

IV RUSSIAN CONFERENCE WITH THE PARTICIPATION OF CIS COUNTRIES ON THE SCIENTIFIC BASES OF CATALYST PREPARATION AND TECHNOLOGY

Scientific Grounds for the Application of Mechanochemistry to Catalyst Preparation

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Abstract—It is shown that mechanochemical activation is efficient in creating waste-free energy-saving methods for the preparation of hydride catalysts, heteropoly acid catalysts, and catalysts for hydrocarbon decomposition into hydrogen and carbon materials, as well for the syntheses of earlier unknown catalytic systems. The capabilities of the mechanochemical methods are demonstrated on modifying the catalytic properties of catalysts and supports: an increase in the strength and catalytic activity, sorption properties, etc. Adhesion theory applied to melts helps to describe the mechanism of mechanochemical synthesis of catalytic systems.

INTRODUCTION

The main task of any chemical technology is to make the reactivity of starting materials effective in the synthesis of a target product. The choice of methods determines the process performance (the yield of a target product, selectivity, energy and capital expenses, economical characteristics, etc.). Traditional methods include an increase in temperature, pressure, the use of solutions as a reaction medium, vigorous stirring, and some others.

All cited methods used in the manufacturing of heterogeneous catalysts require substantial energy and material expenses. In the technology, the main methods are an increase in the reactivity by mixing the components or transferring the components into solutions with their further precipitation and calcination at a high temperature, which is a typical stage in the catalyst preparation. This method is characterized by substantial energy consumption, usual formation of wastewater, and noxious gas emissions: nitrogen oxides, sulfur, ammonia, etc. The purification of liquid and gas emissions contributes to the catalyst cost.

Worldwide catalyst manufacturing is estimated in hundreds of thousands of tons. It covers more than half the periodic table of the elements. Literally speaking, catalyst and support manufacturing is one of the most environmentally dangerous technologies. Therefore, a topical problem is the search for new technologies of catalyst and support manufacturing and the methods to increase the reactivity of solids and overcome limitations mentioned above. In this article, we consider one of such methods, namely the mechanochemical activation (MCA) of solid phases. Numerous examples in material science have proven that MCA is efficient in removing the cited drawbacks.

In our opinion, MCA in catalyst manufacturing can be used for

- catalyst preparation in activator mills (mechanochemical synthesis),
- making the conditions for catalyst preparation milder when conventional methods are used,
- imparting required properties (activity, stability, and others) to catalysts, and
- synthesis of new highly efficient catalytic systems.

Some examples below illustrate the high efficiency of MCA along the four mentioned lines. In addition to solving specific applied and theoretical problems in MCA catalyst preparation, we tried to develop some theoretical grounds for the use of mechanochemistry in catalyst preparation.

PREPARATION OF CATALYSTS BASED ON INTERMETALLIC HYDRIDES OF MAGNESIUM

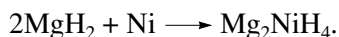
The problems of selective hydrogenation are very topical in the processes of monomer purification from admixtures of alkynes and dienes in the syntheses of polymers of rubber and in the processes of selective hydrogenation of one or several functional groups or multiple bonds in the synthesis of fine organics. Catalysts used for these processes usually contain noble metals and show low selectivity to target products. Therefore, researchers look for new catalytic systems.

Hydrides of intermetallic compounds discovered recently are active in reactions involving hydrogen as was shown in many studies (see, for instance, review papers [1–3]). By the mid-1980s, two methods for the synthesis of intermetallic hydrides were known. These are the hydrogenation of alloys obtained in pyrometallurgy [1–3] and the use of organomagnesium compounds [4]. Shortcomings of the former method are (a) high energy expenses, (b) the necessity of long treatment of the system with alternating hydrogenation and dehydrogenation to make the interaction of metal with

hydrogen more complete, and (c) low specific surface area of materials thus prepared. The latter method is characterized by inconvenience of technological operations with organometallic compounds. The method of hydride synthesis using "mechanical alloys" prepared by MCA of a mixture two metals [5] lacks the cited drawbacks. This method was proposed in the mid-1980s. Mechanical alloys are readily hydrogenated without long-lasting hydrogenation/dehydrogenation treatments. Their specific surface areas are rather high, and energy expenses for mechanochemical activation are much lower than in the case of the pyrometallurgical method. In addition to the previously known hydrides, new compounds have been synthesized [6, 7].

We modified the method of mechanochemical alloying and proposed to carry out mechanochemical activation under the conditions of a high hydrogen pressure. Crushing cylinders of a planetary mill were charged with metal powders and injected hydrogen with a pressure of 25–70 atm. Then, mechanochemical activation was carried out.

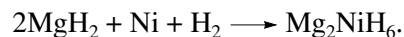
The activation of magnesium–nickel alloy in hydrogen for 30 min at a cylinder rotation intensity of 10 rps resulted in hydrogen absorption in amounts necessary for magnesium hydride or Mg_2NiH_4 formation. However, according to XRD, such a treatment led to sample amorphism. We assumed that activation at low rotation frequencies resulted in the formation of X-ray amorphous phases of magnesium hydride and metallic nickel. If MCA is carried out for a longer time, the phase composition does not change. Analogous results were obtained at 17 rps and 5–10 min of activation. Further treatment for 20–30 min resulted in the formation of Mg_2NiH_4 . This hydride was assumed to be formed via the reaction analogous to hydrogenation of mechanical alloys



Two facts are notable for hydride synthesis using MCA under high pressure. When hydrogen is consumed under the conditions of MCA, its pressure did not decrease below 13 atm. If the initial pressure was lower than 13 atm, hydrides were not formed.

Another feature of this reaction under given conditions is the formation of the high-temperature form of Mg_2NiH_4 , which is stable at room temperature. This is unusual because, according to the published data, reversible phase transition is observed for the hydride of this composition at 503 K. Measurements of the NMR signal from hydride protons showed that the amount of hydrogen corresponds to the formula Mg_2NiH_6 (sodium borohydride was used as a standard). The concentration of hydrogen was determined by two other methods: by measuring the amount of hydrogen evolved during heating and dissolution of the sample in hydrochloric acid. Both methods supported NMR results. Thus, the reason for the stabilization of the high-temperature modification of magnesium–nickel intermetallic compound is the formation of Mg_2NiH_6

rather than Mg_2NiH_4 . The second stage of the interaction of hydrogen with a mixture of metals should be described by the following reaction:



In addition to the magnesium–nickel alloy, other alloys were also hydrogenated under the conditions of mechanochemical activation. For the Mg–Fe system, we failed to obtain the corresponding hydride. For the LaNi_5 alloy, we obtained the known hydride LaNi_5H_7 . An interesting result was obtained for the hydrogenation of the Mg–Cu alloy. After mechanochemical activation at an initial hydrogen pressure of 80 atm, we detected a phase with diffraction maxima that could not be assigned to known compounds in this system. Taking into account that hydrogen is consumed during MCA, we assume that a Mg–Cu intermetallic compound is formed that has not been described in the literature.

Note that the attempts to synthesize such a hydride by traditional methods and by the methods of mechanical alloying were unsuccessful.

Some applications of hydride catalysts were determined. The most promising of them is the purification of monomers from admixtures of alkynes and dienes to α -olefins and *p*-benzoquinone hydrogenation to hydroquinone. The pilot tests of a hydride catalyst in the process of hydroquinone synthesis showed its high efficiency. Advantages of the new technology over known methods are

- (1) Fewer steps in catalyst preparation;
- (2) Absence of pollutants during the catalyst preparation and in the process;
- (3) High hydroquinone yield; and
- (4) Organic solvents are not used.

DEVELOPMENT OF WASTE-FREE METHODS FOR HETEROPOLY ACID SYNTHESIS

Heteropoly acids (HPA) are efficient catalysts for acid–base and oxidation reactions [8–11]. Currently, HPAs are used in several commercial processes: olefin hydration, tetrahydrofuran polymerization, phenol alkylation, metacrolein oxidation, and others [9, 12]. Recent interest in HPA salts is due to their properties as solid acid catalysts [13].

Although the high efficiency of heteropoly acid catalysts was supported in many publications, their commercial applications are restrained by the lack of simple, environmentally clean technologies of HPA manufacturing and a high cost, which is due to complexity in their preparation. Currently, HPAs are obtained by either the synthesis of the corresponding salts with further isolation of acids by extraction with esters or prolonged boiling of the suspensions of initial oxides. These technologies lead to a large amount of liquid acidic waste and deleterious waste gases. These technologies are not fire-safe. Technological charts include

many steps, and the yield of HPA is rather low (60–80%). The loss of deficient, expensive raw materials (molybdenum, tungsten, and vanadium) is not prevented.

The method for direct HPA synthesis by the interaction of molybdenum, tungsten, and vanadium oxides with the compounds of a heteroatom and water is very attractive. These reactions can be carried out in the case of some P–Mo and P–Mo–V HPA with nonquantitative yield under the conditions of prolonged boiling (tens of hours). A drastic acceleration of synthesis becomes possible due to an increase in the reactivity of oxides during MCA. First experiments showed high efficiency of MCA for this purpose. The reactivity of molybdenum and tungsten oxides toward phosphoric acid solutions increases. The interaction yields solutions of the corresponding HPA. The $H_3PW_{12}O_{40}$ was first prepared by the direct interaction of tungsten oxide with the phosphoric acid solution. The reactivity is still higher when the mixture of molybdenum and vanadium oxides is activated. These oxides interact with the solutions of phosphoric acid more rapidly than activated molybdenum oxide. The reactivity of these mixtures increases with an increase in the concentration of vanadium in the mixture.

The reasons for an increase in the reactivity when vanadium oxide was added were studied. The mechanochemical activation of the mixtures of molybdenum and vanadium oxides results in the formation a number of variable-composition compounds $V_2O_5 \cdot nMoO_3$, where $n = 2–22$. These compounds were described earlier and have a crystalline structure close to the structure of orthorhombic MoO_3 . The crystal lattice of these samples consists of alternating layers of molybdenum and vanadium oxides. Available data suggest the existence of new compounds, but a detailed study of their crystal structures is needed to prove them.

The formation of these compounds is probably a reason for an increase in the reactivity of activated mixtures. In our opinion this is due to the fact that disruption in the structure of vanadium oxide leads to the formation of fragments consisting of tetragonal pyramid chains. Similar coordination saturation simplifies the growing-in of the PO_4 group into these fragments with Keggin anion formation in which the coordination sphere of vanadium is completed to an octahedron with oxygen from the PO_4 group. In the case of pure molybdenum oxide, analogous structures consist of octahedra when the bonds between layers are broken and if more complex structural transformations are need to build the PO_4 group in.

For some HPAs, the solid phase syntheses were carried out. The mechanochemical activation of molybdenum and vanadium oxides with phosphoric acid or a mixture of $V_2O_5 \cdot nMoO_3$ with phosphoric acid for $n = 4$ and 6 results in the formation of structures with Keggin anion-like symmetry. ^{31}P NMR data support the formation of HPAs in the solid phase. The salts of heteropoly

acids were obtained in an analogous way: thus, the mechanochemical activation of a mixture of $V_2O_5 \cdot 4MoO_3$ with sodium orthophosphate results in the formation of the corresponding salt $Na_3H_4PMo_8V_4O_4$. Crystallization water plays an important role in this interaction. The salt can be prepared using the mechanochemical method when sodium orthophosphate is used as a crystalline hydrate. When the water-free compound is used, the salt is not formed. Most likely, this is due to the fact that the intensive mechanical mixing of crystalline hydrate leads to an increase in the reactivity. The impossibility of mechanochemical synthesis of P–Mo–V HPAs and their salts in the absence of water is also associated with the stability of the crystalline hydrate of these compounds.

According to IR spectra, the formation of HPAs in the solid phase occurs already after 60 s. When the activation is prolonged, the form of spectra and the solubility in water do not change.

The synthesis of HPAs and their salts in the solid state is hard to explain by sole hydrolytic processes because water was present in activated mixtures in amounts sufficient for the formation of crystalline hydrates but not solutions. Oxides were taken in approximately tenfold excess over water. The differences in the reactivities of $V_2O_5 \cdot 10MoO_3$ and $V_2O_5 \cdot 4MoO_3$ do not explain the hydrolytic mechanism either, because their solubilities in water is about the same, whereas the rates of HPA formation from these compounds differ by several orders of magnitude.

These findings formed the basis for the creation of the new method for HPA synthesis, which is the most efficient for P–Mo–V and P–Mo HPAs. The new method involves only two or three steps: the mechanochemical activation of oxides and their mixtures and the interaction with the solution of phosphoric acid. When necessary, solid acids are concentrated by evaporation. This method was used to synthesize several HPAs described by the formulas $H_{3+m}PM_{12-m}V_mO_{40}$, where $M = Mo$ or W ($m = 0–4$), and $H_6P_2Mo_{18}O_{62}$.

The new method has several advantages over known methods. First, this is a waste-free method. The time need for the synthesis is shortened and the number of steps is reduced. The HPA yield increases. The waste of expensive and deficient materials (compounds of tungsten, molybdenum, and vanadium) is excluded. Energy consumption is reduced. The explosion- and fire-unsafe stages of ester extraction and the decomposition of the ester complex are excluded. For some HPAs, the solid phase synthesis is possible and water consumption is completely excluded, which makes it possible to reduce energy expenses because water need not be evaporated.

The technology was developed for the synthesis of diacetonesorbose, which is an intermediate product in the synthesis of vitamin C, using an HPA catalyst. New catalysts are much more efficient than oleum, which is used for this purpose. The method for mechanochemical recovery of spent catalysts was developed. This

method makes it possible to return catalysts easily to the process without loss of expensive materials.

DEVELOPMENT OF THE METHOD FOR THE PREPARATION OF HYDROCARBON DECOMPOSITION CATALYST

Carbon materials are widely used in different industry sectors. Recently, these materials were recognized as promising sorbents, supports, and catalysts. One of such materials is filamentous carbon, which is formed by the catalytic decomposition of hydrocarbons on iron-subgroup metals or their alloys with other metals.

We developed a method for the preparation of nickel catalysts for methane decomposition into hydrogen and carbon material is another example that makes it possible to replace the method that gives wastewater by a waste-free one. The traditional method is the precipitation of nickel hydroxide and aluminum [14]. Copper hydroxide is used as an additive that increases the catalyst efficiency. The active component is the nickel–copper alloy. The necessary condition for the efficiency of these catalysts is obtaining metal or alloy particles with a largest size of 50 nm [15]. We attempted to obtain such particles using mechanochemical activation. It was necessary to reduce nickel oxide or its mixture with other oxides (copper, iron, or some others) to finer particles of required size and prevent the sintering of metal or alloy particle in the process of reduction under the reaction conditions. To solve these problems we added lamellar-structure compounds to the mixtures to be activated. These were magnesium and aluminum hydroxides and graphite. These procedures allowed us to obtain highly efficient catalysts for methane decomposition.

New catalysts were developed for the decomposition of methane into hydrogen and carbon material that can be used as sorbents, supports, and catalysts. The catalysts work for a long time without deactivation at higher temperatures than those obtained by precipitation. Therefore, they provide higher conversions of methane and higher yields of the carbon material and hydrogen. This enables the use of reaction mixture for hydrogen isolation. The most efficient catalysts are the Ni–Cu–Al–O and Ni–Cu–Fe–Al–O systems obtained by the mechanochemical activation of the mixtures of the corresponding oxides and hydroxides. The optimal composition of the catalyst for methane decomposition includes 10–12% copper oxide and aluminum hydroxide. The Ni–Cu catalyst provides the maximal yields of target products, whereas the Ni–Cu–Fe catalyst is the most stable at the highest temperatures. Furthermore, by varying the catalyst composition, we may change the structure of carbon filament and the properties of the carbon material. We can purposefully impart properties to the material necessary for specific application (sorbent, support, or construction material).

We developed the waste-free technology of catalyst preparation for methane decomposition. This technology includes the following stages:

- (1) mechanochemical activation of the mixture of nickel and copper oxides (iron oxide can also be added) with aluminum hydroxide,
- (2) granulation of the catalyst, and
- (3) reduction with hydrogen.

This technology does not produce liquid and gaseous waste. The use of an APF planetary mill makes it possible to obtain approximately 3 kg of the catalyst per hour. Energy consumed for the MCA step is at most 0.4 kW h kg^{-1} . If we take into account that 1 ton of carbon material requires about 10 kg of the catalyst, it becomes clear that even one mill suffices for the large-scale manufacture.

Our study of mechanically activated samples suggests the reasons for the higher efficiency of the catalysts for hydrocarbon decomposition obtained by the MCA method. It is largely determined by the dispersion of nickel oxide, which is more efficient in the presence of lamellar compounds. These compounds play the role of dispersants for nickel oxide particles and prevent their sintering. The high efficiency of these dispersants is determined by the high homogeneity of the initial component mixing, which is achievable only with mechanochemical activation. The formation of the solid solution of nickel and copper oxides already at the stage of MCA is favorable for its further transformation into the Ni–Cu alloy, the distribution of alloy components is more homogenous than in the case of other preparation procedures. When magnesium hydroxide is used, the reduction of Ni–Cu solid solution in magnesium oxide results in the formation of more dispersed and active metallic-phase particles. All these factors stipulate the formation of active, stable, and temperature-resistant catalysts for the decomposition of methane and other hydrocarbons into hydrogen and carbon materials with interesting properties. The conversion of hydrogen is high enough to make the isolation of hydrogen from these mixtures profitable. The stability of these catalysts at 973–1023 K makes it possible to obtain methane–hydrogen mixtures with a carbon concentration of up to 90%.

The profitability of the process of hydrogen production increases if the carbon material is also a marketable product. As mentioned above, filamentous carbon can be used as a catalyst support, a sorbent, and a filler of the composite material. We found new applications of metal–carbon materials. First of all, this is their use as catalysts in which metallic particles that are fixed at the ends of filaments play the role of an active component. The most promising reactions are selective hydrogenation, namely the purification of synthetic rubber and plastic monomers from alkynes. Another promising application of metal–carbon materials is the purification of gaseous mixtures from dioxins. Our experiments showed that there are materials with certain

Table 1. Dependence of the catalyst strength and pore volume on the conditions of mechanochemical activation

Sample	MCA time, s	Strength, kg/cm ²	Pore volume, cm ³ /g
MCA of the precipitated sample followed by calcination at 620 K			
1-1	0	4	0.50
1-2	600	86	0.20
1-3	1800	91	0.18
1-4	3600	86	0.19
MCA of the precipitated sample followed by calcination at 890 K			
2-1	0	47	0.40
2-2	600	110	0.40
2-3	1800	82	0.30
2-4	3600	71	0.22
MCA of the precipitated sample calcined at 890 K			
3-1	300	64	0.28
3-2	1200	74	0.45
MCA of sample in the presence of 10% water calcined at 890 K			
4-1	300	63	0.27
4-2	1200	79	0.32
MCA of 10% suspension of the sample calcined at 890 K			
5-1	300	50	0.50
5-2	1200	65	0.45

structures of carbon filaments that adsorb dioxins so strongly that they cannot be removed by heating to 673 K. Adsorbed dioxins would probably decompose into carbon, hydrogen chloride, and water over metallic particles if they are heated in a hydrogen atmosphere.

MCA APPLICATION TO INCREASE THE STRENGTH OF THE PHOSPHATE CATALYST FOR DEHYDROGENATION

An increase in the strength of commercial catalysts is one of the most important problems in the technology of their manufacturing. For instance, the Ca–Cr–Ni–P catalyst for the hydrogenation of lower olefins is one of the best, but its mechanical strength is low.

Earlier, we showed that the precipitated mass of the phosphate catalyst consists of hydroxyapatite to 90%. After calcination, it consists of mixed phosphates of calcium with nickel or chromium [16]. Transformations of these compounds determine the mechanical strength of the catalysts.

There are processes that affect the strength of catalyst pellets occur during the formation of the phosphate catalyst [17]:

(1) The hydroxyapatite–whitlockite phase transition. If the catalyst is pelleted in the form of hydroxyapatite, this phase transition leads to the creation of internal stress and a decrease in the strength.

(2) Whitlockite recrystallization. If the mass to be pelleted has a low degree of crystallization, then recrystallization during catalyst operation results in the creation of internal stress and a decrease in the strength. If the degree of crystallization is high, the mass cannot be pelleted.

(3) Sintering. The strength of a catalyst and its porous structure depend on the temperature of thermal treatment.

Kotel'nikov et al. [17] showed that, to achieve a high strength, it is necessary to prevent sintering of mass crystallized to a certain degree. However, this state can be achieved by heating with a certain rate to a certain temperature. This temperature is close to the temperature of exothermic phase transition, and the process of recrystallization is barely controllable because of overheating. Moreover, at these temperatures, sintering is rather intensive. The sintering of particles crystallized to a nonoptimal degree results in a decrease in the strength. In connection with these circumstances, it is difficult to maintain optimal temperatures of catalyst preparation under industrial conditions. This led to the problems in the commercialization of the modified IM-2206 phosphate catalyst.

One of the methods that can solve this problem is a decrease in the temperature of hydroxyapatite–whitlockite phase transition and to carry out the crystallization process under controlled conditions. It is known from published data that MCA usually results in a decrease in the temperatures of crystallization and phase transition. In this work, we attempted to apply MCA to increase the strength of the phosphate catalyst.

According to thermal analysis, whitlockite crystallization in the catalyst after MCA occurs at 610–620 K, whereas in the initial sample it occurs at 920–970 K. Thus, MCA allowed a decrease in the crystallization temperature, and this means that overheating due to isothermal phase transition does not complicate the process of recrystallization to a certain degree. This fact was the reason to hope that the catalyst strength will increase.

Data shown in Fig. 1 suggest that MCA resulted in a substantial increase in the sample strength. This effect is most pronounced in the samples of series 1 (samples 1-1–1-4). In these samples, larger pores dominate, but the overall pore volume and the specific surface area decrease. The presence of such a pore structure results in a decrease in the catalytic activity. More acceptable results were observed for the samples of series 2, which combine the high strength and the pore structure parameters close to the sample obtained according to the standard procedure. This is seen from the comparison of sample 2-1 with 2-2 and 2-3 in Table 1. These results support the conclusions made in [17] on the

Table 2. Effect of MCA on the temperature of supported NiCl₂ reduction

Support	Solvent	MCA time, s	T_{red} , K
ZnO	Water	0	800
	"	60	470
	"	600	520
	Methanol	0	750
	"	60	570
	"	600	570
TiO ₂	Water	0	850
	"	1800 (in air)	600
	"	1800 (in argon)	750
	"	1800 (in Ar + 800 K)	570
	Methanol	0	800
	"	1800 (in air)	620
	"	1800 (in argon)	570
	"	1800 (in Ar + 800 K)	770
ZnAl ₂ O ₄	Methanol	0	800
	"	600	520
	"	1200	590
	"	1800	570
Al ₂ O ₃	Methanol	0	770
	"	300	650

Table 3. Effect of MCA on the sorption properties of supports

Support	Solvent	MCA time, s	[Ni], wt %
ZnO	Water	0	0.18
	"	60	0.20
	"	600	0.30
	Methanol	0	0.15
	"	60	0.19
	"	600	2.07
TiO ₂	Water	0	0.05
	"	1800 (in air)	0.18
	"	1800 (in argon)	0.16
	"	1800 (in Ar + 800 K)	0.16
	Methanol	0	0.04
	"	1800 (in air)	0.18
	"	1800 (in argon)	0.12
	"	1800 (in Ar + 800 K)	0.14
ZnAl ₂ O ₄	Methanol	0	0.51
	"	600	0.64
	"	1200	0.48
	"	1800	0.34
Al ₂ O ₃	Methanol	0	3.40
	"	300	3.76

necessity of the optimal combination of the processes of crystallization and sintering in the technology of phosphate catalyst preparation.

An increase in the strength of the series 3 samples can probably be explained by the fact that mechanochemically activated samples have sites on the surface of particles with excess energy, and the interaction of these sites gives strong contacts between species during heating. The formation of large agglomerates during MCA enables obtaining catalyst pellets with the optimal porous structure, that is, with a rather developed surface area (8–10 m²/g) and large pores (sample 3-2).

The results for the samples of series 4 and 5 support the above idea on the effect of surface hydroxylation on the strength of phosphate catalyst pellets.

The above data show that MCA is an efficient technological means for an increase in catalyst strength. In the case of the phosphate catalyst for dehydrogenation, it is possible to increase the crushing strength of pellets 1.5–2 times while preserving the optimal pore structure.

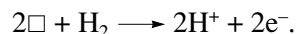
MODIFICATION OF SUPPORT AND SUPPORTED CATALYST PROPERTIES

Mechanochemical activation of solid substances results in the appearance of prolonged defects on the crystalline planes and juvenile, uncontaminated surface

with a large number of unsaturated bonds. These phenomena may affect the regularities of supported catalyst preparation and their catalytic properties.

For several oxide supports, we studied the effect of MCA on the properties of supports and nickel chloride and nickel metal on these supports. For all supports, we observed three phenomena: an increase in the sorption ability of supports with respect to metal, a decrease in the temperature of nickel chloride reduction by hydrogen, and an increase in the activity of supported metals in ethylene hydrogenation and CO oxidation. Each phenomenon is illustrated by a separate table.

A decrease in the reduction temperature of nickel chloride to metal is explained by either the effect of conduction electrons, which appear in some of our support samples after MCA, or by an increase in the electron donor properties of the O²⁻ anion, which is observed for mechanically activated samples:



One of the explanations for an increase in the sorption ability is trivial: the formation of the juvenile surface. Another explanation is the effect of defect wedging out. This was not used to explain changes in the sorption properties of supports. These two factors act together;

Table 4. Effect of MCA on the catalytic properties of supported nickel in the reaction of ethylene hydrogenation

Support	Solvent	MCA time, s	$w \times 10^3$, $\text{mol g}^{-1} \text{s}^{-1}$
ZnO	Water	0	3.6
	"	60	5.3
	"	60 + 630 K H ₂	3.5
	"	600	3.2
	Methanol	0	3.8
	"	60	6.0
TiO ₂	"	600	3.6
	Water	0	0
	"	1800 (in air)	3.7
	"	1800 (in argon)	1.6
	"	1800 (in Ar + 800 K)	1.3
	Methanol	0	0
	"	1800 (in air)	3.3
	"	1800 (in argon)	1.9
ZnAl ₂ O ₄	"	1800 (in Ar + 800 K)	0
	Methanol	0	1.3
	"	600	2.5
	"	1200	3.0
Al ₂ O ₃	"	1800	4.6
	Methanol	0	3.3
	"	300	4.9

only their contributions can differ depending on the conditions of mechanochemical activation.

An increase in the catalyst activity is explained by an increase in the dispersity of metallic nickel due to a decrease in reduction temperature and by the formation of catalytically active metal–defect sites. A decrease in the activity of Ni/TiO₂ activated in an argon atmosphere compared to the same sample activated in air is due to strong metal–support interaction, which is widely discussed in the literature.

Another possibility for the modification of support properties is a change in the coking ability. We illustrate it for alumina. The preliminary study of different crystalline forms of alumina allows us to conclude that acid–base pairs, which are a combination of a coordinatively unsaturated aluminum cation (L-site) and a bridging oxygen anion [18], are active in coking. The strength of the acid site has a dominating effect [19]. A γ -Al₂O₃ (A-2) sample was taken for the study.

In aluminum oxide, there are acceptor sites of two types, which can participate in the formation of carbon deposits. The concentration of strong acceptor sites was determined by ESR, and the concentration of weak acceptor sites was determined by the IR spectroscopy of adsorbed CO molecules. Mechanochemical activa-

tion results in a substantial decrease the specific surface area of the samples, especially if the time of activation is short. The dependence of the concentration of strong acceptor on MCA duration has the same nature. A decrease in the concentration of these sites cannot be explained by a decrease in the specific surface area because the number of sites per unit surface area also decreases. When activation lasts 300 s, the surface concentration of acceptor sites decreases by a factor of three. If activation lasts longer, the concentration changes insignificantly.

To elucidate the role of these sites in alumina coking, let us consider how a change in the concentration of acceptor sites of different types affects the rate of coking. With an increase in the time of activation, the rate of coking decreases. After activation of alumina for 300 s, the rate of coking decreases by a factor of 1.5, whereas the concentration of strong acceptor sites per 1 g of the catalyst decreases by a factor of 7. These data suggest that strong acceptor sites are not a part of the active site responsible for the formation of carbon on the alumina surface.

The concentration of weak acceptor sites (unsaturated aluminum ions at the sites with octahedral coordination) decreases from 440 to 180 $\mu\text{mol/g}$ after 120 s of MCA. When the time of MCA is increased from 120 to 300 s, the concentration of these sites decreases insignificantly and becomes equal to 160 $\mu\text{mol/g}$. Thus, the concentration of weak sites ($\nu\text{CO} = 2190\text{--}2198 \text{ cm}^{-1}$) decreases by a factor of ~ 2.5 after 300 s of MCA. This is a somewhat more pronounced decrease than a decrease in the rate of coking, which becomes 1.5 times lower. This can be explained by the fact that the concentration of weak acceptor sites decreases, but their strength grows, because the frequency of CO vibrations in adsorbed CO increases after MCA from 2190 to 2198 cm^{-1} . This points to an increase in the strength of Lewis sites because νCO is related to the heats of molecule adsorption on the L-sites [20]. We conjecture that an increase in the strength of these sites is due to the distortion of the crystalline lattice of alumina during MCA.

Thus, MCA of γ -Al₂O₃ results in a decrease in the coking rate. The reason for that is a decrease in the concentration of acceptor sites, which constitute the active site for coking in alumina. The strongest acceptor sites disappear at early stages of MCA and have no time to contribute to alumina coking. Weaker acceptor sites, which are more resistant to MCA are responsible for coke formation on the alumina surface.

Comparison of these findings with those considered above for supported catalysts shows that MCA applied to alumina improves several properties: resistance to coking, dispersity of supported metals, and an increase in the catalytic activity of supported catalysts.

The results described in this section show the capabilities of MCA in the modification of different properties of catalysts and supports. One of the most impor-

tant properties of catalysts is their mechanical strength. Analysis of published and our data shows that expedients that can improve mechanical strength are rather common to a variety of catalysts. Surface hydroxylation and the separation of temperature intervals for recrystallization and sintering can be applied to almost all systems.

The effects of mechanochemically induced defects of the support on the properties of supported components are of both theoretical and practical interest. An increase in the catalytic activity and the improvement of sorption properties are important for practical purposes.

A decrease in the activity of alumina toward coking is also of practical interest. This support is widely used in the preparation of different catalysts and coking is observed in any hydrocarbon conversion reaction. Coking decreases the catalyst activity and leads to the necessity of catalyst recovery. MCA decreases the ability of alumina to be coked and improves its sorption properties and the activity of supported components.

To summarize the above findings, it is necessary to note that MCA can successfully be used in the synthesis of catalytic systems (mechanochemical synthesis), it favors interaction in further treatments (calcination, hydration, sorption, etc.), improves performance (formation ability, strength, and sorption properties), and helps to synthesize new efficient catalysts. Some generalizations relevant to mechanochemical synthesis (interactions of compounds in the mill without additional treatment) can be made. Mechanochemical synthesis can be carried out if the crystalline structures of reagents are close, if the interaction is of acid-base type when one of the reactants is a strong acid or base, or if pseudomelts are formed when intensive mechanical mixing can make the molecules of at least one reagent as mobile as in the melt. All these cases, were supported many times in our papers and papers written by others.

In other cases when mechanochemical synthesis does not occur, mechanochemical activation simplifies interaction at later stages of catalyst preparation. This is due to changes in thermodynamic potentials because of the formation of defects, changes in electron properties, clean surface formation, and due to other reasons. The high degree of homogenization of reactant mixtures has the most pronounced effect and favors mass transfer processes. Currently, it remains unclear why mechanochemical synthesis can in some cases be carried out in a mill, whereas in other cases it cannot. In our opinion, during the mechanochemical activation of mixtures, the activated state is formed, which after the removal of load can relax by forming new compounds or by transforming into initial substances with higher dispersity and excess energy compared to their initial state. We failed to find in the literature data the reasons for the realization of that or another relaxation pathway.

In our opinion, it is important that activated substances transfer to the plastic state. In this case we see

analogy with adhesion of liquids and melts and with the mixing of liquids if several reacting components transfer to the plastic state. This state leads to a substantial increase in the number and overall area of contacts between reactants. It accelerates diffusion and creates conditions for chemical interactions. Many of the examples of mechanochemical synthesis considered above refer to the cases when at least one component transfers to the plastic state. When correct methods for the calculation or determination of the thermodynamic potentials for adhesion or mixing will appear, they can be used to predict the possibility of mechanochemical synthesis. Specifically one could use the known formulas for the work function of adhesion and cohesion. If $A_{\text{adh}} > A_{\text{coh}}$, then complete wetting takes place. This condition is always fulfilled when chemical bonds between the components are formed. Adhesion is usually stronger than cohesion (i.e., intramolecular cohesion in the plastic-state phase). This results in the situation when the relaxation of the strain field and further loading of substrate-adhesive particles reveals itself in the breaking of bonds in the plastic-state phase. The mechanical loading of the substrate phase will result in the phenomena analogous to adsorption-stimulated dispersion because the surface energy (an analog of the surface tension for solids) tend to the minimum at the boundary between phases in the case of complete wetting. All these factors result in the formation of lamellar structures during MCA either at the molecular level as we showed for the $\text{V}_2\text{O}_5 \cdot \text{MoO}_3$ system or at the microlevel as it was observed for mechanical alloying.

When there is no complete wetting and none of the interacting phases transfer to the plastic state, the activated phases are dispersed and their particles with sizes of up to several nanometers mix homogeneously. This considerably simplifies diffusional transfer, which is necessary for the interaction during subsequent treatments of activated mixtures. Furthermore, in both cases, the reactivity of components decreases due to changes in thermodynamic potentials.

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