ISSN 0023-1584, Kinetics and Catalysis, 2010, Vol. 51, No. 4, pp. 595–601. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © N.N. Smirnov, A.A. Il'in, Yu.M. Komarov, A.P. Il'in, 2010, published in Kinetika i Kataliz, 2010, Vol. 51, No. 4, pp. 619–625.

Mechanochemical Oxidation of Copper in a Steam–Air–Ammonia–Carbon Dioxide Gas Atmosphere

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Received March 17, 2009

Abstract—The effect of intense mechanical actions on the rate of oxidation of copper metal in a steam–air–ammonia–carbon dioxide gas atmosphere was studied. Based on data on changes in the particle size of copper metal and the rate of its oxidation, the effect of the degree of gas mixture saturation with the components on the efficiency of mechanochemical activation was considered. The effect of the gas mixture composition on the chemical composition of oxidation products was demonstrated.

DOI: 10.1134/S0023158410040208

INTRODUCTION

The preparation of solid compounds with specified physicochemical properties, particle sizes, and defect structures is an important goal of catalyst technologies. Mechanical activation, which implies reactions performed in crushing apparatus, has been widely used for the synthesis of these compounds in recent years. Mechanochemical synthesis is one of the most intensely developed current areas of catalyst technologies [1, 2]. Although there are a great number of publications concerning this subject matter, the mechanisms of processes occurring in the course of mechanochemical synthesis are poorly understood.

The use of mechanochemical treatment for the preparation of catalysts makes it possible to solve a number of problems related to an increase in the catalytic activity of available systems [3], to simplify technologies by decreasing the number of synthetic steps, and to extend the range of raw materials because of the use of high-temperature oxides, metals, and spent catalysts. The use of mechanochemical synthesis shows promise of developing new nontraditional so-called dry processes, which are more environmentally appropriate and efficient than currently available technologies [4].

The participation of a liquid or gas phase at the intermediate stages of synthesis and the optimization of conditions under which these stages are performed can be used to solve energy problems with the use of a mechanochemical technology. The mechanical activation of solids should be considered as a unit in the chain of chemical processes occurring under crushing conditions. The efficiency of chemical reactions occurring at an interface depends on mechanical energy consumption and the rate of chemical reactions. In actual practice, mills used for crushing solids serve as activator reactors (Fig. 1).

Considerable disadvantages of a mechanochemical technology, which prevent it from wide occurrence in industrial practice, are high energy consumptions, mechanical wear of activators, and the pollution of catalyst mass by the material of grinding bodies. Increasing mechanical energy efficiency for the initiation of chemical processes is an important problem of considerable current interest. The occurrence of a liquid phase in a solid-phase system before or after reaction is of special interest because it provides an opportunity to decrease power inputs to the equipment [4]. In this context, studies devoted to the direct mechanochemical synthesis of copper salts with the use of active gas atmospheres are of paramount importance.

In this work, we consider the effects of temperature and the degree of saturation of a CO_2–NH_3–H_2O–O_2 gas mixture in its ingredients on mechanical energy efficiency for the activation of copper metal in the production of copper ammoniates and hydroxocarbonates with various compositions, which are used in the synthesis of complex oxides as catalytic system components.

EXPERIMENTAL

The samples were prepared by mechanochemical synthesis in a steam–air–ammonia–carbon dioxide gas atmosphere with controlled ratios between the components. Copper metal powders with an average particle size of 30–80 μm and a specific surface area of 0.03 m^2/g were used as solid components (Fig. 2). Copper powder (50 g) was loaded in a VM-4 roller-ring vibratory mill. The volume of the working chamber of the mill was 1.2 l; the total volume and weight of grinding bodies were 0.15 l and 1.2 kg, respectively; and the vibration frequency was 930 min^{-1}. The gas mixture (100 ml/min) was supplied to the chamber

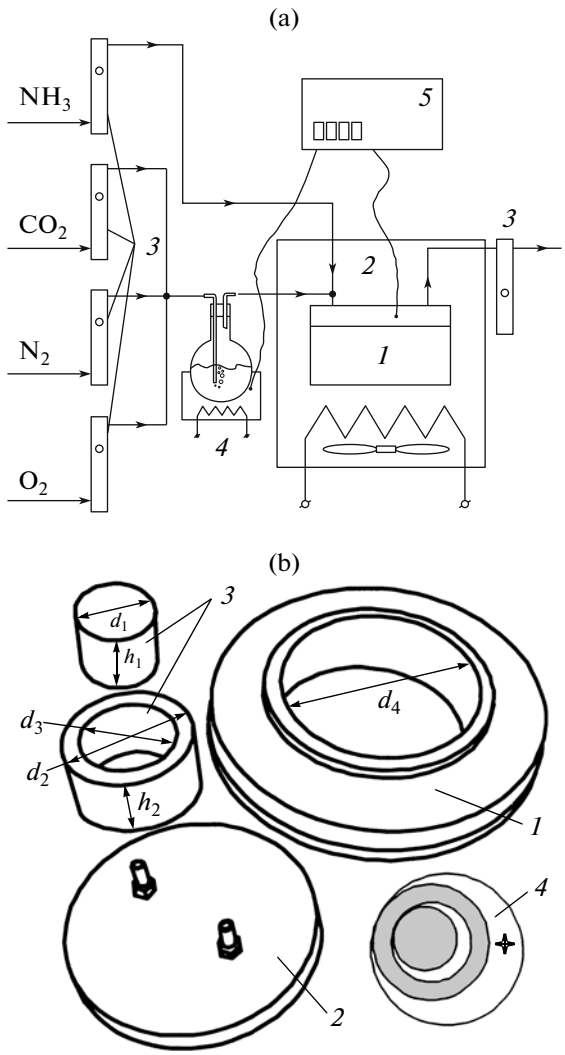

Fig. 1. (a) Schematic diagram of the setup for the synthesis of nanopowders by mechanochemical activation in gas–liquid media: (*1*) vibratory mill, (*2*) air thermostat, (*3*) rotameter, (*4*) steam saturator, and (*5*) potentiometer for temperature measurement and regulation. (b) Roller-ring vibratory mill: (*1*) cup, (*2*) cover, (*3*) grinding bodies, and (*4*) pattern of motions. Main dimensions, mm: $h_1 = 40$, $d_1 = 42$, $d_2 = 80$, $d_3 = 55$, and $d_4 = 180$. Vibration amplitudes in radial and axial directions were ~10 and ~1 mm, respectively.

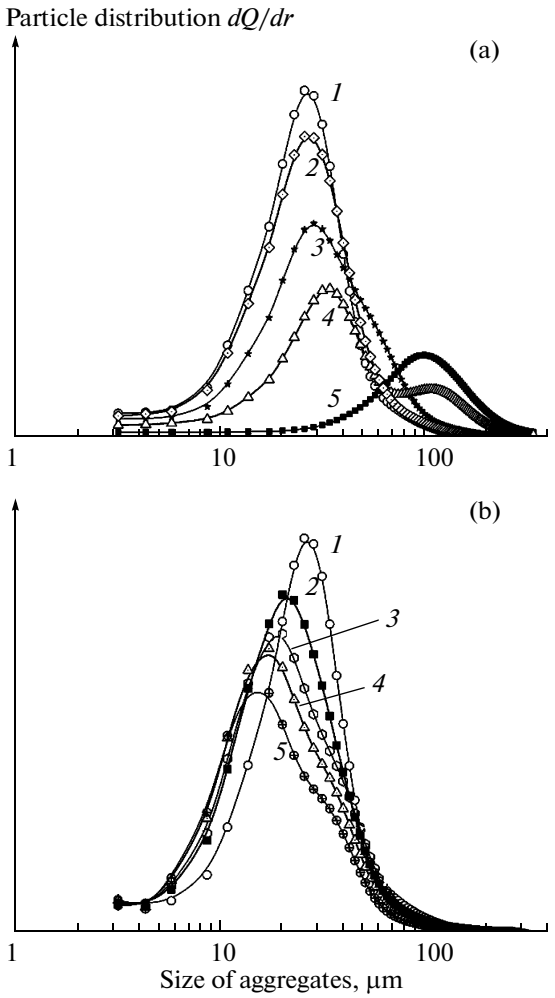

Fig. 2. Effect of activation time and the degree of gas mixture saturation on the particle size of copper metal powders upon their treatment in a mill. The degree of saturation φ: (a) 0.3 or (b) 0.9. The activation times, min: (*1*) 0, (*2*) 5, (*3*) 10, (*4*) 20, and (*5*) 30.

through a connection pipe in the cover of the cup. A constant temperature over the range of 25–100°C was maintained in the course of mechanochemical activation with the use of an air thermostat.

X-ray diffraction and structure analysis was performed on a DRON-3M diffractometer with the use of CuK_α radiation. Substructure parameters were calculated by the harmonic analysis of X-ray line shapes. The sizes of secondary particles were determined on an Analysette 22 instrument. Specific surface areas were determined by the BET method from the thermal desorption of argon. Thermogravimetric analysis was performed on a Q-1500D derivatograph at a heating rate of 5 K/min.

RESULTS AND DISCUSSION

Mechanical energy applied to a solid undergoes redistribution. A portion of this energy is consumed in the formation of a new surface; another portion is consumed in the formation of point and extensive defects and in chemical transformations, and a third portion is converted into heat [1–3]. Preliminary studies of the mechanochemical synthesis occurring in active gas–liquid media demonstrated that chemical reaction is localized in a thin condensation layer on the surface of particles. Thus, to increase the energy efficiency of mechanochemical actions, first of all, it is necessary to choose temperature conditions that afford an optimum condensate amount on the surface and in the pores of a solid phase.

In the presence of active gas atmospheres and liquid media, they interact with the continuously renewed surface of solid components. The layer of products formed on the surface upon the interaction of gas, liquid, and solid phases prevents agglomeration to provide the maximum growth of the interface (Fig. 2). The optimum concentration of a liquid phase on the surface of a metal and the high reactivity of the activated surface facilitate the predominant chemical dissolution of the smallest particles of a polydisperse mixture formed as a result of a mechanical action. The removal of the smallest fraction increased the relative concentration of coarse particles; it is well known that this positively affects the energy efficiency of crushing [3]. In addition, the predominant removal of the smallest particles, which possess a high excessive surface energy acquired in the course of treatment in a vibratory mill, decreases the rate of aggregation.

The character of changes in the particle size as a result of mechanical treatment (Fig. 2) allowed us to represent the interaction of Cu in a CO_2–NH_3–H_2O–O_2 atmosphere under mechanochemical activation in the following manner: In the course of the combined mechanical treatment of solid mixtures with the participation of active gas and liquid media, the crushing and plastic deformation of solids occurred to result in the interaction between the substances. At the first step, the condensation of gas mixture components on the surface of copper metal particles occurred. To control the process of mechanochemical synthesis in a gas–liquid medium, the so-called relative degree of saturation of a multicomponent gas mixture $\varphi = \sum_i \frac{z_i}{K_i(T,P)}$ is used, where z_i is the composition of the initial gas mixture supplied to the reactor (mole fractions), and $K_i(T,P)$ is the phase equilibrium constant. The subscript i denotes gas mixture components (NH_3, H_2O, O_2, and N_2). In engineering calculations, in the absence of data on phase equilibriums in multicomponent systems, the equilibrium compositions of gas and liquid mixtures can be evaluated based on experimental phase equilibrium constants. The phase equilibrium constant [5, 6] $K_i(T,P)$ characterizes the equilibrium distribution of a substance between gas and liquid phases, and it is determined as the ratio between its concentrations in gas (y_i) and liquid (x_i) phases:

$$K_i(T,P) = \frac{y_i}{x_i} \approx \frac{\gamma_i P_i}{P},$$

where P is the total pressure of a gas phase, and P_i is the saturation vapor pressure of the ith component.

Boldyrev et al. [4] found that high-temperature and high-pressure zones can appear upon the mechanical treatment of wet mixtures in high-energy activators. These conditions facilitate the occurrence of processes that are usually performed by a hydrothermal method. Optimum temperature and pressure depend on the composition of an initial gas mixture supplied to the reactor (z_i) according to the equation

$$f(\alpha) = \sum_i \frac{z_i[K_i(T,P)-1]}{1+\alpha[K_i(T,P)-1]} = 0. \quad (1)$$

Solving Eq. (1) for a chosen initial composition of the starting gas mixture at specified temperature and pressure, we find the equilibrium degree of condensation α. With consideration for this value, we calculate the compositions of liquid (x_i) and gas (y_i) phases from the following equations:

$$x_i = \frac{z_i}{1+\alpha[K_i(T,P)-1]}; \quad (2)$$

$$y_i = x_i K_i(T,P). \quad (3)$$

The saturation vapor pressures of NH_3, CO_2, and H_2O over pure components can be determined by the Lee–Kesler method [5, 6]:

$$\ln P_i = f_i^{(0)} + \omega f_i^{(1)};$$

$$f_i^{(0)} = 5.92714 - \frac{6.09648}{(T/T_i^c)} - 1.28862\ln(T/T_i^c) + 0.169347(T/T_i^c)^6;$$

$$f_i^{(1)} = 15.2518 - \frac{15.6875}{(T/T_i^c)} - 13.4721\ln(T/T_i^c) + 0.43577(T/T_i^c)^6;$$

where T_i^c is the critical temperature, K [6]; ω_i is the acentric factor

$$\omega_i = \frac{-\ln P_i^c - 5.92714 + 6.09648(T_i^b/T_i^c)^{-1} + 1.28862\ln(T_i^b/T_i^c) - 0.169347(T_i^b/T_i^c)^6}{15.2518 - 15.6875(T_i^b/T_i^c)^{-1} - 13.4721\ln(T_i^b/T_i^c) + 0.43577(T_i^b/T_i^c)^6},$$

P_i^c is the critical pressure; T_i^b is the normal boiling temperature, K [6]; and $K_i(T,P) \approx \frac{\gamma_i P_i^c}{P}$. The activity coefficient γ_i depends on the composition of the liquid phase, pressure, and temperature with consideration for chemical interactions between the components.

The above calculation scheme indicates that the composition of formed products has a considerable effect on phase equilibrium in the gas–liquid–solid system. To determine gas–liquid equilibrium parameters in the CO_2–NH_3–H_2O–O_2 system, not only the physicochemical properties of the components but also their chemical interactions in liquid and solid

phases should be taken into account in the calculation of vapor pressures.

In the mechanochemical synthesis of copper-containing catalysts, the formation of the ammine complexes, hydroxides, and hydroxocarbonates of copper should be taken into consideration along with the interaction between ammonia and carbon dioxide. The dissolution and crystallization of basic copper carbonates as double hydroxocarbonates occur in a steam–carbon dioxide–ammonia mixture. The precursors of anion-modified oxides are hydroxo compounds: either simple (in the case of one-component systems) or complex, which are formed as a result of the deep interaction of all of the initial components with the formation of a low-temperature oxide solid solution [7].

To determine conditions for performing mechanochemical synthesis at specified initial gas mixture composition and temperature, we evaluated the degree of condensation of gas mixture components based on the calculation of gas–liquid equilibrium with the use of published data [8–11]. By solving a set of equilibrium equations and material balance equations, we calculated the equilibrium concentration of ions in solution. The released condensate was a region in which the main chemical transformations occurred to provide a high rate of mechanochemical synthesis because of the generation of conditions for the occurrence of hydrothermal processes in the system.

In the predominant majority of cases, the oxidation reaction at temperatures lower than 200°C occurred by a so-called electrochemical mechanism: the metal atom and the oxidant species did not directly contact and electron transfer from the metal to the oxidant occurred through a conductivity band. Thus, the oxidation process actually consists of two reactions: anodic metal dissolution and cathodic oxidant reduction. In terms of the electrochemical theory of corrosion [8], the interaction of copper with aqueous ammonia solutions is considered as a two-step process in which the cathode reaction of oxygen reduction

$$1/2O_2 + H_2O + 2\bar{e} \rightleftarrows 2OH^- \quad (E^0 = 0.2005\ \text{V}),$$

occurs at a portion of the metal surface, and the anode reaction of copper oxidation occurs at another portion:

$$Cu + 4NH_3 \rightleftarrows [Cu(NH_3)_4]^{2+} + 2\bar{e} \quad (E^0 = 0.070\ \text{V}).$$

The overall reaction of copper with an ammonia solution in the presence of oxygen is the following:

$$Cu + 4NH_3 + 1/2O_2 + H_2O \rightleftarrows [Cu(NH_3)_4]^{2+} + 2OH^- \quad (E^0 = 0.2075\ \text{V}).$$

Along with the oxidation of copper with oxygen, the dissolution of copper can occur because of interactions between the compounds of Cu(0), Cu(I), and Cu(II). The resulting ammine complex of bivalent copper reacts with copper metal to oxidize it to a univalent state. In solution, the ammine complex of univalent copper is oxidized at a high rate to Cu(II). This mechanism is referred to as an autocatalytic oxidation mechanism [7].

In accordance with the autocatalytic mechanism, the dissolution of copper occurs in the following three steps:

the formation of an ammine complex of Cu(I) [8]

$$2Cu + 4NH_3 + 1/2O_2 + H_2O \rightarrow 2[Cu(NH_3)_2]^+ + 2OH^-;$$

the oxidation of the Cu(I) complex with oxygen

$$2[Cu(NH_3)_2]^+ + 4NH_3 + 1/2O_2 \rightarrow 2[Cu(NH_3)_4]^{+2} + 2OH^- + H_2O;$$

and the interaction of the Cu(II) complex with the surface of copper

$$[Cu(NH_3)_4]^{+2} + Cu \rightarrow 2[Cu(NH_3)_2]^+.$$

As a result of mechanochemical actions, the number of point contacts increased; the agglomeration and continuous renewal of the surface occurred; decomposition processes and the migration of defects on the surface and in the bulk of solids occurred. In this case, the mobility of defects can be sufficient for mixing the substance and intensifying diffusion-controlled reactions. The oxidation of the copper surface with oxygen, which occurred in gas atmospheres and liquid media, prevented the agglomeration of metal particles to increase the interface area.

The study of the kinetics of the interaction of copper metal with aqueous solutions of ammonia in the presence of oxygen demonstrated that two competitive parallel processes occurred simultaneously. The ammine complex $[Cu(NH_3)_4]^{2+}$, which resulted from the reaction of ammonia and oxygen on the surface of copper metal, newly reacted with the surface to increase the overall rate of dissolution. In this case, the copper surface was oxidized by the action of a solution of copper(II) ammine complexes on it with the formation of the ammine complexes of copper(I). The liquid-phase oxidation of $[Cu(NH_3)_4]^+$ to $[Cu(NH_3)_4]^{2+}$ with dissolved oxygen also occurred. In addition, the solution was saturated with copper compounds, the crystallization of interaction products occurred (depending on the concentrations of copper oxides, ammoniates, and hydroxocarbonates in the liquid phase) (Fig. 3).

The oxidation of copper was due to the occurrence of two parallel processes; the overall rate of reaction depended on the sum of their rates:

$$\frac{d[Cu]}{dt} = \frac{2k(\varepsilon,T)k_2(\varepsilon,T)S[O_2][NH_3]}{2k_1(\varepsilon,T)[O_2] + k_2(\varepsilon,T)[NH_3]} + k_3(\varepsilon,T)S[Cu^{2+}]^{0.5},$$

where S is the surface area of the unoxidized metal; $[O_2]$ is the concentration of oxygen in solution; $k_2(\varepsilon, T)$ is the rate constant of the interaction of copper oxide with ammonia with the formation of an ammine complex of copper(II); $k_3(\varepsilon, T)$ is the rate constant of

the reaction between copper and the copper(II) ammine complex; $[NH_3]$ is the concentration of free ammonia in solution; and $[Cu^{+2}]$ is the concentration of the copper(II) complex $[Cu(NH_3)_4]^{+2}$ in solution.

The rate constant of the interaction of oxygen with the surface of copper was determined as a function of the specific input energy ε and the temperature T using the equation

$$k_1(\varepsilon,T) = 0.267[\varepsilon\upsilon(T)]^{0.25}\left(\frac{D(T)}{\upsilon(T)}\right)^{0.75},$$

where $\upsilon(E)$ is the kinematic viscosity of solution, and $D(T)$ is the diffusion coefficient of dissolved oxygen.

An analysis of the temperature dependence of the constant $k_1(\varepsilon, T)$ suggests that the activation energy $E_{k_1} = 15.8$ kJ/mol remains constant over the range of input energies from 0 to 20 W/g; however, an increase in the frequency factor is observed in this case. The greatest increase in the frequency factor occurs at low values of mechanical input energy.

The mathematical treatment of experimental data in the rate of dissolution–input energy ε coordinates demonstrated that the logarithm of the rate constant was adequately linearized at the exponent ε from 0.2 to 0.3.

The rate constant of the interaction of copper oxide with ammonia with the formation of an ammine complex of copper(II) was also determined as a function of the specific input energy ε and the temperature T from the equation

$$k_2^0 = 5.5 \text{ cm/s}, \quad E_2 = 23 \text{ kJ/mol},$$

$$k_2(\varepsilon,T) = k_2^0\varepsilon^{0.3}\exp\left(\frac{-E_2}{RT}\right).$$

In a similar manner, the rate constant of the interaction of copper with an ammine complex of copper(II) was expressed by the equation

$$k_3^0 = 1\times10^3 \text{ s}^{-1}\text{ mol}^{0.5}\text{ cm}^{-0.5},$$

$$E_3 = 45 \text{ kJ/mol}, \quad k_3(\varepsilon,T) = k_3^0\varepsilon^{0.2}\exp\left(\frac{-E_3}{RT}\right).$$

The study of the effect of the degree of gas phase saturation with components indicated that the chemical composition of the gas phase and the temperature regime in the mill are the most important factors responsible for interaction parameters. The temperature and gas composition were varied to regulate the degree of gas mixture saturation. An analysis of the set of data on the chemical and phase compositions and the structures of starting reagents and transformation products allowed us to describe the process occurring at various degrees of gas mixture saturation in the following manner:

(1) At $\varphi > 1.1$, the condensation of high-boiling components from a saturated gas mixture occurred. The liquid occupied the pores and surface of solid particles. A further increase in the degree of condensation resulted in an increase in the thickness of the liquid layer, and the major portion of mechanical input energy was dissipated in the liquid phase. In this case, the main interactions were localized at the interface and in a near-surface liquid layer.

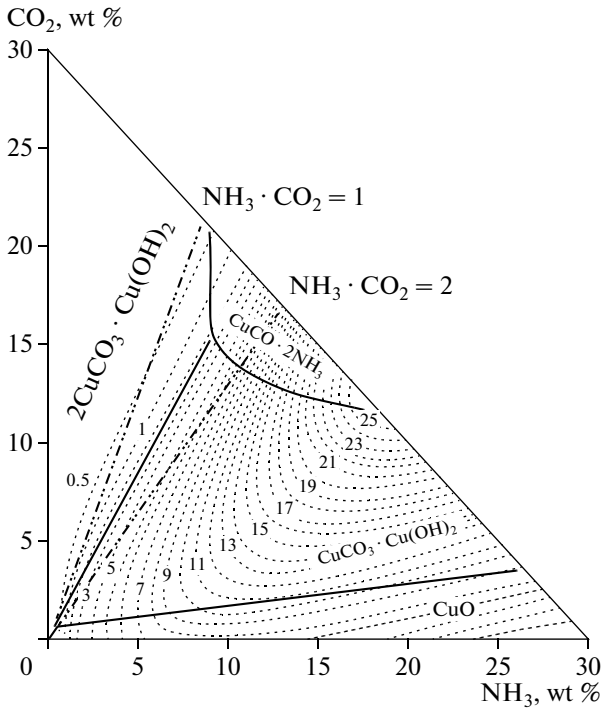

Fig. 3. Isotherms of solubility in the NH_3–CO_2–H_2O–CuO system at 25°C. Isoconcentrates are shown with dashed lines. Numbers at the dashed lines refer to solubility in wt % on a Cu basis. Crystallization fields are shown with solid lines.

(2) At the degree of gas mixture saturation $0.7 < \varphi < 1.0$, the condensation of high-boiling components was observed in the pore space and at individual surface regions. Three phases—gas, liquid, and solid—occurred in direct contact. In this case, a mechanical pulse of pressure primarily affected the liquid phase and then the solid particles to cause their deformation and degradation. Upon the condensation of small amorphized particles, mainly coagulation contacts appeared between them, which did not cause a decrease in the interface area. Under hydraulic discontinuity conditions in the liquid, the interface contacts with gaseous and liquid components.

(3) If the degree of gas mixture saturation is $\varphi < 0.7$, the condensate in a small amount can be present only in the pore space. The liquid on the surface completely lost its hydraulic continuity even before the mechanical action. A mechanical pulse acted only on solid-phase particles to cause their deformation, degradation, condensation, and agglomeration. In this case, condensation and agglomeration processes in dry mixtures occurred at a much higher rate than in the above two cases, when coagulation contacts that are easy to

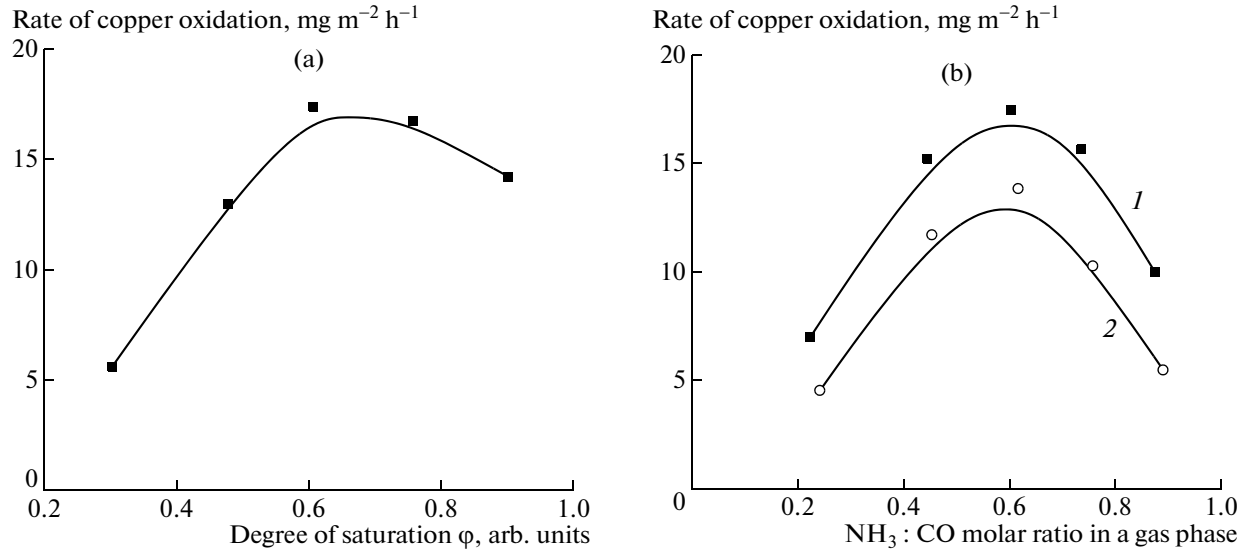

Fig. 4. (a) Dependence of the rate of copper oxidation in a steam–air–ammonia–carbon dioxide atmosphere on the degree of gas mixture saturation φ. Gas mixture composition, mol %: CO_2, 15; NH_3, 15; O_2, 15. (b) Dependence of the rate of copper oxidation in a steam–air–ammonia–carbon dioxide atmosphere on the NH_3: CO_2 molar ratio at 70°C. The concentration of O_2 in the gas mixture was (*1*) 15 or (*2*) 10 mol %.

decompose under mechanical actions were primarily formed.

The interaction of an oxidized surface with a condensed liquid layer occurred at a high rate with the formation of soluble ammine complexes of copper(II) under hydrothermal conditions. Data on the degree of oxidation of copper suggest that, in the case when the gas mixture saturation was from 0.60 to 0.85, the efficiency of intense mechanical actions reached a maximum (Fig. 4). Various chemical processes occur in a condensed liquid layer on the surface of a solid depending on the composition of a gas phase. Along with the oxidation of copper metal, the synthesis of other compounds can also occur.

As found experimentally, the composition of the resulting copper compounds depends on the ratio between gas phase components in accordance with the positions of crystallization fields in the solubility diagram in the NH_3–CO_2–H_2O–CuO system (Fig. 3). Based on experimental and published data on the solubility of copper in ammonia–carbonate solutions, we plotted a solubility diagram for NH_3–CO_2–H_2O–CuO and calculated the corresponding coefficients in the regression equation

$$[\mathrm{Cu}](\mathrm{NH_3},\mathrm{CO_2}) = \frac{a + c[\mathrm{NH_3}] + e[\mathrm{CO_2}] + g[\mathrm{NH_3}]^2 + i[\mathrm{CO_2}]^2 + k[\mathrm{NH_3}][\mathrm{CO_2}]}{1 + b[\mathrm{NH_3}] + d[\mathrm{CO_2}] + f[\mathrm{NH_3}]^2 + h[\mathrm{CO_2}]^2 + j[\mathrm{NH_3}][\mathrm{CO_2}]}.$$

The concentration of $[Cu](NH_3,CO_2)$ in a copper solution was expressed in g/l, and the concentrations $[NH_3]$ and $[CO_2]$, in wt %. The coefficients of the equation were as follows: $a = 0.0253$, $b = 0.0146$, $c = 25.955$, $d = 0.1943$, $e = -14.67$, $f = 0.012$, $g = -0.6122$, $h = -0.00042$, $i = -4.33747$, $j = -0.02123$, and $k = 6.5065$.

The rate of oxidation of copper metal was proportional to the concentration of the copper(II) complex $[Cu(NH_3)_4]^{+2}$ in solution. At the NH_3 : CO_2 molar ratio of 0.6 in a gas phase, it was 3–4 in a liquid phase, which corresponded to a maximum solubility of the complex $[Cu(NH_3)_4]^{2+}$ and a maximum rate of oxidation (Fig. 4b).

Thus, we experimentally found that the mechanochemical synthesis of low-temperature active oxide catalytic systems from copper powders could be performed with the use of medium-energy apparatus. We found that the composition and the degree of saturation of a gas phase exerted a considerable effect on the rate of the oxidation process. The mechanism of the mechanochemical oxidation of copper metal powder under hydrothermal conditions was determined, and it was demonstrated that the energy efficiency of the mechanochemical synthesis reached a maximum at the relative degree of saturation of the multicomponent gas mixture in the range of $0.7 < \varphi < 1.0$. The experimental data can be used in the development of copper-containing catalysts.

Based on an analysis of the oxidation of copper metal in a steam–air–ammonia–carbon dioxide gas atmosphere and the generalized mathematical

description of the crushing–aggregation process in gas–liquid media, we proposed a set of equations for a polydisperse multiphase mixture with consideration for the crushing of disperse phase particles. We analyzed the dissipative function of the system and obtained expressions for the driving force of crushing and a crushing criterion in an explicit form; this allowed us to determine the mechanism of crushing particles. Based on data on the structure of the driving forces of crushing, we found analytical expressions for the probability of degradation and a distribution function, which reflect the stochastic properties of the crushing process. We studied the effect of gas–liquid media on the mechanochemical oxidation of copper metal and proposed to take into consideration the degree of gas phase saturation with components in the evaluation of the energy efficiency of intense mechanical actions. Varying the amount and intensity of input energy, the composition of the atmosphere, and the chemical composition of starting components is the most effective way of controlling the mechanochemical synthesis.

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