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Mechanochemical synthesis of nanoparticles by a dilution method: determination of the particle mixing coefficient in a ball mill

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Experimental study of the kinetics of mechanosynthesis of TlCl nanoparticles in the reaction $2NaCl + Tl_2SO_4 + zNa_2SO_4 = (z+1)Na_2SO_4 + 2TlCl$ with $z = z_1^* = z^* = 11.25$ and comparison of kinetic parameters for this reaction with those determined theoretically for the model reaction $KBr + TlCl + zKCl = (z+1)KCl + TlBr$ with $z = z_1^* = 13.5$ made it possible to estimate the mass transfer (mixing of particles) coefficient in a mechanochemical reactor by the mobile milling tools.

Mass transfer in mechanochemical reactors is a key phenomenon for mechanochemical reactions and processes. However, no attempts were made to experimentally evaluate the mass transfer coefficient in mechanochemical reactors.[1–10] It is evident that, with the addition of a large amount of the diluent, the exchange process should not only slow down but also cease completely after contacts between the initial reagents in the mechanically activated mixture are exhausted. However, this is not observed experimentally.[11] Therefore, the particle transfer mechanism exists in a mechanochemical reactor associated with the interface renewal processes; this mechanism can be connected only with mobile milling tools (balls and walls). In this case, the particle size of the end products should change from a subnanometer scale to a micrometer one, which is characteristic of the reactions in the stoichiometric mixtures of salts.[1,2] Because of this, an optimal time τ of mechanical activation (MA) should exist, which would provide both the completeness of the exchange reaction and obtaining nanoscale particles of the desired reaction product in the diluent matrix.[12,13]

This work presents an experimental verification of the results of theoretical studies of mechanochemical reactions, including the analysis of mass (particle) transfer.[12]

Performing the model exchange MA reaction (z is the dilution parameter[13]) in practice is impeded by the presence of substances with low water solubility both on the left- and right-hand sides of (1), in wt%: TlCl, 0.35 (25 °C); TlBr, 0.05 (25 °C).[12,13] For this reason, the theoretical results were checked by performing reaction (2) in an AGO-2 planetary mill under the conditions described for reaction (1).

$$KBr + TlCl + zKCl = (z+1)KCl + TlBr, \quad \Delta_r G^0 = -12.6 \text{ kJ mol}^{-1} \qquad (1)$$

$$2NaCl + Tl_2SO_4 + zNa_2SO_4 = (z+1)Na_2SO_4 + 2TlCl. \quad \Delta_r G^0 = -40 \text{ kJ mol}^{-1} \qquad (2)$$

Reaction (2) is similar to reaction (1) and satisfies the conditions of synthesizing nanoparticles by the method of dilution with a final product.[13] The solubilities of the initial mixture components for reaction (2) were (wt%): 21.9 (25 °C) for Na_2SO_4, 35.87 (20 °C) for NaCl and 4.87 (20 °C) for Tl_2SO_4.

The conditions of performing exchange reaction (2) in an AGO-2 steel water-cooled two-vial ball mill were as follows (Figure 1, Table 1): steel ball radius $R = 0.2$ cm, number of balls $N = 401$, density of balls $\rho = 7.86$ g cm^{-3}, and overall weight of ball load $m_b = 4\pi R^3 N\rho/3 = 97.1$ g; $\tau = \tau^*$ is the time necessary for exchange reaction completion (by 99% or to the degree of completion $\alpha = 0.99$) in the AGO-2 mill, and $f = 0.189$ s^{-1} is the frequency at which an arbitrarily selected pair of contacting reagent particles gets under the impact action of milling tools.[12] The optimum dilution parameters $z = z^*$ for reaction (2) are as follows:[13]

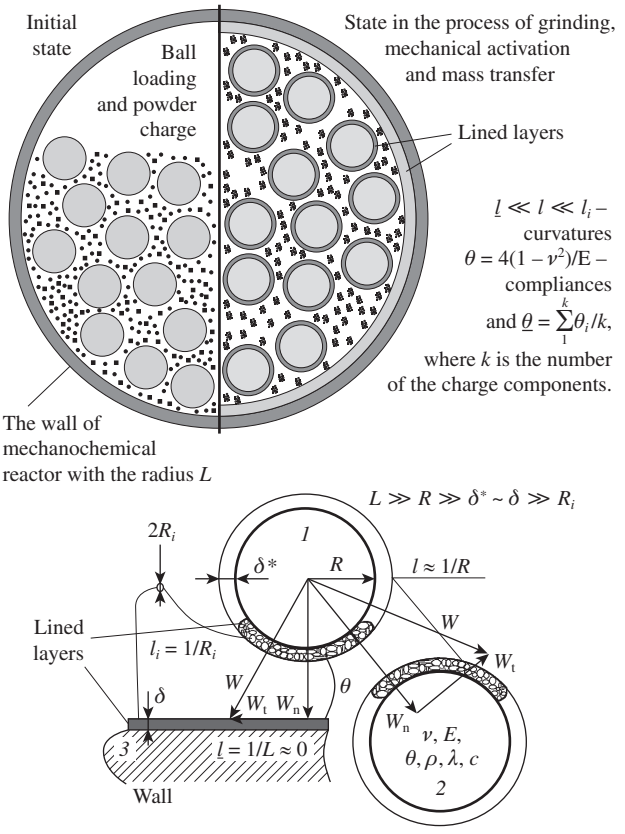

Figure 1 Diagram for the study of various phenomena and processes in mechanochemical reactors owing to the impact-friction interactions of milling tools (for example, ball *1* with ball *2* and ball *1* with wall *3*). Mass transfer occurs as a result of impact-friction interactions of the milling tools (*1* ↔ *2*, *3* ↔ *2* with *W*) through the solid phase of lined layers and the gaseous medium of a mechanochemical reactor with the mass transfer coefficients (Ψ).

$$z_1^* = \rho_3[2\rho_2 M_1 - 0.0937\rho_1 M_2]/0.0937\rho_1\rho_2 M_3 = 11.25; \qquad (3)$$

$$z_2^* = 2.28\rho_3(2\rho_2 M_1 + \rho_1 M_2)/\rho_1\rho_2 M_3 = 5.44, \qquad (4)$$

Table 1 Characteristics and salt sample weights for performing reaction (2).[a]

Property	Object				
	NaCl (i = 1)	Tl_2SO_4 (i = 2)	Na_2SO_4 (i = 3, 3′)	TlCl (i = 4)	AGO-2: steel balls, R = 0.2 cm, N = 401
Hardness, Mohs in arbitrary units[13,14] (Knoop in kg mm^{-2})[15]	2–2.5 (15.2)	— (—)	2.5–3 (—)	— (12.8)	R_b:R_M:R_S ≈ *5:2:1*; 4–5 (~300)
M_i/g	58.44	504.80	142.04	239.85	m_b = *97.1* g;
ρ_i/g cm^{-3}	2.165	6.675	2.663	7.000	τ^* ≈ 6300 s; 7.86
$m_i(z_1^*)$/g	1.106	4.832	14.97	4.491	$m(z_1^*)$ = *20.77*;
$m_i(z_2^*)$/g	1.900	8.206	12.574	7.798	$m_i(z_2^*)$ = *22.68*;
$m_b/m(z_1^*)$	z_1^* =11.25	f =	$m_3 + m_3'$ = *16.300* g		$\Psi(z_1^*, \tau^*)$ ≈ 4.68
$m_b/m(z_2^*)$	z_2^* = 5.44	0.189 s^{-1}	$m_3 + m_3'$ = *14.883* g		0.0046 4.28

[a] In the empty table cells the values of some necessary parameters are printed in italics.

where M_i and ρ_i are the molecular weights and densities of the reaction mixture components. Mass transfer of treated substances occurs as a result of impact-friction interactions of the milling tools through the solid phase of lined layers and the gaseous medium of a mechanochemical reactor (Figure 1).

Data from ref. 13 and equations (3), (4) can be used to find the initial weights of component samples $m_i(z_1^*)$ and $m_i(z_2^*)$. The sum $\sum m_i(z^*)$, where i = 1, 2 and 3, gives the optimum weights of the batch mixture for performing reaction (2) in the AGO-2 mill, $m(z_1^*)$ = 20.77 g and $m(z_2^*)$ = 22.68 g. The values $m_b/m(z_1^*)$ = = 4.68 and $m_b/m(z_2^*)$ = 4.28, $m_3'(z_1^*)$ = 1.33 g and $m_3'(z_2^*)$ = 2.309 g, where m_3' is the mass of diluent Na_2SO_4 formed additionally in reaction (2), have also been obtained.

According to the hardness of the reagents (NaCl, halite, i = 1; Tl_2SO_4, thallium sulfate, i = 2) and the diluent (Na_2SO_4, thenardite, i = 3), the optimum dilution conditions for reaction (2) correspond to the parameter z_1^* = 11.25[13] because, as a rule, the hardness of metal sulfates is higher than that of metal halides.[14–16] However, attempts to find the hardness of Tl_2SO_4 crystals in the literature were unsuccessful, and therefore both compositions listed in Table 1 and given by (3), (4) were used. The reagent mixtures of chemically pure NaCl and Na_2SO_4 and pure Tl_2SO_4 corresponding to the stoichiometric compositions with $z = z_1^*$ and $z = z_2^*$ were first ground and homogenized for 1 h in a Fritsch Pulverisette mill equipped with steel fittings (a mortar 9.45 cm in diameter and one ball 5.16 cm in diameter). The size of particles in the initial mixtures was between 0.005 and 0.015 cm according to optical microscopy data. This was much larger than the quasi-equilibrium particle size of 1.25×10^{-4} cm in MA.[12]

The kinetics of reaction (2) was studied by measuring the conductivity of aqueous solutions of product samples (1 g per 10 ml of deionized water). The only product with a low solubility in water was TlCl. This ensured a fairly high accuracy of measurements based on a decrease in the conductivity of MA product samples with respect to the initial homogenized samples. We thoroughly tested this method by separately determining isomers, namely, ammonium thiocyanate NH_4CNS (pseudohalide) and thiocarbamide $(NH_2)_2CS$ (molecular non-conducting crystal), when they were simultaneously present in solution.[17,18] A unit for conductivity measurements was made from a BM507 Impedance Meter (Tesla, Brno) and a Conductometric Bell type OK-9023 Pt-electrode (Radelkis Electrochemical Instrument, Budapest). The error of measurements was determined from the following characteristics. The maximum possible content of TlCl in a sample (m = 1 g) was 4.491/20.77 ≈ 0.216 g, and that of Tl_2SO_4 was 8.206/20.77 ≈ 0.395 g. Water (1 ml) dissolves ~3.5 mg of TlCl and 48.7 mg of Tl_2SO_4. The solubility of mechanically activated TlCl particles is approximately ten times lower than that of Tl_2SO_4, and 1 ml of water dissolves ~5 mg of TlCl (the solubility of mechanically activated salts can exceed their tabulated equilibrium solubility).[19] Therefore, at a 1 g sample weight, 10 ml of water dissolve ~50 mg of TlCl and, assuredly, all the other system components. For this reason (a) the error in conductivity measurements solely based on the conductivity of solutions of mechanically activated samples would be 0.05/0.216 ≈ 23%; (b) calibration (conductivity curve measurements for different initial reagent mixture compositions) allows the error of measurements to be reduced to (0.05 – 0.035)/0.216 ≈ 7%; (c) the introduction of the correcting coefficient 2 (averaging over the composition or at reaction half completion) allows the accuracy of measurements to be increased to ~4%; the diameter of experimental kinetic curve symbols for reaction (2) in Figure 2 corresponds to this error of measurements.

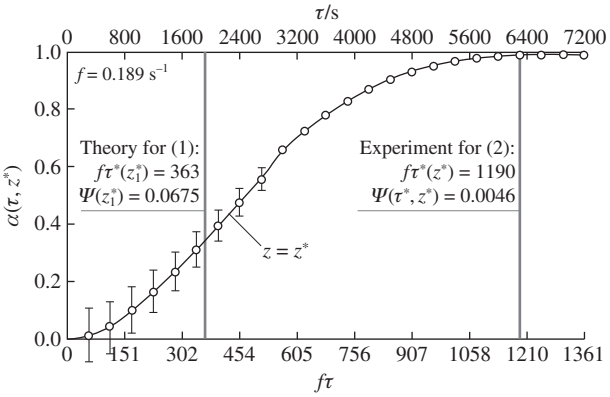

Figure 2 Experimental curve $\alpha(\tau, z^*)$ for the reaction (2) plotted on the basis of conductivity measurements in the solutions of mechanically activated samples in an AGO-2 mill.

Experimental studies of the kinetics of reaction (2) encounter certain difficulties. MA times were expected close to the calculated $\tau^*(z^*)$ values for (1), namely,[11,12] $\tau^*(z_1^*) \approx 1900$ s and $\tau^*(z_2^*) \approx 4800$ s, to be sufficient for the completion of reaction (2). An obviously longer MA time, τ = 7200 s, was used in preliminary experiments. However, the reaction was complete ($\alpha \approx 1$) only for the sample with $z = z_1^*$, whereas α for the sample with $z = z_2^*$ did not exceed ~0.4. The subsequent experiments were performed using samples with $z = z_1^* = z^*$. As the AGO-2 mill had two water-cooled vials (cooling was essential to obtaining certain specific results[20]), one could expect that the experimental MA kinetic curves for reaction (2) could be constructed using two $m(z = z_1^* = z^*)$ loads. The samples were taken in turn from each drum with interrupting MA every 300 s for no more than 1500 s. Sample weights were ~0.3 g, which was very small compared with the weight of the substance to be activated, $m(z^*)$ = 20.77 g (Table 1), and, seemingly, their removal could not affect the development of reaction (2). A comparison of the degrees α of reaction completion for a sample MA for 1800 s = 6×300 s with six interruptions ($\alpha \approx 0.2$) and a sample MA continuously ($\alpha \approx 0.3$), however, showed that pauses in MA influenced the kinetics of reaction (2).[21] The subsequent kinetic experiments were carried out under continuous MA conditions using 24 $m(z^*)$ samples. This corresponds to the number of experimental values in Figure 2.

The following equations describing the kinetic parameters and kinetic curve of model reaction (1) in an AGO-2 mill were obtained for $z = z_1^* = z^*$:[12]

$$\Psi(z^*)_{\tau \to 0} = N_{2B}(z^*)/N_{3B}(z^*) = 1/14.8 = 0.0675; \quad (5)$$

$$s(z^*) = 3g(z^*)d^*(z_1^*)s_{12}(z^*)/4\pi(R_{MS}^3 + R_B^3) = 0.000697; \quad (6)$$

$$-\ln[1 - \alpha(\tau, z^*)] = \Psi(z^*)\Phi^* f\tau[1 - (1 - s)^{f\tau}]/(1 - s)^{f\tau}; \quad (7)$$

$$f\tau^*(z^*)[1 - (1 - s)^{f\tau^*(z^*)}]/(1 - s)^{f\tau^*(z^*)} = 4.60/\Psi(z^*)\Phi^* \approx 105. \quad (8)$$

Here, $\Psi(z^*) = \Psi(z^*)_{\tau\to 0}$ is the calculated mass transfer coefficient at the beginning of MA, $\Phi^* \approx 0.65$, and it follows from $\alpha(\tau = \tau^*, z^*) = 0.99$ that $-\ln[1 - \alpha(\tau^*, z^*)] = 4.60$. These values were used in (8) to find $f\tau^*(z^*) = n^* = 363$ (Figure 2). Using the known frequency $f = 0.189\ s^{-1}$ at which an arbitrarily selected pair of contacting reagent particles experiences the $n^* = 363$ impact action of milling tools, the MA time was obtained for reaction (1) to be completed by 99%: $\tau^*(z^*) = n^*/f = 1920$ s.[12]

In these equations, the only function insufficiently grounded theoretically or in any experimental way is $\Psi(z)$, which is a dimensionless function of the dilution parameter z taking into account mass transfer with mobile balls in an MA batch mixture, which lines the surface of milling tools (balls and mill walls), and the ensuing formation of new contacts between reagent particles (Figure 1). Clearly, if the kinetic curve is known from an experiment, the $\Psi(z^*)$ function can be found from (8) at any particular $\alpha = \alpha'$ value. Moreover, as distinct from published data,[12] the time dependence $\Psi(z^*, \tau)$, that is, the dependence of $\Psi(z^*)$ on the time of MA τ, can also be determined.

Suppose, see (3) and (6), that $s(z_1^* = z^*)$ for (1) is equal to $s(z^*)$ for (2), where the $s(z^*)$ parameter is the fraction of the removed volume V^*/V at the impact-friction contact of a distinguished pair of reagent particles, the total volume of the reagents being V, for test reaction (2).[12] The difference of the $s(z_1^* = z^*)$ and $s(z^*)$ values is only caused by an insignificant difference of the densities ρ_i and compliances $\theta_i = 4(1 - \nu_i^2)/E_i$ of the reagents in reactions (1) and (2); here, E_i are the Young's modules and ν_i are the Poisson's coefficients (see also Figure 2). Only ρ_i and θ_i are different in calculations of $V^* = d^*(z^*)\, s_{12}(z^*)$, where $d^*(z^*)$ is the thickness of reaction volume V^* and $s_{12}(z_1^*)$ is the area of the impact-friction contact for the selected pair of particles.[12]

This allows one (Figure 2) to estimate the mass transfer coefficient $\Psi(z^*)$ during MA experimentally for the first time. Indeed, conductometric measurements show that, after MA for approximately $\tau = \tau^* = 6300$ s, the reaction is complete, and MA ceases to affect the results of measurements. If the τ^* time of MA is used as an indicator of reaction (2) completion by 99%, the following equations and estimate for the $\Psi(z^*, \tau)$ function then follow from (7) and (8):

$$\Psi(z^*, \tau = \tau^*) \approx 7.1(1 - s)^{f\tau^*(z^*)}/f\tau^*(z^*)[1 - (1 - s)^{f\tau^*(z^*)}] = 0.0046; \quad (9)$$

$$\Psi(z^*, \tau) = -\ln[1 - \alpha(\tau)](1 - s)^{f\tau}/\Phi^* f\tau[1 - (1 - s)^{f\tau}]. \quad (10)$$

Equations (7) and (10) are obviously nonlinear, and it is therefore worthwhile to additionally study the $\Psi(\tau)$ function: according to the theory[12,13] or (5), $\Psi(\tau) = \Psi(\tau \to 0) = 0.0675$; according to experimental data and (10), $\Psi(\tau = 300\ \text{s}) = 0.0065$ and $\Psi(\tau = 600\ \text{s}) = 0.0058$ at the starting stage of reaction (2); according to (9), $\Psi(\tau^* = 6300\ \text{s}) = 0.0046$ at the final stage of reaction (2). The $\Psi(\tau)$ values calculated over the range of $1 - \alpha(\tau)$ variations from 0.90 to 0.07, according to (10) or Figure 2, are listed in Table 2. The results show that the $\Psi(\tau)$ function is in all probability described by a damped function and should therefore tend to some equilibrium value, which is, unfortunately, difficult to determine theoretically. $\Psi_{eq}(\tau) = \Psi[\alpha(\tau_{eq}) = 0.5] = 0.0057$ can be recommended as such a value.

Thus, the experimental study of reaction (2) made it possible to determine the following characteristics of mechanical activation and the preparation of TlCl nanoparticles by the method of dilution with a final product: the theoretical estimate of the molar dilution parameter $z = z_1^* = z^* = 11.25$ was substantiated; the kinetic curve for the reaction was obtained, the mass transfer coefficient Ψ with mobile milling tools (ball loading and walls) in an AGO-2 planetary mill was determined. In conclusion, the study of the kinetics of mechanochemical processes can be recommended to find the specific features for the numerical estimation of the mass transfer coefficient in a mechanochemical reactor.

Table 2 Calculations of the mass transfer coefficient $\Psi(\tau)$ as a function of mechanical activation time τ.

τ/s	$f\tau = n$	$\alpha(\tau)$	$\Psi(\tau)\times 10^3$	τ/s	$f\tau = n$	$\alpha(\tau)$	$\Psi(\tau)\times 10^3$
900	170	0.10	7.6	3000	567	0.66	6.0
1200	227	0.16	6.9	3300	624	0.72	4.5
1500	283	0.23	6.5	3900	737	0.83	5.5
2100	397	0.39	6.0	4200	794	0.87	5.4
2400	454	0.47	5.8	4800	907	0.93	5.1
2700	510	0.55	5.6				

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