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Mechanochemical synthesis of nanoparticles by a dilution method: optimization of the composition of a powder mixture

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The suggested trimodal particle-size distribution in a mechanically activated system was used to calculate optimum molar ratios between mixture components that provided the existence of impact-frictional contacts between reagent particles and prevented the aggregation of nanoscale desired product particles; the theoretical results are in agreement with the available experimental data.

The rapid development of nanotechnologies[1,2] includes solid-phase mechanochemical methods for the preparation of nanoscale systems.[2–5] The method of dilution with a final product is of great interest for mechanochemical technologies.[6–9] At the end of the reactions, nanocrystalline powders (grain size of ~10 nm) are obtained within a soluble salt matrix. The final step is washing the salt matrix with appropriate solvents to afford separated nanoparticles. The use of a diluent may be necessary to avoid combustion reactions during milling[2,10] and to reduce the volume fraction of nanoparticles (in this way, it is possible to avoid nanoparticles being agglomerated).[9]

The weight, volume or molar ratio between the reagents and a reaction product (diluent) in the initial powder mixture is selected empirically.[8,9] The same is true of the conditions of mechanically activating the prepared mixture (the geometric and kinematic parameters of a mechanochemical reactor, comparative characteristics of milling tools and the material processed and kinetic characteristics such as the time of mechanical activation, *etc*.). This work is the first attempt at theoretically describing this method and obtaining numerical estimates.

Let us consider classic mechanochemical reactions for the preparation of nanoscale products (B_hD_m, TlBr, ZnS, CdS) in the general form (1) and for several examples (1a)–(1c):

$$kmA_hD_l + hlB_kC_m + zA_kC_l = (z + hm)A_kC_l + lkB_hD_m \quad (1)$$

$$\mathrm{KBr + TlCl} + z\mathrm{KCl} = (z + 1)\mathrm{KCl + TlBr},\ \Delta_rG^0 = -12.6\ \mathrm{kJ\ mol^{-1}} \quad (1a)$$

$$\mathrm{CaS + ZnCl_2} + z\mathrm{CaCl_2} = (z + 1)\mathrm{CaCl_2 + ZnS},\ \Delta_rG^0 = -104\ \mathrm{kJ\ mol^{-1}} \quad (1b)$$

$$\mathrm{Na_2S + CdCl_2} + z\mathrm{NaCl} = (z + 2)\mathrm{NaCl + CdS},\ \Delta_rG^0 = -186\ \mathrm{kJ\ mol^{-1}} \quad (1c)$$

Here, h, k, l and m are integer numbers, and z is an arbitrary positive number. Details concerning the performance of reactions of type (1) for the examples of the preparation of zinc sulfide nanoparticles (1b),[11] cadmium sulfide quantum dots (1c),[12] *etc*., can be found in refs. 6–9. Unfortunately, most of the reagents in reactions (1b) and (1c), CaS, $ZnCl_2$, $CaCl_2$, Na_2S, and $CdCl_2$, are hygroscopic; for this reason, their mechanical properties have not been determined. Therefore, hypothetical reaction (1a) will be considered here. The problem is to estimate $z = z^*$, which determines optimum conditions for the preparation of nanoscale particles of the compound B_hD_m by the method of dilution with the mechanochemical reaction product A_kC_l. Reaction (1a) involves both ionic (KBr, KCl) and covalent (TlCl, TlBr) reagents and products. These compounds are used in infrared technology,[13] and their physicochemical properties have been studied thoroughly.[13,14]

Table 1 Physicochemical properties of reaction (1a) components,[13,14] 'optimum' calculation parameters (*) for a mixture of reagents ($i = 1, 2$) and a diluent ($i = 3, 3'$), and conditions for performing the reaction in a mechanochemical reactor (SPEX 8000 or AGO-2).[a]

Property	Material					
	KBr, $i = 1$	TlCl, $i = 2$	KCl, $i = 3, 3'$	TlBr, $i = 4$	SPEX steel	AGO-2 steel
M	119.01	239.85	74.55	284.31	55.85 (Fe)	
ρ/g cm^{-3}	2.750	7.000	1.988	7.557	7.860	
$E/10^{-12}$ dyn cm^{-2}	0.201	0.245	0.241	0.237	2.232	
ν	0.283	0.326	0.274	0.324	0.285	
$\theta/10^{12}$ cm^2 dyn^{-1}	18.31	14.59	15.35	15.11	1.647	
Knoop hardness H_i	6.45	12.8	8.25	11.9	~300	
Ball radius R^*/cm	*$R_B = 1.25\times10^4$; $\delta^* = 0.03$; $a^* = 0.01$*				0.3	0.2
Number of balls N^*	*$N_B = 6.4\times10^4$; $\Pi^* = 290$ cm^2; $n^* = 5\times10^6$*				170	400
$m_b/m(z_1^*)$	*$z_1^* = 13.5$; $m_{3'} = 0.87$ g; $m_3 + m_{3'} = 12.66$ g*				9.4	6.6
$m_b/m(z_2^*)$	$z_2^* = 6.86$; *$m_{3'} = 1.52$ g; $m_3 + m_{3'} = 11.95$ g*				8.5	5.9
$m_i(z_1^*)$/g	1.39	2.81	11.77	3.33	*$m(z_1^*) = 15.97$*	
$m_i(z_2^*)$/g	2.43	4.89	10.43	5.80	*$m(z_2^*) = 17.75$*	

[a]The values of important parameters obtained in this work are italicized.

All numerical simulation results will be given for the mechanical activation (MA) of this reaction.

Various aspects of modeling the mechanism and kinetics of MA reactions were described previously.[15–18] During a certain initial period of the MA of an initial powdered mixture of stoichiometry (1), the following phenomena occur.

(i) Milling tools (balls and walls, Figure 1) self-lined[19–24] with a layer of thickness δ and porosity $p \approx 1 - \pi/4$,[15–19] this material can be characterized by its eigen mechanical properties (Young's modules E_i and Poisson coefficients ν_i,[13–18] Table 1).

(ii) Homogenization or, in other words, identical chemical composition of the mixture within a definite volume $\Delta V = abc$, which can be chosen at any arbitrary point of the lined layer.[25]

(iii) The maximum linear dimension ΔV should be smaller than the minimum linear dimension of the volume $\pi r^2\delta$, where r is the radius of the area of impact contact between a milling tool (ball) and a layer of particles under processing [Figure 1(*a*)].

(iv) There is dynamic equilibrium[26] with respect to the mean particle radii R_i ($i = 1, 2, 3$) $\ll a \sim b \sim c < \delta$, radii R_i being distributed within one order of magnitude in layer δ (Figure 2).

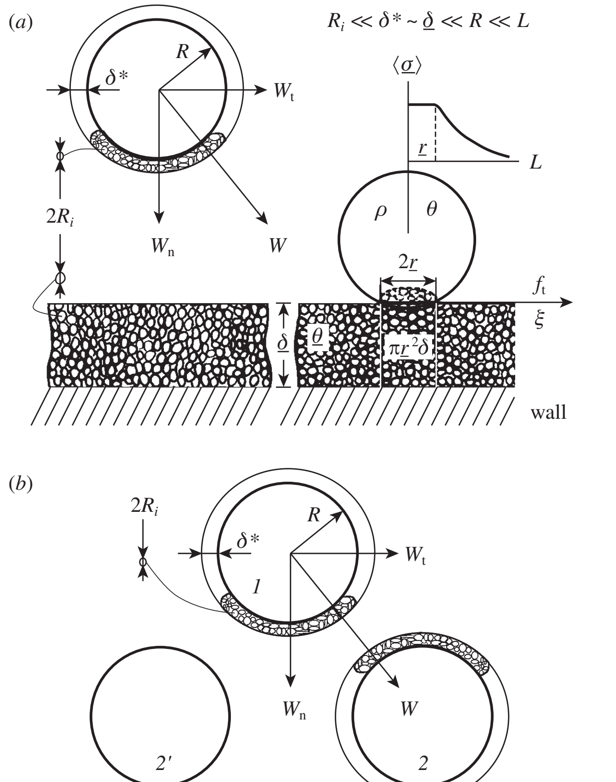

Figure 1 Impact-friction interactions of milling tools with processed particles in a mechanochemical reactor: (*a*) a lined or unlined ball with a lined mill vial wall and (*b*) a lined ball (*1*) with a similar (*2*) or unlined (*2′*) ball.[15,18]

(v) A reaction (transformation degree $\alpha \ll 1$) occurs owing to impact-friction contact of reagents with the formation of nanoscale particles with new properties[27] and mean radii $R_{3'} \approx R_4 \ll R_i$,[6–9,11,12] which are adsorbed on or absorbed by much larger particles R_i ($i = 1, 2, 3$).

The formation and evolution of the lining layer and the evolution of MA are dynamic rather than static phenomena. Mass transfer within the lining layer occurs as a result of impact-friction interactions (Figure 1) with mobile milling tools (ball load and vial wall) accompanied by changes in its chemical (composition), granulometric (R_i) and geometric (δ) characteristics. A fragment of an arbitrary cut of a lining layer of size $a \times b$ is shown in Figure 2; this layer becomes superimposed by similar layers in the c direction. Ideally, large-sized reagent and diluent particles (their number is $N_B = N_{1B} + N_{2B} + N_{3B}$, and their radius is R_B) form close-packing as some superposition of cubic and hexagonal packings. Similar medium-sized particles (their number is N_M and radius $R_M \approx 0.414 R_B$) occupy octahedral voids ($N_O = N_B$), and the smallest particles (N_S particles of radius $R_S \approx 0.225 R_B$) fill tetrahedral voids ($N_T = 2N_B$). To slightly simplify and initiate calculations, the absence of unoccupied voids is postulated; then, $2N_M = 2N_O = 2N_B = N_T = N_S$. In reality, the existence of an always quite definite postulated trimodal particle-size distribution in the lining layer δ and porosity p provides the possibility of impact-friction interactions between all of the three types of particles. However, the formation of reaction products ($N_{3'}$, N_4; $R_{3'}$, R_4) occurs only at contacts between reagent particles ($i = 1, 2$) as a result of their nanoscale abrasive-reactive wear.[19,28] Therefore, the problem is reduced to determining the following optimal MA conditions:

(i) conditions that ensure impact-friction surface of contact between reagent particles;

(ii) conditions that prevent the aggregation of nanoscale particles of the desired reaction product.

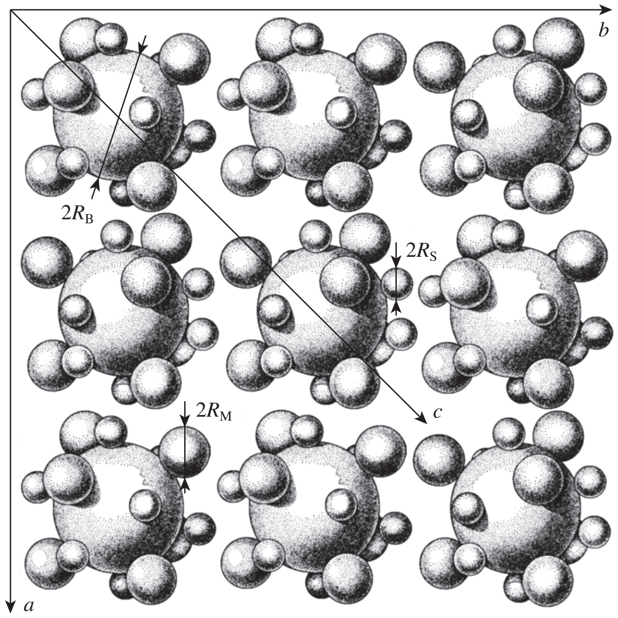

Figure 2 Schematic diagram of a 'unit cell' of a mixture of substances subjected to processing in the lining on the surface of milling tools of a mechanochemical reactor and the sizes of particles in it: R_B is the particle of close-packing; R_M, R_S are the particles in octahedral and tetrahedral holes, respectively; *a*, *b*, *c* are axes.

The most important parameters specifying mechanochemical reactors and MA conditions are the following:[9–12,15–19] the ratio between the mass m_b of mobile milling tools (ball load) and the mass m of the processed substances, $m_b/m = 4\pi R^3 \rho N/3(m_1 + m_2 + m_3)$, where R, ρ and N are the radius, density and number of balls, respectively; and the surfaces area of milling tools $\Pi = \Pi_v + \Pi_b = \Pi_v(L_1, L_2) + 4\pi R^2 N$, where Π_v, Π_b, L_1 and L_2 are the areas of the working surfaces of inside walls and ball load, and the radius and height of the mill vial (usually cylindrical), respectively. Most of the mechanochemical reactors satisfy the condition $L_1 \approx L_2 \gg R$. Numerical estimates were obtained for the two best known mechanochemical reactors.

(1) An AGO-2 steel ($\rho = 7.86$ g cm^{-3}) ball two-vial ($L_1 = 3.1$ cm, $L_2 = 4.6$ cm, $\Pi_v = 2\pi L_1 L_2 \approx 90$ cm^2, volume $V = \pi L_1^2 L_2 \approx 140$ cm^3) water-cooled planetary (carrier radius $L = 5.3$ cm, carrier rotation frequency $\omega = 12$ s^{-1}, opposite number of vial revolutions $\omega_1 = 29$ s^{-1}) mill[28] with the following characteristics[19,29,30] (see Table 1): geometric factor $\Gamma = L/L_1 = 1.7$; kinematic factor $K = \omega_1/\omega = -2.4$ ($|\omega| = 2\pi\omega$); $\cos\varphi = -(1 + K)/\Gamma = 0.82$ determines the angle of ball rebound from walls. The relative velocity W of collisions of milling tools is given by the equation:[18,19,29–32] $|W| = 2\pi\omega L_1[(K + 1)^2 + \Gamma^2 - 2\Gamma(K - 1)\cos\varphi + (\Gamma + 1)^2]^{1/2} \approx 1100$ cm s^{-1}; and the normal (n) and tangential (t) components of W are $W_n = |W|\sin\varphi \approx 900$ cm s^{-1}; and $W_t = |W|\cos\varphi \approx 630$ cm s^{-1}.

(2) A SPEX 8000 steel ball mill[9–12] with the following characteristics[16,33] (see Table 1): $L_1 = 1.9$ cm, $L_2 = 6.4$ cm, $\Pi_v = 2\pi L_1(L_1 + L_2) \approx 100$ cm^2, $V \approx 70$ cm^3, $|\omega(\omega_k)| = 2\pi\omega = 31$ s^{-1}, and $W_t \approx W_n \approx 300$ cm s^{-1}.

In the course of reaction (1), the ratio between five components ($i = 1, 2, 3, 3'$ and 4) dynamically changes. Let m_i and M_i be the sample weight and the molecular weights of the reagents ($i = 1, 2$) and a diluent ($i = 3$), respectively. The hardness (H_i), density (ρ_i), Poisson coefficient (ν_i), Young's modulus (E_i) and compliance $\theta_i = 4(1 - \nu_i^2)/E_i$ for the milling tools (unindexed), reagents, and reaction products are listed in Table 1.

The volume $\delta\Pi$ of the material subjected to processing is formed by the translation of the 'unit cell' $\Delta V = abc$. There are no substantial reasons for some properties of the lining layer to be anisotropic, and the shape of the cell can, therefore, be selected arbitrarily. However, considering the close-packing of particles of the largest size N_B, the cell can conveniently be selected in the form of a regular rhombohedron with the edge $|a|$ multiple to $2R_B$, face area $a^2 3^{0.5}/2$, height $a(2/3)^{0.5}$, volume $a^3 2^{0.5}/2$, and the long diagonal $a6^{0.5}$. The optimum values of $\delta = \delta^*$ and $|a| = |a^*|$ can be found from the MA parameters of the lining layer. According to published data,[15–18] mechanochemical reactions effectively occur only in the volume $\pi r^2 \delta$ of the impact action of milling tools [Figure 1(*a*)].

The minimum diameter $2r = 2r^*$ that corresponds to the diameter $2r^*$ of the contact area of collision between lined balls (see refs. 15, 17, 18):

$$2r^* \text{ (lined ball + lined ball)} \approx 1.5R(\rho\underline{\theta})^{0.2}W_n^{0.4}, \quad (2)$$

where $\underline{\theta}(z) = (km\theta_1 + hl\theta_2 + z\theta_3)/(km + hl + z)$ is the compliance of the lining layer material for reaction (1). Using (2), we obtain $\delta^* = 2r^* = |a^*|6^{0.5}$. Here, the word 'optimum' means that the larger size δ^* and a^* that can be physically grounded, the easier can the condition of homogeneity with respect to mixture composition during MA be fulfilled (Table 1). On the other hand, the condition $m_b/m \gg 1$ should be met.[9–12,16] The number n^* of 'optimum unit cells' that constitute the lining layer of thickness δ^* is $n^* = 2\delta^*\Pi^*/|a^*|^3 2^{0.5} = 2\delta^*(\Pi_v + 4\pi R^2 N)/a^{*3}2^{0.5}$. The greatest convenience provided by the use of the 'unit cell' is its invariance with respect to the type of mechanochemical reactor for any particular test reaction. Obtaining numerical estimates requires finding the 'optimum' value of $z = z^*$.

Consideration of the structure of the lining layer or its 'unit cell' in more detail (Table 1, Figure 2) indicates that the cell contains $N_B = N_{1B} + N_{2B} + N_{3B} = (a^*/\langle 2R_B\rangle)^3$ large-sized particles of radius R_B whose 12-coordinate environment forms the frame of the rhombohedron described above; the same number (N_M) of medium-sized particles of radius of R_M in octahedral voids and twice as many (N_S) small-sized particles of radius R_S in tetrahedral voids. For the distribution of reagent and diluent particles [nine unknown values N_{iJ} (i = 1, 2, 3; J = B, M, S) over three different cell sites], only three normalizing equations including sample weights m_i can be written:

$$R_B^3 N_{1B} + R_M^3 N_{1M} + R_S^3 N_{1S} = 3m_1/n^*4\pi\rho_1; \quad (3\text{-}1)$$

$$R_B^3 N_{2B} + R_M^3 N_{2M} + R_S^3 N_{2S} = 3m_1 hlM_2/n^*4\pi\rho_2 kmM_1; \quad (3\text{-}2)$$

$$R_B^3 N_{3B} + R_M^3 N_{3M} + R_S^3 N_{3S} = 3m_1 z^* M_3/n^*4\pi\rho_3 kmM_1. \quad (3\text{-}3)$$

To solve this system, both objective factors (the mechanical properties of particles such as hardness H) and subjective factors (correct prediction of the relative particle-size distribution) should be invoked. The ratio between the volume occupied by cell frame particles and the total volume of particles in octahedral and tetrahedral interstices (Table 1, Figure 2): $R_B^3/(R_M^3 + 2R_S^3) = (0.414^3 + 2\times0.225^3)^{-1} \approx 11$. Such a large value leads to a very important conclusion, namely, the octahedral and tetrahedral close-packing voids of the lining layer can and must be occupied by most plastic component particles only. Using this conclusion as an axiom, one can see two possibilities for optimizing the structure of the lining layer arises for reaction (1).

(*a*) Let the diluent material (A_kC_l) be the hardest or not most plastic, for instance, let the relative hardness of mixture (1) components be as in (1a), that is, $H_{B_kC_m} > H_{A_kC_l} > H_{A_hD_l}$ (Table 1);

(*b*) The diluent (A_kC_l) has the lowest hardness ($H_{A_hD_l} \sim H_{B_kC_m} > H_{A_kC_l}$), and it will be assumed in numerical estimates that the H_{KCl} of diluent (KCl) in mixture (1a) is minimum (hypothetical case).

In case (*a*), the optimum value of $z = z_1^*$ is found assuming that the most plastic reagent 1 (or A_hD_l) occupies all of the octahedral ($R_M = 0.414R_B$) and tetrahedral ($R_S = 0.225R_B$) voids only:

$$z_1^* = \rho_3[km\rho_2 M_1 R_B^3 - hl\rho_1 M_2(R_M^3 + 2R_S^3)]/\rho_1\rho_2 M_3(R_M^3 + 2R_S^3); \quad (4)$$

$$\text{or } z_1^* = \rho_3[km\rho_2 M_1 - 0.0937hl\rho_1 M_2]/0.0937\rho_1\rho_2 M_3. \quad (4a)$$

Applying (4) to reaction (1a) or assuming that $km = hl = 1$, $z_1^* = 13.5$ is obtained. The ratio between the numbers of diluent (N_{3B}) and reagent 2 (N_{2B}) particles will also be of interest: $N_{3B}/N_{2B} = \rho_3 z_1^* M_3/\rho_2 hlM_2$. In reaction (1a), $hl = 1$ and $N_{3B}/N_{2B} = 14.8$. Therefore, the ratio between the number of 'reaction contacts' of reagent 1 particles in octahedral and tetrahedral interstices and the number of merely 'abrasive' contacts is $N_{2B}:N_{3B} = 1:15$.

In case (*b*), the structure of the lining layer is cardinally different. All the octahedral and tetrahedral voids and a part of close-packing cells are occupied by diluent particles. Reagents 1 and 2 particles fill close-packing cells with radius R_B and a coordination number of 12. The problem is reduced to optimizing the ratio $N_{3B}/(N_{1B} + N_{2B}) = z'$ in the frame of the cell. However, it is necessary first determine the weight loss Δm_3 of the diluent (initial weight m_3) as a result of filling octahedral and tetrahedral voids, $\Delta m_3 = n^*4\pi\rho_3 N_B(R_M^3 + 2R_S^3)/3$. The remaining part of the diluent $m_3 - \Delta m_3$ determines the number of particles N_{3B} and several other obvious relations:

$$N_{3B} = (z_2^* N_{1B}\rho_1 M_3/km\rho_3 M_1) - [N_B(R_M^3 + 2R_S^3)/R_B^3]; \quad (5\text{-}1)$$

$$N_{1B}/N_{2B} = km\rho_2 M_1/hl\rho_1 M_2; \quad (5\text{-}2)$$

$$N_{1B} + N_{2B} + N_{3B} = N_B; \quad (5\text{-}3)$$

$$N_{3B}/(N_{1B} + N_{2B}) = z', \quad (5\text{-}4)$$

where $z = z_2^*$, as previously, determines the required diluent optimum. We see that there are only four equations for five unknowns. The solution at $R_M = 0.414R_B$ and $R_S = 0.225R_B$ to this system is

$$z_2^* = \rho_3(km\rho_2 M_1 + hl\rho_1 M_2)\,[z'R_B^3 + (z'+1)(R_M^3 + 2R_S^3)]/R_B^3\rho_1\rho_2 M_3, \quad (6)$$

$$\text{or, at } z' = 2,\ z_2^* = 2.28\rho_3(km\rho_2 M_1 + hl\rho_1 M_2)/\rho_1\rho_2 M_3. \quad (6a)$$

Close packing symmetry and conditions (i) and (ii) dictate the selection of $z' = 2$ or $z_2^* = 6.86$ for reaction (1a). The number of reaction contacts for an arbitrarily pair of contacting reagent particles is then 3 of 12 at $z' = 0$,[15,17,18] and the number of merely abrasive contacts is 20 with N_{3B} particles, 12 with N_{3M}, and 24 with N_{3S}.

The weights of the other components of reaction (1) with respect to m_1 are $m_2 = m_1 hlM_2/kmM_1$, $m_3 = m_1 zM_3/kmM_1$, $m_{3'} = m_1 hmM_3/kmM_1$, and $m_4 = m_1 lkM_4/kmM_1$. The thickness δ of the lining layer of particles undergoing processing for the initial mixture of reagents 1 and 2 and diluent 3 is related to the weights m_i (i = 1, 2, 3) as follows:[15–18]

$$m_1 = \delta\pi\rho_3\rho_2\rho_1\Pi/4[\rho_3\rho_2 + \rho_3\rho_1(hlM_2/kmM_1) + \rho_2\rho_1(zM_3/kmM_1)]. \quad (7)$$

Return to (2) and use of the condition $2r^*$(AGO) = $2r^*$(SPEX) allows one to find the ratio between the radii of steel milling balls for AGO-2 ($R = R_a$) and SPEX 8000 ($R = R_s$) mills that ensures equal impact contact areas of milling tools with the lining layer of particles: $R_a/R_s = [W_n(\text{SPEX})/W_n(\text{AGO})]^{0.4} = (300/900)^{0.4} \approx 0.65$. As a rule,[30] $R_a = 0.2$ cm; hence, $R_s \approx 0.3$ cm, as in experiments.[12,16,33,34] To obtain identical MA conditions in the test mills, we must also ensure the equality of the surface areas of milling tools, $(\Pi_v + \Pi_b^*)_{AGO} = (\Pi_v + \Pi_b^*)_{SPEX} = \Pi^*$. Assuming[30] that $N_a^* = 400$, we obtain $N_s^* \approx 170$ and $\Pi^* \approx 290$ cm^2 (Table 1).

Next, using (4) and (6), one can estimate the optimum composition of mixtures for reactions (1b) and (1c); this yields

$z_1^*(1b) = 8.30$, $z_2^*(1b) = 4.05$ and $z_1^*(1c) = 17.7$, $z_2^*(1c) = 7.24$. We see that the values of z^* can vary over a broad range depending on the reagent and diluent values of ρ_i and M_i. Comparison of these data with the experimental (e) data,[11,12] according to which $z_{1e}^*(1b) = 8.2$, $z_{2e}^*(1b) = 3.6$,[11] and $z_e^*(1c) = 12 \approx [z_1^*(1c) + z_2^*(1c)]/2$, reveals that the theoretical optimum dilutions of mixtures z^* determined in this work virtually coincide with the experimental values.

Two variants for estimating the optimum ratio (z^*) between powder mixture components for mechanochemically preparing nanoparticles by the method of dilution with the final product are theoretically found. The selection of the variant is determined by the relative mechanical properties of the diluent and reagents. A substantial advantage of the described theoretical investigation is the simplicity of its application. For instance, in order to prepare a mixture of optimal composition for obtaining a nanoscale product of mechanosynthesis according to reaction (1), it is necessary to calculate only the dilution parameter z^* using the simplest and more accurate equations (4a) or (6a) on the basis of the relations between the hardness characteristics of reagents and the diluent. In order to choose the necessary equation and carry out calculations according to (4a) or (6a), we use only the best-known technological parameters: molecular mass M_i, density ρ_i and hardness H_i of the mixture components. As a rule, these components are well-studied chemical elements or individual chemical compounds.

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