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Sonochemical synthesis of inorganic materials

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Abstract. Methods of synthesis of highly dispersed inorganic materials based on the use of ultrasonic treatment are considered. Particular attention is paid to current trends in sonochemistry, namely, ultrasonic hydrothermal treatment and high-temperature ultrasonic processing of liquid- and solid-phase systems. The bibliography includes 218 references.

I. Introduction

The synthesis of modern inorganic materials usually presents significant difficulties. Indeed, such systems are multicomponent and a number of successive stages of formation of intermediates should be carried out in order to obtain target products. The multistage character of the synthesis is responsible for inhomogeneity of chemical and phase compositions (this presents a severe problem in the formation of single phase multicomponent products) and the microstructure of materials. These problems are solved using a variety of chemical homogenisation techniques,[1,2] which make it possible to obtain reaction mixtures in which the starting reactants are in highly dispersed reactive state. Good mixing of reactants provides the possibility of formation of numerous interfacial contacts and, as a consequence, the emergence of a developed reaction interface. The rate of formation of new phases near the developed reaction interface much exceeds the rate of interaction between reactants in conventional state. However, by no means all interfacial contacts formed in the course of homogenisation become reaction interfaces during the synthesis. This is first of all due to the compaction of reactant particles, breakdown of the contacts formed in the course of mechanical mixing of reactants and demixing of reaction mixtures owing to different chemical nature of the reactants.

Solving a number of problems in the synthesis of inorganic materials requires the use of novel methods that allow one to change the character of the reaction zone or the reaction mechanism in a targeted manner and to additionally activate the reaction mixtures.[3] Recently, synthetic methods based on utilisation of microwave radiation have been progressed rapidly.[4–6] Microwave irradiation makes it possible to considerably accelerate such important physicochemical processes as dehydration, decomposition of salt and hydroxide precursors, synthesis of multicomponent composites and sintering of ceramics. This approach is promising due to high rate of heating and short delay of the process in contactless regime (no contact between the heater and the heated body) and to the possibility of selective heating of the components of reaction mixtures.[7] Nevertheless, practice shows that prediction of the behaviour of a system under microwave irradiation is a very complicated task. The reason is that the electrophysical and thermophysical characteristics responsible for the absorbance of compounds strongly depend on temperature. Correct allowance for this factor is a practically insoluble problem. The situation becomes even more complicated for the systems in which chemical processes occur, because changes in the phase composition of such systems cause jumpwise and often uncontrollable changes in their electrophysical and thermophysical characteristics.

Yet another important problem in modern inorganic chemistry and inorganic materials science consists in the need of elaboration of methods for targeted synthesis of nanodisperse materials.[8] Methods of preparation of nanopowders have been studied for a rather long time and many of them are successfully used not only in laboratory practice, but also in industry. The mechanisms of formation of free nanoparticles have been a subject of intensive research and some of them have found experimental substantiation. This made it possible to choose the strategies of the synthesis of nanopowders with preset physicochemical properties, however some problems are still to be solved.[9] In particular, highly dispersed powders have an excess surface energy, which causes their aggregation. Additionally, enhanced reactivity of nanopowders compared to bulk crystals predetermines their instability to the action of various media and rapid degradation. These problems can be solved by introducing nanopowders into

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inert matrices or by using low- and high-molecular-mass surfactants that form a shell on the surface of nanoparticles in the course of the synthesis and thus protect them from aggregation and degradation.[10,11]

A promising method for solving a number of problems mentioned above is sonication. Utilisation of ultrasonic vibrations in chemistry and materials science has long gone beyond research laboratories. Ultrasound is widely used in industry for intensification of many technological processes including degassing of metal melts, dispersion of liquids and solids, extraction, filtration and cleaning of various surfaces.[12,13] Considerable attention has been paid to applications of ultrasound in chemical synthesis including the synthesis of advanced inorganic materials. Progress of research in this field led to emergence of a new branch of chemical science, sonochemistry.†

A number of reviews and monographs devoted to various aspects of application of sonication in inorganic chemistry and materials science have been reported in the last decade.[14–20] At present, chemically- and materials-science-attractive features of sonochemical synthesis have been well documented. The advent of promising sonochemical research avenues, *e.g.*, high-temperature synthesis of complex oxides[21] and synthesis of highly dispersed oxide materials under concurrent hydrothermal and ultrasonic treatment[22] should also be pointed out. In the course of preparation of the present review the authors tried to outline general ideas of the synthetic potential of the methods involving ultrasonic treatment, to consider the mechanisms of processes occurring under sonication and to systematise recent advances in sonochemical synthesis.

II. Methods of generation of acoustic vibrations

Acoustic vibrations are elastic (mechanical) longitudinal vibrations that propagate through a medium. The frequency spectrum of acoustic vibrations is usually divided into three regions, namely, infrasound (frequencies lower than 30 Hz), audible sound (frequency range from 30 Hz to 20 kHz) and ultrasound (frequencies higher than 20 kHz). This classification is to a great extent conditional, being based on human perception of acoustic vibrations.

From the standpoint of applications, ultrasonic vibrations are grouped into low-frequency vibrations (frequency range from 20 kHz to 1 MHz) and high-frequency (frequencies higher than 1 MHz) ones.[23] Low-frequency ultrasonic vibrations are mainly utilised in industry, chemistry and materials science (production of metals and alloys with specified microstructure, ultrasonic cutting and welding,[24] pressing,[25] synthesis of various compounds and materials,[15] sample preparation in analytical chemistry,[26] *etc.*). High-frequency (diagnostic) ultrasound is used in non-destructive methods of analysis (ultrasonic defectoscopy and microscopy, studies of biological objects, *etc.*); in particular, it is widely used for contactless precision measurements of fluid parameters in flow systems.[26] The speed of propagation of an acoustic wave is determined by the properties of the medium through which the wave propagates; therefore, any changes in the liquid phase caused by, *e.g.*, the occurrence of a chemical reactions will change the speed of propagation of the wave and, as a consequence, change the time interval between the generation of an acoustic pulse and reception of the echo signal. Ultrasound diagnostic methods are used if a large number of contactless measuring devices are available (in, *e.g.*, petrochemical industry).[27–29]

Generation of ultrasonic vibrations is based on transformation of electromagnetic oscillations to elastic mechanical vibrations using specific devices. Electrical energy is converted to mechanical energy using the magnetostriction or piezoelectric effect.[30] These phenomena are due to the ability of certain materials to change their linear dimensions upon the action of alternating electric or magnetic field (piezoelectric effect and magnetostriction, respectively).

Magnetostrictive transducers characterised by ultrasound intensity of up to several tens of Watt per cm^2 (electroacoustic efficiency in liquid media exceeds 50%) at frequencies below 30 kHz are best for solving various problems in preparative chemistry and metallurgy. The maximum amplitude of acoustic vibrations is ~ 2 μm for ferrite transducers and more than 10 μm for metallic transducers.

Piezoelectric transducers are mainly used for generation of high-frequency (500 kHz – 100 MHz) ultrasonic vibrations in defectoscopes, sonars and acoustoelectronic devices. The radiation intensity can be as high as 60 W cm^{-2} and even reach the values 200 – 500 W cm^{-2} at an efficiency of 60% – 65% in, *e.g.*, pulsed mode of operation.[13]

In order to increase the acoustic wave intensity in a local spatial domain compared to its intensity at the surface of ultrasonic radiation source, the so-called concentrators are used.[31] Rod-like concentrators (acoustic waveguides) are most widely used because of simple design and ease of replacement. A rod-like concentrator increases the amplitude of vibrations due to a decrease in its cross-section or density in accordance with the momentum conservation law. The gain coefficient of a waveguide (with respect to acoustic wave intensity) depends on the shape of the waveguide. The stepwise and conical concentrators have the simplest design while the highest gains are provided by exponential and catenoidal concentrators. The best materials for manufacturing of concentrators with maximum amplitude of the vibrational speed are titanium and its alloys. However, the maximum operating temperatures of these materials are at most 500 – 600 °C and therefore operation at higher temperatures requires the use of various steels with high acoustic characteristics (*e.g.*, steels with high content of silicon, manganese and chrome).

III. Action of ultrasound on liquid-phase systems

The basic phenomena accompanying propagation of an acoustic wave through a liquid are summarised in Fig. 1. Numerical data presented below (including the acoustic wave intensities) refer to the low-frequency ultrasonic region.

At a rather low intensity (usually, less than 0.1 W cm^{-2}), the behaviour of the system can be quite correctly described using the classical wave equation. In this case no phenomena that could be

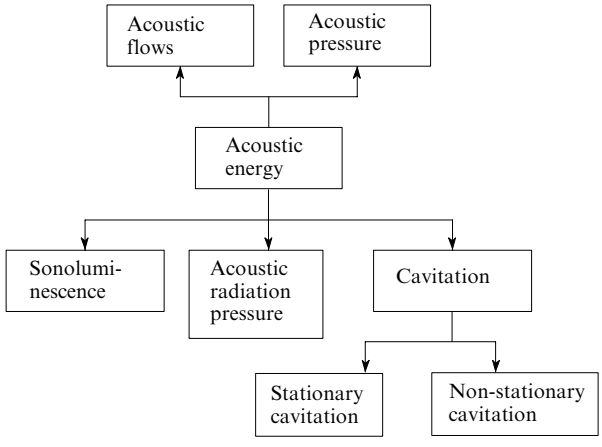


Figure 1. Physical phenomena accompanying the action of high-power acoustic radiation on liquids.

† In 1994, Elsevier B V (now a part of Reed – Elsevier Group) established a scientific journal *Ultrasonics Sonochemistry*. This fact substantiates that research in this field is in high demand.

useful for preparative chemistry and materials science are observed. As mentioned above, low-power ultrasound can only be used for solving particular diagnostic problems.

An increase in the acoustic energy flux density to ~ 1 W cm^{-2} and more causes the onset of some non-linear phenomena in the liquid. Among them, the most important is cavitation.[14, 32–34]

The mechanism of the onset of cavitation can be described as follows.[14, 35] Propagation of acoustic vibrations through a liquid causes the appearance of alternating rarefaction and compression zones in this liquid. A negative pressure is produced in the rarefaction zone. At high acoustic energy densities, it can exceed a critical value corresponding to discontinuity in the liquid and formation of cavitation bubbles in the bulk (Fig. 2, curve *AC* or *ABL*). The critical acoustic pressure for an ideal liquid should be equal to the difference between the atmospheric pressure and the pressure at which boiling of the liquid occurs at a given temperature (P_s). Actually, the critical pressure is much lower than this difference due to the presence of dissolved gases and mechanical impurities in the liquid. In this connection the formation of cavitation bubbles in a real system can be treated as a transition *AF* (see Fig. 2).

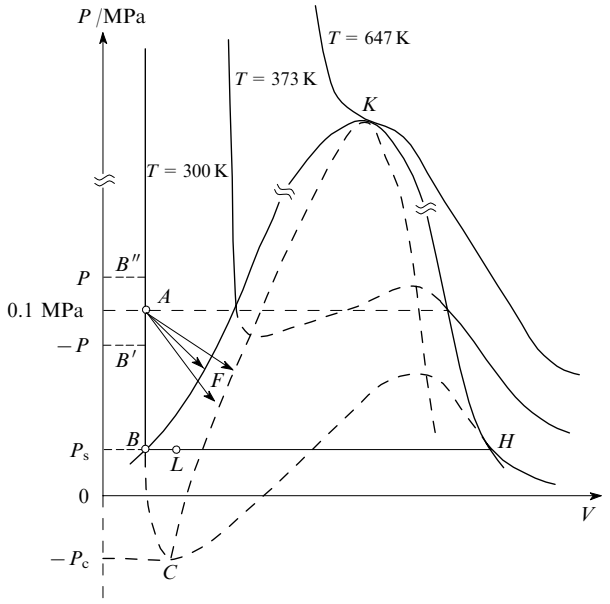


Figure 2. The phase diagram of water.[14]
Notations of points: *AF* is cavitation, *K* is critical point, *BKH* is binodal, *BK* is onset of boiling, *KH* is condensation of vapour, *CK* is spinodal, *P* is acoustic pressure, P_s is saturated vapour pressure, P_c is ultimate tensile stress.

At present, there are two main approaches to explanation of the mechanism of initiation of sonochemical reactions. One approach is usually called the 'hot spot' theory. It is widely used by researchers and is based on the following considerations.

During certain time interval the size of an emerged cavitation bubble and the external acoustic field execute almost in-phase oscillations. Then, due to a large difference between the hydrostatic pressure of the liquid and the pressure within the cavity of the cavitation bubble and to an abrupt increase in the acoustic pressure in the liquid in the compression zone of the ultrasonic wave the liquid moves towards the centre of the bubble and the bubble collapses (Fig. 3).[36] This is accompanied by concentration of energy similarly to the focussing of a converging shock wave. A high pressure developed in the central region of the collapsing bubble causes generation of a diverging spherical shock wave.[37] It is accepted that collapse of a cavitation bubble leads to the formation of a 'hot spot' at the centre, characterised by a local

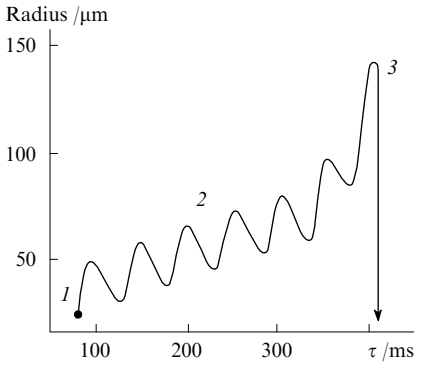


Figure 3. Evolution of a cavitation bubble.[34]
Generation (*1*), growth and oscillations (*2*), collapse (*3*).

temperature of about 5×10^3 K [up to $(2-3) \times 10^4$ K)][38] and a pressure ranging from 500 to 1000 atm.[39] The rate of cooling of the 'hot spot' can be as high as 10^{10} K s^{-1} (Ref. 40). Note that these numerical values were obtained ignoring the effects of heat exchange, surface tension and viscosity of the medium on the parameters of collapse and no correction for non-ideal character of the gas was applied.[41–44]

Thus, the key idea of the 'hot spot' theory is that ultrasonic cavitation causes concentration of acoustic energy within very small spatial domains in the medium. This leads to production of extremely high local energy densities (mainly in the form of heat), which thus initiates the sonochemical reactions.[45]

The second approach to explanation for the mechanism of initiation of sonochemical processes involves analysis of electrical phenomena accompanying the evolution of cavitation bubbles. The approach has been best developed by Margulis,[42, 46–50] who proposed a theory of local electrisation of cavitation bubbles. The key ideas of this theory are as follows. The action of an acoustic energy flux causes partial removal of the electrical double layer near the liquid–cavitation bubble interface. As a result, an uncompensated electric charge appears on the surface of the cavitation bubble. Later on, oscillations of the size of cavitation bubbles under sonication lead to the loss of stable spherical shape and to formation of various microirregularities (branches and jogs) on the surface of cavitation bubbles. In the limiting case, deformation of cavitation bubbles leads to their fission and abstraction of fragment bubbles. Deformation of the bubble surface creates favourable conditions for the appearance of high local densities of uncompensated electric charge, which eventually leads to electrical breakdown. Electrical discharge is accompanied by excitation and splitting of the gas and liquid molecules in the cavitation bubble. Thus, the mechanism of sonochemical reactions is closely related to the processes occurring during electrical discharge in a vapour-gas medium in the cavity of the cavitation bubble.

It should be noted that the local electrisation theory reasonably describes some experimental results that cannot be explained in the framework of the 'hot spot' theory,[42] including the occurrence of sonochemical reactions at very low ultrasound intensities (about 10^{-3} W cm^{-2}) or at high ultrasound frequencies (> 100 Hz) and an increase in the efficiency of suppression of sonochemical reactions using high-boiling additives, *etc.*

IV. Cavitation parameters

Cavitation can be characterised by three main parameters, namely, intensity, cavitation threshold and stationarity.[51]

The cavitation intensity means the volume-average intensity (power) of spherical shock waves generated in a liquid medium upon collapse of cavitation bubbles. The higher the power of the shock waves the higher the cavitation intensity.

The intensity of vibrations I (energy transferred per unit time through a unit surface area) can be estimated from the relation

$$I = \frac{1}{\tau}\int_0^{\tau} I(\zeta)\mathrm{d}\zeta = \frac{P^2}{2\rho c_0} = \frac{\xi^2\omega^2\rho c_0}{2},$$

where τ is time, ζ is the integration constant, $P = \xi\omega\rho c_0$ is the amplitude of acoustic pressure, ρ is the density of the medium, c_0 is the velocity of sound, ξ is the amplitude of acoustic vibrations and $\omega = 2\pi f$ is the angular frequency of vibrations.

It should be noted that the specific power (intensity) of acoustic vibrations is usually expressed in W cm^{-2} (power per unit surface area of acoustic radiator) or in W cm^{-3} (power per unit volume of irradiated sample).[52]

Clearly, the relation presented above is appropriate for determination of the acoustic energy flux density only if the wave propagates through a continuous isotropic medium with no scattering of acoustic power and the propagation of sound through the system treated causes no non-linear physicochemical effects (pre-cavitation regime).

Otherwise, one should use indirect methods of determination of the energy flux density.[52, 53] The most widely used method is a calorimetric technique[54] based on the assumption that a large proportion of the acoustic energy absorbed by the system is released in the form of heat. The main advantage of the technique is simplicity of both practical implementation and corresponding calculations. The method involves measurements of the rate of an increase in the temperature of the medium to which the acoustic wave radiation is transferred followed by calculations of the specific acoustic power using the relation

$$I = \frac{C_p\Delta T v}{S\tau},$$

where C_p is the molar (mass) heat capacity of the medium, ΔT is the experimentally determined change in the temperature during the time interval τ, v is the mass of the substance being processed and S is the radiating surface area of the waveguide (or the volume of the system treated).

Using the definition of specific absorbed acoustic power, it is possible to estimate the efficiency (η_{ef}) of a sonochemical process

$$\eta_{ef} = \frac{m}{SI\tau},$$

where m is the amount of the substance (in moles) involved in the sonochemical reaction. The yield of a sonochemical process (η) can be defined[55] using the transferred power of the source of vibrations W instead of absorbed acoustic power

$$\eta = \frac{m}{W\tau}.$$

However, the calorimetric technique described above has a number of significant drawbacks.[56] First, this is an intense heat exchange between the metallic waveguide contacting the cavitating liquid. Second, the heat capacities of cavitating media may differ appreciably from the heat capacity of the liquid (one should also keep in mind that the properties of the cavitating liquid differ from those of the same liquid in its normal state). Third, large local temperature gradients can be produced in the liquid in the course of experiments.

An alternative method is the comparative calorimetric technique.[57] This approach involves initial irradiation of the liquid with ultrasound over a short period (τ) and measurements of the dependence of the temperature of the liquid on the duration of the treatment stage (curve A). After cooling, the liquid is heated again using a conventional technique (by, *i.e.*, an electrical resistive heater) and the dependence of the temperature of the liquid on time (curve B) is also measured. Then, by varying the power of the heater the shape of curve B is changed in order to match curve A. Once matched, the output power of the heater is considered equal to the acoustic power absorbed by the liquid. The most favourable conditions for calorimetric measurements are as follows: a slight increase in temperature (0.1 – 0.4 °C), short-term operation of the source of ultrasound (5 – 15 s) and efficient mixing of the liquid.

The cavitation threshold is a minimum intensity of ultrasonic waves at which cavitation emerges. Cavitation is quantitatively characterised by the so-called critical cavitation number (χ_c) defined by the relation

$$\chi_c = \frac{P_0 - P_s}{P_c},$$

where P_0 is the external pressure. Interestingly, the χ_c value corresponding to the onset of cavitation usually differs from the value corresponding to its disappearance, *i.e.*, hysteresis occurs. The χ_c value depends on many parameters that characterise both the state of the liquid (content of dissolved gases, temperature, presence of impurities) and the acoustic field (frequency, pulse duration, *etc.*). For instance, the cavitation threshold increases as the concentration of gas dissolved in the liquid decreases, the frequency of acoustic vibrations increases, the pulse duration decreases and the flow turbulence enhances.

Depending on the lifetime of cavitation bubbles, cavitation is classified into two types,[23] stationary and non-stationary cavitation. Non-stationary cavitation bubbles are formed at an acoustic energy density of the order of 10 W cm^{-2} and exist during one or a few acoustic cycles. The bubble radius becomes at least twice as large as the initial radius and then the bubbles are rapidly collapsed in the liquid compression stage. Some bubbles disintegrate into smaller bubbles that in turn form cavitation centres. Non-stationary cavitation is characterised by high intensity because the vapour pressure in the bubble cavities is very low owing to short bubble lifetimes.

Stationary cavitation bubbles are characterised by relatively long lifetimes and high vapour pressure in cavities. They are formed at rather low ultrasound intensities (1 – 3 W cm^{-2}).

It has been accepted for long that only non-stationary cavitation can induce sonochemical processes. However, recent calculations showed that the temperature and pressure produced in the collapsing stationary bubbles are only slightly lower than in the collapsing non-stationary bubbles. Additionally, the stable cavitation bubbles have much longer lifetimes and therefore a stronger effect on the course of the sonochemical reaction.[14]

The key parameters of acoustic cavitation (cavitation intensity and threshold) depend on various factors. The most important factors are listed below.

Ultrasound power and frequency. The ultrasound power necessary for carrying out a sonochemical reaction should be chosen taking into account the need of overcoming the power threshold associated with the onset of cavitation (1 – 5 W cm^{-2} for aqueous solutions) and the optimum power (10 – 50 W cm^{-2} for aqueous solutions), because further increase in acoustic power makes the process less efficient.[23] The limitation imposed on the second parameter is due to the formation of a cavitation cloud near the radiating surface at high ultrasound power, which precludes the development of cavitation in the bulk of the liquid.[14]

Sonochemical processes are usually carried out with 20 – 500 kHz ultrasound, because at lower frequencies the role of vapour cavitation increases appreciably, which reduces the overall cavitation intensity. At the same time at acoustic frequencies of 2 – 3 MHz the cavitation threshold substantially increases[14] and the efficiency of the sonochemical processes decreases.

Physical properties of solvent. It is accepted[40] that an increase in the viscosity of the medium causes a substantial increase in the cavitation threshold and a decrease in cavitation intensity.

According to calculations [58] for acoustic vibrations at 23 kHz, an increase in the viscosity of the medium from 0.001 to 0.1 Pa s leads to more than twofold decrease in cavitation intensity. As the viscosity of the liquid phase increases to 1.0 Pa s, cavitation almost disappears.

Based on analysis of experimental data, the following relation between the viscosity of the liquid medium η and cohesion pressure p_{co} (characterises the hydraulic resistance of the liquid to the formation of cavitation bubbles) was proposed [59]

$$\log\left(\frac{\eta}{\eta_0}\right) = -3.05 p_{co},$$

where $\eta_0 = 0.13$ MPa s and the empirical constant -3.05 is expressed in atm^{-1}.

The cohesion pressure cannot be measured directly, but it can be expressed through the experimentally measured parameters, namely, the amplitude of acoustic pressure (p_{min}) and the intensity of ultrasonic waves corresponding to the onset of acoustic cavitation (I_{min}), *i.e.*, the cavitation threshold [60]

$$p_{co} = p_0 - p_{min} = p_0 - \sqrt{2 I_{min} \rho \upsilon_{us}},$$

where p_0 is the hydrostatic pressure and υ_{us} is the speed of ultrasonic waves in the liquid medium.

Not only the viscosity, but also the surface tension of the liquid phase has a strong effect on the cavitation intensity and threshold. Experiments [61] showed that a decrease in the surface tension of the liquid from 0.072 to 0.040 N m^{-1} causes a more than threefold acceleration of sonochemical reactions. The main reason for this effect is the decrease in the cavitation threshold.[61]

According to calculations,[58] the surface tension of the liquid sonicated at 23 kHz has no pronounced effect on the cavitation intensity. At the same time an increase in the surface tension of the liquid medium from 0.020 to 0.1 N m^{-1} reduces the cavitation intensity by a factor of nearly 2.5 for sonication at high frequencies (2–3 MHz).

Thus, a correct choice of the medium is of crucial importance for carrying out sonochemical reactions, namely, the liquid media of low viscosity (weak intermolecular interaction) and surface tension are more appropriate for the onset of intense low-threshold acoustic cavitation.

Presence of dissolved gases and purity of reaction system. An abrupt drop of external pressure in a liquid causes liberation of gas dissolved in it. If an acoustic wave is in the rarefaction phase, the dissolved gases liberate in the form of small bubbles, which can act as nuclei of cavitation centres, and the cavitation threshold decreases appreciably.[62] Additional cavitation nuclei are usually produced by bubbling an inert gas (nitrogen or argon) through the liquid.

Any microinhomogeneities or free surfaces present in the liquid medium also act as nuclei of cavitation bubbles; this considerably decreases the cavitation threshold.[63]

Temperature. Experiments [62] showed that raising the temperature favours a decrease in the cavitation threshold on the one hand and an increase in the rate of solvent evaporation and in the partial pressure of the solvent inside the bubble on the other hand. Because of this, a transition is possible from gas cavitation to vapour cavitation [64] characterised by an abrupt decrease in the efficiency of collapse of cavitation bubbles and in the intensity of acoustic cavitation. For instance, the oxidation of aqueous $FeSO_4$ solution under sonication is suppressed at 50 °C and sonolysis of water resulting in the formation of H_2O_2 is suppressed at 67 °C.[62] Thus, the operating temperature for sonochemical processes in open systems should be much lower than the boiling point of the solvent.

External pressure. The cavitation threshold depends on the pressure developing in the rarefaction phase. This pressure exceeds the hydrostatic pressure of the liquid medium in absolute value. An increase in external pressure reduces the difference between the acoustic pressure in the rarefaction phase and the hydrostatic pressure. At high external pressure, this difference can appear to be insignificant for formation of cavitation bubbles in the liquid medium. In this case the onset of cavitation requires a substantial decrease in the acoustic pressure in the rarefaction phase (increase in the amplitude of acoustic vibrations). Experimental studies [14] showed that the optimum external pressure for sonochemical processes in open systems ranges from 0.1 to 0.5 MPa.

Thus, cavitation emerged upon sonication of liquid-containing systems enhances the efficiency of ultrasonic treatment due to concentration of acoustic energy in small spatial domains. Using this effect, one can solve a number of chemical, materials science and technological problems, *e.g.*, fabrication of metal slabs with homogeneous microstructure,[65–68] finely dispersed powders,[69] emulsions [60,70] and aerosols.[71–73] Additionally, sonication is successfully utilised for etching of surfaces,[23] regeneration of catalysts,[74] monitoring of precipitation,[23] *etc.*

Ultrasonic dispersion procedure is based on violation of symmetry of collapse of a cavitation bubble near the interface (*e.g.*, liquid–solid interface, Fig. 4).[15] As a result, intense local fluid microflows towards the phase boundary are produced; the speed of propagation of such flows reaches several tens of metres per second. Physicochemical consequences of this phenomenon can be followed taking ultrasonic treatment of various suspensions as examples.

It was experimentally established [75] that sonication of suspensions of inorganic oxide and sulfide materials in organic solvents causes a considerable increase in the surface area of target powders (20–30-fold increase after ~45 min at an initial specific surface area of 0.3–0.5 $m^2\ g^{-1}$) due to collisional disintegration of particles. Chemical processes in the liquid–solid systems can also occur at higher rates under these conditions;[76] this particularly concerns molecular intercalation into layered inorganic materials. For instance, the intercalation rate of amines, metallocenes, metallic sulfide clusters and some other compounds into ZrS_2, V_2O_5, TaS_2, MoS_2 and MoO_3 under sonication increases by more than two orders of magnitude compared to conventional intercalation rates. Ultrasonic treatment of suspensions under normal conditions can initiate reactions giving binary compounds from elements (Fig. 5).[77]

A common feature of the fields of application of high-power ultrasound mentioned above is utilisation of mainly mechanical effects of sonication of liquids. At the same time there is a broad spectrum of pure chemical problems that can also be solved using acoustic treatment of the liquid phase.

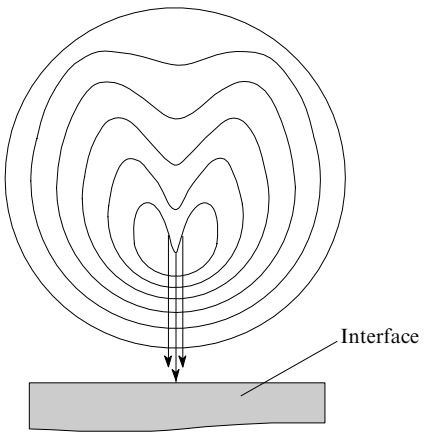


Figure 4. Collapse of a cavitation bubble near interface.[15]
The direction of the liquid flow after collapse of the bubble is shown by arrows.

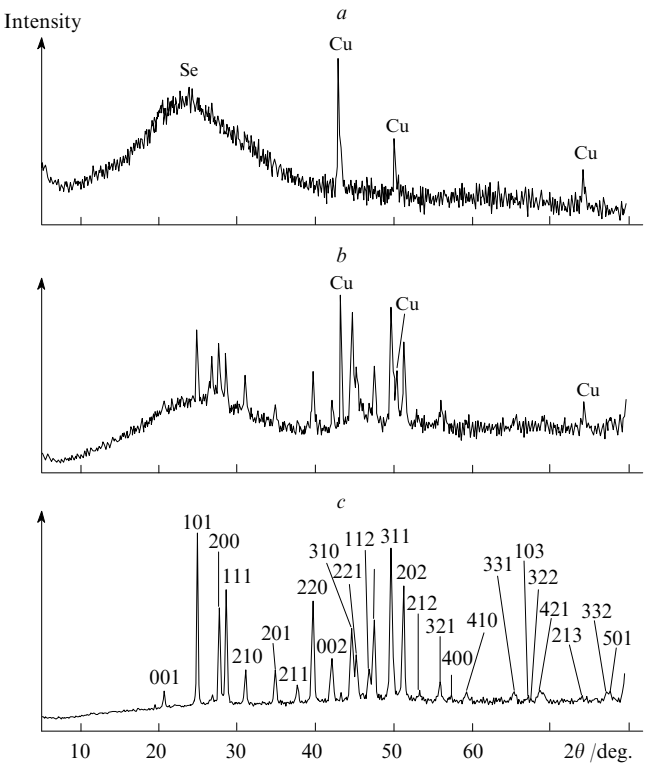


Figure 5. Powder X-ray diffraction data of the samples obtained upon irradiation of a suspension of Cu/Se mixture in methanol with ultrasound for 30 (*a*), 120 (*b*), and 480 min (*c*).[77]
The X-ray diffraction pattern in Fig. *c* corresponds to single Cu_3Se_2 phase; the reflections were indexed according to [PDF 47-1745].

V. Sonochemical reactions in aqueous media

The chemistry of aqueous solutions under sonication has been studied in considerable detail.[8, 14, 33, 78] In most cases sonochemical reactions in aqueous solutions are due to the fact that water vapour present in the cavity of a cavitation bubble at the instant of bubble collapse experiences the action of high temperature and high pressure; as a consequence, water molecules undergo the so-called sonolysis [79, 80]

$$H_2O \xrightarrow{)))} H^{\bullet} + HO^{\bullet},$$

$$HO^{\bullet} + HO^{\bullet} \longrightarrow H_2O_2,$$

$$H^{\bullet} + O_2 \longrightarrow HO_2^{\bullet},$$

$$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2.$$

The rate of formation of $HO^{\bullet}$ radicals in solutions in the absence of oxygen dissolved in water is $\sim$25 μmol litre^{-1} min^{-1} and the rate of formation of hydrogen peroxide in air-saturated solutions is 0.6 mmol litre^{-1} min^{-1} (Ref. 81).

Sonication of water causes ionisation of water molecules at the instant of collapse of the cavitation bubble and emergence of hydrated electrons [82]

$$e^- + z\,H_2O \longrightarrow e_{aq}^-.$$

The presence of solvated electrons in an aqueous solution strongly depends on the acidity of the medium.[83] For instance, in an acidic medium the solvated electrons participate in the formation of hydrogen atoms following the reaction

$$e_{aq}^- + H^+ \longrightarrow H^{\bullet},$$

whereas another process occurs in a basic medium

$$H^{\bullet} + OH^- \longrightarrow H_2O + e_{aq}^-.$$

Thus, sonication of aqueous solutions should initiate redox and radical reactions in them. For instance, sonication of an acidified aqueous solution of Mohr's salt in air causes oxidation of Fe(II) to Fe(III) as follows [84]

$$Fe^{2+} + H_2O_2 + H^+ \longrightarrow Fe^{3+} + HO^{\bullet} + H_2O. \quad (1)$$

The oxidation of iodide ions in aqueous KI solution occurs under similar conditions

$$I^- + HO^{\bullet} \longrightarrow 0.5\,I_2 + OH^-, \quad (2)$$

$$I_2 + I^- \longrightarrow I_3^-. \quad (3)$$

Reactions (1)–(3) are considered as reference reactions in sonochemistry. They are used, in particular, for dosimetric purposes in the determination of specific acoustic power from the data of kinetic experiments, because it is clear that the rates of these redox reactions are related to the acoustic power absorbed by the solution.[53] In addition to the oxidation reactions of divalent iron and iodide anion, the decomposition reactions of various porphyrin derivatives, *e.g.*, 5,10,15,20-tetrakis(4-sulfophenyl)porphyrin (TPPS) [85] (Fig. 6), are also used as reference reactions.

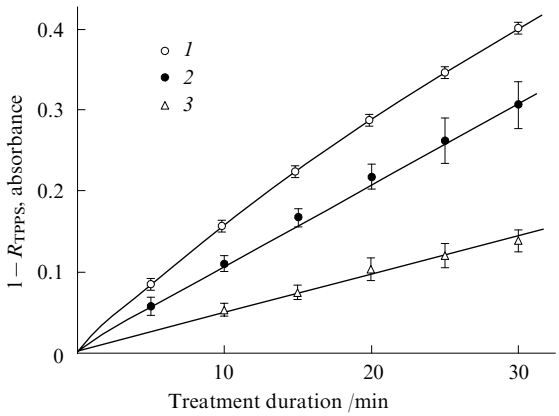


Figure 6. Extent of decomposition of TPPS (*1*) and absorbances of Fe^{3+} (*2*) and I^- (*3*) solutions plotted *vs.* duration of ultrasonic treatment.[85]
$R_{TPPS} = c_{TPPS}/c^0_{TPPS}$ is the ratio of the TPPS concentration after ultrasonic treatment to the initial TPPS concentration.

Reduction reactions, *e.g.*, reduction of Fe(III) upon sonication of weak acid or neutral aqueous solution of complex $K_3[Fe(C_2O_4)_3]$ in air [86] can also proceed in aqueous solutions

$$Fe^{3+} + HO_2^{\bullet} \longrightarrow Fe^{2+} + O_2 + H^+.$$

Reduction of Ce(IV) to Ce(III) under ultrasonic treatment of acidified aqueous cerium(IV) sulfate solution proceeds analogously.[87]

Particular attention should be paid to a series of studies of oscillation processes in ultrasonic field taking the Belousov–Zhabotinsky reaction as an example; the results obtained are summarised in a monograph.[14] It was shown that the parameters of the self-oscillatory chemical process (frequency, intensity, duration of vibrations) strongly depend on the instant (within the period of oscillations of the concentration of reaction mixture components) at which the acoustic energy is transferred to the irradiated medium.

Radical processes occurring under high-power ultrasound in aqueous solutions saturated with an oxygen–nitrogen mixture have also been studied.[88–90] It was established that molecular nitrogen undergoes a series of chemical transformations involving the formation of nitrate and nitrite ions at nearly the same rates (about 0.03 μmol litre^{-1} W^{-1}).[90]

As mentioned above, sonolysis of water in the course of ultrasonic treatment of aqueous and aqueous alcoholic solutions creates favourable conditions for redox reactions, which can be used for the synthesis of various compounds in highly dispersed state. In this connection it is convenient to consider direct and indirect sonochemical redox reactions. In the former case the chemical reaction is solely driven by hydrogen peroxide formed in the course of sonolysis while in the latter case the oxidising (or reducing) agent is added to the reaction mixture during the synthesis.

It should be noted that often the role of sonication during the synthesis of disperse powders from aqueous solutions is reduced to intensification of the mixing of the reaction medium, disaggregation of particles, renewal of their surfaces, fabrication of uniform heterogeneous mixtures of solids, *etc*. Thus, sonolysis of water has almost no effect on the physicochemical features of synthesis.

1. Reduction of metals from aqueous solutions

Metals characterised by large positive redox potentials corresponding to semireactions (gold, platinum, palladium) can be reduced by direct sonochemical reduction (no additional reducing agents) to give disperse elements. For instance, ultrasonic treatment of aqueous tetrachloroaurate solutions in argon atmosphere makes it possible to prepare colloidal solutions of 10-nm gold particles [91] with very narrow size distribution. The addition of aliphatic alcohols to the reaction mixture significantly accelerates the formation of colloidal solution, the effect being even more pronounced with enhancement of the hydrophobic properties of the alcohol. Similar results were obtained [92] in a study of the influence of aliphatic alcohols on the rate of reduction of platinum from H_2PtCl_6. The effect seems to be due to the fact that the interaction of alcohols with primary radicals $H^{\bullet}$ and $HO^{\bullet}$ formed in the sonolysis of water results in more stable and long-lived secondary radicals, which then act as reducing agents. As the hydrophobic fragments of molecules increase, the concentration of alcohol at the cavitation bubble–solution interface increases. As a consequence, most primary radicals interact with the alcohol molecules, thus favouring an increase in the yield of the secondary radicals. Therefore, the highest rate of sonochemical reactions in aqueous solutions is expected in the presence of surfactants.

Indeed, the rate of sonochemical reduction of some metals in the absence of surfactants is very low. For instance, the reduction of hexachloroplatinum acid and formation of nanodisperse platinum particles with the size of 3 nm occurs only in the presence of anionic surfactants (sodium dodecyl sulfate, sodium dodecylbenzene sulfonate or polyethylene glycol sodium monostearate); moreover, the reaction rate remains almost unchanged if the surfactant concentration becomes higher than the critical micelle concentration ($0.1-5$ mmol litre^{-1}).[93]

The effect of the surfactant concentration on the micro morphology of nanodisperse powders formed under sonochemical reduction conditions was studied.[94] With no surfactant, ultrasonic treatment of aqueous hydrogen tetrachloroaurate solution in the presence of poly-*N*-vinyl-2-pyrrolidone resulted in the formation of highly dispersed almost spherical gold particles (average size ~ 7 nm). The particles formed in the presence of $NaO_3SC_{12}H_{23}$ have different morphologies including spherical, needle-shaped, disk-like and triangular crystals (Fig. 7). As the $[HAuCl_4]:[NaO_3SC_{12}H_{23}]$ ratio decreased from 1 to 0.05 with an increase in the surfactant concentration, the average particle size reduced from 18 to 10 nm and almost all triangular particles disappeared (only disk-like or spherical gold particles formed at high surfactant concentrations).

A negative consequence of the presence of surfactants in solution consists in reduction of cavitation efficiency due to the decrease in the surface tension of the solution. Because of this, the efficiency of formation of primary radicals decreases.

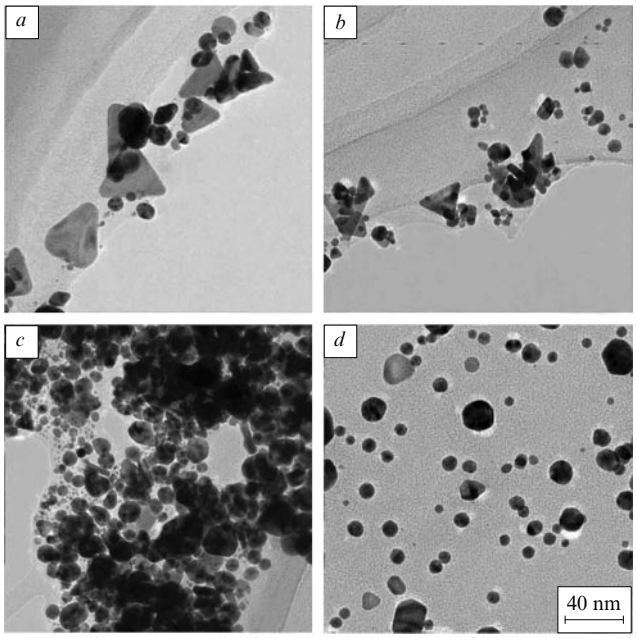


Figure 7. Micrographs of nanodisperse gold particles prepared by ultrasonic treatment for 1 h at a $[HAuCl_4]:[NaO_3SC_{12}H_{23}]$ ratio of 1 (*a*), 0.2 (*b*), 0.1 (*c*), 0.05 (*d*).[94]

A study [94] of the effect of the acoustic power on the micromorphology and average size of gold particles showed that an increase in the acoustic power from 30 to 90 W causes the average particle size to decrease from 20 to 10 nm. Additionally, nearly perfect spherical particles formed under high-power treatment, whereas low-power sonication resulted in the formation of disk-like, prismatic and needle-shaped particles. The authors believe that an increase in the ultrasound power increases the reduction rate of gold ions and the nucleation rate of the new phase and, correspondingly, the average particle growth rate decreases. Hydrogen peroxide that is formed during sonolysis of water is not a unique reducing agent; other compounds can also play this role. The mechanism of sonication is most likely associated with initiation of redox reactions due to the appearance of reactive radicals in the aqueous solution. The synthesis [95] of nanodisperse copper particles of size $50-70$ nm from copper(II) hydrazine carboxylate can also be treated as indirect sonochemical reduction.

The results obtained in a study [96] of sonochemical reduction of potassium dicyanoaurate(I) in the presence of ascorbic acid deserve particular attention. It was shown that strongly aggregated gold particles of irregular shape are formed in aqueous solution. At the same time, gold nanoparticles formed in polyethylene glycol (PEG-400) have a needle-shaped morphology (diameter ~ 40 nm at an anisotropy coefficient of about 15). It was assumed that the mechanism of formation of needle-shaped particles is due to the fact that individual 3-nm gold particles formed in the redox reaction form chains owing to coordination by OH and C–O–C groups of the polymer solvent molecules. Then, these chains aggregate to form needle-shaped particles. This mechanism was confirmed by the results of a study of the effect of potassium dicyanoaurate(I) concentration on the micromorphology of particles formed. The size and anisotropy coefficients of aggregates formed upon sonochemical reduction of gold from solutions with higher salt concentrations considerably increased and the content of particles with dendritic morphology also increased.

At present, studies on the synthesis of inorganic composite materials based on simple metals using sonochemical reduction techniques are scarce. In particular, direct sonochemical reduction of $HAuCl_4$, $AgNO_3$ and $PdCl_2$ was successfully used [97–101] for preparation of nanocomposites based on SiO_2 xerogels and containing 4–7-nm nanoparticles of corresponding metals. The matrix (SiO_2) plays an important role in the formation of nanodisperse metal particles. First, the xerogel pore diameter determines the size of the metal particles and, second, the matrix precludes aggregation of individual particles. Nanodisperse ruthenium particles were synthesised in a similar fashion by sonochemical reduction of ruthenium trichloride in the presence of mesoporous silica SBA-15.[102]

Sonochemical reduction of $HAuCl_4$ and H_2PtCl_6 was also employed to prepare conducting composite materials based on polypyrrole [103] and polyaniline.[104] It was shown that acoustic treatment makes it possible to significantly accelerate (by $\sim$50 times) the formation of the composite and to increase the yield of the reaction product.

2. Sonochemically induced reduction of metal oxides and hydroxides from aqueous media

Iron, chromium and manganese cannot be obtained from aqueous solutions by sonochemical reduction (standard electrode potential of semireactions is negative or has a small positive value). However, sonication can be utilised for preparation of corresponding highly dispersed oxides. In particular, nanocrystalline Fe_3O_4 powder comprising needle-shaped particles (average size 14×48 nm) was obtained by ultrasonic treatment of $Fe(OAc)_2$ solution under argon bubbling.[105] Good examples of typical publications in this field are provided in Refs 83, 106 and 107. In particular, highly dispersed (50–200 nm) powders of X-ray amorphous manganese and chromium oxides Mn_2O_3 and Cr_2O_3 were synthesised from potassium permanganate and ammonium bichromate, respectively.[107] The addition of ethanol to the reaction mixture considerably increased the rate of sonochemical synthesis due to the formation of secondary radicals (α-hydroxyethyl radical). A study of the effect of temperature of the solution treated on the sonochemical reaction showed that the yield of the reaction product increases (but not decreases) with the increase in temperature due to a decrease in the cavitation intensity. Probably, in this case the thermodynamic and kinetic factors predominate. Recently, various modifications of the sonochemical synthesis of manganese oxides from aqueous solutions have attracted considerable attention because these compounds are promising in the design of materials for d.c. sources.[108–110]

As mentioned above, in some cases the mechanism of sonochemical synthesis does not involve the redox processes and the role of cavitation is reduced to various mechanical effects. The reaction products obtained under sonication can differ in phase composition and micromorphology from those synthesised under similar conditions without sonication. In particular, this was observed [111] in the course of preparation of nanodisperse α-$Ni(OH)_2$ powder (particle size 20 nm) by precipitation from aqueous solutions of nickel salts under ultrasonic treatment. The reaction carried out under similar conditions with no sonication resulted in the β-modification of nickel hydroxide characterised by somewhat larger particle size (70 nm).

A number of highly dispersed simple metal oxides were prepared in a similar fashion by sonohydrolysis.[8] In particular, nanodisperse ceria was synthesised [112, 113] from cerium ammonium nitrate, hexamethylenetetramine, and polyethylene glycol. The procedure resulted in relatively small particles (size 2–4 nm) with narrow size distribution. Additionally, it was shown that the micromorphology of powder obtained by precipitation from a solution containing cerium nitrate and azoformamide noticeably changes upon addition of some bases. In particular, the addition of quaternary ammonium bases gave monodisperse CeO_2 powder with a particle size of 3.3 nm.

Recently, extensive literature on the synthesis of titania powders under sonication has been published.[114–122] Interest in preparation of highly dispersed titania is first of all due to the fact that this compound is a promising photocatalyst, which founds application in cleaning of waste water from organic waste. Most often, the sonochemical synthesis of TiO_2 is carried out by hydrolysis of titanium tetraisopropoxide in ethanol–water mixture followed by thermal annealing of the product at relatively low temperatures (400–500 °C). In this case spherical dense or mesoporous monophase anatase particles (average size 100–500 nm) or a mixture of anatase with brookite are formed depending on the reaction conditions.[117, 119] In some cases preparation of spherical particles during the synthesis requires the addition of high-molecular-mass compounds, *e.g.*, polyethylene glycol [115] or octadecylamine.[118] It should be noted that synthesis of titania from titanium tetrachloride results in monophase rutile [119, 121] with needle-shaped or dendritic morphologies.

Acoustic treatment of rutile suspensions in sodium hydroxide solution [122] leads to formation of nanotubes and needle-shaped particles of approximate composition $H_2Ti_3O_7 \cdot 0.5\,H_2O$. No such structures are formed without sonication. The authors assumed that this is due to partial dissolution of TiO_2 upon sonication.

The photocatalytic activity of titania can be considerably enhanced by carrying out the photodegradation reaction under sonication (Fig. 8).[123] This effect is due to continuous renewal and activation of the surface of titania particles.

A study [114] of the photocatalytic activity of titania powders synthesised by sonohydrolysis of titanium tetraisopropoxide in aqueous and aqueous-alcohol media showed that this procedure makes it possible to prepare photocatalysts whose catalytic activities are at least comparable with those of the samples of commercially available materials (comparison with the Degussa-P25 sample was made, see Fig. 9).

More complex compounds, in particular aluminates,[124] nickelates and manganites [8] were synthesised using similar sonochemical procedures (addition of precipitating agent to aqueous metal salt solutions).

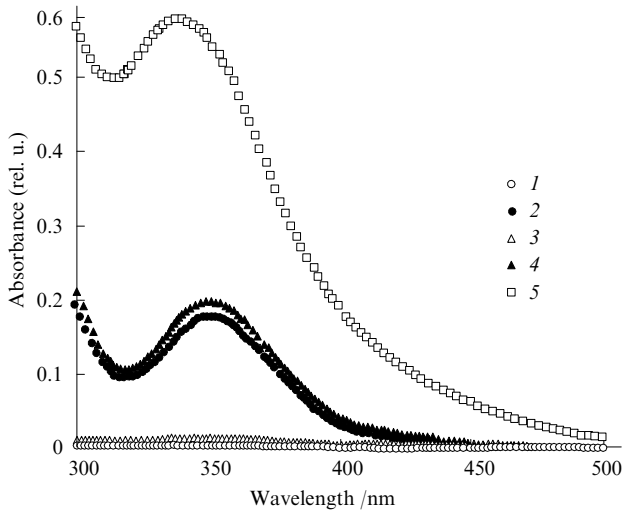


Figure 8. Absorption spectra of: aqueous KI solution irradiated with UV light (*1*) and ultrasound (*2*), aqueous KI solution with TiO_2 additive (*3*), pure aqueous KI solution (*4*) and aqueous KI solution with TiO_2 additive simultaneously irradiated with UV light and ultrasound (*5*).[123]

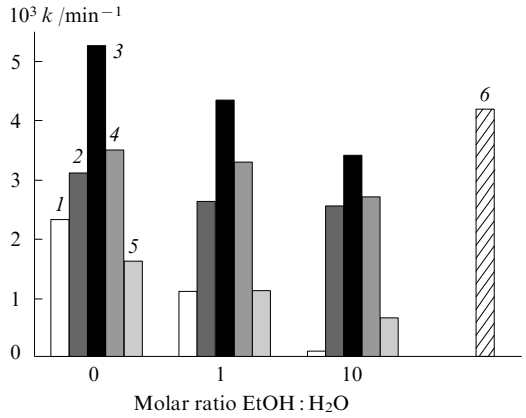


Figure 9. Apparent rate constants (k) for photocatalytic degradation of acetone plotted *vs.* solvent compositon and calcination temperature of titania samples prepared by ultrasonic irradiation.[114]
T/°C: 100 (*1*), 400 (*2*), 500 (*3*), 600 (*4*) and 700 (*5*); Degussa-P25 sample (*6*).

3. Sonochemical synthesis of metal chalcogenides

Recently, extensive literature has been devoted to sonochemical synthesis of transition metal chalcogenides. This method was used for preparation of nanodisperse ZnS,[125–127] Sb_2S_3,[128,129] HgSe,[130] HgS,[131] SnS_2,[132] CdS,[133–137] CdSe,[133,138] PbX (X = S, Se, Te),[139–141] CuS,[96,142] $Cu_{2-x}Se$, Cu_3Se_2, CuSe,[143–145] $Bi_2Se_xTe_{3-x}$, Ag_2Se, Ag_2Te, Cu_5Se_4, PbSe, Ni_3Se_4,[146] Ag_2Se, $NiS_{1-x}Se_x$,[142,147] MoS_2,[148] Ag_2S,[149] $RuS_{1.7}$,[150] Bi_2S_3,[151] HgTe,[152] $MoTe_2$,[153] and Bi_2Te_3 powders.[154]

Here, salts are most widely used as the source of metal. First of all, these are acetates,[125,130,139] nitrates and chlorides.[132] The source of sulfur is provided by thioacetamide, thiourea, elemental sulfur or sodium thiosulfate. Selenides and tellurides are mainly synthesised from elemental selenium and tellurium as the sources of the non-metals; at the same time, the syntheses of selenides and tellurides using sodium selenite or tellurite were reported.[138,146]

The most often used solvents are water or aqueous-alcohol solutions;[125,134,136] however, in some cases ethylenediamine[145,147,149,152,155] or polyethylene glycol[130,140] is more appropriate. This concerns the reactions involving elemental sulfur (or selenium) as the source of the non-metal, because sonication of a suspension of a chalcogen in ethylenediamine induces the reaction

$$S + H_2N-CH_2-CH_2-NH_2 \xrightarrow{)))} \longrightarrow \text{—[—}S_n-NH-CH_2-CH_2-NH\text{—]}_m + H_2S$$

resulting in liberation of hydrogen sulfide.[149] Nanodisperse sulfides are formed as a result of the interaction of hydrogen sulfide with a metal salt or a metal complex.[156] By carrying out reactions in polyethylene glycol it is possible to substantially reduce the minimum acoustic power necessary for the sonochemical synthesis of chalcogenides.[130] In some cases polyethylene glycol also acts as a reducing agent.[130] Additionally, the synthesis of metal chalcogenides in the presence of polyethylene glycol or other polymers capable of playing the role of complex-forming agents (*e.g.*, hydroxyethylcellulose[136]) permits fabrication of submicron disperse particles with strip and dendritic morphologies. A similar procedure [sonochemical oxidation of iron(II) acetate in aqueous solution in β-cyclodextrin matrix] was used for preparation[105] of needle-shaped magnetite (Fe_3O_4) nanoparticles.

It should be noted that low-molecular-mass complex-forming agents affect the micromorphologies of the powders formed in the course of sonochemical synthesis. This concerns, in particular, sodium tartrate and sodium citrate.[143,151] However, the most interesting results were obtained using ethylenediaminetetraacetic acid (EDTA) as complex-forming agent. Namely, the reactions of formation of needle-shaped or strip-like nanodisperse Bi_2S_3,[151] PbS,[141] and CdS[136] particles in the presence of EDTA were substantially accelerated. The formation of highly anisotropic particles in the presence of EDTA was explained using a mechanism involving the formation of a very stable pentadentate complex between EDTA (Y^{4-}) and Cd^{2+} ion. Steric hindrances allow the interaction between Cd^{2+} and S^{2-} ions

$$CdY^{2-} + S^{2-} \longrightarrow CdS + Y^{4-}$$

to follow only one direction.[16] Correspondingly, the chalcogenide particles grow in this direction (Fig. 10).

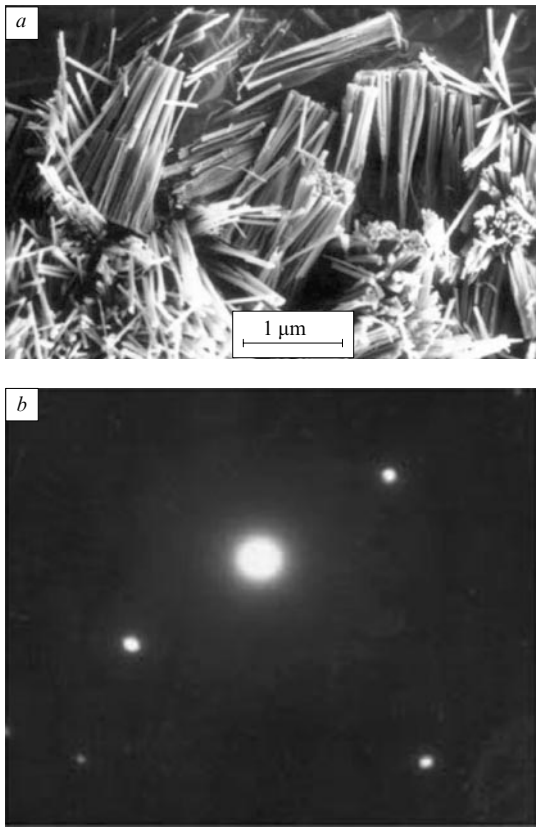


Figure 10. Micrograph of rod-like CdS crystals (~80 nm in diameter, ~1.3 μm long) formed under ultrasonic treatment in the presence of EDTA (*a*) and an electron diffraction pattern of an individual rod (*b*).[16]

When chalcogenides are synthesised in aqueous media, the compositions and structures of reaction products are strongly influenced by the pH value of the solution. Taking mercury sulfides as examples, it was shown that nanodisperse α-HgS powders can only be synthesised from solutions with pH 9–11.[131] In more acidic media, coarse-grained precipitate is formed rapidly. If the medium pH is controlled by adding ammonia (triethanolamine), the powder formed is characterised by an average particle size of ~35 nm (10–15 nm, spherical particles). The smaller particle size in the case of triethanolamine was explained[131] by the fact that this compound is an effective ligand that forms stable complexes with Hg^{2+}. The synthesis of nanodisperse β-HgS powder only proceeds at pH values from 3 to 5. Reactions in media of lower acidity result in coarse-grained β-HgS precipitate. Additionally, it was shown that the β-HgS particle size also depends on the treatment duration, namely, the average particle size changes from 13 to 20 nm as the duration of sonochemical synthesis increases from 0.5 to 1 h. This effect can be due to recrystallisation and growth of nanodisperse particles.

By and large, the micromorphologies of products of sonochemical synthesis are to a great extent determined by the reaction conditions. For instance, the synthesis of Sb_2S_3 gave both amor-

phous nanospheres and needle-shaped nanoparticles.[128] Star-like Sb_2S_3 particles were synthesised under somewhat different conditions.[129]

The mechanism [139] of sonochemical formation of nanodisperse lead sulfide powders can probably be extended to other metal sulfides and selenides provided that the source of the non-metal is elemental sulfur or selenium. Sonication of such systems increases the rate of dissolution of the non-metal (conventionally, this is the limiting stage of the chalcogenide formation reactions) and, hence, the formation of E^{2-} (E = S, Se, Te) ions. Additionally, ultrasonic treatment precludes aggregation of chalcogenide particles.

VI. Sonochemical processes in non-aqueous media

As shown above, in the course of sonochemical reactions in aqueous media the cavity of a cavitation bubble is only filled with water vapours and dissolved gases, because usually the volatilities of other components of the aqueous solution are negligible. The mechanism of sonochemical processes in aqueous solutions involves the formation of mainly $H^{\bullet}$, $HO^{\bullet}$, and $HO_2^{\bullet}$ radicals upon collapse of cavitation bubbles and subsequent interacton of these species with compounds in solution.

In the case of non-aqueous solutions the number of compounds capable of competing with the solvent in volatility considerably increases and includes, *e.g.*, various metal complexes. Large amounts of such compounds can be present in the gaseous phase within the cavitation bubble along with the solvent molecules. Collapse of the cavitation bubble causes their decomposition and formation of solid-phase products of sonolysis. Since each collapsing cavitation bubble can be treated as a specific microreactor, sonochemical decomposition products are characterised by very high degree of dispersion.

Sonolysis of non-aqueous solutions makes it possible to obtain simple (metals) and complex substances (*e.g.*, binary compounds including nitrides, carbides, oxides, sulfides, silicides, borides) and composites based on them.[15] The compositions and structures of nanomaterials strongly depend on the characteristics of the reaction medium, namely, the type of solvent, chemical inertness of the solvent or its ability to interact with the substance treated; the presence of surfactants and/or high-molecular-mass compounds; the oxidative, reductive or inert character of the atmosphere in which ultrasonic treatment is carried out.

1. Synthesis of nanodisperse metals and alloys

Sonication of solutions of transition metal carbonyls [$Fe(CO)_5$, $Ni(CO)_4$, $Co(CO)_3NO$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Cr(CO)_6$, $Mo(CO)_6$] in high-boiling alkanes leads to formation of nanosized clusters of amorphous metal particles.[39, 157–161] In particular, high-power ultrasonic treatment of a solution of iron pentacarbonyl in decane under argon bubbling at 0 °C led to weak aggregation of amorphous particles of elemental iron of size at most 5–6 nm.[39] Subsequent heat treatment of the powder thus obtained in inert atmosphere at 350 °C resulted in partial crystallisation of iron.

Starting from a mixture of metal carbonyls, one can prepare nanodisperse alloys. For instance, sonication of a solution of iron and cobalt carbonyls in decane gave a highly dispersed Fe–Co alloy (particle size 6–10 nm).[162] By varying the concentrations of the starting compounds it is possible to obtain a continuous series of iron–cobalt alloys from pure iron to pure cobalt.[162, 163] Similar results were obtained in the synthesis of Co–Ni and Fe–Ni alloys.[164, 165]

Not only elemental iron, but also carbonyl complexes of more complex structures are formed [39]

$$2\,Fe(CO)_5 \xrightarrow{)))} Fe(CO)_3 + Fe + 7\,CO,$$

$$Fe(CO)_3 + Fe(CO)_5 \xrightarrow{)))} Fe_2(CO)_8,$$

$$Fe_2(CO)_8 + Fe(CO)_5 \xrightarrow{)))} Fe_3(CO)_{12} + CO;$$

$$Fe(CO)_5 \xrightarrow{)))} Fe(CO)_4 + CO,$$

$$Fe(CO)_4 + Fe(CO)_4 \xrightarrow{)))} Fe_2(CO)_8.$$

It is impossible to obtain $Fe_3(CO)_{12}$ by thermolysis of photolysis of $Fe(CO)_5$ as well as by other methods. Therefore, the synthesis of compound $Fe_3(CO)_{12}$ can be considered as specific sonochemical reaction.

Small metal and alloy particles formed in the sonochemical reaction undergo strong aggregation. The degree of dispersion of powders obtained can be considerably increased using surfactants and some other compounds. A method of synthesis of stable colloidal solutions of elemental iron and cobalt using high-power sonication was proposed.[166–168] The technique is based on sonochemical decomposition of iron pentacarbonyl or cobalt carbonyl-nitrosyl in decane in the presence of stabilisers (poly-*N*-vinyl-2-pyrrolidone, oleic acid [8, 15] or higher aliphatic alcohols).[167, 168] As a result, a stable colloidal solution of nanosized paramagnetic iron particles (size range 8–10 nm) is formed (Fig. 11). A modified procedure was used for the synthesis of colloidal Fe_2O_3 solution stabilised with oleic acid.[8]

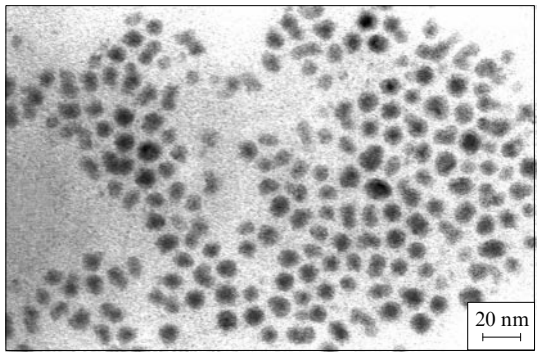


Figure 11. Micrograph of colloidal iron sample obtained under sonochemical irradiation and stabilised by oleic acid.[15]

It should be noted that nanodisperse metals can be sonochemically synthesised in non-aqueous media not only from carbonyls, but also from other volatile metal compounds. For instance, a colloidal solution of nickel particles (size 3.9–4.3 nm) in diethyl ether was prepared from nickel acetylacetonate in the presence of triphenylphosphine with diethyl aluminium hydride as reducing agent at −40 °C.[169] Colloidal particles can be separated and redispersed in another polar solvent, *e.g.*, pyridine. Colloidal particles are stabilised by the triphenylphosphine shell on the surface.

The use of transition metal β-diketonates instead of carbonyl and carbonyl-nitrosyl complexes is not very promising because of rather high metal–oxygen and oxygen–carbon bond energies. Therefore, sonolysis of solutions of transition metal β-diketonates (even carried out in high-boiling alkanes C_{12}–C_{17}) only results in partial decomposition of these compounds and formation of products with high content of organic residues.[170, 171]

Catalysis is one of the largest fields of application of nanodisperse metals.[172] The vast majority of metals used as heterogeneous catalysts represent supported catalysts. Here, compounds characterised by large specific surface area (usually, alumina or silica) act as substrates. A conventional method of synthesis of heterogeneous catalysts involves the soaking of a porous substrate with a corresponding metal salt solution followed by heat treatment in reductive atmosphere. Clearly, in this case metal particles

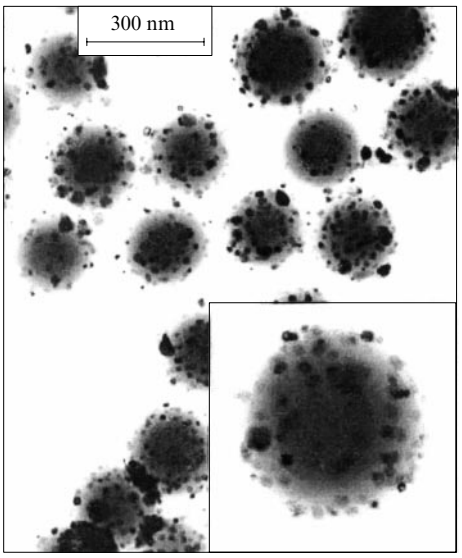


Figure 12. Micrograph of a sample prepared by sonolysis of iron pentacarbonyl in decalin in the presence of silica microspheres followed by hydrogen reduction.[174]

are adsorbed not only on the surface, but also within the pores of the substrate, which significantly reduces the specific activity of the catalyst. In this connection the development of sonochemical methods for the synthesis of catalysts with uniformly distributed nanodisperse metal particles with narrow size distribution (Fig. 12) on the substrate surface seems to be quite promising.[173, 174]

Sonolysis of iron pentacarbonyl in decane in the presence of silica gel results in nanodisperse powders of amorphous metallic iron (3–8 nm); the powder particles are uniformly distributed over the surface of silica particles.[175] The catalytic activity of the material thus obtained was studied taking the Fischer–Tropsch reaction as an example. A comparison of its catalytic activity with that of a catalyst prepared by the soaking technique showed that at the same loading the activity of the sonochemically prepared catalyst was nearly tenfold higher than the activity of the 'soaked' catalyst. The former catalyst exhibited a high activity at relatively low temperatures (<250 °C), whereas the activity of the latter catalyst in this temperature range was very low (Fig. 13).

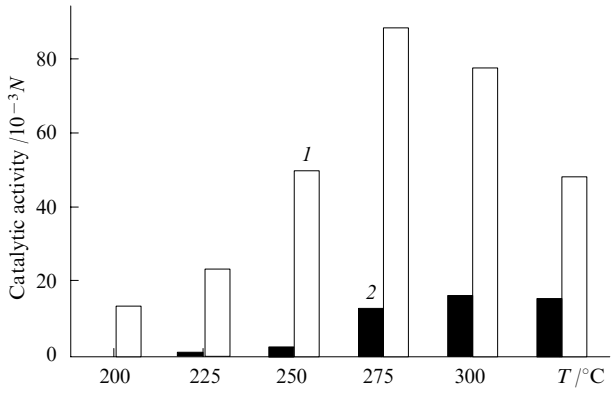


Figure 13. Catalytic activity of Fe/SiO_2 plotted *vs.* hydrogenation temperature of carbon monoxide.[175]
N is the number of hydrogenated CO molecules per active site per second; catalysts were prepared by ultrasonic treatment (*1*) and by soaking (*2*).

2. Synthesis of binary compounds

Metal carbonyls can serve as precursors in the synthesis of binary metal compounds, *e.g.*, carbides and chalcogenides. Depending on the synthesis conditions and the character of subsequent treatment, a variety of products can be obtained.[176] Often, preparation of the end product involves high-temperature heat treatment of an intermediate. For instance, the sonochemical decomposition of molybdenum hexacarbonyl in hexadecane followed by heating of the product in CH_4-H_2 atmosphere resulted in a nanosized $Mo_2C_{1.02}$ powder with particle size of 3–5 nm.[162]

In order to synthesise metal chalcogenides, the corresponding carbonyl and elemental chalcogen are sonicated in a high-boiling non-polar solvent. In particular, ultrasonic treatment of a solution of molybdenum hexacarbonyl and sulfur in tetramethylbenzene under argon bubbling results in the formation of nanocrystalline MoS_2 (particle size $\sim$15 nm) with unusual morphology (aggregates of porous spherical particles).[148] Molybdenum telluride $MoTe_2$ was synthesised [153] by sonicating tellurium and $Mo(CO)_6$ in decalin under argon bubbling for 4 h. The product obtained immediately after sonication was X-ray amorphous powder characterised by high degree of aggregation of particles of size 50–150 nm. The powder obtained at shorter duration of the synthesis had a different micromorphology and comprised plate-like particles of nearly the same size (50–150 nm). Subsequent thermal annealing of the products of sonochemical synthesis at 650 °C for 10 h gave a molybdenum telluride powder the particles of which were nanotubes of length 100–500 nm and 20–50 nm in diameter.

Nanosized amorphous cobalt ferrite ($CoFe_2O_4$) powder was obtained by sonochemical decomposition of iron carbonyl $Fe(CO)_5$ and cobalt carbonyl-nitrosyl $Co(CO)_3NO$ in decalin at 0 °C under oxygen flow.[177] Nanosized amorphous nickel ferrite $NiFe_2O_4$ was prepared under similar conditions.[178] Subsequent annealing of the amorphous products at 450 °C led to partial crystallisation with retention of the nanosized state.

Composite materials can also be synthesised using the procedure described above. Considerable advances in this field were made by a research group headed by Prof. Gedanken. Most studies of researchers from this group were devoted to preparation of reactive catalytic materials.[8, 15] In particular, a novel method of fabrication of molybdenum oxide–silica and molybdenum carbide–silica composites was reported.[179] These materials were synthesised by ultrasonic treatment of a suspension of silica microspheres and molybdenum hexacarbonyl in decane. Treatment in air gave amorphous powder of $Mo_2O_5-SiO_2$ composite, whereas ultrasonic treatment in argon atmosphere resulted in amorphous Mo_2C-SiO_2 composite.

Preparation of nanodisperse amorphous oxides, in particular, nickel and cobalt oxides can also be treated as specific methods of sonochemical synthesis. It is believed [180] that similar compounds can be synthesised only under sonochemical treatment, because one should attain unusually high cooling rates (up to $10^{10}-10^{11}$ K s^{-1}).

It should be noted that sonochemical reactions in non-aqueous media are far from being reduced to the transformations of metal carbonyls. Extensive literature is devoted to sonochemical transformations of organic (alkanes, halogenated hydrocarbons) and organometallic compounds; Diels–Alder synthesis, Friedel–Crafts reaction, *etc.* under sonication. It was shown that concurrent microwave and ultrasonic treatment is promising for acceleration of hydrazinolysis of esters.[181] A scheme of a setup for combined microwave–ultrasonic treatment is shown in Fig. 14. A number of reviews concerned with various aspects of liquid-phase and heterophase sonochemistry of non-aqueous media are available.[14, 23, 33, 182]

Thus, at present the most often used starting compounds for sonochemical synthesis of nanodisperse inorganic materials in non-aqueous media are transition metal carbonyl and carbonyl-

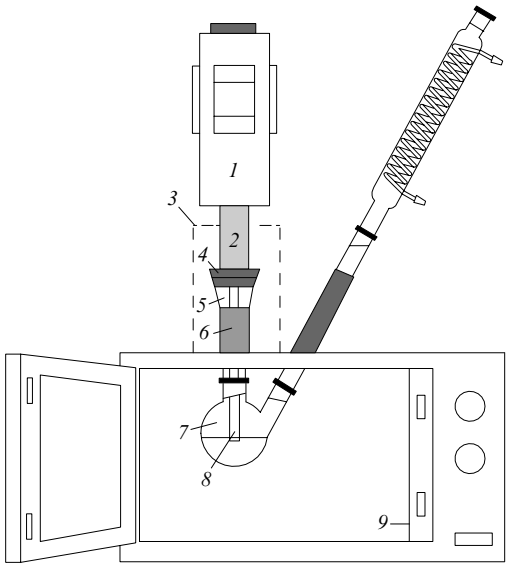


Figure 14. Scheme of an apparatus for combined microwave – ultrasonic treatment of solutions.[181]
Transducer housing (*1*), upper part of the waveguide (*2*), copper mesh screen (*3*), rubber stopper (*4*), adapter (*5*), port (*6*), flask (*7*), detachable horn (*8*), microwave oven (*9*).

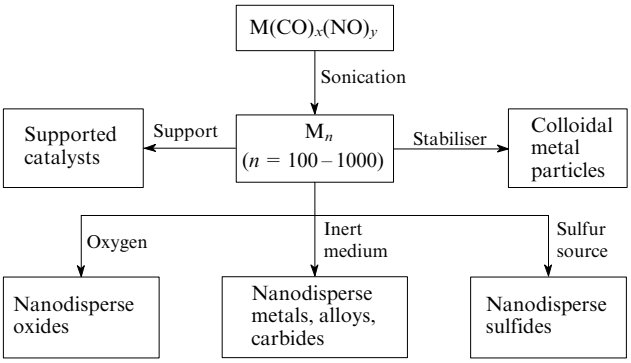


Figure 15. Sonochemical methods of synthesis of various nanodisperse inorganic materials in non-aqueous media.[15]

nitrosyl complexes. Possible methods of synthesis of such materials are shown in Fig. 15.

VII. Sonochemical processes under hydrothermal conditions

Initially, hydrothermal synthesis was used as efficient method of growth of single crystals of various inorganic compounds and for production of high-purity inorganic materials.[183, 184] Later on, the method was shown to be promising for the synthesis of highly dispersed (including nanodisperse) inorganic materials. At present, hydrothermal method is widely used for preparation of both single crystals and highly dispersed powders of simple and complex oxides, chalcogenides, hydroxides, phosphates, zeolites, supramolecular and many other classes of compounds.[185]

The promise for using concurrent hydrothermal and ultrasonic treatment for the synthesis of disperse powders has been documented.[22, 186–188] The authors assumed that the main effects accompanying sonication of liquid-phase and heterogeneous liquid – solid systems under conventional conditions (cavitation, sonolysis and sonochemical redox reactions, intense local microflows of liquids and shock waves) should also be observed under hydrothermal conditions. At the same time the possibility of onset of cavitation in aqueous solutions at temperatures above 100 °C required experimental substantiation. This was done in analysis of the level of acoustic noise in an aqueous medium measured by a broadband hydrophone.[186] It was established that the cavitation intensity at 250 °C is 70% – 80% of the cavitation intensity at room temperature. Unfortunately, the temperature dependence of the cavitation intensity in the temperature range from 100 to 250 °C was not measured. Additionally, the influence of the physicochemical properties of liquid media at temperatures above 100 °C (viscosity, surface tension, saturated vapour pressure, *etc.*) on the cavitation parameters was also not studied.

It was also shown[186] that sonication of hydrothermal solutions initiates redox processes in them. The authors assumed that the oxidation of divalent cobalt salts and hydroxide to Co_3O_4 involves $HO^{\bullet}$ radicals generated in aqueous solutions during sonolysis of water. It should be noted that nanodisperse Co_3O_4 particles formed under concurrent hydrothermal and ultrasonic treatment of a cobalt nitrate solution have a well-developed mesoporous structure (Fig. 16). Under conventional hydrothermal treatment of solutions, mesoporous metal oxide powders are formed at such concentrations at which the rates of nucleation processes (they dominate at low concentrations) and growth of crystallites (they dominate at high concentrations) are commensurable.[189] It was shown experimentally that the growth of crystallites predominates under hydrothermal treatment of solutions of cobalt(II) salts. At the same time sonication probably increases the rate of nucleation of the new phase, which leads to a shift of the hydrothermal synthesis towards the transient 'nucleation – crystallite growth' region characterised by the best conditions for the formation of mesoporous oxide powders.

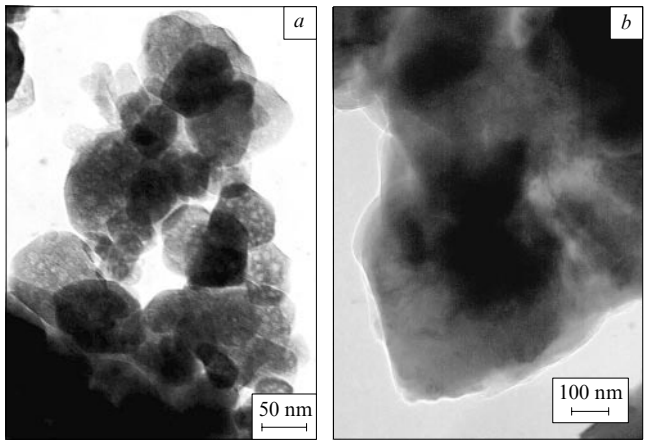


Figure 16. Micrographs of Co_3O_4 samples synthesised by concurrent hydrothermal and ultrasonic treatment (*a*) and by conventional hydrothermal treatment (*b*).[186]

A study[190] of the synthesis of mixed nickel – zinc ferrites showed that ultrasonic treatment under hydrothermal conditions causes a slight increase (by 10% – 20%) in the size of nanodisperse product crystallites and the formation of powders with a narrower crystallite size distribution compared to the particle size distribution typical of conventional hydrothermal synthesis.

Sonication under hydrothermal synthesis also has a moderate effect on the micromorphology of titania and zirconia powders prepared by crystallisation of X-ray amorphous zirconyl and titanyl hydroxide gels.[190] At the same time the TiO_2 and ZrO_2 powders synthesised under concurrent hydrothermal and ultrasonic treatment are characterised by significantly different phase compositions compared to powders prepared under conventional hydrothermal conditions. For instance, hydrothermal treatment of amorphous zirconyl hydroxide gel for 3 h at 250 °C results in the formation of a mixture of two crystalline polymorphs of

zirconia, namely, a thermodynamically stable monoclinic modification (~12%) and a metastable tetragonal modification (~88%). Hydrothermal treatment of amorphous gel $ZrO_2 \cdot n\,H_2O$ under similar conditions with concurrent sonication leads to appreciable acceleration of crystallisation of the amorphous phase and to an increase in the content of thermodynamically stable monoclinic modification of zirconia (to ~30%) in the reaction product.

Similar results were obtained in the synthesis of nanodisperse titania by high-temperature hydrolysis of aqueous $H_2TiO(C_2O_4)_2$ solution.[190] A conventional hydrothermal treatment of the solution gave a mixture of thermodynamically stable (rutile) and metastable (anatase) TiO_2 polymorphs, the content of rutile being at most 10%. Concurrent hydrothermal and ultrasonic treatment led to an increase in the content of rutile to 20%.

At the same time sonication in the course of hydrothermal synthesis of ZrO_2 and TiO_2 from zirconyl nitrate and X-ray amorphous $TiO_2 \cdot n\,H_2O$ gel, respectively, had almost no effect on the phase composition of reaction products.

Thus, sonication during the hydrothermal synthesis of oxide powders can be accompanied by (i) substantial acceleration of crystallisation of X-ray amorphous gels and formation of highly dispersed and nanodisperse powders, (ii) an increase in the content of thermodynamically stable phases in the products of synthesis provided that the oxide being synthesised exists as a number of polymorphs and (iii) initiation of redox reactions in aqueous solutions resulting in highly dispersed (including mesoporous) particles.

VIII. Solid-phase sonochemical processes

The mechanisms of liquid-phase sonochemical reactions are closely related to a number of non-linear effects emerging upon sonication of solutions and suspensions (first of all, cavitation). Clearly, cavitation cannot be the driving force of the processes occurring in the solids irradiated with high-power ultrasound. Therefore, the mechanism of the action of ultrasound on solids should be fundamentally different.

Consider the effect of acoustic vibrations on the real structure of solids. At present, such studies are only carried out for polycrystalline metals and alloys [191] as well as for single crystals of ionic compounds (alkali metal halides) and $A^{II}B^{VI}$ and $A^{III}B^{V}$ semiconductor crystals.[192] Main trends in the behaviour of these systems under alternating stresses are similar.

Sonication causes the following processes in solids to occur.

1. Dislocation motion and redistribution over the volume of the crystal, which is only possible upon attainment of a threshold amplitude of ultrasonic vibrations ($\xi_{threshold}$).[193, 194] Translational motion of dislocations mainly follows one direction in spite of periodic changes in the sign of the stress, because the chain of point defects, small dislocation loops and dislocation dipoles formed behind the moving dislocation precludes the change in the direction of the dislocation motion. The speed of translational motion of dislocations in various crystals varies from 0.2 to 2.4 μm min^{-1} (Ref. 192). The action of ultrasound on crystals induces the appearance of stable dislocation patterns, thus having much in common with thermal annealing.[195, 196]

2. Dislocation multiplication and an increase in the concentration of dislocations to a certain limiting value (saturation) occur at stresses corresponding to the dynamic yield stress σ_t^0. Sonicaton causes an increase in the concentration of dislocations by several orders of magnitude to $10^8 - 10^{10}$ cm^{-2} (Ref. 194). The dislocation distribution over the volume is highly non-uniform; dislocations are mainly concentrated near sources (at grain boundaries, cracks and other macroscopic structural defects).

3. Formation of point defects, which can occur at dislocation jogs or follow the mechanism of annihilation of dislocations of opposite sign.[197, 198]

It should be noted that the concentration of structural defects in ultrasonically treated material is a non-linear function of both the acoustic power and the treatment temperature. Here, a considerable (by more than an order of magnitude) increase in defectiveness of the crystal is observed in particular temperature and ultrasound power ranges,[191] *i.e.*, there is well-defined synergism between acoustic and heat treatment. Clearly, such a change in the real structure of a solid should lead to considerable enhancement of the diffusion mobility of ions in the crystal structure and, correspondingly, to acceleration of certain solid-phase reactions.

The simplest types of solid-phase reactions are polymoprhic transformations and phase decomposition. In the text below we summarise the results of studies on the effect of sonication on solid-phase austenite transformations in steels.

The effect of ultrasonic radiation on the kinetics of intermediate (beinite) transformation of 30ХГСН2А steel was studied.[199] The ultrasonically treated samples showed a considerable increase in the content of beinite, *i.e.*, acoustic treatment favoured acceleration of the austenite transformation. Electron microscopy studies revealed that the dislocation density in the untreated samples was an order of magnitude lower (10^8 cm^{-2}) than in the samples exposed to ultrasonic irradiation (at least 10^9 cm^{-2}). The ultrasonically treated steel samples showed that dislocations are present both in the interior of grains and at grain boundaries. Additionally, the dislocation structure of austenite developed under sonication rapidly disappears upon short-term heat treatment of the steel samples. The authors [199] suggested the following mechanism of austenite transformations. The interaction of point defects that are formed abundantly under sonication with dislocations during high-temperature annealing is due to diffusion and subsequent annihilation of the defects. Acceleration of the beinite transformation under ultrasonic treatment results from enhancement of the mobility of carbon atoms, which in turn is a consequence of an increase in the density of lattice defects (dislocations and vacancies).

The effect of sonication on the reverse martensite transformation in iron/nickel (29% Ni) alloy pre-annealed from 950 °C was a subject of yet another study.[200] It was established that the process slows down upon ultrasonic treatment. The authors [200] pointed out that austenisation on heating causes the formation of concentration inhomogeneities, namely, regions with higher and lower concentration of nickel atoms. According to the phase diagram of the Fe–C system, the nickel-enriched martensite phase should transform into austenite at lower temperatures compared to the Ni-depleted phase. Continuous ultrasonic irradiation results in a high concentration of vacancies and, as a consequence, enhanced mobility of nickel atoms. Here, the formation of the nickel-enriched zones becomes less probable. As a result, the reverse martensite transformation is shifted towards the higher-temperature region.

Studies of the effect of acoustic activation on polymorphic transformations were carried out for a few oxides, in particular, PbO [201] and zirconia.[202] For instance, it was shown [201] that ultrasonic treatment of β-PbO initiates the β-PbO → α-PbO phase transition even in the absence of additional heat treatment; the degree of transformation was about 5%. The efficiency of sonication in the course of phase transition appreciably increases as the temperature increases. At 400–475 °C, the α-PbO phase formed under sonication is partially oxidised to Pb_3O_4. A kinetic study of the β-PbO → α-PbO phase transition and oxidation of α-PbO to Pb_3O_4 at 425 °C showed that an increase in the duration of ultrasonic treatment of β-PbO causes the overall extent of the transformation β-PbO → α-PbO + Pb_3O_4 to increase. Then, the rate of the phase transition decreases and the curve of the β-PbO content reaches saturation stage. The maximum extent of transformation of β-PbO under concurrent sonication and heat treatment is 0.85, which is in good agreement with the results obtained in studies of mechanochemical activation of the β-PbO → α-PbO transition.[203]

Sonochemical initiation of the phase transformation 'metastable polymorph → stable polymorph' of zirconia proceeds in a

similar fashion.[202] Under conventional heat treatment the tetragonal polymorph of zirconia remains stable on heating up to 600 °C, whereas under concurrent high-temperature and ultrasonic treatment the monoclinic modification is formed at 500 °C (the content of the latter is 18%).

More complex types of solid-phase reactions undoubtedly include processes in binary and multicomponent systems, because reactions in such systems occur at grain boundaries.

Enikolopov *et al.*[204] were the first who studied the possibility for solid-phase chemical processes to occur under ultrasonic treatment in mixed (not pure metallic) systems. The following reactions were carried out under sonication:

(1) decomposition

$$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4\,H_2O;$$

(2) substitutions in metal–oxide systems (metallothermy)

$$3\,CuO + 2\,Al \longrightarrow Al_2O_3 + 3\,Cu,$$

$$3\,CuO + 2\,Fe \longrightarrow Fe_2O_3 + 3\,Cu,$$

$$Fe_2O_3 + 2\,Al \longrightarrow Al_2O_3 + 2\,Fe;$$

(3) exchange in the citric acid–iron oxide system

$$2\,HO_2CCH_2C(OH)(CO_2H)CH_2CO_2H + Fe_2O_3 \longrightarrow$$
$$\longrightarrow 2\,(O_2CCH_2C(OH)(CO_2)CH_2CO_2)Fe + 3\,H_2O;$$

(4) azo couplings in solid-phase synthesis of some azo dyes (Bismarck brown, pigment Red G) from stoichiometric mixtures including an aromatic amine and sodium nitrite.

It was shown that in all these systems ultrasonic treatment favours initiation of solid-phase reactions. For instance, irradiation of metal–metal oxide systems with ultrasound (vibrational amplitude 5 μm) initiated reactions that completed in 15–25 s depending on the system. An increase in the amplitude had no effect on the reaction rate. Sonication had similar action on the reactions of ammonium bichromate decomposition and interaction of iron(III) oxide with citric acid. In the latter case the maximum extent of transformation was only 50% and did not increase with an increase in the duration of ultrasonic treatment and in the acoustic power delivered, apparently, due to the formation of a dense layer of reaction product on the Fe_2O_3 surface. On the contrary, the synthesis of azo dyes appeared to be sensitive to the ultrasonic power, namely, the rate of the reaction increased on the average by 30%–40% upon an increase in the vibrational amplitude from 10 to 15 μm.

It was established that each system studied is characterised by a particular threshold amplitude of ultrasonic vibrations (no reaction initiation occurs at smaller amplitudes). Solid-phase sonochemical reactions require a rather high density of compaction of the starting powder.[204] For instance, initiation of the decomposition of ammonium bichromate under sonication occurred only if the density of the starting pellet was at least 80% of the theoretical value. This is probably due to the need of creation of good acoustic interparticle contacts in powder (if no contacts are available, acoustic power substantially dissipates at interfaces and the efficiency of sonication considerably decreases).

It was assumed[204] that the initiating action of ultrasound causes an appreciable reduction of diffusion limitations, which allows solid-phase reactions to proceed at rather high rates under relatively mild conditions. However, in this case the role of acoustic activation is likely reduced to initiation of the solid-phase reactions mentioned above. In particular, it is known that metallothermic processes and decomposition of ammonium bichromate release much heat. Ultrasonic deformations can cause local heating in powder systems; for instance, heat release occurs at interparticle contacts at the instant of reaction initiation. At high density of compacted samples, the energy released is almost not dissipated, being completely spent for heating of the surrounding particles and thus initiating further interaction. Then the reaction proceeds by a mechanism similar to high-temperature self-propagating synthesis (in this case ultrasound acts as initiator of the reaction). This assumption is consistent with the fact that an increase in the amplitude of ultrasonic vibrations upon attainment of a threshold value does not accelerate the reaction, because after initiation the effect of sonication on the process becomes negligible compared to the effect of heating of the reaction mixture due to heat released.

Obviously, the data on the formation of complex organic compounds[204] could not be interpreted in the framework of the diffusion formalism. In this case the reaction mixtures are multicomponent systems including not only ionic, but also molecular compounds, and the chemical reaction involves formation of numerous intermediate products.

The effect of sonication on high-temperature self-propagating synthesis of Ti_5Si_3 and $TiSi_2$ in the titanium–silicon system was studied.[205] This is a multiphase system and therefore the reaction product can contain a variety of intermediates depending on the blend composition and synthesis conditions. Sonication causes changes in both the temperature profile of the combustion wave (heating zone is extended) and the rate of combustion. Ultrasonic treatment reduces the reaction rate and the maximum temperature of the synthesis. It was assumed that alternating stresses produced at contacts between the reactant particles induce local heating of the starting mixture. This can cause the formation of intermediate reaction products in the heating zone and thus change the reaction conditions; as a consequence, the amount of heat released will be smaller compared to the combustion of mixtures without sonication.

A study by Khanukaev and Khanukaeva[206] was a logical continuation of an earlier investigation.[204] The authors[206] also studied a number of solid-phase processes occurring under ultrasonic treatment:

(1) decomposition of ammonium bichromate, chromate and sulfate;

(2) dehydration of copper(II) and magnesium sulfate crystal hydrates;

(3) decomposition of $Mg(OH)_2$ and $Fe(OH)_2$;

(4) synthesis of copper(I) phthalocyanine from *o*-phthalonitrile

$$4\,o\text{-}C_6H_4(CN)_2 + 2\,CuCl \longrightarrow Cu(C_8N_2H_4)_4 + CuCl_2\,.$$

The results obtained in both studies appeared to have much in common. The vast majority of the reactions studied were characterised by a threshold amplitude of ultrasonic vibrations (~ 5 μm) and by a threshold density of compact samples (no reaction at lower densities). Acceleration of the reactions under ultrasonic treatment was associated with the overcoming of diffusion limitations.

New information was as follows. First, it was found that the amplitude of ultrasonic vibrations has a strong effect on the reaction kinetics in these systems. In particular, the mass loss rates during the decomposition of hydroxides, $Mg(OH)_2$ and $Fe(OH)_2$, appeared to be proportional to the squared amplitude of vibrations at the end face of the waveguide at the same treatment durations (*i.e.*, the reaction rates are proportional to the transferred acoustic power). Additionally, almost all reactions were characterised by rather long induction periods (3–8 min), which was associated with the need of accumulation of the energy necessary for initiation and keeping up the reactions in the reaction volume. The distribution of the reaction product over the sample volume has a cylindrical symmetry.

The threshold pattern of ultrasonically treated solid-phase reactions was explained as follows. First, effective mixing of reactants occurs under such conditions where the stress due to ultrasonic vibrations exceeds the corresponding yield points. The threshold amplitude was estimated at ~ 5 μm, which coincides with experimental data. Second, it is well known that initiation of any chemical reaction requires the overcoming of an energy barrier (threshold amplitude of $\geqslant 10-11$ μm).

According to a model proposed,[206] the key factors responsible for acceleration of ultrasonically treated solid-phase reactions are renewal of the reactant surfaces and removal of the reaction product layer between the interacting particles rather than the overcoming of diffusion limitations by generation of structural defects.

We believe that both mechanisms of acoustic activation of solid-phase processes take place in real systems.

The fact that sonication of a solid-phase reaction mixture can accelerate the interaction between the mixture components due to elimination of diffusion limitations was first experimentally proved in studies[207–209] on the kinetics and mechanism of ultrasonically treated high-temperature reaction

$$MgO + Fe_2O_3 \longrightarrow MgFe_2O_4 .$$

At 800 °C, the rate of magnesium ferrite formation under ultrasonic activation was noticeably higher (by 15% – 20%) than the rates of the blank reactions (no activation). On the contrary, the rate of the solid-phase reaction carried out at 700 °C under ultrasonic activation decreased to some extent. At 900 °C, ultrasonic treatment of the samples had almost no effect on the rate of ferrite formation. The results obtained correlate with the characteristics of the defectiveness of the iron(III) oxide samples, which is formed upon ultrasonic treatment in the temperature range 700 – 900 °C.[209,210] The character of changes in the defectiveness of α-Fe_2O_3 directly affects the formation kinetics of $MgFe_2O_4$, namely, if the sonicated Fe_2O_3 samples have less defect structures compared to the products of the blank reactions (700 °C), the formation of $MgFe_2O_4$ and the yield of the reaction product in the former case is lower than in the latter case. However, if the reaction is carried out at 800 °C, both the defectiveness of the Fe_2O_3 samples and the rate of $MgFe_2O_4$ formation from the ultrasonically treated samples are higher than those for the blank reactions. At 900 °C, the ultrasonically processed samples and the untreated ones are characterised by the same defectiveness and the formation of $MgFe_2O_4$ occurs at nearly the same rates.

Additionally, alternating stresses at 700 – 900 °C should obviously cause the same mechanical effect of renewal of the reactant surfaces. Thus, it is the diffusion mobility of ions that governs all changes in the reaction rates under ultrasonic treatment compared to the rates of the blank reactions.

These non-linear changes in the defectiveness of α-Fe_2O_3 crystallites and in the rate of solid-phase reactions of α-Fe_2O_3 were explained[207–209] by the occurrence of the following concurrent processes in the system: generation of structural defects under sonication; thermal annealing of defects, which dominates at 900 °C; and annihilation of extensive defects in the acoustic field upon ultrasonic annealing.

The effective activation energies of the solid-phase reactions carried out under ultrasonic treatment and without it were determined from formal kinetic analysis of experimental data. It was found that in both cases the formation of $MgFe_2O_4$ is a diffusion-limited process. Analysis of the Arrhenius relation $\ln k = f(T^{-1})$ (k is the rate constant for the reaction in the framework of the kinetic model chosen) gave an apparent activation energy of 180 kJ mol^{-1} for the samples formed in the blank reactions. The relationship between $\ln k$ and T^{-1} for the reaction conducted under combined heat and ultrasonic treatment is non-linear. The temperature range studied can be divided into two intervals, 700 – 800 °C and 800 – 900 °C, which are characterised by the apparent activation energies of 320 and 100 kJ mol^{-1}, respectively.

The efficiency of sonication performed to accelerate diffusion was also demonstrated taking the solid-phase reaction of iron(III) oxide with lithium carbonate as an example.[211]

An additional substantiation of interrelation between the mechanism of ultrasonic activation of solid-phase reactions and elimination of diffusion limitations is provided by the results of a study[212] of ion exchange in acid tantalum and zirconium phosphates in the presence of caesium chloride under ultrasonic treatment.

It was shown that dehydration of mixtures of acid tantalum phosphate with caesium chloride upon sonication occurs at a higher temperature, being characterised by smaller mass loss. This effect is most pronounced for the decrease in the mass loss in the low-temperature region corresponding to the loss of weakly bound water. This is due to partial substitution of caesium ions for $(H_5O_2)^+$ ions in acid tantalum phosphate. The ultrasonically treated samples also show a smaller mass loss corresponding to solid-phase ion exchange accompanied by liberation of HCl. The major effect of sonication is achieved in the initial stages of treatment; additional processing of the samples in the reactor has a much weaker effect. Probably, this is due to the fact that solid-phase ion exchange between $(H_5O_2)^+$ and caesium ions is controlled by cation diffusion through the layer of reaction product. Therefore, initially (at zero degree of conversion and diffusion layer thickness) the reaction rate is rather high, being exponentially decreased with the development of the reaction.[213] The overall extent of ion exchange and dehydration reduces on the average by 15% – 20% due to ultrasonic treatment.

Sonication has a similar effect on ion exchange between acid zirconium phosphate $Zr(HPO_4)_2 \cdot H_2O$ and alkali metal chlorides. The ultrasonically treated samples were also characterised by the mass loss at higher temperatures compared to the untreated samples. This effect was observed for both dehydration (80 – 350 °C) and ion exchange (T > 450 °C). As in the preceding case, this is an indication of solid-phase ion exchange induced by ultrasonic vibrations.

A series of recent studies[21,214–218] was devoted to detailed investigations of the effect of ultrasonic activation on high-temperature solid-phase synthesis of various ferrites including $LiFe_5O_8$, $ZnFe_2O_4$ and $NiFe_2O_4$ (Fig. 17). Kinetic studies of the solid-phase reactions of iron(III) oxide with zinc oxide, nickel oxide and lithium α-orthoferrite and investigations of the evolution of the structure of the reactants during the synthesis of the final phases revealed similarity of the mechanisms of ultrasonic

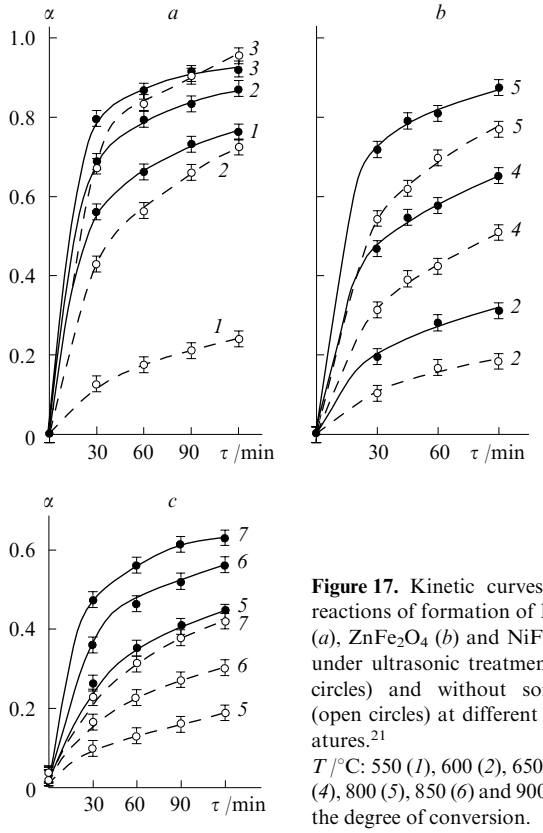


Figure 17. Kinetic curves of the reactions of formation of $LiFe_5O_8$ (*a*), $ZnFe_2O_4$ (*b*) and $NiFe_2O_4$ (*c*) under ultrasonic treatment (filled circles) and without sonication (open circles) at different temperatures.[21]
T /°C: 550 (*1*), 600 (*2*), 650 (*3*), 700 (*4*), 800 (*5*), 850 (*6*) and 900 (*7*); α is the degree of conversion.

activation of these reactions. With no sonication, the reaction products ($LiFe_5O_8$, $ZnFe_2O_4$, $NiFe_2O_4$) are formed only on the outer surface of iron(III) oxide particles representing dense aggregates of primary Fe_2O_3 crystallites. The microstructure of the starting Fe_2O_3 shows no significant changes [the size of the coherent scattering domains (CSD) in iron(III) oxide remains almost unchanged in the corresponding temperature ranges for all reaction mixtures] and small particles of reaction products rapidly aggregate into relatively large crystallites, as indicated by rapid increase in the CSD size in the initial stages of the reactions.

At the same time the reactions of ferrite formation under ultrasonic treatment are characterised by a decrease in the size of the primary iron(III) oxide crystallites and by prolonged retention of small size of the CSDs in lithium, zinc and nickel ferrites that are formed. This indicates non-uniformity of the reaction front, which penetrates into the bulk of Fe_2O_3 aggregates with the development of the reaction due to intensification of ion transfer through diffusion along Fe_2O_3 grain boundaries (Fig. 18).

IX. Conclusion

An undoubtful advantage of ultrasonic treatment consists in the possibility of concurrent use of the technique and other methods of activation of reaction mixtures including conventional thermal activation procedures. Such 'combined' methods are characterised by manifestation (to some extent) of characteristic physical effects of sonication. Targeted use of ultrasonic treatment makes it possible to considerably enhance the possibilities of the available synthetic approaches and to synthesise novel inorganic materials in a targeted manner. The main effects accompanying the action of high-power ultrasound on liquid- and solid-phase systems are listed below.

Liquid-phase systems	Solid-phase systems
Processes accompanying sonication	
1. Cavitation. Local heating to ~5000 K, local increase in pressure to ~1000 atm, microflows of liquids with velocities of up to 100 m s^{-1}, intense local electric discharge. 2. Considerable intensification of mass transfer.	1. Motions, generation and multiplication of dislocations (nearly 1 000-fold increase in concentration). 2. Nearly tenfold increase in effective diffusion coefficients. 3. Formation of interparticle contacts through mutual motions of particles.
Main physicochemical consequences of ultrasonic treatment	
1. Decomposition of volatile components of solutions. 2. Initiation and acceleration of redox reactions. 3. Disaggregation of particles. 4. Formation of stable suspensions and emulsions. 5. Degassing of solution.	1. Acceleration of solid-phase reactions. 2. Reduction of reaction temperature
Main fields of application of high-power ultrasonic waves	
1. Organic and inorganic syntheses. 2. Preparation of nanodisperse materials based on amorphous and crystalline metals, simple and complex oxides, *etc*. 3. Design of materials with preset morphologies of aggregates.	1. Activation of solid-phase reactions; synthesis at lower temperatures. 2. Targeted formation of the structure of solids.

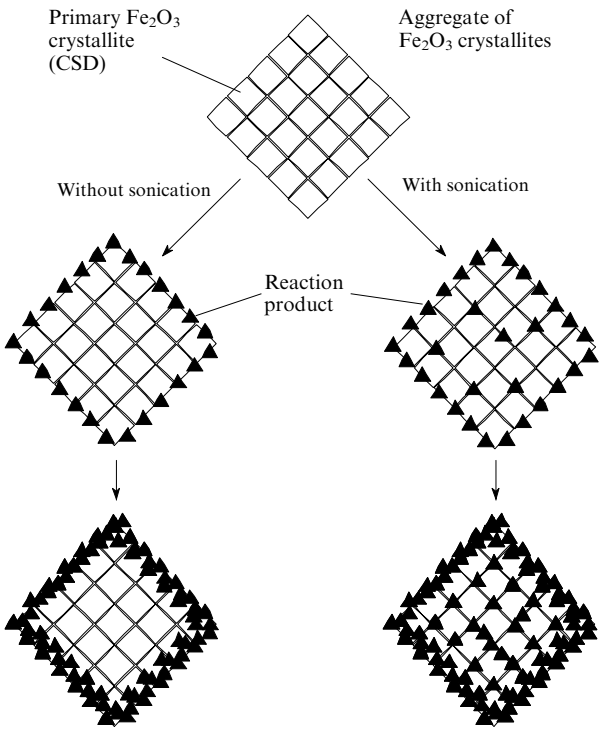


Figure 18. Mechanisms of reactions of ferrite formation under ultrasonic treatment and without it.[21]

Summing up, it should be emphasised that sonication techniques open new prospects for targeted synthesis of various inorganic materials. Sonochemical treatment allows one not only to considerably accelerate chemical transformations (first of all, in heterogeneous systems), but also often to prepare highly dispersed phases with controllable micromorphology.

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