Mechanochemical Synthesis as a Method for the Preparation of Nanodisperse Particles of Oxide Materials

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Abstract

Using various versions of mechanochemical synthesis for the preparation of nanodisperse particles of oxide materials is considered. The results of investigations of some solid-phase reactions in mixtures of reagents subjected to mechanical activation and subsequent thermal treatment are presented. The role of the salt matrix in preventing aggregation of ultradisperse particles has been studied. The efficiency of soft mechanochemical synthesis is compared with that of the sol-gel method. Both methods make it possible to obtain nanodisperse particles close in size.

INTRODUCTION

Mechanochemical synthesis is a rather simple and accessible method for the preparation of inorganic compounds [1–4]. However, it is less known as a method giving nanodisperse particles. Disperse particles are formed during mechanochemical synthesis as a result of pulverization of the reagents and chemical interaction between the components. Particles of the reaction products are formed as two-dimensional nuclei at points of contact between reagents; then they grow in volume. Particle size can be controlled by varying the temperature and time of the subsequent heat treatment of the activated mixtures. It was noted earlier that oxides with particles 1–5 μm in size are available through pulverizing, and particles sized 0.02–0.2 μm could be obtained by using mechanochemical reactions [3].

A large number of compounds were synthesized by mechanical activation, and some regularities of mechanochemical reactions have been established [5–8]. In particular, it was demonstrated that interpenetration of the solid components forming the product phase is predominantly observed in systems characterized by the negative values of the thermodynamic potential (Gibbs energy) of the reactions [6]. It was also shown that the reaction rate (for example, for tungstates) with close values of reaction heat is controlled by the hardness of reagents [8]: the smaller the hardness, *i. e.*, the higher the plasticity of the substance, the closer the contact between the particles and the higher the reaction rate. Based on the assumption that the reaction rate is proportional to the area of the contact sites, equations adequately describing the dependence of the product yield on the time of mechanical activation have been derived [8, 9]. For the case of the surface of powders increasing linearly with activation time

$$\alpha/(1 - \alpha) = K_1 t^2 \quad (1)$$

where α is fractional conversion, t is the operating time of the device, and K_1 is a constant.

If the initial components already are of maximally high dispersity and mechanical activation only makes them react, the equation is simplified to

$$\alpha/(1 - \alpha) = K_2 t \quad (2)$$

This equation is similar to the equation of a bimolecular reaction, except that the constant

K_2 has a different sense compared to the molecular kinetic theory of reactions.

Formation of disperse materials during mechanochemical synthesis was repeatedly registered earlier. The authors of [10] studied the reaction between hydrated aluminum chlorides and soda. Activation of the mixture was followed by washing the product with water and then by heat treatment. At 500 °C, the resultant basic aluminum carbonate decomposes to form disperse aluminum oxide (specific surface 40 m^2/g). Oxalic complexes of various metals were also produced in the course of mechanical activation of solid oxalic acid with hydroxides and basic salts of metals [11]. Ultrafine and highly active catalysts, pigments, and other practically significant substances were obtained by thermal decomposition of the complexes.

It was reported [12–16] that a series of compounds had been synthesized in the nanodisperse state by mechanical activation of mixtures of anhydrous oxides and salts. The synthetic procedure is based on substitution reactions realized during activation and subsequent heat treatment. Introduction of one of the reaction products as an additive in the starting mixture prevents aggregation of another product and is used as a method to control particle size for the main product.

It should be noted that mechanochemical synthesis using anhydrous compounds as starting products often occurs at low rates even for high mechanical stress. The reactions are promoted by using hydrated compounds as the starting substances. Activation of a mixture of compounds with acid-base properties is accompanied by neutralization reactions, which considerably accelerate the interaction. This method is known as “soft mechanochemical synthesis” [17].

As some hydrated compounds have low melting points, they are likely to form a melt (gel paste) during mechanical activation of their mixture; in the melt, a new phase nucleates. For this reason, one can anticipate the soft mechanochemical synthesis to be similar to the sol-gel method. In any case, synthesis involves hydrated compounds, and crystallization of the dehydrated products occurs after subsequent heat treatment. It is common knowledge that the sol-gel method is widely employed for the preparation of nanodisperse particles. The soft mechanochemical method can also be used for this purpose, but is less actively investigated.

CHANGE IN PARTICLE SIZES DURING MECHANICAL ACTIVATION

According to modern knowledge, ultradisperse substances have primary (crystallites), secondary (globules), and tertiary (agglomerates) particles (see, for example, [18]). Crystallites have a regular structure; they are relatively free of point defects and dislocations and reach 10–100 nm in size. Globules are formed from primary particles due to noncompensated superficial chemical bonds, and agglomerates (grains) are derived from globules due to van der Waals forces. Formation of such particles is predetermined by the mosaic structure of solids [19].

To illustrate the above classification, Table 1 lists experimental data on particle sizes of hydrargillite for different mechanical activation times (planetary mill EI-2 × 150, acceleration 40 *g*).

The average size of crystallites (in coherent scattering regions) was determined by the Selyakov – Scherrer formula from X-ray line broadening [20]. The size of globules was calculated from the specific surface and density based on the assumption that the globules have a spherical or oval form [21]. The size of agglomerates was estimated by laser granulometry (with stirring and ultrasonic treatment of the aqueous slurry).

As can be seen from Table 1, the size of the primary particles monotonically decreases with activation time (with simultaneous amorphization of the product), the size of globules passes through a minimum, and the size of agglomerates decreases only slightly. The minimal size of globules equals 3 or 4 sizes of the primary aluminum hydroxide particle. It was demonstrated [22] that long activation of hydrargillite leads to splitting of crystals into plates up to 4–5 nm in diameter and 1–2 nm in thickness. Note that agglomerates of the activated compound in an aqueous slurry are practically identical in size.

TABLE 1

Changes in the particle size of $Al(OH)_3$ for different activation times

Charac-teristic	Activation time, min								
	0	1	2	3	6	9	12	15	18
d, nm	31	31	25	22	16	11	10	7	6
D, nm	690	335	225	210	55	155	195	300	250
V, μm	3.9	2.7	3.5	4.4	3.7	3.8	3.5	3.0	3.1

Note. d, D, V are the sizes of crystallites, globules, and agglomerates (grains), respectively.

COMPARISON OF SOL-GEL AND MECHANOCHEMICAL METHODS FORMING COMPLEX OXIDES

Aluminotitanium mixtures with different component ratios were synthesized by the sol-gel method [23]. The calcinated samples exhibit delayed crystallization of both aluminum oxide and titanium dioxide compared to crystallization of the individual compounds. The effect of mechanical activation of a mixture of aluminum hydroxide and hydrated titanium dioxide (titanic acid) on subsequent formation of particles during synthesis of aluminum titanate by the reaction

$$2Al(OH)_3 + H_2TiO_3 \rightarrow Al_2TiO_5 + 4H_2O \quad (3)$$

is described in [24]. Table 2 gives particle sizes for particles produced by heat treatment of aluminotitanium mixtures in the course of tialite formation (β-Al_2TiO_5).

The mechanochemical and sol-gel methods allow crystalline aluminum titanate (β-Al_2TiO_5) to be synthesized at a temperature of 1340 °C with an average size of globules of less than 10 μm; the size of crystallites is 35–40 nm. There is certain evidence suggesting that an amorphous hydrated compound, which is stable up to temperatures of 450–700 °C, is formed in the course of synthesis. At elevated temperatures, this compound dissociates into ultrafine oxides, which give rise to tialite formed at a temperature of about 1340 °C.

The case is opposite for synthesis of zirconium titanate. Using the sol-gel method led to xerogels whose calcination at 600 °C gave rise to crystalline $ZrTiO_4$ [25]. Synthesis by the soft mechanochemical method also gives rise to crystalline zirconium titanate formed at 600 °C [26] by the reaction

$$Zr(OH)_4 + H_2TiO_3 \rightarrow ZrTiO_4 + 3H_2O \quad (4)$$

In both cases, formation of X-ray amorphous hydrated zirconium titanate occurs before $ZrTiO_4$ crystallization. Comparison of the particles available by different methods is given in Table 3.

As aggregation of particles prevents the use of the developed surface of the samples, there is a serious problem of how to prevent formation of globules from primary particles. One of solutions to this problem lies in choosing solid-phase reactions where one of the products is the compound acting as an inert matrix and hampering aggregation of nanosized particles of the target product.

USING MECHANOCHEMICAL EXCHANGE REACTIONS TO OBTAIN NANOSIZED PARTICLES

To study exchange reactions forming a salt matrix, we investigated reactions between zirconium chlorides (nitrates) and hydroxides or carbonates of alkaline and alkaline earth elements [27], in particular, the reaction

$$ZrOCl_2 \cdot 8H_2O + 2NaOH \rightarrow ZrO_2 + 2NaCl + 9H_2O \quad (5)$$

TABLE 2

Particle sizes after calcination of a mixture of hydrated aluminum and titanium oxides (Al/Ti = 2) produced mechanochemically (numerator) and by the sol-gel method (denominator)

Charac-teristic	T, °C		
	25	450	1340
d, nm	r/am	r/am	40/35
D, nm	110/–	24/10	9100/2700

Note. r/am is an X-ray amorphous state.

TABLE 3

Size of zirconium titanate particles on calcination of samples obtained by mechanical activation of a mixture of hydrated oxides (numerator) and by the sol-gel method (denominator)

Characteristic	T, °C				
	25	400–450	600	800–900	1200
d, nm	r/am	r/am	12/17	13/15	34/–
D, nm	68/–	84/17	91/180	285/206	3260/–

The resulting hydrated zirconium oxides or oxycarbonates rather easily decompose on heating, giving nanosized particles of zirconia within the matrix of alkaline or alkaline earth element chlorides (nitrates). The matrix is readily soluble in water and can be easily removed from the system. Particle sizes of zirconia obtained by reaction (5) after thermal treatment of the mixture are presented in Table 4.

In this case, the observable crystallites are 2–3 times smaller than the globules. As can be seen from Table 4, the size of globules remains virtually constant over a wide temperature range (up to 900 °C). The dispersity of the target ZrO_2 is controlled by the dispersity of the intermediate of the reaction. The solid (NaCl) matrix keeps zirconia particles from aggregation, which is one of the advantages of mechanochemical synthesis.

Low-temperature mechanochemical treatment gave a cubic solid solution of ZrO_2–Y_2O_3 in the nanodispersed state [28]. The exchange reaction

$$3(ZrO(NO_3)_2 \cdot 2H_2O) + Y_2(CO_3)_3 \cdot 3H_2O \rightarrow (3ZrO_2{-}Y_2O_3) + 3CO_2 + 9H_2O + 6HNO_3 \quad (6)$$

forms zirconium oxycarbonate and yttrium nitrate. A solid solution is produced by heating the mixture at temperatures of up to 400–500 °C. Particle sizes of the solid solution obtained by reaction (6) are presented in Table 5.

In this case, the size of crystallites is much smaller than that of globules. Treatment above 900 °C results in a sharp growth of particle size, and sintering of the samples occurs. The average grain size V depends on the composition of the resultant solid solution: 8 % Y_2O_3 – 15.2 μm, 15 % – 17.2 μm, 20 % – 23.3 μm, 25 % – 23.1 μm. Incorporation of yttrium into the solid solution promotes growth of the grain size in high-temperature samples. The possibility to obtain a solid solution of the samples in the nanodisperse state at rather low temperatures is also an advantage of the mechanochemical method.

CONCLUSIONS

The above data, in our opinion, clearly demonstrate that the mechanochemical method has a great potential in obtaining nanodisperse particles of various inorganic compounds. While

TABLE 4

Sizes of zirconia crystallites and globules obtained by reaction (5) at different calcination temperature

Characteristic	T, °C					
	25	320	450	600	900	1200
d, nm, before washing out NaCl	r/am	r/am	24 (T > 95 %)	21 (T, 40 %)	31 (T, 20 %)	
				21 (M, 60 %)	28 (M, 80 %)	86 (M, 100 %)
The same, after washing out	r/am	r/am	21 (T > 95 %)	19 (T, 30 %)	31 (T, 20 %)	
				19 (M, 70 %)	29 (M, 80 %)	86 (M, 100 %)
D, nm, after washing out NaCl	51	41	42	43	70	1630

Note. T is the tetragonal modification of ZrO_2, and M is the monoclinic form.

TABLE 5

Particle sizes of the solid solution of cubic $3ZrO_2-Y_2O_3$ obtained mechanochemically

Characteristic	T, °C			
	450	600	900	1200
d, nm	3	4	8	48
D, nm	60	12	40	1820
V, μm	–	–	–	23.1

this is a relatively simple procedure, there is a real possibility to expand its applications, for example, to improve the quality of ceramics.

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REFERENCES

1 V. V. Boldyrev, E. G. Avvakumov, *Uspekhi khimii,* 40 (1971) 1836.

2 P. Yu. Butyagin, *Ibid.*, 40 (1971) 1935.

3 G. S. Khodakov, Fizika izmelcheniya, Nauka, Moscow, 1972.

4 G. Heinike, Tribochemistry, Academie-Verl., Berlin, 1976.

5 J. S. Benjamin, *Scientific America,* 5 (1976) 40.

6 E. G. Avvakumov (Ed.), Mekhanokhimicheskiy sintez v neorganicheskoy khimii, Nauka, Novosibirsk, 1991.

7 E. Gaffet and O. Tillement, *Annales de Chimie*, 22 (1997) 417.

8 E. G. Avvakumov, Mekhanicheskiye metody aktivatsii khimicheskikh protsessov, Nauka, Novosibirsk, 1979.

9. F. Miani and F. Maurigh, in: Encyclopedia of Nanoscience and Nanotechnology, California, Marcel Dekker, 2004.

10 Yu. M. Polezhaev, N. E. Darienko, *Zhurn. prikl. khimii,* 66 (1993) 1618.

11 Sw. Payakoff, *Õsterr. Chemie Zeit.*, 3 (1985) 48.

12 T. Ding, T. Tsuzuki and P. McCormick, *J. Am. Ceram. Soc.*, 79 (1996) 2956.

13 T. Ding, T. Tsuzuki and P. McCormick, *Nanostruct. Mater.*, 8 (1997) 75.

14 T. Ding, T. Tsuzuki and P. McCormick, *Ibid.,* p. 739.

15 T. Tsuzuki and P. McCormick, *Materials Transactions*, 42 (2001) 1623.

16 T. Tsuzuki, K. Pethick and P. McCormick, *J. Nanoparticle Res.,* 2 (2000) 375.

17 E. Avvakumov, M. Senna, N. Kosova, Soft Mechanochemical Synthesis: a Basis of New Chemical Technologies, Kluwer Academic, Boston *etc.,* 2001.

18 G. G. Saveliev, T. A. Yurmazova, M. I. Lerner *et al.*, Physical Chemistry of Ultradisperse (Nano) Systems, Proc. 6th All-Russian Conf., August 19–23, 2002, Tomsk, p. 212.

19 V. R. Regel, A. I. Slutzker, E. I. Tomashevkiy, Kineticheskaya priroda prochnosti tverdykh tel, Nauka, Moscow, 1980.

20 S. S. Gorelik, Yu A. Skakov, L. N. Rastorguev, Rentgenograficheskiy i electronno-opticheskiy analiz, Moscow, 1994.

21 A. P. Karnaukhov, Adsorbtsiya. Tekstura dispersnykh i poristykh materialov, Nauka, Novosibirsk, 1999.

22 S. M. Paramzin, O. P. Krivoruchko, B. P. Zolotovskiy *et al., Izv. SO AN SSSR. Ser. khim. nauk,*6 (1984) 39.

23 L. G. Karakchiev, T. M. Zima, N. Z. Lyakhov, *Neorgan. materialy*, 36 (2000) 852.

24. L. G. Karakchiev, E. G. Avvakumov, O. B. Vinokurova *et al., Khimiya v interesakh ustoichivogo razvitiya*, 9 (2001) 27.

25 L. G. Karakchiev, T. M. Zima, N. Z. Lyakhov, *Neorgan. materialy*, 37 (2001) 469.

26 L. G. Karakchiev, E. G. Avvakumov, O. B. Vinokurova *et al., Khimiya v interesakh ustoichivogo razvitiya*, 11 (2003) 493.

27 L. G. Karakchiev, E. G. Avvakumov, O. B. Vinokurova *et al., Zhurn. neorgan. khimii,* 48 (2003) 1589.

28 L. G. Karakchiev, E. G. Avvakumov, O. B. Vinokurova *et al., Ibid.*, 49 (2004) 5.