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Effects of ultrasound on catalytic processes

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Abstract. The results of studies on sonochemical catalytic reactions are generalised. The effects of ultrasound on processes of preparation, activation and regeneration of catalysts as well as its influence on the course of catalytic reactions are considered. The advisability of ultrasonic treatment in different stages of catalytic processes is discussed. The bibliography includes 143 references.

I. Introduction

The effect of ultrasonic waves on chemical reactions was first revealed in 1927.[1] The number of publications devoted to studies of reactions which change considerably their rates or direction in an ultrasonic field is increased every year. As regards their sensitivity to acoustic vibrations, all sonochemical reactions may be divided into two groups: some reactions are accelerated in an ultrasonic field and can also occur in its absence, though at a lower rate, whereas others cannot occur at all without the action of ultrasound vibrations. For both groups of reactions, high-frequency (2 – 10 MHz), medium-frequency (20 – 100 kHz) and low-frequency (from 10 Hz) vibrations are applied.[1–7] The classification of sonochemical reactions proposed by Margulis[2] envisages their following division:

— redox reactions in aqueous solutions between solutes and the products resulting from ultrasonic degradation of water (H, OH, H_2, H_2O_2);

— reactions between dissolved gases and substances in the vapour state under high pressure inside cavitation bubbles;

— chain reactions induced not by radical products obtained upon ultrasonication of water, but rather by another compound present in the system which is split upon cavitation;

— reactions involving macromolecules, including oscillatory reactions which acquired wide popularity in recent years;[1,8]

— sonochemical reactions in non-aqueous systems;

— initiation of explosion in liquid and solid explosives.

According to this classification, nearly all the catalytic processes can be referred to the reactions in non-aqueous systems, because the main solvent or reagent in them is an organic substance, although water can also participate. For this reason, it seems more appropriate to divide catalytic processes with regard to the type of catalysis (*e.g.*, homogeneous, heterogeneous) and also to classify them by the type of catalyst and the kind of reaction (hydrogenation, oxidation, *etc.*). This approach has been used in fundamental studies on sonochemistry[1–5,9] and has become classical in the theory of catalysis.[10,11] It was proposed to divide the results of the impact of acoustic vibrations on chemical processes into the so-called effects of the first and the second order.[12–14] These are non-linear effects developing in a liquid upon propagation of high-intensity acoustic waves. However, this approach does not allow estimation of the extent of the influence of individual parameters of ultrasound on chemical reactions. Nonetheless, the equations describing each of these parameters and effects can be used for formalising the problems of mathematical simulation of the corresponding chemical processes.[9,15]

The action of acoustic vibrations is highly diverse.[16] Ultrasonic waves can accelerate chemical reactions owing to emulsification of liquid components,[17] dispersion of solid components and catalysts, erosion of their surfaces, degassing, prevention of sedimentation or coagulation of the products, intense mixing, *etc.*[18–20] The action of ultrasound on solid catalysts is far from being always reduced solely to dispersion, since under definite conditions their activities are much higher than those which could be expected after mere grinding of particles.[1–3] Dispersion results in the increased interface area of reactants and occurs due to both the fragmentation of solid phase particles and the surface friction between the solid and liquid phases.[21,22] As the thickness of the diffusion boundary layer is decreased, the number of effective collisions between the molecules of reactants is increased.[23] Erosion of solids under the action of low acoustic frequencies has the following feature: the use of medium- and high-frequency acoustic fields crumbles out rather large particles from the surface and it becomes rough, whereas low frequencies cause smoothing and 'polishing' of the surface, apparently owing to the crumbling out of microscopic particles.[2,24,25]

The increase in the rates and selectivities of most chemical reactions in ultrasonic fields appears to be due to the occurrence of cavitation:[26–29] acoustic waves induce the formation and growth of vapour/gas bubbles in a liquid, which oscillate, pulsate and coalesce. There are two basic approaches to the explanation of high-energy effects caused by cavitation, *viz.*, the thermal and electrical ones. In the thermal approach, these effects are associated with high temperature inside a cavitation bubble upon its adiabatic compression at a continuously increasing rate, whereas in the electrical approach these are related to a discharge inside the bubble resulting from the accumulation of electric charges on its walls.[1,2,6,12] The electrical action of ultrasound can be exempli-

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fied in the formation of hydrogen peroxide.[1] H_2O_2 is generated in microbubbles upon electric discharge in water vapour. First, the elementary processes of ionisation and excitation take place:

$$H_2O + e^- \longrightarrow H_2O^+ + 2e^-,$$

$$H_2O + e^- \longrightarrow H_2O^* + e^-,$$

$$H_2O^+ \longrightarrow H^+ + OH^\bullet,$$

$$H_2O^* \longrightarrow H^\bullet + OH^\bullet.$$

Hydrogen peroxide is formed upon recombination:

$$OH^\bullet + OH^\bullet \longrightarrow H_2O_2.$$

Hydrogen peroxide cannot be obtained by adiabatic compression of water vapour and a noble gas since this process occurs at high temperature. Hydrogen peroxide decomposes at a lower temperature than does water and therefore is not accumulated to an appreciable extent if only the thermal factors are involved in the adiabatic compression of a cavitation bubble under the action of ultrasound.

The effects of ultrasonic action are the reason for the ever-increasing interest in the use of sonochemical methods in organic synthesis and catalysis.[30–37] Clearly, the necessity of joint investigation of such complex phenomena as catalysis and sonochemical effects does not promise rapid advances in the elucidation of the mechanism of catalysis in an ultrasonic field. Nonetheless, in some instances the action of ultrasound on catalytic processes has been studied in sufficient detail and the number of publications devoted to catalytic reactions in ultrasonic fields is rather large.[38–46] Most experimental studies merely state the facts of intensification of processes, increased yields of products and higher catalytic activity without considering the mechanisms underlying the ultrasonic impacts leading to the above-mentioned effects.

As organic liquids are widely used as solvents or reagents, studies of sonochemical reactions in non-aqueous systems are of special significance. In most cases, the use of acoustic vibrations intensifies drastically chemical reactions in such systems.[9, 21, 22, 47–49] Investigations into the mechanisms of sonochemical reactions in non-aqueous systems are complicated for the following three reasons: the results of these reactions are simultaneously affected by usual thermal and sonochemical effects; such processes occur in rather diverse systems; the action of ultrasound also leads to other concomitant physicochemical and colloidal-chemical effects, *e.g.*, emulsification, dispersion of solids, formation of microscopic bubbles, *etc*.

The present review is devoted to the consideration of the effects of ultrasonic vibrations on catalytic systems and catalysts in different stages of preparation for, and implementation of, chemical reactions.

II. Pre-reaction conditioning of catalysts

1. Ultrasonic treatment in the process of catalyst preparation

Acoustic vibrations are applied to the process of catalyst preparation in order to enhance its activity.[50]

Ultrasound influences substantially the properties of platinum and palladium blacks.[51–53] The blacks prepared by the reduction of H_2PtCl_6 or $PdCl_2$ with 40% formaldehyde under the action of ultrasonic waves (USW) of different frequencies in the presence of various gases increased their activities 1.5–2-fold compared to that of USW-nontreated blacks. The surface areas of platinum catalysts increased on the average from 15 to 18 $m^2\ g^{-1}$. The basic characteristics of Pt and Pd blacks are listed in Table 1.

Magnetic susceptibility of catalysts is enhanced under the action of ultrasound. Paramagnetism of 'ultrasonic' blacks obtained under nitrogen is increased appreciably (about twofold), and it is almost not changed in the course of further training of these catalysts in vacuum. X-ray patterns of 'ultrasonic' blacks exhibit noticeable enhancement of the background, which points to the presence of a substantial amount of the atomic metal phase.

Table 1. Relative activity of platinum and palladium blacks prepared by ultrasonication in an atmosphere of different gases.

Preparation conditions		Activity in reactions [a] (%)		
gas medium	frequency /kHz	of H_2O_2 decomposition	of hex-1-ene hydrogenation	of EtOH oxidation
Pt black				
H_2	3000	195	119	69
N_2	20	135	113	74
	548	175	104	84
	3000	260	138	140
Air	20	226	90	118
	548	226	87	110
	3000	116	79	125
Pd black				
H_2	3000	150	150	82
N_2	20	320	130	240
	548	200	140	135
	3000	100	175	79
Air	20	–	84	–
	548	158	79	173
	3000	58	70	30

[a] The activity of USW-nontreated black in the corresponding reaction is taken as 100%.

The increase in the activity of Pt black in hydrogenation of hex-1-ene and oxidation of ethanol may be explained by the catalyst's increased surface. It is noteworthy that in the process of decomposition of H_2O_2 the effect due to USW is $\sim$2.5 times stronger than that related to the increased surface. Consequently, ultrasound has a specific effect on the active centres of the catalyst. In the oxidation of ethanol, the Pt and Pd blacks prepared under definite conditions in an ultrasonic field proved to be less active than the control catalysts.

Probably, the application of an ultrasonic field induces the formation, on the surface of crystals, of the most disordered amorphous phase which contains active centres for decomposition of H_2O_2, whereas in the reactions of hydrogenation of hex-1-ene and oxidation of ethanol the amorphous phase possesses a decreased catalytic activity.[51] The reason for enhanced activities of the ultrasonicated Pt blacks in the catalytic decomposition of hydrogen peroxide and their relatively low activities in the reactions of hydrogenation and oxidation consists in virtually all the amorphous phase being active in the reaction of decomposition of H_2O_2 since this simplest reaction can occur on active centres of any type. On the contrary, hydrogenation or oxidation require active centres with a more ordered structure which are not formed abundantly under the action of ultrasound. The increase of the reaction order[1] of hydrogenation of hex-1-ene on the ultrasonicated Pt black from zero to first order points to changes in the reaction mechanism. Thus, when discussing an increase or a decrease in the activity of a heterogeneous metal catalyst under the action of ultrasound, it should be indicated to what kind of reaction these changes are referred. This circumstance first established by Kobozev *et al.*[51] should be taken into account in studies of heterogeneous catalytic systems.

As can be seen from Table 1, the nature of gases used in the preparation of blacks has a similar influence on different catalysts. Thus in the decomposition of H_2O_2, the blacks obtained under nitrogen are the most active. The blacks prepared in an ultrasonic field in air are noticeably deactivated possibly due to the adsorption on their surface of nitrogen oxides formed with the participation of the water sonolysis products.[53] Deactivation of 'ultrasonic' catalysts prepared in air is most strongly manifested in the hydrogenation reactions. Apparently, the enhanced chemisorption of nitrogen oxides and oxygen in an ultrasonic field

Table 2. Activity of platinum blacks (mmol s^{-1} g^{-1}) prepared by the reduction of H_2PtCl_6 solutions of different concentrations with hydrogen using ultrasonic fields and mechanical stirring.

Concentration of H_2PtCl_6 (mass %)	Decomposition of H_2O_2		Hydrogenation of hex-1-1ene	
	I	II	I	II
0.05	0.37	0.72	–	–
0.10	0.28	0.14	0.19	0.25
0.25	0.21	0.065	0.17	0.071
0.50	0.27	0.062	0.068	0.049

Note. I, mechanical stirring; II, ultrasonication.

prevents the hydrogen uptake by the catalyst and reduces its hydrogenation activity.

It is noteworthy that the catalysts obtained from dilute solutions in an ultrasonic field are more active in the reactions of decomposition of H_2O_2 and hydrogenation of hex-1-ene (Table 2) than those prepared in the absence of USW. It appears that upon reduction of dilute solutions of H_2PtCl_6 in an ultrasonic field the dispersive action of ultrasound is better manifested, whereas upon reduction of concentrated solutions the effects of acceleration of crystallisation and coagulation under the action of ultrasound are predominant.[51] One should, however, bear in mind that the results of studies [51–53] were interpreted in terms of N I Kobozev's theory of active ensembles, which was not fully confirmed subsequently in the theory and practice of catalysis.

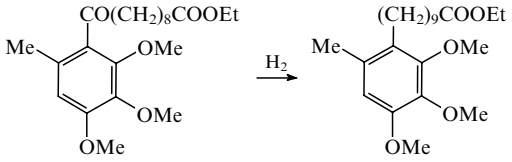
Some specific effects appear under the action of ultrasound in the process of preparation of adsorption catalysts.[52, 53] For example, ultrasonication (frequency 550 kHz, flux density 5.4 W cm^{-2}) of a system H_2PtCl_6–silica gel, in which the support does not virtually adsorb H_2PtCl_6, in a hydrogen atmosphere leads to the formation of a mechanical mixture of platinum black and silica gel, whereas in a system H_2PtCl_6–alumogel, in which the support adsorbs H_2PtCl_6 well, the latter is reduced directly on alumogel under the action of ultrasound. The catalyst thus obtained is active in the hydrogenation of hex-1-ene, whereas the alumogel adsorption catalyst prepared without ultrasonication is inactive.

Ultrasound is successfully used for the preparation of catalysts supported on silica gel, alumina or lamellar inorganic materials. Thus the reduction of ammonium hexachloroplatinate in an acoustic field (frequency 440 kHz, intensity 5 W cm^{-2}) in the presence of suspended silica gel leads to an 80% increase in the surface of the metal compared to that of a sample obtained by mechanical stirring. This may rationalise the increase in the activity of highly dispersed catalysts Pd/Al_2O_3 or Pd/C in the reaction of reduction of acetophenone by hydrogen.[54]

One of the stages in the proposed mechanism of catalytic hydrogenation is migration (spillover) of hydrogen to the adsorbed substrate molecules.[55] This explains the enhancement of the activity of a Pd/C catalyst obtained by the reduction of a palladium salt with formaldehyde under the action of ultrasound in the reaction of hydrogenation of nitrobenzene at 303 K.[56] In the case of ultrasonic treatment, the amount of hydrogen capable of participating in the spillover increases appreciably: after ultrasonication of the Pd/C catalyst (0.8 mass % Pd) the H : Pd ratio may reach 6.8.

Preliminary ultrasonic treatment of a Pt/SiO_2 catalyst intended for the hydrogenation of cinnamaldehyde resulted in a considerable increase in the selectivity of formation of cinnamic alcohol (up to 80%) and a twofold increase in the reaction rate. This effect is explained [57] by the formation on the support of effective metal centres providing for stronger substrate adsorption involving the C=O bond.

Comparative studies of the profound reduction of the C=O groups on H_2SO_4-unmodified and -modified Pt catalysts with and without ultrasonic treatment also confirmed the activating action of USW.[58, 59] This conclusion was drawn from the results of hydrogenation of the carbonyl group of ethyl 9-(2,3,4-trimethoxy-6-methylbenzoyl)nonanoate on a Pt/sibunit catalyst.



In the course of the experiment, the extent of the catalyst dispersion was monitored by a conductometric method. Analysis of the results obtained allowed one to conclude that the granulometric composition of the catalyst remained invariant under the action of USW with the intensity of up to 1 W cm^{-2}, while the reaction rate increased as the duration of ultrasonic pretreatment was prolonged from 15 to 30 s. The catalyst subjected to the USW action for 60 and 120 s exhibited lower activity. The increase in the ultrasonic flux density from 0.1 to 1 W cm^{-2} favoured the catalyst's activity, while its further increase to 3 W cm^{-2} resulted in the decrease in activity (Fig. 1). Deactivation of the catalyst upon increase in the duration and intensity of sonication may be explained by the restructuring of active centres associated with an appreciable modification of the morphology of the catalyst's surface. Examination of the catalyst's samples before and after sonication by electron microscopy confirmed this conclusion, which is in full agreement with the data reported by Garibyan *et al.*[25] X-Ray photoelectron spectroscopic data showed that the Pd(II) : Pd(0) ratio increased after ultrasonic treatment. Assuming that the hydrogenation of the C=O group proceeds on a bifunctional active centre $Pd(0)-Pd^{\delta+}$, the higher catalyst activity may be explained by the increased proportion of Pd(II) under the action of USW.[31, 32]

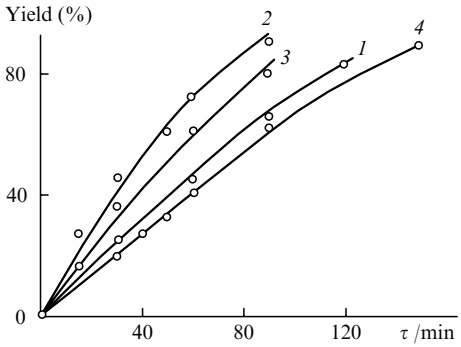


Figure 1. Dependence of the yield of the hydrogenation product of ethyl 9-(2,3,4-trimethoxy-6-methylbenzoyl)nonanoate on a Pt/sibunit catalyst on the reaction time (τ) and the USW intensity (W cm^{-2}): (*1*) 0.1; (*2*) 1; (*3*) 3; (*4*) without USW. The duration of ultrasonication was 30 s.

Systematic investigations of the impact of ultrasound on novel polymeric palladium catalytic systems containing metal colloids have led to a conclusion about an appreciable effect of acoustic vibrations on the activity of these catalysts in the selective hydrogenation of the triple bond of acetylenic alcohols to the double bond.[60, 61] High dispersion of the catalyst's active phase was attained also by ultrasonication in the stage of preparation of supported ruthenium catalysts.[62] Ultrasound has a strong effect on the genesis and properties of alumogel,[63] which is widely used as the support for hydrogenation and dehydration catalysts and also as the support for the active phases of adsorption catalysts. The application of an ultrasonic field accelerates crystallisation of alumogel and its surface is increased by 40% compared to that of ultrasound-nontreated samples. This results in the formation of a secondary structure consisting of smaller aggregates with a

strongly developed surface and in higher hydrophilicity of particles, which prevents their aggregation.

The relevant literature carries a suggestion that cleavage of the carbon–carbon bonds occurs after their activation on 'metal' active centres.[55] The number of such centres appears to increase as a result of changes in the dispersion under the action of ultrasound leading to the acceleration of hydrogenolysis. Supported palladium and rhodium catalysts prepared on the base of TiO_2-SiO_2 gels under ultrasonic treatment possess higher activity than analogous systems non-treated with ultrasound and ensure the required selectivity in the hydrogenolysis of n-butane.[64]

The catalytic activity of nickel obtained by the reduction of nickel oxalate at 583 K under the action of acoustic vibrations with a frequency of 25 kHz and an intensity of 3000 W cm^{-2} is increased by 87% in the reaction of hydrogenation of benzene (see Ref. 9). Probably, as in the case of Pt and Pd,[5, 59] this is related to the modification of the structure of the catalyst's surface under the action of ultrasound. Similar effects were also observed when other nickel catalysts were used. Sonication in the course of reduction of nickel iodide with lithium has led to activated nickel which catalysed 1,4-addition of phenylsilane to α,β-unsaturated ketones and nitriles providing high yields (after hydrolysis) of hydrogenation products.[65] Activated nickel powder is also used in the synthesis of aminoarenes by reduction of nitroarenes. This catalyst is prepared by the reduction of anhydrous nickel chloride with potassium subjected to dispersion by ultrasound.[66]

Ultrasonication gives a positive effect in the preparation of promoted and supported oxide catalysts which are used in the oxidative addition of methane (Na_2O-ZnO, Li_2O-MgO, La_2O_3-MgO, Sm_2O_3-MgO), oxidation of propylene (Na_2O-ZnO) and total oxidation of methanol to CO_2 ($CuO-SiO_2$).[67] Application of USW in the stage of impregnation increases the catalytic activity of oxides in oxidative processes. The use of the 10% Na_2O-ZnO catalyst thus obtained increases the methane conversion from 14% to 18% and raises the selectivity from 40% to 54%. On the activated 1% La_2O_3-MgO catalyst, the degree of conversion is increased insignificantly, whereas the selectivity is increased from 54% to 60%. The $C_2H_4:C_2H_6$ ratio is changed in favour of ethylene. A similar effect of an increase in the catalytic activity of manganese and chromium oxides was also observed in the heterogeneous oxidation of 1-hydroxyphosphonates.[68]

According to Garibyan *et al.*,[67] the improvement of catalytic properties of oxides upon sonication may be due to changes in the number and structure (composition) of active centres, which is in agreement with the conclusions[52] drawn from the study of oxidation of ethanol on platinum and palladium. The electron microscopy analysis of samples prepared with and without application of USW has shown that the application of ultrasound provided a more uniform distribution of components. This inference is consistent with the results of analysis of palladium catalysts.[24, 25] Promoter oxides present on ZnO or MgO in the form of agglomerates are dispersed on the support surface. The promoter increases the efflux of $^{\bullet}CH_3$ and $^{\bullet}C_2H_5$ radicals to the gas phase;[69] consequently, a uniform distribution of sodium and lanthanum ions reached under the action of USW favours the formation of radicals and prevents their capture by the surface. This results in an increased yield of C_2 hydrocarbons.

The use of the EPR method has shown that the activation of methane and ethane on ultrasound-treated catalysts provides higher concentrations of free radicals in the gas phase. On the USW-nontreated Sm_2O_3-MgO catalyst, the ratio of desorbed radicals $[^{\bullet}CH_3]:[^{\bullet}C_2H_5]$ is equal to 0.9, whereas upon ultrasonication it increases to 1.75. This implies that in the latter case additional disintegration processes with the release of C_2H_4 take place in the course of formation of $^{\bullet}C_2H_5$ radicals. Experiments on CH_4 conversion under atmospheric pressure showed that under the action of USW the $[C_2H_6]:[C_2H_4]$ ratio is shifted in favour of ethylene. The ethyl radicals are decomposed either on the surface or in the gas phase, *i.e.*, a radical mechanism without participation of a solvent is realised:

$$^{\bullet}C_2H_5\,(\text{ads}) \longrightarrow C_2H_4 + H^{\bullet},$$

$$^{\bullet}C_2H_5\,(\text{ads}) + CH_3{}^{\bullet}(\text{gas}) \longrightarrow C_2H_4 + CH_4,$$

$$^{\bullet}C_2H_5\,(\text{gas}) + {}^{\bullet}CH_3\,(\text{ads}) \longrightarrow C_2H_4 + CH_4.$$

Incorporation of ions of a different valence (M^+) into the lattice of alkaline-earth metal oxides leads to changes in the defect structure of the catalyst and its higher activity in the process under study. Ultrasonication results in the enhancement of this effect.

The extent of oxidation of propylene on the Na_2O-ZnO catalyst activated by 60-min ultrasonication increased by 4% compared to that on the USW-nontreated catalyst; the composition of products also changed:[67] the yield of hexadiene increased, while the amount of hydrogen and benzene decreased (Table 3). The Na_2O-ZnO system contains numerous unprotected ZnO centres on which oxidation does take place. Considerable content of hydrogen in the products is related to the possible dehydroaromatisation of hexadiene on zinc oxide. In the catalyst subjected to the action of USW, sodium oxide covers the surface of zinc oxide uniformly and suppresses this process thus increasing the yield of hexadiene.

Table 3. Composition of the propylene oxidation products on a 10% Na_2O-ZnO catalyst. Reaction conditions: temperature, 843 K; contact time, 5.5 s; pressure, 1 atm.

$[C_3H_6]$ (vol.%)	Conversion (%)	Conditions of catalyst treatment	Composition of products (vol.%)				
			$CO + CO_2$	H_2	C_2H_6	$(C_3H_5)_2$	MeOH
3.5	30	mechanical stirring	8.32	2.7	0.112	0.01	0.081
3.9	33.9	ultrasonication	9.00	0.5	0.082	0.08	0.103

The same approaches were used in studies of the total oxidation of methanol on the 5% $CuO-SiO_2$ catalyst. The data on the temperature dependence of conversion of methanol in this system are listed in Table 4. The selectivity of CO_2 formation was found to be equal to 100% at all the temperatures studied. As can be seen from Table 4, irrespective of the SiO_2 porosity (catalysts 1 and 2 have the pore size 10^2-10^5 and 10–100 Å, respectively), the ultrasonic treatment in the stage of catalyst preparation increased the degree of conversion, which reached 86% at 668 K. The ultrasound-treated catalysts preserve their activities for a prolonged time. The phase composition of catalysts prepared by the method of thermal treatment at 623 K with and without sonication was also studied. The diffractograms of the catalysts of oxidation of methanol that have operated for the same time period point in both cases to the presence of only CuO phase,

Table 4. The temperature dependence of the methanol conversion into CO_2 on the 5% $CuO-SiO_2$ catalyst (1.5 vol.% MeOH in air).

Conditions of treatment	Conversion (%) at the temperature /K				
	573	598	623	648	668
Sample No. 1					
Mechanical stirring	20	43	56	66	75
Ultrasonication	43	60	65	77	86
Sample No. 2					
Mechanical stirring	33	43	48	67	73
Ultrasonication	40	50	66	70	86

although the activity of the ultrasound-treated catalyst remains at a high level. The sonication favours uniform distribution of the CuO phase over the SiO_2 surface. The $CuO-SiO_2$ samples prepared at 623 K with and without ultrasonication were studied before and after the reaction by the EPR method. The concentration of paramagnetic Cu^{2+} ions in the catalyst ultrasonicated before the reaction was one order of magnitude higher than that in the catalyst prepared in the usual manner. After the reaction, nearly equal low concentrations of copper ions were found on both catalysts. This may be explained by the degradation of the intermediate $Cu_2(OH)_3NO_3$ phase into CuO during the reaction.

Thus, the application of ultrasound for the preparation of promoted and supported catalysts enhances appreciably the efficiency of catalytic systems.

Ultrasonication of a suspension in the co-precipitation and ageing of copper, zinc and aluminium oxides enhanced noticeably the activity of the catalyst of methanol synthesis.[70] It was suggested that under the action of ultrasound the Cu : Zn : Al ratio in the catalyst precursor becomes the same as in the compound $Cu_3Zn_3Al_2(OH)_{16}CO_3 \cdot 4H_2O$, *i.e.*, 3 : 3 : 2. The specific surface of the thus obtained highly dispersed $Cu(Cu^+)$, ZnO and Al_2O_3 particles as well as the yield of methanol depend linearly on the content of this hydrate-like phase.

Ultrasound is also used in the stage of precipitation in the preparation of catalysts and their precursors.[71] Formation of agglomerates in mixed half-precipitated suspensions of $(Cu/Zn)_2(OH)_2CO_3$ under the action of acoustic waves of different intensity was studied. The application of ultrasound influences substantially the size of particles and the surface of agglomerates. The precursors precipitated by the low-intensity ultrasonication have basically small specific surface and are composed of small agglomerates. The precursors prepared using high-intensity USW are characterised by a more developed surface and formation of larger agglomerates. The MnO_2 catalyst prepared under the conditions of high-intensity ultrasonic treatment possesses higher activity as regards evolution of oxygen from H_2O_2 than that of an analogous but USW-nontreated catalyst.

The ultrasound treatment is also used for the preparation of electrode catalysts of the solid-oxide fuel cell.[72] For example, the anode catalyst $La_{1.8}Al_{0.2}O_3$ is prepared by pyrolysis of an aqueous mixture of lanthanum and aluminium nitrates. This technique provides higher activity of the anode catalyst than that attained using other methods. The optimum conditions for the ultrasonic treatment are determined experimentally by monitoring the particle size and from the dependence of the quantity of deposited particles and their size on the concentration of an aqueous solution and temperature.

There is a possibility of sonochemical synthesis of various nanostructured materials using high-intensity ultrasound.[73] In the decomposition of organometallic compounds under the action of ultrasound, the specific surface of the solid phase composed of agglomerates and nanoclusters is increased. This technique was used to synthesise nanostructured metals and alloys from iron pentacarbonyl and cobalt tricarbonylnitrosyl; molybdenum carbide was prepared in this way from molybdenum hexacarbonyl. These materials represent active heterogeneous catalysts for reforming of hydrocarbons and hydrogenation of CO.

The use of surface acoustic waves and resonance vibrations makes it possible to prepare heterogeneous catalysts with artificially controllable functions.[74] For instance, thin films of catalysts were precipitated using horizontal surface-active waves generated on ferroelectric single crystals of $LiNbO_3$ and $LiTaO_3$. This resulted in an appreciable increase in the activities of Ag, Pd and Ni catalysts in the oxidation of ethanol and of Pd catalyst in the oxidation of CO. The enhancement of catalytic activity is related to the modification of the coefficients of electromechanical adhesion of ferroelectrics and to the state of the catalyst surface.

It should be noted that ultrasound not only influences the process of catalyst preparation but also enhances the activities of ready-to-use catalysts in various reactions.[59]

2. The action of ultrasound on ready-to-use catalysts

Ultrasonication influences the genesis of crystalline catalysts, their properties and catalytic activities in various reactions and favours the increase in the size of solid particles irrespective of the nature of the material used.[75] An appreciable decrease in the particle size is particularly noticeable at a low metal content.[76] The removal of impurities from the metal surface makes an additional contribution to the enhancement of the catalyst's activity.[59]

Asymmetric catalysis on metals implies the interaction of a substrate with an active centre formed as a result of coordination of a chiral modifier with the metal component of the catalyst.[77] Ultrasonic treatment of catalysts leads to an increased enantioselectivity of many processes, *e.g.*, hydrogenation of ethyl pyruvate to ethyl lactate on various platinum catalysts (Pt/C, Pt/Al_2O_3, Pt/SiO_2 and Pt/montmorillonite).[78] After the action of USW on the Pt/SiO_2 and Pt/montmorillonite catalysts, the enantioselectivity is enhanced substantially, the hydrogenation rate is increased by an order of magnitude compared to that on the untreated catalyst, while the yield of the target product reaches 100%. The enhanced activity can be due to the decreased size of the catalyst's particles (Table 5) and changes in their morphology. Initially, the size of platinum crystals ranges from 5 to 60 nm. After ultrasonication, small particles (3–5 nm) become predominant and their distribution is almost uniform. Apparently, this favours the formation of a large number of reactive different-ligand complexes and, consequently, enhances the catalyst's activity. Analogous results were obtained in the sonochemical treatment of a catalytic system Pt/Al_2O_3 – quinidine in acetic acid.[79] In addition, sonication made possible the repeated use of the catalyst without its regeneration, *i.e.*, made the catalyst more stable.

Table 5. Mean diameter of metal particles in supported platinum catalysts before and after 30-min ultrasonication.[78]

Catalyst	Diameter of particles /nm	
	before treatment	after treatment
5% Pt/C	3.0	2.5
3% Pt/SiO_2	6.7	4.2
5% Pt/montmorillonite	3.7	3.8
5% Pt/Al_2O_3	23.1	12.6

A number of studies were devoted to the investigation of the ultrasonic treatment of Raney nickel.[22, 80–87] Sonication in water[80] with subsequent asymmetric modification yielded a highly efficient catalyst of enantioselective hydrogenation. The complex tartaric acid – NaBr – modified Raney nickel exhibits high enantioselectivity and catalytic activity in the hydrogenation of β-diketones and β-keto esters.[81, 82]

According to Suslick and Casadonte,[22] ultrasonic treatment (20 kHz, 50 W cm^{-2}) of a nickel powder (particle size 5 μm) in octane increased 10^5 times its ability to catalyse hydrogenation of alkenes. Though, such a strong effect is in part due to the fact that the results were compared with an inactive form of nickel. The application of an acoustic field simplifies considerably the preparation of the catalyst. The initial hydrogenation rate reaches its maximum after preliminary 60-min ultrasonication of a sample, whereas further action of ultrasound decreases its catalytic activity (Fig. 2). The use of scanning electron microscopy showed that the acoustic field does not modify the particle size but influences noticeably the surface morphology. Sonolysis allows preparation of nickel with a specific surface close to that of Raney nickel. Initially, the surface of the crystalline structure is smoothed under the action of ultrasound and then the particles 'stick' to each other,[22, 86] which is presumed to be the main reason for the decrease in the hydrogenation rate upon prolonged action of ultrasound. However, the effect of particle sticking is difficult to explain from the physical viewpoint, since for this process to occur, the particles should be heated to their melting temperature,

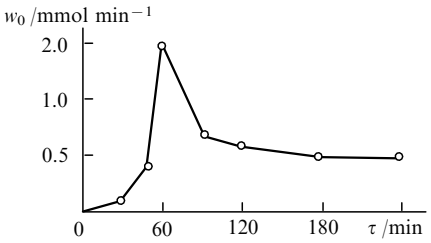


Figure 2. Dependence of the initial rate of hydrogenation of non-1-ene (w_0) on the duration of ultrasonic activation (τ) of nickel powder; temperature 273 K, pressure 1 atm.

which is possible if their minimal relative speed at the moment of collision [1] is 15 000 m s^{-1}, which is 30 times as high as the really observed one (500 m s^{-1}) and almost 10 times higher than the velocity of sound propagation in the liquid.

The ultrasound-treated platinum (mainly Pt/C), nickel and palladium catalysts are successfully used in reactions of hydrogenation and hydrosilylation of alkenes.[83–85]

A catalytic system metal hydride–dialkylzinc activated by ultrasound is effective in the reduction of carbonyl compounds and epoxides (like the ultrasound-nontreated system) and in reactions of partial reduction of carboxylic acids to aldehydes.[88] This system is highly attractive owing to its accessibility, inexpensiveness and simplicity of handling and, hence, it may be particularly useful for the implementation of large-scale reduction processes.

The possibility of ultrasonic activation of polymerisation, aldol condensation, allylation and oxidation catalysts should also be noted. Ultrasonic treatment (20–500 kHz, 4–20 W cm^{-2}) of octane-suspended titanium trichloride, belonging to the group of the Ziegler–Natta catalysts, led to the decrease in the particle size from 15–40 to 0.1–5 μm. Crystalline polymers formed in the presence of this catalyst are more uniform with regard to their molecular mass than are polymers obtained on the ultrasound-nontreated catalyst. Similar results were also derived using other Ziegler–Natta catalysts.[5] The application of ultrasound enhances the catalytic activity of the metal iodide-promoted $BiCl_3$ used as the catalyst of the Mukaiyama and Mukaiyama–Michael reactions.[89] The ultrasound has an accelerating effect on the systems $BiCl_3$–1.5 $ZnCl_2$ or $BiCl_3$–1.5 SnI_2 (5 mol.%), which catalyse the crossover aldolisation of acetophenone and benzaldehyde.

Ultrasound-activated palladium catalyses the heterogeneous allylation of carbonyl compounds with γ-substituted allyl alcohols in the presence of $SnCl_2$ in non-polar solvents (diethyl ether, diisopropyl ether and toluene).[90] The reaction proceeds regioselectively with high yields of 1,4-disubstituted but-3-en-1-ols; the regioselectivity (α-selectivity) of the reaction on ultrasound-activated palladium is the opposite of the regioselectivity (γ-selectivity) of the palladium-catalysed homogeneous carbonyl allylation in polar solvents.

Garibyan *et al.*[25] studied the effect of ultrasound in the stage of preparation of catalysts on their activities and selectivities in the oxidative condensation of methane, oxidation of propylene on Na_2O/ZnO and profound oxidation of MeOH on CuO/SiO_2.

It is noteworthy that the most interesting results were obtained when the ultrasound was involved in catalytic processes.

III. Sonochemical catalysis

1. Homogeneous catalysis

The application of ultrasound with the intensity sufficient for inducing cavitation leads to the acceleration of chemical reactions, which appears to be determined by the formation of free radicals.[91]

An extensive series of homogenous catalytic processes carried out under sonication have been studied. Thus Müller *et al.*[92] demonstrated the possibility of the ultrasound-induced highly effective enantioselective chain elongation of labile fluorenylmethoxycarbonyl-protected amino acids by means of Wolf rearrangement of the corresponding α-diazo ketones at room temperature catalysed by silver ions. Donatti and Vollet [93] investigated hydrolysis of tetraethoxysilane at 312 K and mixtures of tetramethoxysilane and tetraethoxysilane at 308 K catalysed by hydrochloric or oxalic acid in an ultrasound field. It was shown that Lewis acids or sonication catalyse the condensation of imines with H-phosphonates bound to the Wang resins resulting in high yields of the corresponding α-aminoalkylphosphonates.[94] A number of diterpenoids were obtained by highly regioselective cycloaddition of styrenes to substituted 1,4-benzoquinones under the action of ultrasound in the presence of Lewis acids as catalysts.[95] The application of ultrasound increased appreciably the rate of addition of aldehydes to methyl acrylates catalysed by 1,4-diazabicyclooctane.[96] Ultrasonic waves with an amplitude of 120 μm accelerate decomposition of 2-chlorophenol in the presence of 200 mg litre^{-1} of H_2O_2.[97] Under the action of ultrasonic vibrations, the condensation of indene or 2-nitrofluorene catalysed by bis(*p*-methoxyphenyl) telluroxide leads to the corresponding fulvenes in high yields.[98] Ultrasound is also used in the reactions involving fatty acids.[99] For example, an isomer of methyl 8-(5-hexyl-4,5-dihydro-3*H*-pyrrol-2-yl)octanoate can be synthesised from methyl ricinoleate in several ways. The highest yield (42%) is achieved and the minimum reaction time is necessary in the case where USW (20 kHz, 53 W cm^{-2}) are applied.

Let us consider in more detail oxidation and isomerisation reactions occurring under the action of USW. The results of studies of the effect of ultrasound on the liquid-phase oxidation of hydrocarbons by the radical-chain mechanism in the presence of 0.3% cobalt stearate are presented in Table 6. It is seen that the accumulation of oxygenated compounds is increased by 15%–30% under the action of USW. As the pressure increases, the oxidation rate also increases. The maximum acceleration of the process is reached at a frequency of ~300 kHz. It is of essence that in an ultrasonic field the oxidation rate remains invariant for a long time, whereas without ultrasonic treatment it reaches a maximum and then decreases appreciably. In the process of oxidation, cobalt stearate usually forms a micelle with the hydrocarbon, which is a reason for the decrease in the catalyst's activity. In an ultrasonic field, complexes of this type decompose or are not formed at all, and this prevents shielding of the catalyst by hydrocarbon molecules and enhances their stabilities because of which the reaction rate remains constant.

Table 6. Characteristics of the product of n-tetradecane oxidation at 385 K in the presence of cobalt stearate catalyst.

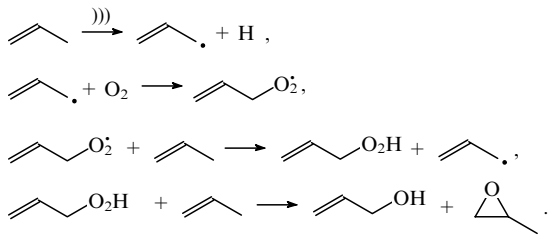
Characteristic	Without ultrasonic treatment	Under the action of ultrasound with a frequency of /kHz		
		300	600	1000
Acid number [a]	21.0	29.2	27.2	25.0
Ester number	10.6	14.9	14.2	13.7
Carbonyl number	22.4	28.1	26.4	27.4
Hydroxyl number	7.2	7.5	6.2	5.5
Sum of oxygenated compounds	61.2	79.1	73.9	71.6

[a] In mg KOH per 100 g product.

It is of note that the oxidation rate decreases appreciably at an USW frequency of 16 kHz. This effect may be explained by several reasons: intense degasification of the hydrocarbon at low frequencies and high intensity of irradiation; chemical modification of the

catalyst's molecules; higher decomposition rate of peroxide compounds formed in the oxidation.

Oxidation of alkenes by oxygen in the presence of $Mo(CO)_6$ with the formation of enols and epoxides was performed under the action of ultrasound.[5] The primary sonochemical act in this process is presumed to be homolysis of the allylic C–H bond under the action of cavitation.



Under ultrasonic stirring, the homogeneous cationic ferroporphyrins become effective catalysts of cyclohexane oxidation in the presence of MeCN. At a total yield of 93%, the ratio of selectivities of the formation of epoxide, alcohol and ketone is 77 : 12 : 11.[100]

Margulis[26] investigated the catalytic isomerisation of alk-1-enes into alk-2-enes in an ultrasonic field in the presence of metal carbonyls. In the presence of $Fe(CO)_5$, isomerisation of pent-1-ene under the USW action (frequency 20 kHz, intensity 100 W cm^{-2}) proceeds at a constant rate for 1 h, then the catalyst's activity drops for a period of several hours due to the formation of dispersed metallic iron and a small amount of $Fe_3(CO)_{12}$. High initial activity of carbonyl $Fe_2(CO)_9$ decreases rapidly, since under the conditions of sonolysis it is transformed at a high rate into the complex $Fe(CO)_5 \cdot Fe_3(CO)_{12}$; however, even under prolonged exposure to ultrasound the complex does not undergo degradation with the liberation of metallic iron. The initial rate of catalytic isomerisation of pent-1-ene measured 5 min after the beginning of sonication is increased more than 10^6 times compared to the rate in the control experiment (without ultrasound).

It was shown that the efficiency of isomerisation decreases when alk-1-enes have substituents creating steric hindrances (Table 7). Therefore, isomerisation of 2-ethylpent-1-ene and allylbenzene is appreciably slower than that of pent-1-ene. Isomerisation of *cis*-stilbene virtually does not occur because of either the non-terminal position of the double bond or the difficulty of forming an intermediate complex with $Fe(CO)_5$. According to the data from Table 7, the isomerisation rate of linear alk-1-enes changes in the order: pent-1-ene $\approx$ hex-1-ene $\gg$ oct-1-ene > dec-1-ene.

Isomerisation of alkenes in an ultrasonic field in the presence of other metal carbonyls, not only iron carbonyls, was also studied. It is seen from Table 7 that in the presence of iron carbonyl *trans*- and *cis*-pent-2-enes are formed in the ratio

Table 7. Isomerisation of alk-1-enes in an ultrasonic field in the presence of $Fe(CO)_5$.

Initial alkene	Products [a]	Relative isomerisation rate
Pent-1-ene	*trans*-pent-2-ene (77%) *cis*-pent-2-ene (23%)	1.0
Hex-1-ene	*trans*-hex-2-ene (74%) *cis*-hex-2-ene (26%)	1.1
2-Ethylpent-1-ene	2-ethylpent-2-ene	0.31
Oct-1-ene	*trans*- and *cis*-oct-2-enes	0.17
Dec-1-ene	*trans*- and *cis*-dec-2-enes	0.05
Allylbenzene	β-methylstyrene	0.02
cis-Stilbene	*trans*-stilbene	0.02

[a] Yields are indicated in parentheses.

virtually close to the thermodynamic equilibrium. This ought to be expected, since irrespective of the presence or the absence of the ultrasonic field the same species remain catalytically active. However, in the presence of $Ru(CO)_5$ and $Ru_3(CO)_{12}$ other ratios of *cis*- and *trans*-isomers are obtained, which points to a different mechanism of catalytic action of ruthenium carbonyls and to the participation of different intermediates in the reaction. The catalytic activities of carbonyls in the isomerisation reaction under the action of USW decrease in the series: $Ru_3(CO)_{12}$ > $Fe(CO)_5$ > $Mo(CO)_6$ > $Fe_3(CO)_{12}$ $\gg$ $W(CO)_6 \approx Cr(CO)_6$. The rates of photocatalytic isomerisation change in a different sequence: $Fe(CO)_5$ > $Fe_3(CO)_{12}$ > $Ru_3(CO)_{12}$ > $W(CO)_6 \approx$ $Mo(CO)_6 \gg Cr(CO)_6$. In many cases, the ratios of *trans*- and *cis*-isomers in the sonocatalytic and photochemical isomerisations are similar; however, when $Ru_3(CO)_{12}$ is used, they differ considerably and amount to 2.8 and 6.0, respectively.

These results suggest the existence of substantial differences in the mechanisms of sonochemical and photochemical initiation of the catalytic processes, the catalytic activity being higher in the first case. Experimental data support the suggestion that in both cases the stages in which hydrogen migrates from the β-position of the alkene to form an intermediate hydride, *viz.*, π-allyllic complex, are analogous. In accordance with the commonly accepted scheme, sonolysis of $Fe(CO)_5$ in the presence of an excess of pent-1-ene yields $[Fe(CO)_4(C_5H_{10})]$, which is confirmed by IR spectroscopy.

Exposure to ultrasound not only enhances the rates of homogeneous catalytic reactions, but also increases the number of catalytic cycles. Ultrasound is a factor which influences the catalytic activity of iron(III) *meso*-tetrakis(2,6-dichlorophenyl)-porphyrin chloride [Fe(TDCPP)Cl] in a homogeneous system[101] where cyclohexanol is formed from cyclohexane by a classical mechanism of hydroxylation with the participation of iodosylbenzene: PhIO is reduced to iodobenzene with the oxidation of Fe(TDCPP)Cl resulting in the formation of catalytically active species of iron(IV)oxoporphyrin radical, which directly hydroxylate cyclohexane. The optimum conditions of this reaction have been established: $[Fe(TDCPP)Cl] = 3 \times 10^{-4}$ mol litre^{-1} in 1,2-dichloroethane, ultrasonic stirring at 273 K in an excess of PhIO. Ultrasound makes it possible to achieve an unusually high yield of cyclohexane (96%) and to increase more than twofold (from 45 to 96) the number of reaction cycles. The catalyst [Fe(TDCPP)Cl] acting in an ultrasonic field may be regarded as a good biomimetic model. This is a stable and selective catalyst allowing the preparation of cyclohexanol as the single product.

Application of an ultrasonic field (35–40 kHz) increases considerably the number of catalytic cycles involving a water-soluble rhodium catalyst for the hydroformylation of alkenes.[5] The number of such cycles in the preparation of aldehydes under a pressure of 2.5 MPa in an aqueous solution containing a 1 : 1 mixture of carbon monoxide and hydrogen, hex-1-ene and the rhodium complex $HRhCl(CO)[P(C_6H_4SO_3H)_3]_3$ under the action of ultrasound is 11.34, whereas with mechanical stirring at a rate of 500 rpm it is 3.24.

Thus, ultrasound accelerates homogeneous catalytic reactions by modifying in some cases their mechanisms and increases the stability of homogeneous catalysts.

2. Heterogeneous catalysis

Acoustic vibrations can exert a dual effect on heterogeneous catalytic reactions. On the one hand, they favour mass transfer and, on the other hand, enhance the activity of catalysts.[51, 102, 103] The use of ultrasound in heterogeneous reactions opens broad possibilities for the application of physical and chemical factors of acoustic impact. Difficulties of studying such factors are related to the absence of unequivocal and clear-cut concepts of the nature of the ultrasound effect on heterogeneous catalytic processes. At present, several tentative mechanisms of the effects observed may be discussed, but there is no answer so far to the question about which of them is predominant.[26]

Table 8. Rates of NH_3 formation (μmol litre^{-1} min^{-1}) in the sonolysis of water saturated with a mixture of N_2 and H_2 in the presence of metal catalysts.[51]

Catalyst	Rate of NH_3 formation [a]	Catalyst	Rate of NH_3 formation [a]
Rh (from $RhCl_3$)	2.5, 3.0	Rh black	1.4, 1.3
Pt (from H_2PtCl_6)	1.6, 2.0	Pt black	1.0, 0.9
Pd (from $PdCl_2$)	1.3, 1.5	Pd black	0.73, 0.80
Without catalyst	0.4	Rh black (without USW)	0.00

[a] In most cases, there are two values derived from parallel experiments.

Let us consider the mechanism † of a heterogeneous catalytic reaction in an ultrasonic field exemplified in the synthesis of NH_3. A remarkable effect has been observed: in water saturated with a mixture of N_2 and H_2 in the stoichiometric proportion, the rate of NH_3 formation under ultrasonic irradiation in the presence of platinum group metals as catalyst is rather high, whereas without ultrasound no reaction occurs whatsoever.[51]

Table 8 lists the rates of the NH_3 formation in the presence of different catalysts in the sonolysis (550 kHz, 4–5 W cm^{-2}) of water saturated with a mixture of N_2 and H_2. The rate of NH_3 formation in the absence of catalysts is close to the rate of HNO_2 formation in the sonolysis of water in the nitrogen atmosphere (in addition to nitrous acid, H_2O_2 and HNO_3 are also formed as the reaction products).[104] Accordingly, it may be presumed that NH_3 is synthesised in an ultrasonic field non-catalytically in the gas phase with cavitation bubbles involving the excited nitrogen molecules, *e.g.*, the long-living metastable term $N_2^*(A^3\sum_u^+)$

$$N_2^* + H \longrightarrow N + NH.$$

In this case, ammonia is formed according to the following scheme:

$$N + H_2 \longrightarrow NH + H,$$

$$NH + H_2 \longrightarrow NH_3,$$

$$N + H_2 \longrightarrow NH_2,$$

$$NH_2 + H_2 \longrightarrow NH_3 + H.$$

It is possible [105] that, as in the case of the reaction in an electric discharge, the primary act in the sonochemical synthesis of NH_3 is the ionisation of nitrogen followed by the stage

$$N_2^+ + H_2 \longrightarrow N_2H^+ + H$$

and then by the stage which ultimately leads to the formation of ammonia.

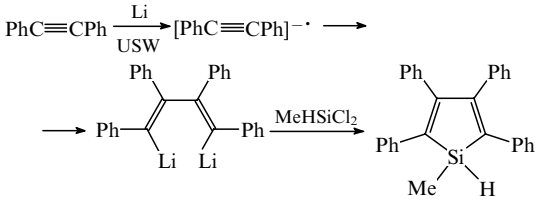
Ultrasonic fields accelerate appreciably hydrogenation of unsaturated compounds,[81] *e.g.*, indene, acenaphthylene, non-1-ene, α-methylstyrene and *trans*-benzylideneacetone.

Hydrogenation was carried out on a catalyst obtained by deposition of 10% Pd on activated carbon in the presence of formic acid as the hydrogen carrier. In an ultrasonic field, 100% hydrogenation of the double bonds at 298 K was reached within 1 h, whereas the aromatic rings remained intact. Without ultrasound, the reaction was considerably slower and the yield was 70% after 1 h and 90% after 2 h.

Ultrasonic field increased appreciably the hydrogenation rate of alkenes in anhydrous media in the presence of platinated carbon. It should be noted that the hydrogenation of acyclic alkenes is accelerated to a greater extent than that of unsaturated cyclic hydrocarbons.[26]

The rate of hydrogenation of acrylic acid on Pt black at 298 K in an acoustic field (440 kHz, 5 W cm^{-2}) is three times as high as that under mechanical stirring at 1000 rpm (see Ref. 106). The use of ultrasound (1 MHz, 3 W cm^{-2}) in the catalytic hydrogenation of olive oil on Raney nickel made it possible to reduce appreciably the residual concentration of unsaturated compounds in the product (the iodine number was 77.0 after hydrogenation for 3 h and 50.0 after hydrogenation in the ultrasonic field).[107]

Under the action of ultrasound, anthracene can be reduced by lithium to its dianion. Addition of water leads to the formation of 9,10-dihydroanthracene. Under similar conditions, diphenylacetylene yields a radical anion which then dimerises. This dianion may be captured by some species,[5] as is shown in the scheme:



Ultrasonic waves speed up not only hydrogenation, but also dehydrogenation, which seems to be due to the fact that both reactions occur by the same mechanism. For example, the degree of dehydrogenation of tetrahydronaphthalene to naphthalene in the presence of 3% Pd/C as a catalyst in diethylene glycol at 473 K reaches 55% after 6 h.[108] The use of ultrasound makes it possible to decrease the temperature to 453 K and to achieve the total conversion within the same time. The use of pulse ultrasound is as effective as continuous ultrasound. Dehydrogenation of triethylene glycol in dimethyl ether is much less sensitive to ultrasound.

Ultrasound makes it possible to increase the efficiency of the preparation of deuterium-labelled compounds.[109] The Raney nickel-catalysed hydrogen exchange for deuterium in a monosaccharide was performed in different solvents under the action of ultrasound. Deuterium was introduced with a high stereospecificity and regioselectivity.

Ultrasonication of a reaction mixture containing barium hydroxide increased the rates of the reactions and the yields of products involving aromatic aldehydes. For example, 4-chlorobenzaldehyde does not enter into the Cannizzaro reaction in the absence of ultrasound. The use of catalytic poisons which affect selectively the oxidative active centres made it possible to establish that this reaction occurs on the reduction centres, the catalytic cycle being initiated by a single-electron transfer from the catalyst to the substrate.[5]

Acceleration of the aldol condensation of ketones in an ultrasonic field in the presence of Al_2O_3 is confirmed by the following data:[110] sonolysis of 1-tetralone in an argon atmosphere at 353 K for 24 h produces the hydroxy ketone in 80%–90% yield, whereas in the absence of ultrasound its yield is not more than 52% after 144 h.

The rate of the Ullmann coupling of 2-iodonitrobenzene in dimethylformamide in the presence of copper bronze at 333 K is increased 64-fold upon sonication.[111] If this process is performed in the usual manner, but using the pre-sonicated copper bronze, its rate also increases compared to the reaction rate on the ultrasound-nontreated copper bronze, though to a much lesser extent. This effect may be easily explained by the decrease in the size of metal powder particles under ultrasonic treatment. An appreciable acceleration of the reaction under the direct action of ultrasound results from the constant activation of the metal surface. In addition, the sonochemical process has two other advantages: it requires a considerably smaller excess of copper and excludes sticking of metal powder to the walls of the reaction vessel.

Sonication was also employed in the synthesis of α-amino acids using amino acid γ-anion equivalents.[112] The reaction of

† Unfortunately, the mechanism of catalytic synthesis of NH_3 in an ultrasonic field is not considered in the relevant literature; therefore, only some suggestions may be discussed.

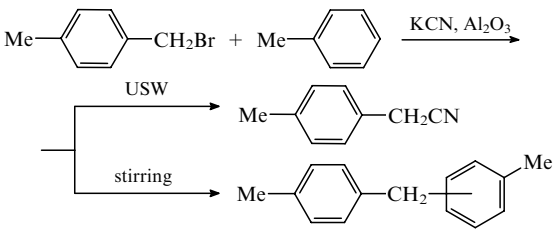
activated zinc with a iodohomoalanine derivative yields alkylzinc iodide, which reacts in the presence of palladium catalysts with a number of electrophiles (aryl iodides and acid chlorides) producing the corresponding α-amino acid derivatives. Sufficiently high yields are obtained using tetrahydrofuran as the solvent in the former case; to reach high yields in the reactions with acid chlorides under the action of ultrasound, it is necessary to use a combination of toluene and dimethylacetamide. Furthermore, alkylzinc iodide may be transformed into a zinc–copper couple, which reacts with allyl halides and reactive acid chlorides to give sufficiently high yields of the corresponding adducts.

The accelerating effect of ultrasonic treatment was exemplified in the liquid-phase alkylation of benzene by cyclohexene yielding cyclohexylbenzene.[113] The reaction was conducted on an $AlCl_3$ catalyst prepared by the method of chemical deposition on SiO_2 from the vapour phase. These catalysts are active below 273 K and can be regenerated. Despite the fact that the activity of the catalysts becomes lower in successive experiments, they can be used repeatedly. At least until the sixth cycle, the turnover number was 110. Apparently, reactions on solid catalysts are limited by the diffusion of reagents and/or products into the catalyst's pores. The ultrasonic impact in the course of catalytic reaction provides an accelerating effect, so that, depending on the size of the catalyst's particles, the reaction rate can increase by even one order of magnitude.

It is of note that the action of surface acoustic waves changes appreciably the activation energy and the reaction orders on oxidised catalytic surfaces, whereas on the reduced surfaces these changes prove to be much smaller. At a resonance frequency, oxidation of ethanol on palladium is accelerated 140–160 times, which may be explained by a stronger distortion of the lattice under these conditions.[72]

The application of USW speeds up substantially β-hydroxylation of acrylonitrile at room temperature (the same effect was also revealed in a homogeneous reaction [101]) on a catalytic system comprising copper(I) oxide and tetramethylethylenediamine. With the use of USW, the yield of the β-adduct also increases from 30% (stirring) to 70%–75%.[114] Ultrasonic acceleration of reactions on non-metal catalysts (using $HSiCl_3$ as the silylation agent) was not studied as thoroughly as that on metals;[115, 116] nonetheless, in these cases too the increase in the reaction rate is related to the increase in the specific surface of the solid reagent due to the decrease in the particle size upon cavitation and the improvement in the mass transfer of a liquid reagent to the solid phase surface.

The reaction route can also be changed under the action of ultrasound.[5] Stirring aluminium oxide with KCN in a mixture of *p*-methylbenzyl bromide and toluene leads to the formation of products of the Friedel–Crafts reaction (in this case, aluminium oxide acts as a catalyst). Under the action of ultrasound, this reaction follows a different route: *p*-methylbenzyl cyanide is formed as a result of direct substitution of CN for Br.



The change in the composition of products upon sonication is presumed to be due to the saturation of the Lewis acid centres on the aluminium oxide surface with CN^- ions, which induces nucleophilic substitution.[5]

The reaction of aryl iodides with zinc powder accelerated by ultrasound yields arylzinc compounds which contain the electron-withdrawing groups, *viz*,. CO_2Me, $C(O)NMe_2$, CN, Br, Cl and CF_3. The presence of these groups provides fairly good yields of asymmetric multifunctional biaryls in the catalytic synthesis with participation of Pd(0).[117]

Ultrasonication is also employed in electrochemical processes for intensifying the electrode reactions, which may be exemplified in the sonovoltammetric reduction of nitrobenzene on glassy carbon and gold electrodes.[118] The four-electron reduction of nitrobenzene in an alkaline solution (pH 13) was studied as a model. The mechanism of electrochemical reduction is known to be complex; it includes protonation and dehydration, the processes proceeding both on the surface and in bulk depending on the nature and the state of the electrode. In the absence and in the presence of ultrasound, the reduction of nitrobenzene on the glassy carbon electrodes includes a chemically reversible process followed by the irreversible three-electron reduction. The combined use of a rotating disc and sonovoltammetry permits one to decrease the capacity of the double layer.

Electrochemical dehalogenation of organic compounds in microemulsions of a system didodecyldimethylammonium bromide–water–dodecane under the action of ultrasound in the presence of zinc phthalocyanine as a catalyst proceeds faster than in a homogeneous system including toxic and expensive organic solvents.[119]

Thus, ultrasound accelerates the heterogeneous catalytic reactions owing to a better mass transfer, smaller size of the surface particles and creation of active centres on which the substrate undergoes specific transformation.

3. Phase-transfer catalysis

Ultrasound initiates and accelerates reactions in phase-transfer catalysis.[120, 121] The chemical effect of ultrasound in this case is also explained by the coalescence of cavitation bubbles, whereas its mechanical impact is associated with the formation of a highly dispersed emulsion which increases appreciably the interface area.

The mechanism of a typical phase-transfer reaction resembles the substitution mechanism. The overall equation

$$RX(org) + MY(aq) \longrightarrow RY(org) + MX(aq)$$

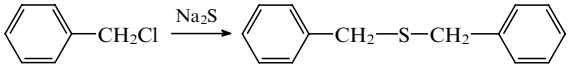
includes the catalytic cycle

$$RX + [Q^+Y^-] \longrightarrow RY + [Q^+X^-] \quad \text{(organic phase)}$$

$$M^+X^- + [Q^+Y^-] \rightleftharpoons M^+Y^- + [Q^+X^-] \quad \text{(aqueous phase),}$$

where Q^+ is the cation of the phase-transfer catalyst (PTC).

Combined action of PTC and ultrasound in heterogeneous reactions can be exemplified in the reaction of benzyl chloride with solid sodium sulfide in the presence of tetrabutylammonium bromide as PTC and acetonitrile as the solvent.[122]



The proposed mechanism includes two phase-transfer ion-exchange stages and the main reaction in the organic phase:

$$Na_2S(sol) + 2Q^+Br^-(org) \longrightarrow 2NaBr(sol) + Q^+S^{2-}Q^+(org),$$

$$Q^+S^{2-}Q^+(org) + 2\,PhCH_2Cl(org) \rightleftharpoons$$

$$\rightleftharpoons PhCH_2SCH_2Ph(org) + 2Q^+Cl^-(org),$$

$$Na_2S(sol) + 2Q^+Cl^-(org) \longrightarrow 2NaCl(sol) + Q^+S^{2-}Q^+(org).$$

The results obtained upon the use of PTC and ultrasound and upon their combined action are shown in Fig. 3.

The catalytic cycle of transformation of benzyl chloride includes the transfer of sulfide anions to the organic phase. The influence of ultrasound on the molecular diffusion and dissolution of sodium sulfide in acetonitrile is minimal, whereas a slight increase in the conversion occurs owing to the development of

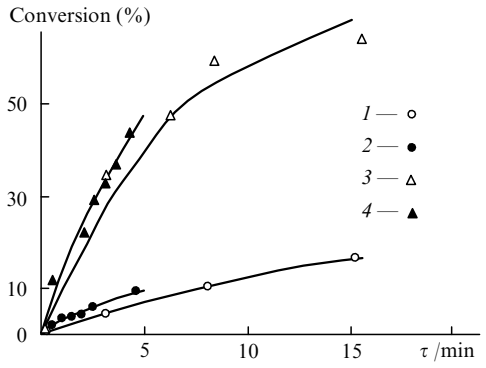


Figure 3. Results of the use of PTC and ultrasound in the reaction of benzyl sulfide formation (USW intensity, 150 W cm^{-2}): (*1*) without USW and PTC; (*2*) with USW; (*3*) 0.4% PTC; (*4*) 0.4% PTC + USW.

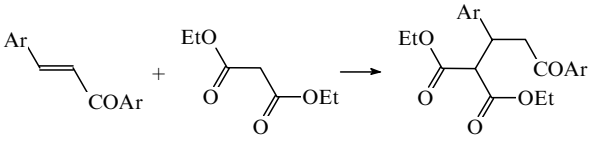
the interface where the reaction takes place, facilitation of mass transfer and effective stirring of the reagents as a result of cavitation. Combination of PTC and ultrasound gives a maximum increase in the conversion owing to the additive effect of their individual impacts on the system.

Ido *et al.*[123] investigated the possibility of the multiple use of phase-transfer catalysts. The catalyst (hexadecyltri-n-butylphosphonium bromide) is concentrated in the third phase formed between the organic (dodecane) and the aqueous (saturated KBr solution) phases. This interface catalyses substitution in benzyl chloride by bromide, the former being in the organic phase and the latter, in the aqueous phase. After completion of the reaction, the organic phase was removed and a new phase was introduced. The application of USW made it possible to avoid direct contact between the organic and the aqueous phase. The three phases were not mixed, the reagents were transferred across the interface under the impact of ultrasonic vibrations.

According to the theoretical concepts,[48] the chemical action of ultrasound is limited by the unpaired electron transfer. In this case, the reaction mechanism includes only ionic species; therefore, the effect of ultrasound is of physical nature. Ultrasound in fact increases the catalyst surface area since cavitation prevents agglomeration of particles.

Sonochemical acetylation of tertiary alkyl halides in the presence of zinc acetate was accomplished in the presence of PTC and under the action of ultrasound.[124] Alkylation of a glycine derivative by activated organohalogen compounds under the conditions of ultrasonic acceleration of phase transfer and subsequent hydrolysis of the products yielded aminoacylsultams and then, upon mild saponification, pure α-amino acids in a rather high overall yield.[125]

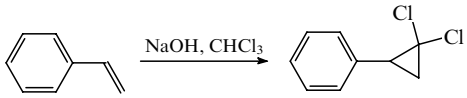
In the example of the addition of ethyl malonate to chalcone in the presence of KOH and trimethylbenzylammonium chloride as PTC (the Michael reaction) it was shown that with ultrasonic stirring the reaction is complete in 2 min, instead of 1 h.[89]



Allylation and benzylation of sodium 5-β-D-glucopyranosyl-1,3-dimethylbarbiturate in water were carried out with benzyl bromide in Me_2SO or allylic and benzylic bromides in the presence of PTC under sonication.[126]

The application of ultrasound in combination with phase-transfer catalysts, crown-ethers and lithium chloride accelerated the transformation of 6-methoxytetralins into 8-methoxytetralins including the stages of cleavage and cyclisation by the intermolecular Friedel–Crafts alkylation.[127]

It is noteworthy that in many cases the application of ultrasound makes it possible to avoid PTC. An example is the cyclopropanation of styrene in which the yield of 96% was reached within 1 h without PTC.[128]



In the control reaction carried out under mechanical mixing the yield was only 30% after 16 h.

4. Enzymic catalysis

Recent studies show the possibility of the ultrasonic influence on enzymic reactions. Acoustic vibrations increase substantially the activity and decrease the size of subtilisin particles which catalyse trans-esterification in organic solvents, the changes in the USW amplitude having no effect on the reaction rate.[129] It was shown that the activity of enzymes depends on the duration of sonication. Thus a short-term action of ultrasound activates butyryl cholinesterase, whereas a prolonged action brings about partial dissociation of the tetrameric enzyme and its irreversible inactivation.[130] Total inactivation of peroxidases (lipoxenases and phenol oxidases) under the action of ultrasound and elevated temperatures is used in food technologies.[131]

Ultrasound was shown to influence hydrolysis of sucrose catalysed by invertase.[132] The effect of ultrasound was studied over a wide range of changes in biochemical and physical conditions, such as pH, sucrose concentration and USW intensity. It was found that the reaction rate increases at low sucrose concentrations. At high concentrations, continuous ultrasonic vibrations have a more substantial influence on this enzymic reaction.

The rate of reactions catalysed by lipase from porcine pancreas is increased 3–60 times under the conditions of azeotropic distillation and 7–83 times under the action of ultrasound, the enantioselectivity being preserved in both cases.[133, 134]

IV. Regeneration of catalysts

Traditional techniques for the regeneration of catalysts include their high-temperature calcination in the atmosphere of oxygen to remove organic residues.[135] However, the initial catalyst's activity is not recovered completely. The physical components of the ultrasonic action make it possible to use acoustic treatment for the effective regeneration of catalysts. Thus the initial activity of a brass catalyst used for the preparation of acetone from propan-2-ol recovered to 83% under the action of ultrasound (18–22 kHz, 6–20 W cm^{-2}) in a solution of sulfuric and nitric acids and sodium bichromate.[5] Without ultrasound, the activity of this catalyst recovered only to 63%.

Ultrasound intensifies considerably the oxidative regeneration of the deactivated rhodium triphenylphosphine catalyst used in the hydroformylation of alkenes.[136]

A nickel-molybdenum catalyst used for the cracking of hydrocarbons was regenerated by oxidation in air with the subsequent action of USW in low-viscosity oils.[5] Similarly, a 30-min action of an acoustic field in water led to the regeneration of the activity of a catalyst of denitrification of waste gases (TiO_2–V_2O_3).

Ultrasound restores totally the specific surface, porosity and activity of the palladium–aluminium catalyst APK-Z, which is used for the removal of nitrogen oxides from exhaust gases.[137] The activity of the 3% Pd/C catalyst in diethylene glycol used for the dehydrogenation of tetrahydronaphthalene and studied earlier in an analogous reaction without ultrasound[138] decreases in the course of the reaction, but it can be restored with the aid of ultrasound.[108]

A series of studies[24, 139–143] were devoted to the regeneration of the industrial ShPAK-0.5 catalyst (0.5% Pd/Al_2O_3) modified by zinc acetate, pyridine and KOH. This catalyst is used for the selective hydrogenation of the triple bond of acetylenic alcohols to

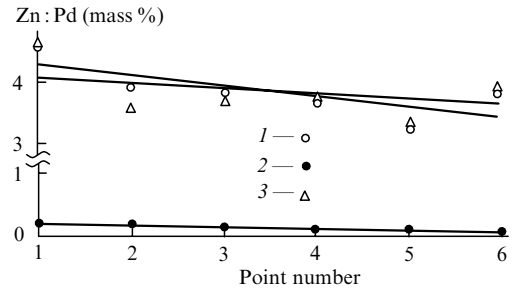


Figure 4. Changes in the Zn : Pt ratio across the granule in subsurface layers of a fresh catalyst (*1*), exhausted catalyst (*2*) and a catalyst following sonication (*3*). The distance between the points is 0.05 mm.

the double bond in the synthesis of vitamin A and E intermediates. In the course of hydrogenation, the catalyst loses its activity and its selectivity is decreased. Besides, the use of physicochemical methods (X-ray spectral microanalysis, electron microscopy and X-ray photoelectron spectroscopy) showed that the catalyst's surface is changed substantially. The ultrasonic treatment with an intensity of 1 W cm^{-2} and a 3-min duration leads to the total recovery of the initial properties of the catalyst (Fig. 4).[54] After the ultrasonic treatment, the content of zinc and palladium in the surface layers of the regenerated catalysts becomes the same as that in the fresh sample. Probably, this is explained by the purification of the surface from coke deposits and the diffusion of the zinc atoms into the subsurface layer. The XPES data also point to a possible amorphisation of the structure of the catalyst's surface, which is at variance with the conclusions made in Refs 54 and 66.

V. Conclusion

The application of ultrasound in chemistry, particularly in catalysis, is one of the most fortunate examples of the use of non-conventional physical methods influencing a reaction system. The present review reflects only the basic results of studies of the applicability of USW for the preparation, activation and regeneration of various catalytic systems as well as for conducting catalytic reactions. The unique results of the action of ultrasound make rather attractive the prospects of its technological uses and are also of appreciable interest for fundamental research. Summing up the above considerations, let us emphasise the following most important moments.

It has been established that ultrasound increases the specific catalyst's surface, because cavitation prevents the agglomeration of particles. The action of ultrasound on solids, including catalysts, increases the content of small particles (3–5 nm) and modifies their lyophilicity. Under ultrasonic treatment, the increase in the activity of catalysts is often several orders of magnitude larger than the increase in their specific surface. This may be associated with a specific action of ultrasound on the nature of the active centres. The change in the nature of the active centres influences not only the catalytic activity but also the reaction selectivity, including enantioselectivity. In an ultrasonic field, the rate of catalytic reactions remains constant for a long time, *i.e.*, the stability of a catalyst is enhanced. In addition, the acoustic waves can change the activation energy and the reaction orders. The combined use of phase-transfer catalysts and ultrasound provides a maximum increase in the degree of conversion owing to the addition of their individual impacts on the system. In a number of cases, the application of ultrasound makes it possible to conduct reactions without phase-transfer catalysts.

A topical problem is the use of USW and resonance vibrations for the creation of heterogeneous catalysts with adjustable functions. Heterogeneous reactions in a liquid phase are limited by the diffusion of the reagents and/or the product in the catalyst's pores. The application of ultrasonic vibrations in the course of a catalytic reaction leads to a several-fold increase in its rate depending on the size of the catalyst particles.

The optimum USW parameters are individual for each catalyst and catalytic reaction. The ultrasonic treatment increases appreciably the spillover of hydrogen which explains higher activity of ultrasound-treated catalysts in hydrogenation reactions. The phenomenon of catalyst's deactivation, which is sometimes observed at a longer duration and a higher intensity of ultrasonic treatment, may be explained by the rearrangement of active centres, which is in turn related to the modification of the catalyst's surface.

The fundamental question about a detailed mechanism of catalysis in an ultrasonic field remains still open to debate. Solution of this problem is a priority issue in the catalysis and determines the prospects of the technological use of USW.

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