Chemistry for Sustainable Development **22** (2014) 345–355

UDC 541.18.053; 546.07

Prospects of Soft Mechanochemical Synthesis

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Abstract

Analysis of the works recently published on the soft mechanochemical synthesis of oxide compounds is presented in the review. Specific features and advantages of this method in comparison with other ones are considered. The possibilities of this method in obtaining materials through easier and readily realizable procedures avoiding solvents are demonstrated. Specific examples of the synthesis of fireproof oxides, spinels, catalysts, lithium-containing compounds, pigments are presented, and the prospects of their implementation are considered.

Key words: mechanical activation, hydrated oxides and salts, mechanochemical synthesis, thermally activated synthesis, nanometer-sized particles

INTRODUCTION

Reactions in the mixtures of hydrated oxides are widely used to obtain various products by means of high temperature thermal treatment of co-precipitated hydroxides. As a rule, reactions proceed in these mixtures through dehydration stage with the formation of simple oxides, and subsequent interaction at high temperature. At the same time, it was shown in some works that a more efficient mechanism is possible. It involves conjugation of dehydration and synthesis reactions. However, it is necessary for its implementation that the mixtures would be characterized by close dehydration temperatures; rather narrow range of mixtures meets these requirements [1]. To broaden this range, it was proposed to subject the mixtures to mechanical activation. This underlay a novel method called soft mechanochemical synthesis (SMS). This method includes mechanical activation of the mixtures of solid compounds containing different oxygen-hydrogen groups (solid acids and bases, hydrated oxides, basic and acid salts, crystalline hydrates *etc.*). Reactions proceeding under the conditions of mechanical activation are distinguished by higher rates in comparison with the reactions in the mixtures of anhydrous oxides, which points to the important role played by these groups. The interaction in these mixtures is due to the participation of surface-active centres, both intrinsic ones and those induced by the action of mechanical activation. The features and advantages of this method were considered for the first time in the review published in 1994 [4] and somewhat later in a monograph [3]. The SMS method obtained recognition of specialists and intense development for different classes of compounds. The works dealing with the use of this method for synthesis of different classes of compounds are discussed in the present review.

SOME PATTERNS OF THE REACTIONS INVOLVED IN SOFT MECHANOCHEMICAL SYNTHESIS

Chemical reactions in the mixtures of hydrated compounds proceed with the participation of water which is present in these compounds in different forms. This may be crystallization or constitution water incorporated in solids and released during mechanical activation, physically adsorbed water, chemically bound water, capillary or free water. The properties of water at the interface between liquid and solid phases differ from bulk properties. The principles known from colloid chemistry and governing the properties at the interface between a solid particle and water are also applicable to mechanochemical phenomena [4]. Water adsorbed on the surface of solids forms a double layer the structure of which includes the region of strong ordering of water near the surface and some transient region containing water clusters in ordinary water [5, 6].

Water affects grinding process and chemical interaction between solids, which is determined by different factors: the nature of a solid body (porous, non-porous, crystalline, microcrystalline, amorphous, hydrated or anhydrous *etc.*), genesis and amount of water, the type and power of the apparatus and so on. During mechanical treatment, water promotes particle destruction and activates the reactions of solids with water (the formation of hydrates and oxyhydrates on the surface, *etc.*) [7]. Accelerated destruction and the efficiency of grinding are due to a decrease in the strength of solids as a result of a decrease in surface tension (Rebinder effect), an increase in the mobility of dislocations and their annihilation, neutralization of the surface charge and delays in closing fresh cracks. Aggregation and agglomeration phenomena are also connected with water. In the presence of water, molecular-dense aggregates of solid particles disintegrate to form primary particles, and fine grinding is improved. However, in the case if water forms 1?3 layers on the surface of the particles, it acts as a binding agent and strengthens the agglomerates through the formation of hydrogen and coordination bonds between water molecules and hydroxylated surface. As a result of structuring of water layers and the action of the surface field of a solid on water layers, hydrogen bonds become stronger, their energy increases more than 2–2.5 times in comparison with their energy in bulk water, while water itself exhibits different properties (density: 1.2 g/cm^3, permittivity: 5) [7, 8].

Numerous data show [9] that grinding and chemical interaction in the presence of water turn out to be more efficient than those during dry grinding, as a result of the above-described processes. With a decrease in particle size, the probability of their interaction increases.

It was established, on the basis of the entire set of results obtained by present that the difference in the acid-base properties of reagents plays an essential part in these reactions. It should be stressed that this generally recognized and available principle of chemistry is widely implemented in inorganic synthesis. There are many theoretical and experimental works explaining the acid and base properties of solids depending on the nature of chemical bonding, structure (coordination number) and degree of oxidation of the constituent ions. A strong difference in acid-base properties leads to a decrease in activation energy and to spontaneous reactions in many cases. The larger is the difference, the higher is interaction rate and the larger is its depth. However, in the case of anhydrous oxides this principle does not work, even if the mixtures are subjected to long-term grinding [9]. This is due to the presence of high activation barriers for reactions between solids. The activation barrier in the reactions involved in SMS is much lower because a reaction proceeds with the participation of protons and hydroxide groups according to neutralization mechanism with the formation of water.

From the viewpoint of thermodynamics, more profitable reactions are those in which a definite optimal amount of water is formed. This may be seen from the calculations of reaction enthalpies (for standard conditions), which were carried out for the reactions listed below:

$$CaO + Me_xO_y = CaMe_xO_{y+1} \quad (1)$$

$$CaO + H_2Me_xO_y = CaMe_xO_y + H_2O \quad (2)$$

$$Ca(OH)_2 + Me_xO_y = CaMe_xO_y + H_2O \quad (3)$$

$$Ca(OH)_2 + H_2Me_xO_y = CaMe_xO_y + 2\ H_2O \quad (4)$$

where Me_xO_y = Al_2O_3, Fe_2O_3, SiO_2, TiO_2, V_2O_5, WO_3; $H_2Me_xO_y$ = $Al_2O_3 \cdot 3H_2O$, $Fe_2O_3 \cdot 3H_2O$, H_2SiO_3, H_2TiO_3, $H_2V_2O_6$, H_2WO_4.

One can see in the data presented in Fig. 1 that more profitable reactions are those in which one mole of water is formed per one mole of the product. For higher water content, if both reagents (acid and base oxides) are hydrated, the reactions are less profitable from the thermodynamic point of view. Reactions of solid anhydrous oxides have high negative Gibbs

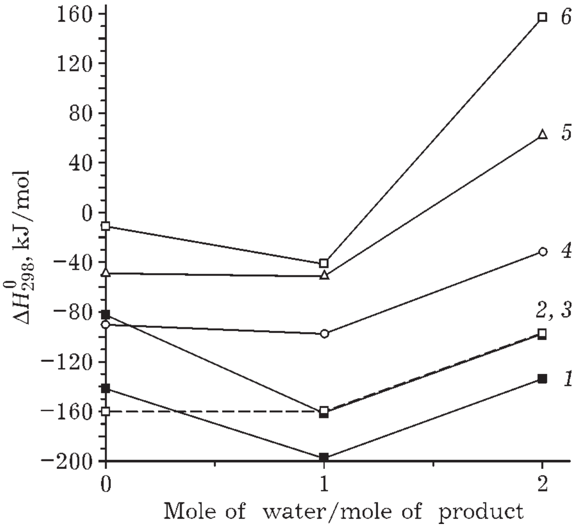

Fig. 1. Changes of the enthalpy of synthesis of calcium salts according to equations (1)–(4) depending on water content in reaction products: *1* – CaV_2O_6, *2* – $CaTiO_3$, *3* – $CaSiO_3$, *4* – $Ca_2Fe_2O_5$, *5* – $CaAl_2O_3$, *6* – $CaWO_4$.

energy values; however, they have a high activation barrier.

In the kinetic aspect, the higher rate of SMS reactions is due also to lower hardness of hydrated compounds and hence their higher plasticity. The rate of solid-phase reactions depends on the area of regions in contact at the boundary between particles, so in the case of more plastic substances this area is substantially larger than that in the case of non-plastic ones. The formation of the agglomerates of solid particles promotes contacts between them at the moment of mechanical action. Depending on the concentration of water (bound in initial reagents or added), reaction rate passes through a maximum. In the case of low water content (mainly adsorbed), the properties of water differ from its bulk properties, which enhances its reactivity. In addition, hydrothermal effects of reactions, caused by local heating at the contacts with milling bodies during the work of grinding devices, are realized to the highest extent [10, 11]. All these data allow one to distinguish an intermediate region differing from purely solid-phase reactions and reactions in aqueous solutions: the reactions of solids in the presence of small amounts of water originating from mechanical activation.

It was shown experimentally that the amorphous phase of the product gets stabilized in the presence of insignificant amounts of water added. To obtain the product in the crystalline form, its subsequent thermal treatment is necessary. In the case of the high power of apparatuses for mechanical activation, thermal treatment may be unnecessary, but expenses for synthesis increase substantially in this situation. In this connection, the most economical methods to carry out the synthesis are those in which low energy mechanical activation is combined with low temperature thermal treatment. Soft mechanochemical reactions meet these requirements to a higher extent.

Nanometer-sized particles are obtained mainly with the help of chemical methods (hydrolysis, sol-gel procedure, precipitation), as well as condensation-based and plasmachemical methods. All these methods have disadvantages, such as low productivity, ecological problems in operations involving solutions *etc.* To obtain oxides in nanodispersed state, it was proposed to use SMS. One of the advantages of this method is the possibility to obtain nanometer-sized and nanostructural materials which may be used to produce materials with qualitatively new properties, not through grinding but due to the reaction between solid particles. Nanometer-sized particles of the product arise at the contacts between particles; if the product is formed in the amorphous state, one may obtain the particles of required size by varying treatment temperature and time. A comparative analysis of the efficiency of SMS and sol-gel procedure, which is considered to be one of the best methods for this purpose, was carried out. It was shown that it both cases the particles of nearly the same size are obtained. However, SMS differs from the sol-gel procedure by simplicity and higher productivity.

SYNTHESIS OF REFRACTORY OXIDES, SILICATES, AND ALUMINOSILICATES

Oxide ceramics is widely used in many branches of technology. Its application for obtaining heat-proof barrier coatings on metal parts working under the conditions of high temperature and are subject to oxidation is of special interest [12]. As a rule, fire-proof oxides are used for these purposes, such as zirconium oxide ZrO_2 stabilized by yttrium (melting point 2700 °C), $MgAAl_2O_4$ spinel (melting point 2135 °C), aluminium oxide a-Al_2O_3 (m. p. 2050 °C), forsterite $2MgO \cdot SiO_2$ (m. p. 1890 °C), mullite $3Al_2O_3 \cdot 2SiO_2$ (m. p. 1870 °C), celsian BaO $AL_2O_3 \cdot SiO_2$ (m. p. 1740 °C), cordierite $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ (m. p. 1465 °C) with inexpensive and available raw material sources. Many works [13, 14] deal with the development of coatings based on these oxides, involving the formation of intermediate layers composed of other materials.

The quality of coatings depends on many parameters, including the size of the particles of the material to be deposited. At present, the attention of researchers is concentrated on developing the new class of coatings based on nanometer-sized and nanocrystalline particles less than 100 nm in size, which provides the unique properties of nanocoatings.

Mechanical activation is carried out using grinding and activating devices of various designs. We used centrifugal mills of the periodic and flow types realizing the principle of shock destruction in combination with attrition [15, 16], in particular planetary mill [17], and a flow centrifugal mill [18].

For each of the oxides listed above, we chose reactions that have been realized with the participation of mechanical activation and subsequent thermal treatment. The difference in acid-base properties of interacting substances determining the rate of interaction between them was taken into account. The results of the studies were published in [19–27].

ZrO_2–8 mol. % Y_2O_3 [20, 21]. After mechanical treatment of the reagents mixture corresponding to equation

$$3ZrO(NO_3)_2 \cdot 3H_2O + Y_2(CO_3)_3 \cdot H_2O \rightarrow (3ZrO_2{-}Y_2O_3) + 3CO_2 + 6NO_2 + 10H_2O \quad (5)$$

in the mills of periodic and flow types under heating to 450 °C a solid solution $ZrO_2{-}Y_2O_3$ is obtained. After thermal treatment at 600 °C, the only identified product is the tetragonal modification of zirconium oxide, with crystallite size 15–17 nm and lattice parameter equal to 0.5135 nm. The powder is readily mouldable by means of dry moulding and is sintered in the air at a temperature of 1450–1600 °C to the density 99 % of the theoretical value.

α-Al_2O_3 [22]. At the stage of mechanical activation, the interaction between the components takes place, leading to the formation of an intermediate compound $AlO_x(CO_3)_4(OH)_y \cdot nH_2O$:

$$2AlCl_3 \cdot 6H_2O + 3Na_2CO_3 \cdot 10H_2O = \gamma\text{-}Al_2O_3 + 6NaCl + 42H_2O + 3CO_2 \quad (6)$$

The obtained product is washed to remove sodium chloride, and annealed. The decomposition process is finished at 500 °C; fine dispersed and highly active γ-Al_2O_3 is formed (specific surface 40 m^2/g). Annealing at a temperature above 1000 °C is accompanied by the transition of this oxide into α-Al_2O_3.

$2MgO \cdot SiO_2$ [23]. For the same method of mechanical activation in the planetary mill under identical conditions of thermal treatment (1200 °C), exchange reactions between salt reagents

$$2Mg(OH)_2 + H_2SiO_3 = Mg_2SiO_4 + 3H_2O \quad (7)$$

$$2(MgCl_2 \cdot 6H_2O) + Na_2SiO_3 \cdot 9H_2O + 2NaOH = Mg_2SiO_4 + 4NaCl + 22H_2O \quad (8)$$

proceed with much higher efficiency than the interaction between magnesium hydroxide and silica gel according to equation (7). At temperatures above 1000 °C, sodium chloride evaporates and is practically absent from the reaction product. Forsterite formed after thermal treatment at 1200 °C according to equations (7) and (8) has uniform particle size equal to 40–45 nm.

$3Al_2O_3 \cdot 2SiO_2$ [24–28]. As a result of mechanical activation, completely amorphized product is formed in the mixture according to equation

$$6Al(OH)_3 + 2(SiO_2 \cdot 0.6H_2O) = 3Al_2O_3 \cdot 2SiO_2 + nH_2O \quad (9)$$

At a temperature of 1300 °C, single-phase mullite with particle size 54 nm is crystallized from amorphized mixture. However, mullite powder does not possess sufficient activity, which is exhibited as its inertness during sintering. In order to improve its sintering properties, it is recommended to subject the powder to additional short-term mechanical activation.

Mechanical activation of the mixture according to equation

$$6(AlCl_3 \cdot 6H_2O) + 2(Na_2SiO_3 \cdot 9H_2O) + 14NaOH = 3Al_2O_3 \cdot 2SiO_2 + 18NaCl + 61H_2O \quad (10)$$

is accompanied by the formation of X-ray amorphous product and well crystallized NaCl. The appearance of reflections of sodium chloride in diffraction patterns provides unambiguous evidence of the exchange reaction between the components during activation. The product was subjected to thermal treatment after washing with water to remove sodium chloride. At a temperature of 750 °C, the signs of mullite formation appear in the diffraction patterns, while at a temperature of 1000 °C it is recorded reliably; its particle size is equal to 28 nm. An increase in annealing temperature to 1200 °C is accompanied by an increase in crystallite size to 43 nm but does not affect the lattice parameters. So, the exchange reaction of aluminium chloride with sodium silicate in the presence of sodium hydroxide, proceeding during the mechanical activation of the mixture, provides a decrease in the temperature of the synthesis of mullite in nano-dispersed state nearly by 300 °C.

$BaO \cdot Al_2O_3 \cdot 2SiO_2$ [28]. Mechanically activated mixtures obtained according to equation

$$BaO + 2Al(OH)_3 + 2H_2SiO_3 = BaO \cdot Al_2O_3 \cdot 2SiO_2 + 5H_2O \quad (11)$$

were subjected to thermal treatment for 2 h at a temperature of 1200 °C. According to the XPA data, hexagonal celsian is formed. In comparison with non-activated mixtures, the synthesis proceeds at 1200 °C instead of 1400 °C.

$2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ [29–31]. Mechanical activation of mixtures according to equations

$$2MgO + 4Al(OH)_3 + 5H_2SiO_3 = 2MgO \cdot 2Al_2O_3 \cdot 5SiO_2 + 11H_2O \quad (12)$$

$$4(3MgO \cdot 4SiO_2 \cdot H_2O) + 7(Al_2O_3 \cdot 2SiO_2 \cdot H_2O) + 10Al(OH)_3 = 6(2MgO \cdot 2Al_2O_3 \cdot 5SiO_2) + 33H_2O \quad (13)$$

leads to the formation of X-ray amorphous phase from which cordierite is crystallized as a result of heating. The synthesis of cordierite proceeds at lower temperature than in the case of non-activated mixtures (1200 and 1400 °C, respectively) for 2–3 h. Almost pure cordierite is obtained; it does not contain admixture phases. The synthesized cordierites was ground in the planetary mill for 1 min. The achieved average particle size was nearly 6 μm, and specific surface was 2.6 m^2/g. Then cordierite power was subjected to plasticization, extrusion and sintering at 1400 °C. The texture of the resulting samples is a porous polycrystalline matrix composed of crystallites connected with each other through contact sites. The density of the ceramics is 2.3 g/cm^3, porosity is 5–8 %. Compression strength of the ceramics was 130–240 MPa.

It follows from the listed data that nanoparticles of the product are formed during thermal synthesis of complex oxides with the use of mechanical activation at the stages preceding thermal treatment and with the use of hydrated compounds at substantially lower temperatures than in the case of the mixtures of anhydrous compounds. The use of exchange reactions participated by hydrated salts is more efficient than the reactions of hydrated oxides; in addition, the formation of smaller particles is provided in the case of hydrated salts.

SYNTHESIS OF SPINEL

Spinel synthesis procedures are based on chemical and solid-phase reactions. The major methods include hydrothermal reactions, co-precipitation, sol-gel procedure, solid-phase reactions. The SMS procedure is becoming important, as it is considered to be efficient method of obtaining new and cheap materials. Usual solid-phase reactions require high temperatures. Under the action of mechanical activation, the interaction may proceed till the formation of final products or precursors, the synthesis from which proceeds at substantially lower temperature.

$MgAl_2O_4$ [32–35]. The synthesis of aluminomagnesium spinel can be carried out according to reactions

$$MgO + Al_2O_3 = MgAl_2O_4 \quad (14)$$

$$Mg(OH)_2 + Al_2O_3 = MgAl_2O_4 + H_2O \quad (15)$$

$$MgO + 2Al(OH)_2 = MgAl_2O_4 + 3H_2O \quad (16)$$

$$Mg(OH)_2 + 2Al(OH)_2 = MgAl_2O_4 + 4H_2O \quad (17)$$

The synthesis according to these reactions was carried out with the help of high-energy grinding followed by thermal treatment at 900 °C. It was shown that after mechanical activation for 65 min the maximal yield of spinel was achieved in the case of equation (17). Activation energy was determined; it was 127 and 22 kJ/mol for equations (15) and (17).

According to the data reported in [34, 35], an X-ray amorphous compound is formed during the treatment of a mixture of magnesium and aluminium hydroxides in the grinding apparatus. Thermal treatment of this compound involves its dehydration, and nanodispersed spinel composed of the particles 7–10 nm with the high degree of microdeformations is formed at a temperature above 750 °C. An increase in temperature is accompanied by crystallite

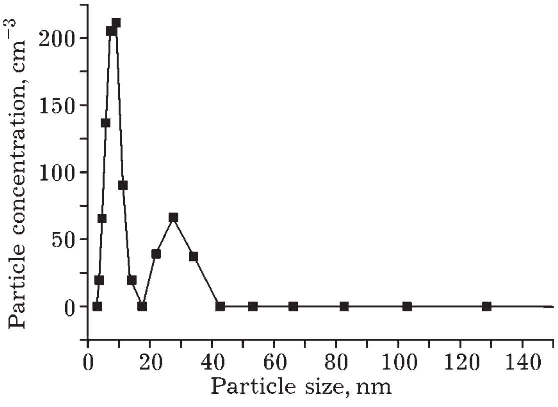

Fig. 2. Particle size distribution for $MgAl_2O_4$ spinel sample obtained by means of the soft mechanochemical synthesis.

growth and a decrease in the degree of microdeformations. The data on particle size determined by means of laser ablation are shown in Fig. 2 [35]. One can see that the particles with the narrow size distribution within the range 5–7 nm and larger particles 20–40 nm in size are detected in the products of synthesis. According to XPA data, these are secondary formations (agglomerates) composed of the particles 5–7 nm in size, and it is difficult to destroy these agglomerates under the conditions of the method used. However, the very fact of the existence of nanometer-sized particles obtained with the use of mechanical activation demonstrates the possibilities of this method.

$NiFe_2O_4$ [36–41]. Monophase $NiFe_2O_4$ was obtained at 500 °C from the mixtures of nickel and iron hydroxides after mechanical activation for 5 h in a Fritsch Pulverisette 7 planetary mill [36]. For comparison, the same mixtures were heated without activation, and spinel was not formed. In the synthesized ferrite, the amount of iron cations Fe^{3+} in tetrahedral surroundings is smaller than in usual nickel ferrite (31 and 50 %, respectively). Their number increases as a result of heating and reaches the values characteristic of usual ferrite.

In [37], the synthesis of nanocrystalline $NiFe_2O_4$ was realized also by means of SMS from a mixture of $Ni(OH)_2$ and $Fe(OH)_3$ powders activated in the planetary mill. Monophase nanometer-sized product was synthesized after mixture treatment for 25 h and thermal treatment at 1100 °C for 2 h. According to XPA data, a single phase with the cubic structure is formed. Electric measurements showed that the conductance is connected with intergrain boundaries and has a negative coefficient characteristic of semiconductors. Judging from the activation energy value, the conductance is due to electron transitions between Fe^{2+} and Fe^{3+}.

The same authors in another work [38] succeeded in obtaining nickel and manganese ferrites by means of SMS, with the size of 30–40 nm, avoiding the stage of thermal treatment, according to reactions

$$Ni(OH)_2 + Fe_2O_3 = NiFe_2O_4 + H_2O \quad (18)$$

$$Mn(OH)_2 + Fe_2O_3 = MnFe_2O_4 + H_2O \quad (19)$$

It was shown that mechanical activation leads to amorphization of initial materials and the formation of NiO, NiO(OH), FeO(OH) phases after treatment for 10 h. The $NiFe_2O_4$ phase appears only after activation for 25 h for reaction (18), while in the case of reaction (19) phases MnO, FeO(OH) are observed after 12 h. Pure ferrite $MnFe_2O_4$ is detected only after activation for 25 h. The transitions of cations from the octahedral coordination into tetrahedral one were detected by means of Mössbauer spectroscopy. The amount of Mn^{2+} cations in the tetrahedral surroundings decreases with a decrease in particle size.

$MgFe_2O_4$ [39]. The synthesis of iron-magnesium spinel was realised through the activation of $Mg(OH)_2 + Fe_2O_3$ and $Mg(OH)_2 + Fe(OH)_3$ in a planetary mill. Spinel formation started after activation for 5 h and was finished after activation for 15 h. The particles of synthesized spinel were 10 and 15 nm in size for the indicated mixtures, respectively. Measurements of magnetization after activation for 15 h showed the values of 15–23 and 10–14 J/(T · kg), respectively.

In [40–43], the following exchange mechanochemical reactions were used to obtain nanometer-sized ferrites:

$$2FeCl_3 + CoCl_2 + 3Na_2CO_3 + Ca(OH)_2 \rightarrow CoFe_2O_4 + CaCl_2 + 6NaCl + H_2O + 3CO_2\uparrow \quad (20)$$

$$FeSO_4 + 2FeCl_3 + 8NaOH \rightarrow Fe_3O_4 + Na_2SO_4 + 6NaCl + 4H_2O \quad (21)$$

$$LiCl + 5FeCl_3 + 8Na_2CO_3 \rightarrow LiFe_5O_8 + 16NaCl + 8CO_2 \quad (22)$$

$$MgCl_2 + 2FeCl_3 + 4Na_2CO_3 \rightarrow MgFe_2O_4 + 8NaCl + 4CO_2 \quad (23)$$

$$MnO_2 + 2FeCl_3 + 6NaOH \rightarrow MnFe_2O_4 + 6NaCl + 0.5O_2 + 3H_2O \quad (24)$$

$$CuCl_2 + 2FeCl_3 + 4Na_2CO_3 \rightarrow CuFe_2O_4 + 8NaCl + 4CO_2 \quad (25)$$

The initial reagents for the synthesis were salts in the form of crystal hydrates, except for manganese oxide, sodium carbonate and hydroxide; all reagents were at least Kh. Ch. (chemically pure) reagent grade. In order to prevent aggregation of nanoparticles, an inert component (sodium chloride) at a ratio of 1 : 2 was introduced additionally during mechanical activation. The mixture of reagents and sodium chloride was sealed in quenched steel cylinders with steel balls 5 mm in diameter. Mechanical activation was carried out in a planetary mill (acceleration was 60*g*) with the powder to balls mass ratio equal to 1 : 20 for 30 min. The products were washed on the filter with distilled water till complete removal of the salts, dried at room temperature and then treated with ultrasound and centrifuging.

The phase composition, morphology, disperse state and structural parameters of nanometer-sized powders were determined by means of X-ray structural analysis and transmission electron microscopy; the specific surface of the synthesized samples was determined by means of thermal desorption of nitrogen using a SORBI N 4.1 instrument. Particle diameter (D) was calculated using equation

$$D = 6 \cdot 10^{-4}/\gamma S$$

where γ is density, g/cm^3; S is specific surface, m^2/g. According to the data of electron microscopy, nanometer-sized particles of all the synthesized oxide ferrimagnetics have a spherical shape. The particle size distribution of magnetite particles (Fe_3O_4) is unimodal and includes the particles 3–14 nm in diameter; nearly 60 % of them are 3–7 nm in size. The compound $CoFe_2O_4$ is composed of nanometer-sized grains (3–15 nm) weakly bound with each other; the fraction of the particles 4–8 nm in diameter is approximately equal to 65 %. Magnesium ferrospinel $MgFe_2O_4$ contains the particles with the average size of (6±2) nm, but also larger particles (50±20) nm in size occur. The powder of lithium ferrospinel contains two size classes. The first one includes rather coarse particles (44±2) nm in diameter, their fraction reaches 30 %, while the second class includes the particles of medium size (D = (9±2) nm); their fraction reaches 60 %. For $CuFe_2O_4$ and $MnFe_2O_4$ samples, the particles (4±2) and (5±2) nm, respectively, are characteristic. The parameters of the synthesized spinels are shown in Table 1.

The transition of ferrite spinel into the nanometer-sized state is accompanied by a substantial change in its magnetic properties, first of all magnetization, the field of magnetic crystallographic anisotropy and Curie temperature. These materials are of substantial interest for medicine and biology because they may be involved in solving the problems connected with the separation and purification of biological substances, with pharmacokinetic studies, targeted delivery of medicines and genes, and enhancement of contrast of magnetic resonance images [43].

SYNTHESIS OF CATALYSTS

The development of SMS during the recent years opened a novel direction in the area of catalyst preparation. A number of catalysts based on simple and complex oxides were developed with the help of SMS. These catalysts are distinguished by phase purity, high crystallinity and small grain size with narrow distribution. Also one of the advantages of SMS is the absence of waste water, which is important from the ecological point of view. Due to a decrease in the time and temperature of thermal treatment, energy consumption for the preparation of catalysts decreases substantially.

TiO_2 [44, 45]. Titanium dioxide and its derivatives possess good photocatalytic properties; these compounds are used to purify air and water from various pollutants [46]. The charac-

TABLE 1

Specific surface, particle size and microdeformations in the powder of mechanochemically synthesized ferrospinel

Samples	S_{sp}, m^2/g	D_{calc}, nm	$D_{cl(XSA)}$, nm/ D_{el}, nm	$10^3\Delta d/d$
Fe_3O_4	150	8	11/13	7.4
$MnFe_2O_4$	103	11	11/5	7.4
$LiFe_5O_8$	119	10	10/9	8.7
$MgFe_2O_4$	132	10	11/7	8.3
$CoFe_2O_4$	113	10	9/8	8.8
$CuFe_2O_4$	162	7	9/5	8.5

teristics of these compounds depend on particle size, crystallinity, phase composition, specific surface, microstructure and morphology of powders. Among the known seven polymorphous modifications [47], four modifications are used most frequently: anatase, brookite, rutile and the high pressure phase. The photocatalytic properties of anatase and rutile were studied; it was established that anatase exhibits higher activity.

The SMS procedure was used in [44] to obtain nanometer-sized TiO_2 particles according to reaction

$$TiOSO_4 \cdot xH_2O + Na_2CO_3 \rightarrow TiO_2 + Na_2SO_4 \cdot xH_2O + CO_2 \quad (26)$$

It was established that nanocrystals rutile with particle size 15 nm is formed as a result of mechanical activation of the initial mixture taken in the stoichiometric ratio 1 : 1 for 60 min; the traces of TiO_2 high pressure phase were also detected. To separate the particles of titanium dioxide from the salt, reaction products were treated with water. In order to obtain anatase modification, the time of mechanical treatment was decreased to 5 min, but then the mixtures were subjected to thermal treatment at 300–600 °C; particles 5–35 nm in size were obtained. Under irradiation with light, anatase powders exhibit good activity in forming free radicals, which is recorded by means of EPR. It was demonstrated that mechanical activation of initial products containing no water does not involve interaction.

Dissolution and separation of solid nanoparticles from the salt solution are rather inconvenient, so it was proposed in [44] as a development of this method to carry out exchange reactions with ammonium salts, for example with ammonium carbonate:

$$MeCl_4 \cdot xH_2O + 3(NH_4)_2CO_3 = MeO_2 + 4NH_4Cl + 3CO_2 + xH_2O + 2NH_3 \quad (27)$$

During heating of the mixture, which is necessary to crystallize the target product, ammonium salts decompose at a temperature above 350 °C and evaporate from the reaction zone.

$LaCoO_3$ [48, 49]. Lanthanum cobaltite is a highly active catalyst for the oxidation of carbon monoxide. This catalyst is obtained mainly using labour-intensive thermal synthesis, which involves long-term thermal treatment at temperatures above 1000 °C and multiple intermediate grinding. Heating at high temperature causes powder agglomeration and hinders the formation of powders with highly developed surface, which is essential for the use as catalysts. In [48], a method was proposed to synthesize this compound from mechanically activated mixtures of hydrated carbonates of lanthanum and cobalt followed by thermal treatment at a temperature of 400–900 °C according to reaction

$$La_2(CO_3) \cdot 6H_2O + CoCO_3 \cdot Co(OH)_2 \cdot 2H_2O + 1/2O_2 = 2LaCoO_3 + 9H_2O + 4CO_2 \quad (38)$$

According to XPA data, the synthesis is carried out completely with the formation of well crystallised lanthanum cobaltite at a temperature of 700 °C; the formation of the product is observed even at 550 °C. An increase in temperature results in an increase in crystallite size and a decrease in specific surface. The maximal specific catalytic activity is demonstrated by the samples annealed at 600 °C; their activity is higher than the catalytic activity of the samples obtained using the thermal method. So, the optimal conditions for the synthesis of fine and active $LaCoO_3$ were determined: mechanical activation of a mixture of hydrated carbonates of cobalt and lanthanum for 5 min in the AGO-2 planetary mill, followed by annealing at a temperature of 700 °C.

Another version of the synthesis of $LaCoO_3$ was proposed in [49]. A mixture of $LaCl_3$, $CoCl_2$, NaOH at a ratio of 1 : 1 : 6 was subjected to mechanical activation for 3 h in a planetary mill. The formation of $La(OH)_3$, $Co(OH)_3$, NaCl phases during the treatment was detected. Pure $LaCoO_3$ was obtained by thermal treatment of the mixture at 600 °C. After removal of water, the specific surface of the powder was 10 m^2/g.

$Cr_2(MoO_4)_3$ [50]. This compound is the catalyst of the soft oxidation of alcohols; its synthesis was realised by means of SMS as described in [49]. A stoichiometric mixture of $Cr(OH)_3$ and MnO_3 at the molar ratio of 2 : 3 was subjected to intense mechanical activation in a Fritsch Pulverisette-7 planetary mill for different time intervals, and then to thermal treatment at different temperatures. Treatment for 5 h results in the complete amorphization of initial products. Heating of the activated mixture allows one to decrease the synthesis temperature to 400 °C instead of 700 °C, which is necessary for usual solid-phase synthesis.

$LaCrO_3$ [51]. Mixtures of $Cr(OH)_3 \cdot nH_2O$ and La_2O_3 were taken for SMS. Before mechanical activation, hydrated chromium hydroxide was heated to 200 °C to remove part of its water. After activation for 3 h, $LaCrO_3$ with specific surface equal to 5 m^2/g was obtained.

$MoS_2–Ni_3S_2$ [52]. The catalyst composed of molybdenum and nickel sulphides possesses good catalytic properties in hydrodesulphurization reactions. In [52], a precursor was obtained by means of SMS from initial compounds $NiCO_3 \cdot 2Ni(OH)_2 \cdot xH_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$; annealing of this precursor gives $NiMoO_4 \cdot xH_2O$. This compound is readily sulphidized; the resulting sulphide catalyst possesses high activity and stability in hydrodesulphurization, hydrogenolysis and hydrogenation.

SYNTHESIS OF LITHIUM-CONTAINING MATERIALS

Promising materials for lithium current sources are the complex oxides of lithium and transition metals with layered and spinel structure. Among them, the compounds and solid solutions based on $LiCoO_3$, $LiNO_3$, $LiMn_2O_4$ have been studied in detail. The leading compound in this group is lithium manganese spinel which is distinguished by high power intensity, low cost and non-toxic properties.

$LiMn_2O_4$ [53, 54]. The synthesis of this compound is usually carried out using the thermal method at a temperature above 800 °C. Thus obtained spinel possesses low dispersity, small specific surface and insufficient electrochemical activity. The application of SMS allowed one to obtain spinel in fine dispersed state and stabilize the cubic structure due to the higher Mn(IV) content than that in the case of thermal synthesis. Initial reagents were lithium compounds LiOH, $LiOH \cdot H_2O$ and MnO, Mn_2O_3, MnO_2. Spinels of both stoichiometric and non-stoichiometric composition were obtained. The interaction proceeds with the highest efficiency in the mixtures of $LiOH \cdot H_2O$ with manganese dioxide MnO_2, which is due to the largest difference in their acid-base properties.

The development of this method in application to lithium-containing materials allowed the development of a number of new compositions based on solid solutions possessing increased conductivity and cycling ability. Detailed information on the synthesis and properties of these materials was reported in reviews [54–58].

SYNTHESIS OF PIGMENTS

By analogy with spinel synthesis, the synthesis of pigments for glazing and overglaze paints was realized with the help of SMS. The blue overglaze paints $CoAl_2O_4$ is obtained by the mechanical activation of a stoichiometric mixture of cobalt oxide Co_3O_4 and aluminium hydroxide in a centrifugal planetary mill, followed by thermal treatment at 1100 °C for 2 h [59]. Using aluminium hydroxide and iron oxide, a pigment of red-brown colour was obtained according to this procedure. In the case of zinc hydroxide and cobalt oxide, a pigment of light-green colour was obtained [60].

The advantages of SMS procedure are evident for the synthesis of the whole spectrum of pigments based on hexacyanoferrates (II, III) of 3*d* elements as realized in [61] according to reactions

$$2MeSO_4 + K_4[Fe(CN)_6] = Me_2[Fe(CN)_6] + 2K_2SO_4 \quad (29)$$

$$3MeSO_4 + 2K_3[Fe(CN)_6] = Me_3[Fe(CN)_6] + 3K_2SO_4 \quad (30)$$

where M = Mn, Co. Cu, Zn, *etc*. The initial reagents were crystal hydrates of sulphates and anhydrous sulphates (for comparison). The mixtures were activated in a ball vibratory mill for 15 min. The synthesis proceeds in the mixtures with the participation of both anhydrous sulphates and crystal hydrates, but the rate and yield are substantially higher in the latter case. The authors explain an increased yield in the

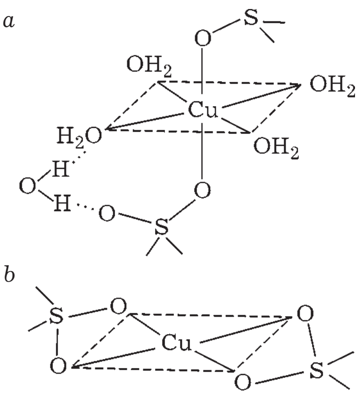

Fig. 3. Structural fragments of crystal hydrate (*a*) and anhydrous copper (II) sulphate (*b*).

reactions participated by crystal hydrates in comparison with anhydrous sulphates (for copper as example) by substantial differences in the structures of initial states (Fig. 3).

The coordination number of copper ion in crystal hydrate is 6, while in the anhydrous sulphate it is 4; the corresponding strength of Cu–O bond in crystal hydrate is substantially lower than in anhydrous sulphate. For this reason, rearrangement of the structure is simplified, and reaction yield increases.

The pigments of a broad spectrum obtained by means of SMS according to the indicated reactions may be used to paint polymeric composite materials.

CONCLUSION

Examples described in the present review show that SMS is being successfully introduced into the practice of scientific and applied research, and the range of its applications broadens every day. Substantial attention is paid to this method, along with other developing directions, in the reviews on mechanochemistry and mechanochemical synthesis published recently in home and foreign journals [62–64].

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