent that they could be considered as new substances having the same composition as the initial substance.

This brief description of the present-day concepts on the mechanism, regularities and peculiar features of MCA is aimed at promoting the interest to this promising method and its application in the development of the scientific basis for preparation of catalysts [1].

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

1. Substitution of the process stages employing solutions by mechanically activated homogenization of systems or mechanical alloying, which permits one to obtain new structures and prevent ecologically harmful wastes; direct synthesis of catalysts under MCA conditions (mechanochemical synthesis).
2. Synthesis of new solid materials (catalysts) due to an increase in the reactivity of reacting solid phases under MCA conditions.
3. Preparation of non-equilibrium solid systems that cannot be prepared by traditional methods, including solid solutions with concentrations significantly higher than the equilibrium ones.
4. Temperature decrease and easy interaction of phases during further treatments such as calcination, hydration, sorption, reduction, etc.
5. Decrease in the synthesis temperature of binary and more complex systems owing to MCA, resulting in improved structural and other characteristics.
6. Modification of the operation properties (formability, strength, texture, etc.).
7. Preparation of finely dispersed and nano-sized systems.
8. Simplification of technologies by reducing the number of stages and aggregate costs.

3.2. Some MCA applications for catalyst synthesis

We would like to present several examples to illustrate the MCA potential in the preparation of catalysts.

The treatment of powdered mixtures of magnesium and iron group metals by MCA produced a number of mechanical alloys that after subsequent hydrogenation in hydrogen at 10–17 atm yield new intermetallic hydrides Mg_2MH_x (where M = Co, Fe and $x = 5–6$). These hydrides are efficient catalysts for hydrogenation of acetylene and diene hydrocarbons to mono-olefins with the selectivity close to 100% [10]. The hydride Mg_2CoH_5 shows 100% selectivity in hydrogenation of acetylene to ethylene performed at 473 K, with the hydrogen to acetylene ratio equal to 5 at the reaction mixture flow rate 1500 h^{-1}. Under the same conditions, hydride Mg_2FeH_6 shows 99.2–99.7% selectivity in hydrogenation of butadiene to butane. The hydrogenation mechanism has been determined. Hydrogenation follows a stage mechanism at low temperatures and a heterogeneous–homogeneous radical mechanism at relatively high temperatures [11].

Mechanochemical activation of the metal powders at hydrogen pressure 100 atm led to the synthesis of two earlier unknown intermetallic hydrides Mg_2NiH_6 (stable at ambient temperature) and $MgCuH_2$ exhibiting hydrogenating activity [12].

It was established that MCA strongly affects the properties of supports as well as nickel chlorides and nickel metal 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 with respect to the metal; (2) a decrease in the temperature of nickel chloride reduction with hydrogen by 200–300 °C; and (3) an increase in the activity of the supported metals in the reactions of ethylene hydrogenation and CO oxidation. For γ-Al_2O_3 MCA allows one to increase the coke resistance, dispersion of supported metals and the catalytic activity of supported catalysts [13,14]. Table 1 shows the above mentioned effect using ZnO as an example.

A new method for synthesis of heteropolyacids from molybdenum, tungsten and vanadium oxides was developed. The method is very efficient for synthesis of phosphorous–vanadium–molybdenum and phosphorous–molybdenum 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 aqueous phosphoric acid. We synthesized a number of heteropolyacids described by the following formulas: $H_{3+m}PM_{12-m}V_mO_{40}$, $H_3PMo_{12-m}W_mO_{40}$ and $H_6P_2Mo_{18}O_{62}$, where M = Mo or W, and $m = 0–4$.

These HPA are efficient catalysts in many commercial processes [15].

The basic advantages of the new technology are:

- Total absence of manufacturing water and gas exhausts.
- Cutting down the synthesis time from tens of hours to tens of minutes.
- Low water and energy consumption.
- Lack of the losses of expensive and toxic molybdenum and vanadium reagents.
- Quantitative yields of heteropolyacids.
- Lack of the explosive and fire-dangerous stages (ether extraction).

A new catalytic system based on metal particles that are definitely incorporated into carbon filaments (Fig. 1) via catalytic decomposition of hydrocarbons on such particles was developed.

Table 1
The influence of MCA on the properties of ZnO.

MCA time (s)	Ni content (mass%)	T_R (K)	W ($\times 10^3$mole C_2H_6 s^{-1} g^{-1})
0	0.18	800	3.6
60	0.30	470	6.0

T_R is the temperature of $NiCl_2$ reduction by hydrogen; W is the specific rate of ethylene hydrogenation per gram of Ni.

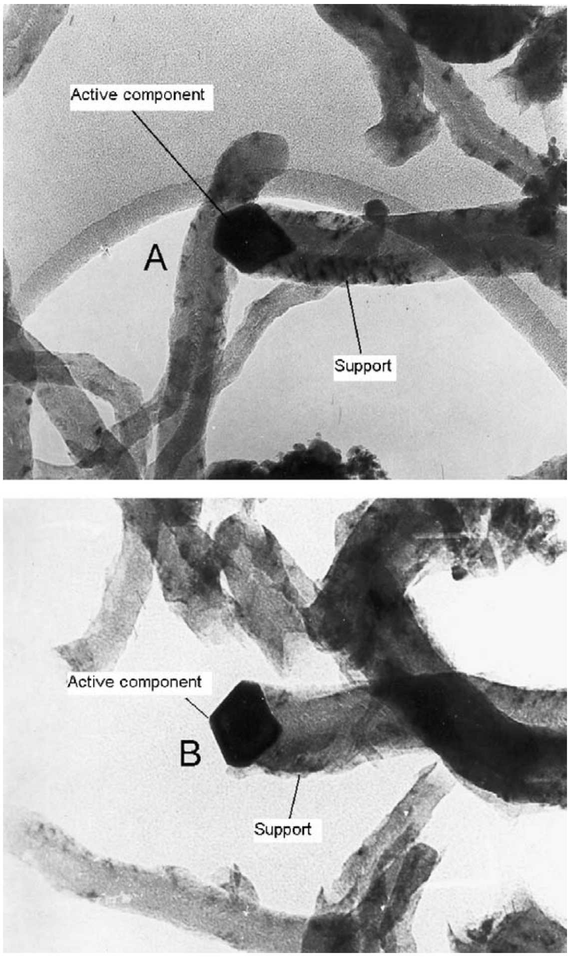


Fig. 1. TEM image of new metal–carbon catalysts: (A) C/Ni = 1.5 and (B) C/Ni = 10.

The preparation method allows one to control the nature of the crystallographic planes on the surface (Fig. 1, A and B). The as-prepared catalysts can be used in a number of catalytic processes such as hydrogenation, dehydrogenation, Fischer–Tropsch synthesis, CO oxidation, vapor- and CO_2-conversion of methane. The more efficient field of these catalysts application is selective hydrogenation of acetylenic and dienic hydrocarbons to olefins and purification of the monomers from admixtures of the above hydrocarbons [16].

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 the following reduction. The layered structure of hydroxides allows one to disperse more efficiently the iron group metal oxides. To prevent sintering of the metal particles, substances with layered structure, magnesium or aluminum hydroxides, were introduced into the activated mixture [16].

MCA makes it possible to synthesize new forms of alumina, such as π-Al_2O_3. This crystal modification results from dehydration of mechanically activated gibbsite. The modification is characterized by layered structure similar to that of gibbsite and the presence of four-, five- and six-coordinated ions. Two neighboring Al(III) ions coordinated by five oxygen atoms are pair Lewis sites exhibiting catalytic activity [17,18].

It was established that preliminary activation of gibbsite, boehmite and bayerite reduces the temperature of their phase transformation to corundum by 200–300 °C [18].

4. 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 action. However, the task is complicated by the fact that the traditional problem definition involves also phenomena of the MCA system.

In this context we suggest two possible applications of MCA for increasing the catalytic activity [19]:

1. Effect of the preliminary MCA catalyst treatment on the catalytic properties. In this case, partially relaxed catalyst system treated by MCA preserves some part of its defectiveness and the excess free energy associated with it.
2. Effect of MCA during a catalytic process on the catalytic properties. In this case, the effect of MCA depends on its power density, that is, on the level of energy dissipation and properties of the catalyst dissipation state.

Catalysis takes place on the surface of heterogeneous catalysts. The properties of atoms on the solid surface differ from those in the bulk. Their reactivity is affected by steric and energy properties of the surface defects. For this reason we are primarily interested in the phenomena and processes occurring on the surface due to MCA [5,8].

In some reports, defects in the crystal structure are associated with the catalytic action, whereas the chemical nature of the catalytic sites is not mentioned at all. Meanwhile, the catalytic action is based on the formation of a chemical intermediate (active complex) on the surface. This leads to another question: what are the relations and the contributions of chemical and structure–energy components to the nature and properties of catalytically active sites? This question can be subdivided into a number of particular questions such as:

1. What is the nature of the MCA effect on the activity of the catalytic sites?
2. Are there individual active sites for the target and side reactions?
3. Can MCA destroy active centers or initiate generation of alternative active sites?
4. If 100% conversion of the initial product is composed of the conversion to the desired and side products, can we use MCA to control the selectivity to the desired product, etc.?

At present, the answers to the above questions are still under development and there are no unambiguous answers to them. We have just indicated the problems as guiding lines for future research.

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 determines the physicochemical properties of solids, including reactivity. Their nature varies in a wide range: we know ionic, covalent, metallic, molecular and hydrogen bonds. MCA affects chemical bonds in different ways. These are responsible for the anisotropy of the crystal properties and distinctions between different crystal faces in the surface energy and reactivity.

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

During MCA the inhomogeneity range of the catalyst surface properties sharply increases, extending the variety of active sites.

In our case, the question on the nature and mechanisms of the MCA effect on the efficiency of active sites is reduced to the elucidation of a relation between structure–energy properties of an active site and its reactivity. Furthermore, one should assume that different defects (that is, carriers of excess energy in the solid) affect the chemical, catalytic and other properties of catalysts in different manner.

Relaxation in a heterogeneous catalyst structure can proceed through several channels of different nature. However, the main reason for increasing the catalytic activity is a feature of defects in the crystal structure. The system tends to minimize its Gibbs energy by localizing it on the defects [3]. Such distribution of free energy is thermodynamically more efficient than uniform distribution of elastic stresses throughout the crystal lattice bonds. As it follows from Ref. [8], the chemical activity of the catalytic sites is increased by extended defects such as block boundaries formed by dislocation array and shift defects resulting from shifts and turns of the layers. Such areas are characterized by the highest concentrations of the surface atoms with unsaturated bonds and increased reactivity. An increase of the free energy of the above areas reduces the potential activation barrier of the catalytic reactions.

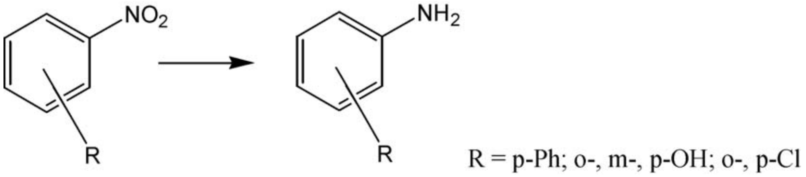
One should expect the strongest effect of MCA on the catalytic activity from a combination of MCA and a catalytic act. In this case, a catalytic system can be approximately treated as a dissipative one [20]. The system state will depend on the intensity of energy dissipation. At each dissipation level, the corresponding dynamic order and a non-equilibrium stationary structure will appear. Thus, as the catalysis and MCA are used at the same time, one may talk about a statistically defined set of the system dynamic states with its own potentials. These states appear only in the impact areas, but not in the bulk of the particles. For this reason, the observed increase in the catalytic activity should be attributed to the input of this area alone.

Pulse action of MCA on the catalyst is responsible for two counteracting processes occurring in the system at each instant of time. These are deformations accompanied by increasing Gibbs energy and relaxation. Due to formation of defects, 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 and the channels of energy dissipation [9]. As the MCA action decreases, the main role is played by the rate of "quenching" in the relaxation process. One can suggest that after MCA the relaxation rate is described by equations similar to those of the radioactive elements half-life.

The relaxation energy can be rather high due to conversion of the elastic energy to 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 bond destruction, which also increases the activity of the catalytic sites [3,4]. In any case, the as-activated catalytic complex acquires some excess energy providing for surpassing the potential barrier of a catalytic reaction. This is the manner how a specific energy relaxation channel (here it is a catalytic reaction) acts. Qualitative analysis of the thermodynamic and kinetic parameters of the catalytic processes under MCA conditions [19] has shown that the catalyst activity should increase if the nature of active sites does not change. In this case, the selectivity can vary with the relation between the rates of the main and side reactions. Some information on the selectivity can be obtained by studying correlations between the rates of separate reactions and the presence of the corresponding structural defects.

When MCA is combined with a catalytic process, a special pathway for the process appears. Under these conditions, fresh surfaces with broken and distorted bonds with radical active sites are continuously generated. The appearance of excited atoms on such surface determines their reactivity. The lifetime of these atoms is comparable with the chain termination rate. In this case, the reaction with a gas goes without an activation barrier [2]. Radical reactions are defined by the rates of formation and consumption of the active sites that are proportional to the reproduction rate of fresh surfaces. The sites are consumed by spontaneous annihilation and interaction with gases during the catalytic act [2].



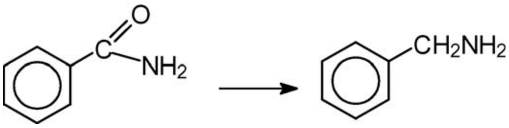
4.3. MCA affecting both activity and selectivity of catalysts

Earlier [8] we presented a detailed analysis of publications considering the effect of MCA on the activity and selectivity of catalysts. The present article considers a number of new examples.

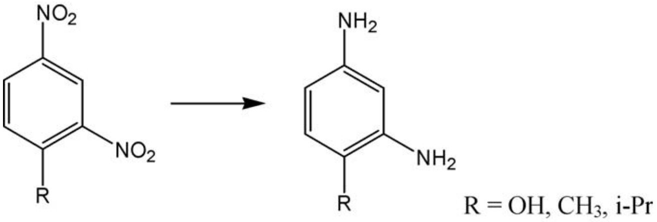
Performing catalytic reactions under the MCA conditions makes it possible to increase their activity and selectivity and substantially extend the range of possible processes. Of particular interest are new MCA applications under the reactant pressure: synthesis of new compounds, selective catalytic reactions in the solid phase, and new efficient ways of performing reactions. For example, hydrogenation of a number of organic compounds in the solid phase promotes selective reduction of functional groups and unsaturated bonds.

The most illustrative example is hydrogenation of caryophyllene-α-oxide [21]. MCA of caryophyllene-α-oxide (I) for 10 min at the barrels rotation frequency of 10 s^{-1} in the presence of the hydride Mg_2NiH_4 at the hydrogen pressure 5 atm leads to hydrogenation of double bond and to 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 epoxy group with formation of alcohols (III) at a selectivity of 90%. Finally, MCA for 20 min at the barrels rotation frequency of 17 s^{-1} leads to complete removal of hydroxyl groups and to the formation of dihydrocaryophyllene (IV).

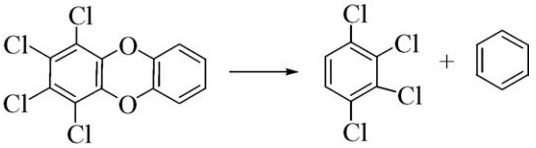
Quantitative transformation of benzamide to benzamine was observed on hydride Mg_2NiH_4 after MCA for 30 min at barrels rotation frequency 17 s^{-1} and hydrogen pressure 15 atm.



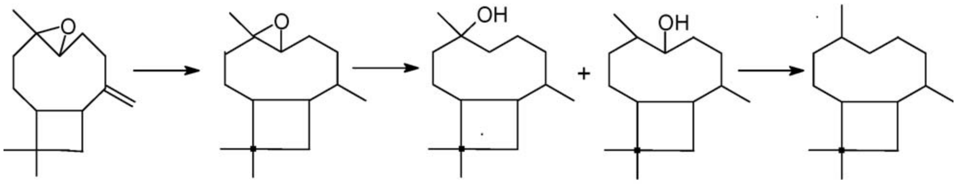
The high efficiency of this method was demonstrated for the hydrogenation of nitroaromatic compounds. MCA of a number of nitroaromatic compounds for 30 min at hydrogen pressure of 50–100 atm (barrels rotation frequency 17 s^{-1}) in the presence of hydride Mg_2NiH_4 results in hydrogenation of nitro groups with the formation of corresponding amines.



Hydrodechlorination of toxic chlorine aromatic compounds, including complete destruction of 1,2,3,4-tetrachlordibenze-n-dioxin, was performed.



At elevated ammonium pressure ursolic acid amide was obtained. Copper salts were used as the catalysts. Without solvents the amide yield could not be obtained higher than 8–10%. Amination in the presence of methanol or acetic acid as solvents allows obtaining ursolic acid amide at a yield of 65%. Under the same conditions without the catalysts ammonia salt of ursolic acid was obtained.



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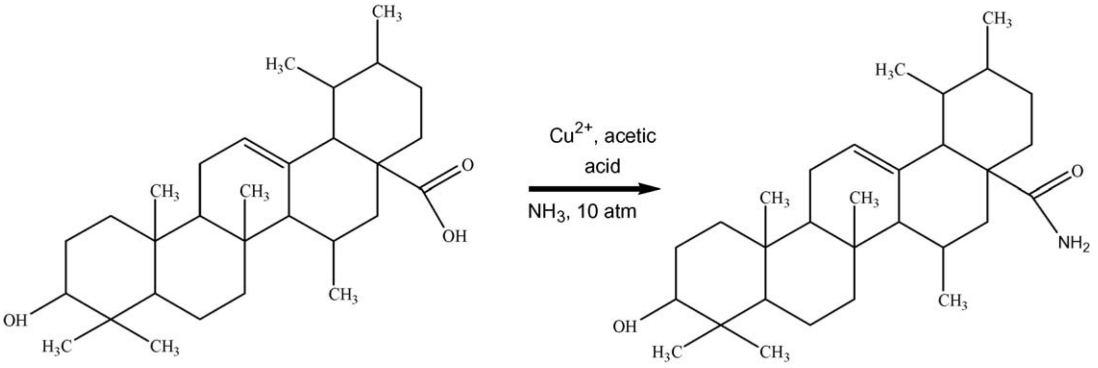

In the mentioned cases, the chemical processes were initiated by simultaneous mechanochemical activation of the catalysts and solid reactants [21]. Hydrides were shown to be active in the reduction of other functional groups, such as epoxides and hydroxides [22].

Of particular interest is the catalytic action of ammonia observed in the synthesis of intermetallic complex hydrides performed during mechanochemical activation of the reacting metals in the presence of the gas phase (H_2 + 5% NH_3). Adding ammonia to hydrogen made it possible to change the mechanism and the rate of nickel–magnesium intermetallide hydride formation. Ammonia was adsorbed on the solid activated particles (reaction participants), activated by them and led to the stage mechanism involving the hydrogen atom transfer [23]. This exotic phenomenon meets the earlier concepts of the universal stage mechanism in heterogeneous catalysis [24].

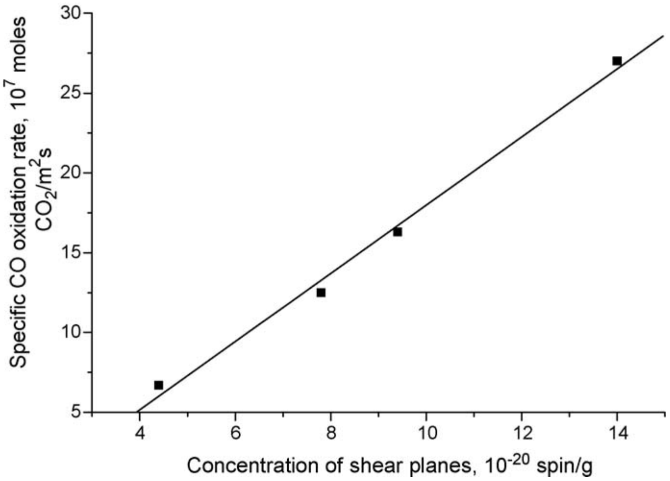

Fig. 2. Dependence of specific CO oxidation rate on the concentration of crystallographic shear planes.

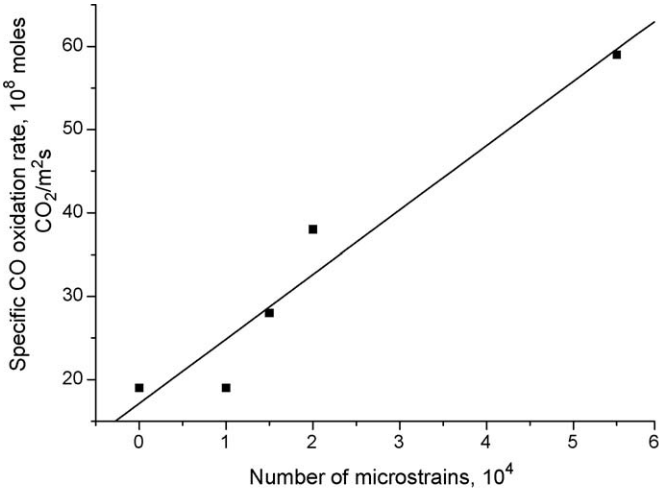

Fig. 3. Dependence of specific CO oxidation rate on the number of microstrains.

It was established [25] that the specific CO oxidation rate on TiO_2 linearly depended on the concentration of crystal shear planes (Fig. 2). This dependence can be considered as an unambiguous proof of the role of extended defects.

MCA tripled the specific catalytic activity of zinc oxide in CO oxidation. This was accompanied by a substantial decrease of activation energy, which indicated generation of alternative active sites. This observation was associated with the formation of low-angle block boundaries and appearance of exits of dislocations and packing defects onto the surface. A linear dependence of the specific CO oxidation rate on the number of microstrains was established (Fig. 3). Zn^{2+} ions involved in the defects are the sites of oxygen chemisorption acting as catalytically active sites providing for the stage mechanism of CO oxidation. It was also established that point defects do not affect the activity of ZnO in this reaction [26].

Of special interest are our recent unpublished results concerning the changes in the catalyst selectivity towards desired and side products caused by MCA. The results prove the possibility of generating some active sites while annihilating other sites. It was established that MCA affected the selectivity of vanadium oxide in the formaldehyde oxidation to formic acid and by-products. In addition, the selectivity of zinc oxide was found to change in the reaction of isopropyl alcohol following two routes yielding acetone by dehydrogenation and propylene by dehydration.

In both cases, the selectivity was changed by the formation of Lewis acid sites by MCA and decrease in the concentration of Bronsted acid sites.

5. Conclusions

Our review considers the role of structure–energy properties of mechanically induced defects in the crystal structure of heterogeneous catalysts. The main theoretical concepts of the MCA effect on the activity and selectivity of catalysts are considered. We discussed the most promising trends of research in this field.

The wasteless and energy-saving methods of preparation of some catalysts are presented. Rigorous experimental proofs of the influence of defects in the crystal structure of catalysts on their specific catalytic activity are obtained. High performance of mechanochemical catalysis application for hydrogenation and amination processes is shown. For the first time catalytic reactions under the conditions of mechanochemical activation at elevated pressure of gases are carried out.

The increasing interest to MCA applications in catalysis reflects the tendencies in this field. There is a good reason to believe that the basic research on the nature and mechanisms of the MCA action performed in all divisions of the catalytic science will promote general progress in practical implementation of this method.

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